13. The university will not be able to meet the demands placed on it by a changing technological society. (Clarification: Many individuals commented that the university lacks the structure and resources to deal with a rapidly changing technological society.)

a. Of greatest concern at: (check as many as necessary)
___ provincial level ___ school level
___ regional level ___ university level
___ system level ___ other level, please specify ___________

b. Recommended strategies for reducing probability:

14. Subject areas and grade levels will compete for placement of computing equipment.

a. Of greatest concern at: (check as many as necessary)
___ provincial level ___ school level
___ regional level ___ university level
___ system level ___ other level, please specify ___________

b. Recommended strategies for reducing probability:

15. Most of the newly acquired equipment will be placed in high schools. (Clarification: Many individuals felt that some of this equipment should be placed in other areas.)

a. Of greatest concern at: (check as many as necessary)

___ provincial level
___ regional level
___ system level
___ school level
___ university level
___ other level, please specify ___________

b. Recommended strategies for reducing probability:

16. In relation to computers, external groups will continue to make conflicting demands on the educational community (i.e. the A.S.T.A., the A.T.A., the Home and School Assoc., the University, the Department of Education, Advanced Education).

a. Of greatest concern at: (check as many as necessary)

___ provincial level
___ regional level
___ system level
___ school level
___ university level
___ other level, please specify ___________

b. Recommended strategies for reducing probability:

SECTION II

ROUND II STATEMENTS REGARDED AS HIGHLY DESIRABLE WITH LITTLE AGREEMENT REGARDING PROBABILITY

(If you disagree with the overall group response for any of the statements please use the space available in part b to state the reason(s) why you disagree.)

1. There will be development of a local software industry tailored to provincial curriculum.
   a. Of greatest concern at: (check as many as necessary)
      ___ provincial level ___ school level
      ___ regional level ___ university level
      ___ system level ___ other level, please specify ___________
   b. Recommended strategies for increasing probability:

2. Computer related in-service will be compulsory for teachers.
   a. Of greatest concern at: (check as many as necessary)
      ___ provincial level ___ school level
      ___ regional level ___ university level
      ___ system level ___ other level, please specify ___________
   b. Recommended strategies for increasing probability:

3. Teachers will be adequately trained to deal with the social impact of computers.

   a. Of greatest concern at: (check as many as necessary)

___ provincial level	___ school level
___ regional level	___ university level
___ system level	___ other level, please specify ___________

   b. Recommended strategies for increasing probability:

4. Computers will foster more parent involvement in the school.

   a. Of greatest concern at: (check as many as necessary)

___ provincial level	___ school level
___ regional level	___ university level
___ system level	___ other level, please specify ___________

   b. Recommended strategies for increasing probability:

SECTION III

ROUND II STATEMENTS REGARDED AS HIGHLY PROBABLE WITH LITTLE AGREEMENT REGARDING DESIRABILITY

(If you disagree with the overall group response for any of the statements please use the space available to state the reason(s) why you disagree.)

1. The introduction of computers will contribute to stress within all educational organizations.

a. Of greatest concern at: (check as many as necessary)

___ provincial level
___ regional level
___ system level
___ school level
___ university level
___ other level, please specify ___________

b. To what degree will computers contribute to dysfunctional stress within educational organizations? (Circle one)

to a large degree 1 2 3 4 5 very little

c. To what degree will computers contribute to stress within educational organizations that leads to positive changes?

to a large degree 1 2 3 4 5 very little

d. Additional comments:

2. Despite the increased use of computers the role of teacher, student, and principal will remain primarily the same.

a. Of greatest concern at: (check as many as necessary)

___ provincial level
___ regional level
___ system level
___ school level
___ university level
___ other level, please specify ___________

b. Additional comments regarding the desirability of the above statement:

SECTION IV

ROUND II STATEMENTS REGARDED AS HIGHLY UNDESIRABLE WITH LITTLE AGREEMENT REGARDING PROBABILITY

(If you disagree with the overall group response for any of the statements please use the space available in part c to state the reason(s) why you disagree.)

1. The inertia of all the existing software will discourage upward capability of hardware. (Clarification: Some individuals felt that resources already invested in existing software would discourage the purchase of any newer generation equipment that was incompatible.)
   a. Of greatest concern at: (check as many as necessary)
      ___ provincial level ___ school level
      ___ regional level ___ university level
      ___ system level ___ other level, please specify ________
   b. A matter of (circle one): great concern 1 2 3 4 5 little concern
   c. Potential strategies for reducing probability of such a development:

2. Apart from the area of technology itself, curriculum content in other areas will remain much the same as it is at present.
   a. Of greatest concern at: (check as many as necessary)
      ___ provincial level ___ school level
      ___ regional level ___ university level
      ___ system level ___ other level, please specify ________
   b. A matter of (circle one): great concern 1 2 3 4 5 little concern
   c. Potential strategies for reducing probability of such a development:

SECTION V

ADDITIONAL COMMENTS:

Your cooperation is greatly appreciated! A summary of the findings will be forwarded to you when the study is completed.

APPENDIX G

MATRIX OF ROUND III QUESTIONNAIRE ITEMS AND RECOMMENDED STRATEGIES

MATRIX OF ROUND III QUESTIONNAIRE ITEMS AND RECOMMENDED STRATEGIES

RECOMMENDED STRATEGIES QUESTIONNAIRE ITEMS	SOFTWARE/COURSEWARE (73)	Establish Educ. Criteria (12)	Communicate Educ. Criteria (10)	Software/Courseware Dev. (5)	Software/Courseware Eval. (4)	Courseware Evaluation (16)	Provincial Development (13)	Provincial Involvement (3)	More Educators Involved (10)	FUNDING (61)	Funding (32)	Change Formula (9)	Designated (8)	Courseware and Facilities (5)	In-service (2)	Pay Incentives (4)	Subsidize Recom. Courseware (1)	IN-SERVICE (38)	In-service (20)	Expertise (6)	Training (11)	Administrator (1)	POLICIES (26)	Guidelines (11)	Re: Allocation (2)	Re: Access (5)	Re: Equipment Migration (2)	Re: Information Stored (3)	Usage (3)	CURRICULAR DEVELOPMENT (17)	Development (14)	Restructure (3)	PRE-SERVICE (9)	Pre-service (5)	Training (4)	PLANNING (8)	SECURITY PROCEDURES (7)	COMMUNICATION (7)
Section I																																						
1. Underutilization of equipment				5	3																11				2						4				4	2		
2. Courseware development lacking educational input		4	6			6	4		6								1																					
3. Software inappropriate for education		4	1			10	5												1															1				
4. Software piracy																								5														
5. Confidentiality of information																										5		3									7	
6. Lack of computing skills a handicap at post-secondary																															4			1				
7. Differential rates of adoption contributing to inequities													8							6				1														
8. Continued funding for hardware														5	2														3									
9. Computers diverting needed funds																			2					5							4							
10. Problem developing courseware		4	3		1		4		4		6																											
11. Resistance to change											2								8															1		2		
12. Migration of talent																4																						
13. Increased demands on universities											9								1													3						
14. Competition for equipment											3											1														3		
15. High schools acquiring equipment												9							1								2											
16. Conflicting demands on education																																						5
Section II																																						
1. Local software industry								3			6																									1		
2. Compulsory in-service											5								2																			
3. Teachers trained to deal with social impact of computers																			5												2			2				
4. Increased parental involvement											1																											2

RECOMMENDED STRATEGIES QUESTIONNAIRE ITEMS	COPYRIGHT LAWS (5)	INDUSTRY LIAISON (5)	RELEASE TIME (5)	SPECIAL PRICING AGREE. (5)	PARENT CLASSES/COMM. (5)	CHANGE MANAGEMENT STRUC. (4)	IMPLEMENTATION (4)	"SPECIAL" ENTRY COURSES (4)	COMPULSORY COURSES (3)	EMPHASIS ON ETHICS (3)	INTERPROV. CO-OPERATION (3)	MANDATORY CERTIFICATION (3)	RECOGNITION (3)	REDUCED PRICES (2)	SET MINIMUM STANDARDS (2)	SHARING ARRANGEMENTS (2)	SOFTWARE SECURITY (2)	AVOID OVERLOADING (1)	BOARD ALLOCATIONS (1)	LITIGATION (1)	MAINTENANCE SUPPORT (1)	NETWORKING (1)	PILOT TESTING (1)	PIRACY PREVENTION (1)	REMOVE TENURE (1)	SCHOOL ALLOCATIONS (1)	SCHOOL BASED BUDGETING (1)	SOFTWARE HARDWARE AVAIL. (1)	SYSTEM MAINTENANCE (1)	TAKE-HOME COURSEWARE (1)	TIME AND EXPERIENCE (1)	DISAGREE
Section I																																
1. Underutilization of equipment							2																				1		1			1
2. Courseware development lacking educational input											1																					0
3. Software inappropriate for education											1												1									0
4. Software piracy	5			5						2				2			2			1												2
5. Confidentiality of information										1																						1
6. Lack of computing skills a handicap at post-secondary								4	3																							0
7. Differential rates of adoption contributing to inequities															2																	2
8. Continued funding for hardware																			1		1					1						0
9. Computers diverting needed funds																																0
10. Problem developing courseware											1																					1
11. Resistance to change							2																					1			1	1
12. Migration of talent			4										3					1														2
13. Increased demands on universities		1				4																			1							1
14. Competition for equipment																2																1
15. High schools acquiring equipment																																1
16. Conflicting demands on education																																1
Section II																																
1. Local software industry		4																						1								1
2. Compulsory in-service			1									3																				3
3. Teachers trained to deal with social impact of computers																																1
4. Increased parental involvement					5																	1								1		2

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Title of Thesis – Titre de la thèse

Identification of Reactive Intermediates in the Photochemistry of Furan and Thiophenes.

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IDENTIFICATION OF REACTIVE INTERMEDIATES IN THE PHOTOCHEMISTRY OF FURAN AND THIOPHENES

by

W. ALAN RENDALL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL 1985

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled IDENTIFICATION OF REACTIVE INTERMEDIATES IN THE PHOTOCHEMISTRY OF FURAN AND THIOPHENES submitted by W. ALAN RENDALL in partial fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

Otto P. Strausz

Supervisor

George Kotovych

Frederick F. Cantwell

Loren G. Hepler

External Examiner

DATE June 18/85

For D.L., and J.T. or K.L.

ABSTRACT

Solution phase photolysis and trapping experiments, and also photolysis experiments in low temperature (10 K) matrices have been utilized to identify some of the short-lived reactive species in the photochemistry of furan and thiophenes.

In the case of thiophene, two Diels-Alder adducts between Dewar thiophene and furan were isolated and characterized following the UV irradiation of thiophene in furan. These same adducts were also obtained when thiophene was irradiated in a frozen glass at -170°C, followed by post-photolysis trapping with furan, thereby demonstrating that the furan trapping process intercepts a true intermediate as opposed to an excited state of thiophene.

By comparison, the room temperature irradiation of neat liquid furan led to the characterization of four furan Diels-Alder adducts, two with each of cyclopropene-3-carboxaldehyde and 2,3-butadienal. Owing to their reactive nature none of these species are isolable products of the solution phase irradiation of furan or thiophene at room temperature.

In the low temperature matrix isolation experiments those photolysis products trapped in solution were again observed. In addition, a number of other primary photolysis products were identified. For thiophene the most significant new species produced by matrix photolysis was the cyclopropenyl thioaldehyde, while with matrix isolated furan the Dewar isomer was formed.

Dewar and cyclopropenyl species have often been suggested as intermediates in the photoinduced scrambling responsible for the positional isomerization observed in many substituted furans and thiophenes following UV irradiation, but only limited success had previously been achieved in demonstrating the existence of such species. We have demonstrated the photochemical formation of the Dewar and cyclopropenyl isomers of both furan and thiophene. In addition, a new and efficient methodology for probing the exact role of these species in the photoinduced scramblings of five-membered heterocyclic systems has been developed. Some experiments with substituted thiophenes have also been performed, but at present we are unable to offer a definite explanation of the role of Dewar and cyclopropenyl species in these photorearrangements.

ACKNOWLEDGEMENTS

I wish to express my most sincere thanks to Dr. O.P. Strausz under whose patient supervision this research was guided to a successful conclusion.

In addition, I would particularly like to acknowledge the contributions of two members of Dr. Strausz's research group: Dr. M. Torres for his valuable advice during the course of this research, and Mr. A. Clement for his expertise in low temperature matrix isolation (and his passion for sports - particularly hockey).

The considerable efforts of Dr. E. Lown in the preparation of this thesis are greatly appreciated.

The fluorescence lifetimes of the phenylthiophenes were determined by Drs. D. James and W. Ware at the University of Western Ontario. We are grateful for their assistance in performing these measurements, which were beyond the capabilities of our lifetime instrumentation.

I am also deeply indebted to all those members of the various departmental analytical laboratories (MS, NMR, IR, ...) who have been of so much assistance.

The efforts of Miss A. Wiseman in typing this manuscript are gratefully acknowledged.

Finally, I should like to extend a sincere, collective thanks to everyone in the Chemistry Department whom I have come to know these past few years. While research must inevitably be an endless course of victories and defeats, these friendships have always served to brighten my daily routine. Although in most cases our paths in life will seldom cross again, I will always have many cherished memories of these individuals.

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INTRODUCTION

PHOTOCHEMICAL REARRANGEMENTS

Many photoreactions interconverting isomeric compounds have been reported. The current investigation is concerned with photorearrangement in heteroaromatic ring systems, especially thiophenes, where isomerizations occur by scrambling of the ring carbon atoms. Before reviewing heteroaromatic photochemistry from the current perspective, two intimately related subjects should be discussed briefly. The first is the nature of photoisomerization as a route for radiationless transitions. The second one is the thoroughly investigated photorearrangement reactions of benzenes. Chronologically, benzene photoisomerizations were detected before those of thiophene systems. Consequently, ideas regarding the benzenes influenced the course and interpretation of thiophene experiments.

A. Radiationless Energy Dissipation by Photoisomerization

The fate of the energy which a molecule receives during electronic excitation is described by a collection of processes. For the photochemist these are conveniently summarized in a modified Jablonski diagram, Figure 1, and subdivided into two types: radiative and radiationless transitions, conventionally represented by solid and wavy lines, respectively. The occurrence of unimolecular radiationless transitions such as internal conversion and inter-

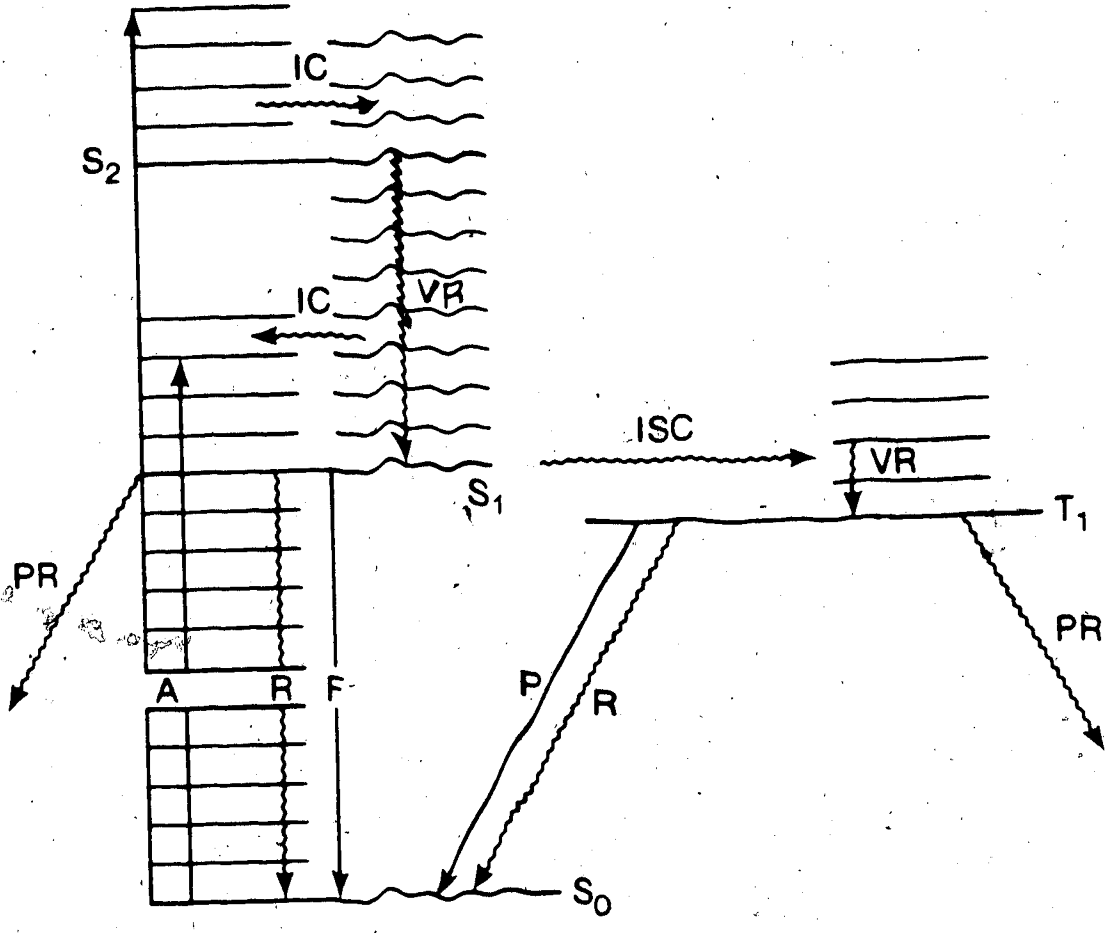


Figure 1. Modified Jablonski diagram.

S_0	Ground state singlet	F	Fluorescence
S_1	First excited singlet	P	Phosphorescence
S_2	Second excited singlet	R	Radiationless decay
T_1	First excited triplet	IC	Internal conversion
A	Absorption	VR	Vibrational relaxation
PR	Photochemical reaction	ISC	Intersystem crossing

system crossing is inferred from quantum yield measurements. The yields of processes like decomposition and emission are measured experimentally. The fraction of molecules not accounted for by this sum is attributed to radiationless transitions.

The observation of no net chemical reaction following irradiation is common. It must be realized that reversible photochemistry (dark back-reactions, cage effects) in addition to purely photophysical transitions, may also be responsible for the apparent reaction inefficiency.

Phillips et al. [1] discussed the concept of internal conversion, and possibly intersystem crossing to the ground state, occurring by formation of a thermodynamically unstable isomer in its ground state, Figure 2. The isomer's potential curve provides an additional vibrational ladder for energy dissipation. Let us define an isomer as a nuclear configuration producing an energy minimum on the potential surface. The thermodynamic stability of each isomer depends on the depth of its minimum. Since the ground states of all isomers for particular numbers and types of atoms will lie on the same potential surface, one isomer can in theory be converted to any other by surmounting the appropriate energy barrier. Experimentally, the formation of certain isomers may not occur thermally because of competition with other processes having lower barriers.

This concept of excitation energy dissipation through the formation of a thermodynamically unstable isomer was used by Lamola et al. [2] in 1965 to help explain their results on stilbene photochemistry. The cis-trans photoisomerization of many ethylene derivatives

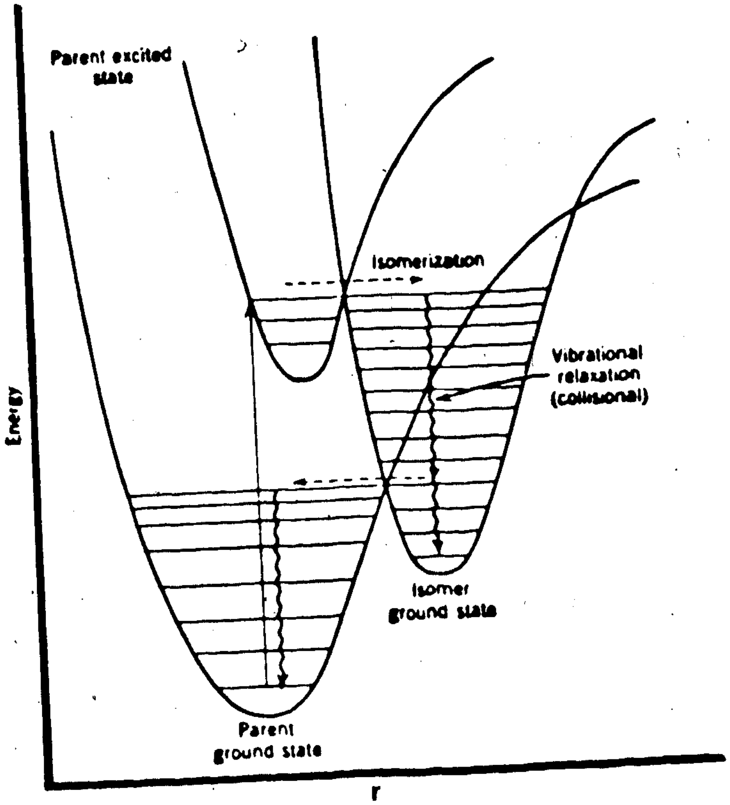


Figure 2. A representation of the formation of a thermodynamically unstable isomer in its ground state as a mode of radiationless transition. Reproduced from Ref. [1].

has been reported and stilbenes (1,2-diphenylethylenes) are possibly the most extensively investigated. Lamola et al. suggested that if a higher energy stilbene isomer, with possibly a twisted geometry, was formed it might yield either the trans product or return to cis-stilbene and also provide a means of energy dissipation. More recently, exciting picosecond pulse spectroscopic techniques have further probed the details of stilbene photoisomerization, revealing the rapid deactivation ($k \sim 1.1 \times 10^{10}\ s^{-1}$) of the first excited singlet state of trans-stilbene by twisting about the central double bond - the first step in the isomerization process [3].

Sometimes radiationless transitions are separated into photophysical and photochemical processes, however, because this distinction can become blurred it may be preferable to concentrate on the energy surface pathways of a photoreaction, Figure 3. Most organic photoreactions are believed to be diabatic. In case (b) the excited and ground state surfaces approach closely at some geometry intermediate between reactant, R, and product, P. Near this geometry the radiationless transition probability is relatively higher because of the smaller energy separation. If return to S_0 is imagined to occur "to the left" of the maximum on this surface then reformation of R results. The overall process might be termed net photophysical. Crossing "to the right" of the maximum yields P, a net photochemical process. Clearly the distinction implied by the terms photochemical and photophysical may become less meaningful than the energy surface description. Case (b) also provides a picture of how reversible photochemistry can occur.

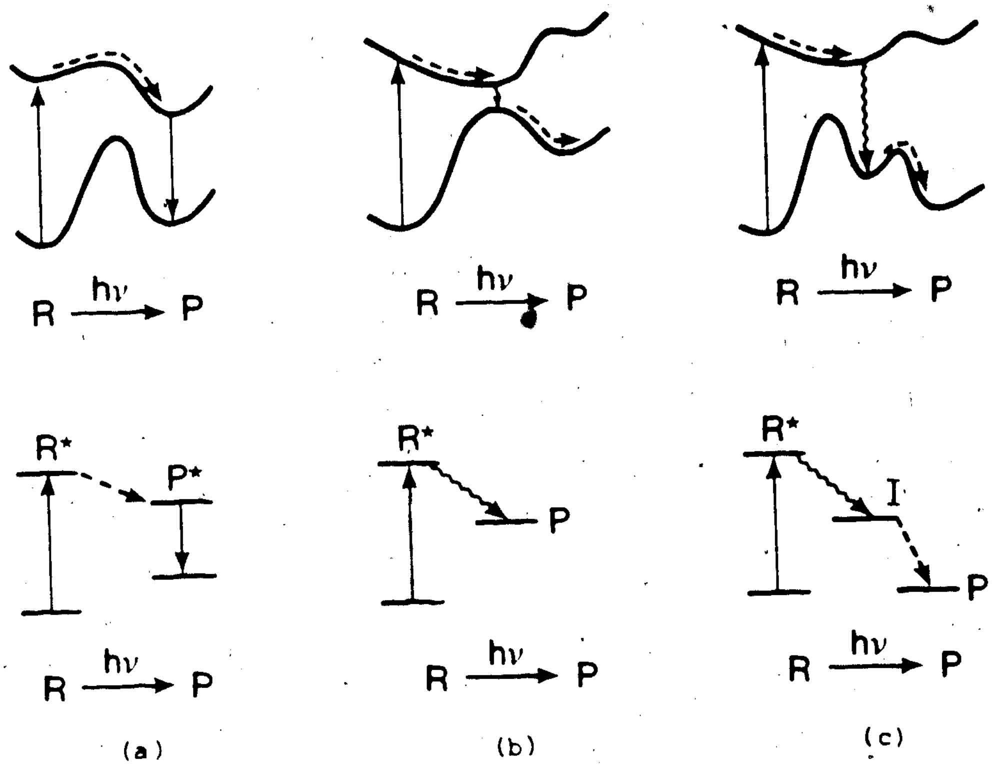
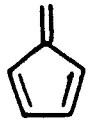


Figure 3. The classifications of photoreactions: (a) adiabatic, (b) diabatic, and (c) "hot" ground state reaction.

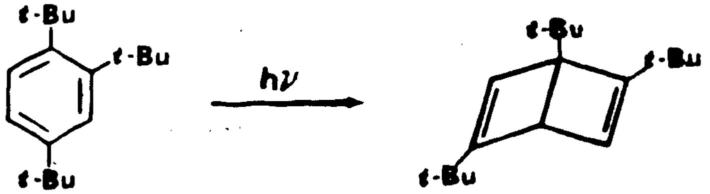
Case (a) represents an adiabatic photoreaction, because the conversion from reactant to product occurs entirely on the excited surface. Case (c) illustrates a "hot" ground state reaction. The intermediate, I, is formed in its ground state with sufficient excess energy to produce P. This is actually a specific case of a diabatic reaction.

B. Benzene Photoisomerizations

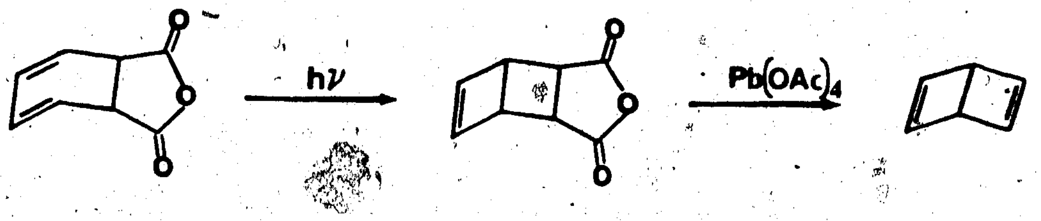
Prior to 1957 benzene itself was believed to be stable to UV irradiation. In that year however, Blair and Bryce-Smith [4] reported fulvene, **1**, formation on irradiation (254 nm) of liquid benzene. The first substituted Dewar benzene was obtained by van Tamelen and Pappas [5] in 1962. They rationalized that bulky substituents would stabilize the nonplanar bicyclohexadiene structure of Dewar benzene relative to the aromatic form, and proceeded to isolate 1,2,5-tri-t-butylbicyclo[2.2.0]hexa-2,5-diene (1,2,5-tri-t-butyl Dewar benzene). Shortly after they prepared the parent Dewar benzene [6] from the precursor:



1

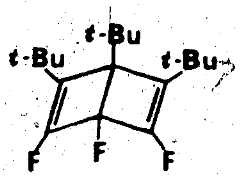


(1)



(2)

In 1964 Viehe et al. [7] isolated three important classes of benzene valence bond (VB) isomers. The Dewar, 2, Landenburg or prismane, 3, and benzvalene, 4, structures were all formed by the trimerization of t-butylfluoroacetylene.



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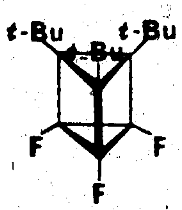

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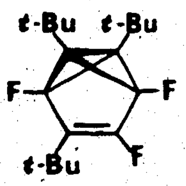


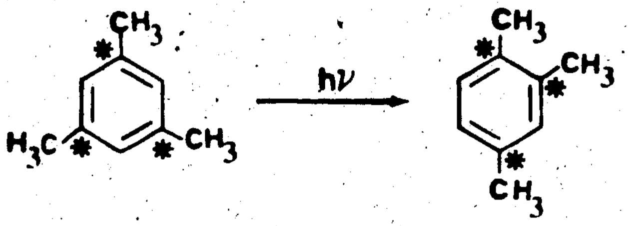
4

Although not isolated until comparatively recently the existence of such C_6H_6 VB isomers had been postulated much earlier. Dewar had illustrated his alternative to the Kekulé formulation of benzene almost one hundred years earlier [8]. Ladenburg's prismatic formulation dates from nearly that same time [9] and Hückel discussed a tricyclohexene structure in 1937 [10], though it later became known as benzvalene [7].

The UV photolysis of benzene is wavelength dependent. Irradiation of liquid benzene at 254 nm populates the S_1 state, producing a mixture of fulvene and benzvalene, but no Dewar benzene [11-15]. The quantum yields are ca. 0.01-0.03. Increasing the temperature promotes both fulvene and benzvalene formation with limiting concentrations of 300-500 mg/L of each isomer being obtainable from neat benzene at 50-60°C. There is evidence that fulvene may be a secondary product arising by benzvalene photolysis [14]. The irradiation of liquid benzene at shorter wavelengths produces Dewar benzene, fulvene and benzvalene [16]. Selective excitation of only the S_2 state demonstrated that it is the precursor to Dewar benzene [17].

Nearly coincident with the early reports of VB isomers were other investigations describing the photoisomerization of substituted benzenes. During UV photolysis apparent substituent migration occurred, generating at least one new positional isomer. The phototranspositions of alkyl groups in dialkyl benzenes were observed in different laboratories [18,19]. In each case o-dialkylbenzene photolysis produced the corresponding m- and p-dialkylbenzenes. Time studies revealed that the para isomer was formed by secondary photolysis of the m-dialkylbenzene.

From a mechanistic standpoint the 1,2-alkyl shift was suggested to occur by either radical formation, migration and recombination; or formation of a benzene isomer, such as Dewar benzene, prismane or benzvalene, followed by rearomatization to a new positional isomer. Burgstahler and Chien [19] suggested using an appropriately ^{14}C labelled benzene ring to distinguish the two mechanisms. Wilzbach and Kaplan [18] reported a small O_2 effect on xylene photoisomerization, concluding that neither radicals nor triplet states were involved. They also performed the ^{14}C labelling experiment [20]. Solution photolysis (254 nm) of 1,3,5-^{14}C-mesitylene (1,3,5-trimethylbenzene) produced some 1,2,4-trimethylbenzene. It was shown, by ozonolytic degradation, that this product was labelled exclusively in the 1, 2 and 4 positions, providing experimental proof for the phototransposition of the benzene ring carbon atoms. Thus positional isomerization was concluded to proceed via the formation and rearomatization of a VB isomer.



(3)

Subsequent photolysis studies of substituted benzenes may be divided into two categories: (a) formation of fulvenes, Dewar benzenes, prismanes and benzvalenes, and (b) formation of positional isomers presumably involving at least some category (a) members as intermediates. In most category (b) studies however, the intermediacy of such compounds has never been experimentally demonstrated.

The photoisomerization of tri-t-butylbenzenes [21] provided the first direct experimental evidence for a specific VB intermediate. Three tri-t-butyl VB isomers were isolated and determined spectroscopically to be the Dewar benzene, prismane and benzvalene. All three were stable at room temperature but underwent rearomatization after several hours at 100°C. The quantum yield for conversion of 1,3,5-tri-t-butylbenzene to the 1,2,4 isomer was 0.02 in methylpentane solution. Photolysis and thermolysis of each separated VB isomer showed that benzvalene was definitely an intermediate in the rearrangement. The prismane structure was formed from the Dewar isomer by an intramolecular [2+2] cyclization. There was some indication that either the Dewar or the prismane structure might be involved in the 1,3,5-tri-t-butylbenzene photoisomerization but this was not regarded by the authors as clearly established.

As will become apparent during this introduction, photolysis of completely perfluoroalkylated derivatives often generates stable VB isomers of benzene or the heteroaromatics. For instance, hexakis-(trifluoromethyl)benzene produced the corresponding Dewar, prismane and benzvalene isomers. The ratios of these isomers were time dependent due to their photochemical interconversion [22]. The isomers were much more resistant to thermal rearrangement than were the VB isomers of alkylbenzenes. Hexakis(trifluoromethyl) Dewar benzene had the greatest stability, rearomatizing with $t_{1/2} \sim 135$ h at 170°C in C_6F_6. The least stable isomer was the benzvalene, $t_{1/2} \sim 9$ h, under these conditions.

The photochemistry of benzene has been reviewed in detail in two articles by Bryce-Smith and Gilbert [23,24]. The first is an extensive two part review, concerned in Part 1 with photoisomerization reactions, and dealing in Part 2 with photoaddition and photosubstitution processes. Their more recent review covers both photochemical and nonphotochemical rearrangements of the benzene ring.

Although the rate of publications concerning benzene photoisomers has decreased markedly in the last decade some interesting studies have been reported recently. The photochemistry of fulvene, dimethylenecyclobutene, benzvalene and Dewar benzenes has been investigated [25]. The only product, formed in high yield from fulvene, benzvalene or Dewar benzene, was benzene. These results do not entirely agree with earlier experiments. For instance, Turro et al. [26] studied the direct and triplet sensitized photolysis of a dideuterobenzvalene, discovering that excitation energies lower than 270 $kJ \cdot mol^{-1}$ produce a [1,3]-sigmatropic rearrangement, while higher energies induce rearomatization. Photolysis of dimethylenecyclobutene produced polymer and no volatile products.

The kinetics of the gas phase thermal isomerization of some fluoro-Dewar benzenes has been investigated [27]. The photophysics of C_6F_6 was examined by picosecond techniques [28]. Two transient absorptions were detected, both of which decayed single exponentially and with lifetimes of 0.71 and 5.3 ns. The short-lived species was a $C_6F_6^+C_6F_6^-$ geminate pair formed in C_6F_6 clusters. The other absorption was attributed to an intermediate in the isomerization to the Dewar structure. This intermediate was assigned the biradical structure, **5**. The first study of the benzvalene radical cation was recently performed by mass spectrometry (MS) [29].

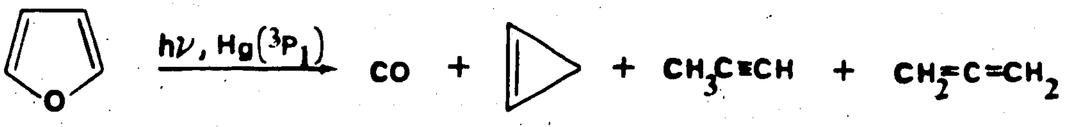
5

Although studies of benzene photoisomers continue, heterocyclic systems have become the focus during the past twenty years. A staggering number of heterocyclic compounds, differing in size, as well as in numbers and types of heteroatoms, have been photolyzed. Due to this explosive growth their literature is too cumbersome to describe in its entirety, and the brave reader is advised to seek those reviews which provide a broader scope [30-32]. For the present purpose only photoisomerizations of the heteroaromatics; furan, pyridine, pyrrole and thiophene, will be considered in detail. The material presented in each section is arranged essentially chronologically.

C. Photoisomerizations of the Heteroaromatics

1. Furans

Srinivasan investigated the direct irradiation and Hg($^3P_1$) photosensitization of furan vapour. The sensitized reaction led to decarbonylation and the formation of a C_3H_4 fraction consisting of cyclopropene and propyne, with small amounts of allene at high conversions, suggesting that the allene was formed by a secondary process [33,34]. A significant pressure dependence was discovered.



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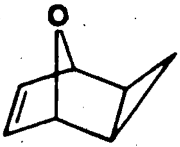
A maximum decarbonylation quantum yield of about 0.4 was reached at the lowest furan pressures utilized (~0.67 kPa) and the C_3H_4 fraction was primarily propyne (~80%) under these conditions. With increasing furan pressure the CO yield decreased and the cyclopropene/propyne ratio increased [34]. In addition, at furan pressures of 20-100 kPa two compounds of molecular formula C_7H_8O and one of formula $C_8H_8O_2$

were obtained. The former were exo, 6, and endo, 7, Diels-Alder adducts (DAa) of furan with cyclopropene, while the latter, 8, was its DAa with cyclopropene-3-carboxaldehyde. The stereochemistry of 8 was unknown [34,35].



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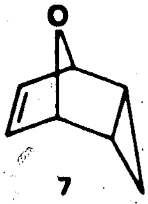

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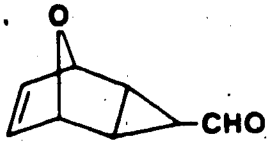

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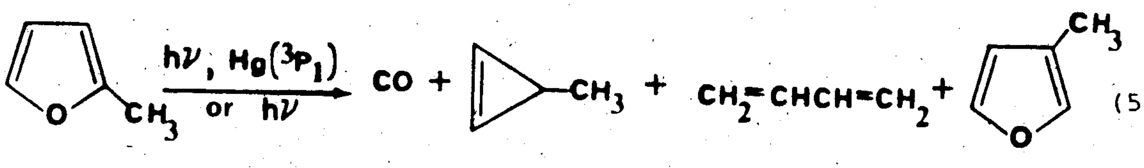
By comparison, the direct irradiation of furan vapour showed different behaviour from the photosensitized reaction [36]. The quantum yield for CO formation was pressure independent and propyne now constituted most of the C_3H_4 fraction, which also contained a substantial allene yield and little or no cyclopropene. Srinivasan also irradiated solutions of furan. Although the formation of an insoluble yellow solid indicated that photodecomposition had taken place, no fragmentation products or adducts similar to those from the gas phase experiments could be detected. Irradiation in the presence of methanol (10%) or cyclopentene (10%) also failed to produce adducts [34,35].

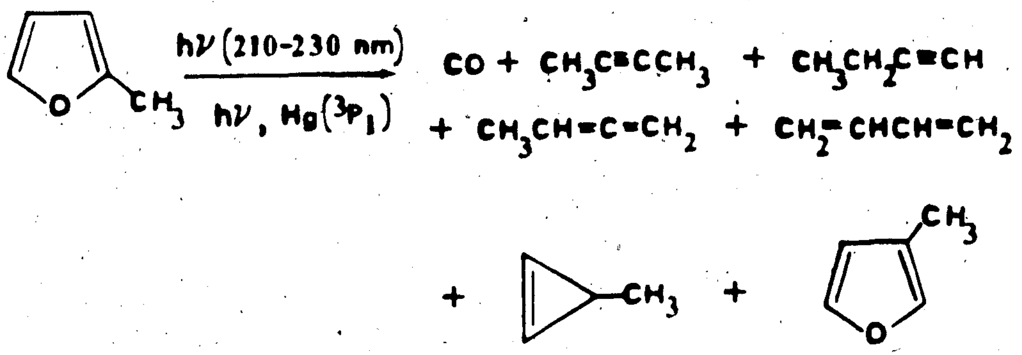
The photochemistry of alkylfurans showed the occurrence of positional isomerization. In the vapour phase, either direct irradiation or Hg($^3P_1$) photosensitization of 2-methylfuran gave decarbonylation products and 3-methylfuran [37]. Similarly, the direct irradiation of 2,5-dimethylfuran produced 2,4-dimethylfuran among other compounds. The photosensitized decomposition of 2,5-dimethyl-



(5)

furan was later studied in detail and yielded a complex product mixture [38]. Hg($^3P_1$) sensitization of 3-methylfuran led only to decarbonylation and 2-methylfuran was not detected [37].

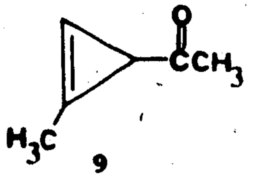
Subsequently, more complete details of the monomethyl furans were published [39]. In the case of both isomers more complex product mixtures were found. For instance, for 2-methylfuran,



(6)

Most importantly, while the photosensitized reaction of 3-methylfuran produced no 2-methylfuran as previously reported [37], the latter was formed in low yield on direct irradiation. The only cyclopropene detected in this photosensitized reaction was 1-methylcyclopropene. Under direct irradiation however, both 1-methyl and 3-methylcyclopropene were formed. The Hg($^3P_1$) photosenstized reaction of 2,4-dimethylfuran gave no isomeric dimethylfurans but a number of decarbonylation products were observed. The single cyclopropene product obtained in this case was 1,3-dimethylcyclopropene [39].

The above results prompted the suggestion of a common decarbonylation and photoisomerization mechanism for furan, with a cyclopropene carboxaldehyde intermediate central to both processes. Such a species had been trapped as its furan Diels-Alder adduct, **8**, in the photosensitization of furan vapour [35]. A footnote in this same paper reported the isolation of ketone 9, derived from 2,5-



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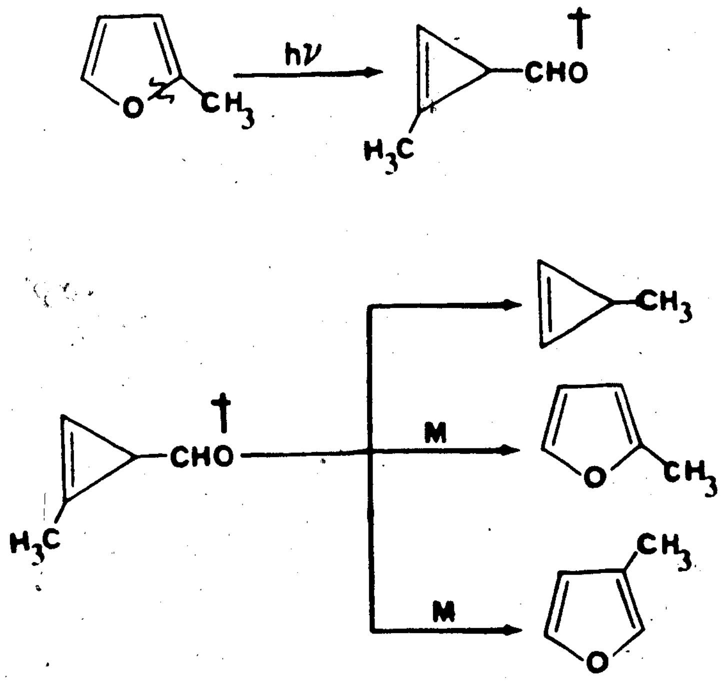
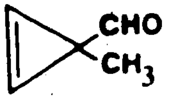
dimethylfuran. It was suggested that a consistency between the photoisomerization and decarbonylation results would exist if such intermediates were common to both systems. Scheme A summarizes the postulated 2-methylfuran mechanism. The initially generated 1-methylcyclopropene-3-carboxaldehyde must be vibrationally excited. It may decarbonylate to produce 3-methylcyclopropene or undergo ring expansion, generating a mixture of 2- and 3-methylfurans. Scheme A is incomplete because it does not include the pathways by which 3-methylcyclopropene molecules



Scheme A

containing excess vibrational energy isomerize to the ring-opened isomers shown earlier (reaction 6) as opposed to being vibrationally deactivated.

Hiraoka has used similar reaction schemes for the cases of 3-methyl and 2,4-dimethylfuran [39]. The crucial feature in his interpretation is a presumed selectivity in the initial furan ring opening that produces the cyclopropenyl derivative. As an example, in 3-methylfuran two possible ring openings can be imagined. If the initial bond rupture takes place in the C_5-O position then the cyclopropene carboxaldehyde formed, **10**, can decarbonylate giving 1-methyl



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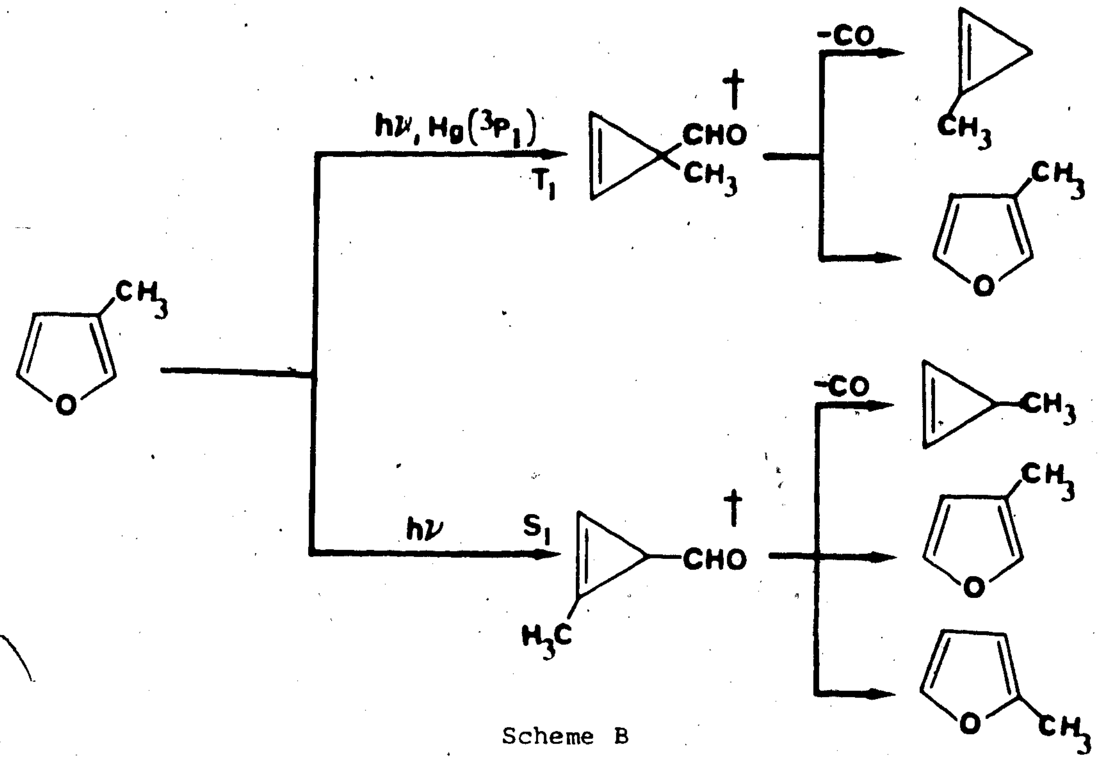
cyclopropene, which is detected experimentally, or regenerate 3-methylfuran. The formation of 2-methylfuran is not possible. However, if the C_2-O bond cleaves initially the same intermediate as from Scheme A is generated and the same products are therefore expected. Thus, the formation of both 1-methyl and 3-methylcyclopropene as well as of 2-methylfuran in the direct vapour phase photolysis of 3-methylfuran can be explained by initial C_2-O bond rupture (Scheme B). Presumably, some excited singlet furan formed on direct photolysis can undergo intersystem crossing to the triplet, thereby accounting for the appearance of 1-methylcyclopropene as a product.

Having reviewed the photochemistry of furan and the methylfurans, some discrepancies worthy of attention should be discussed.



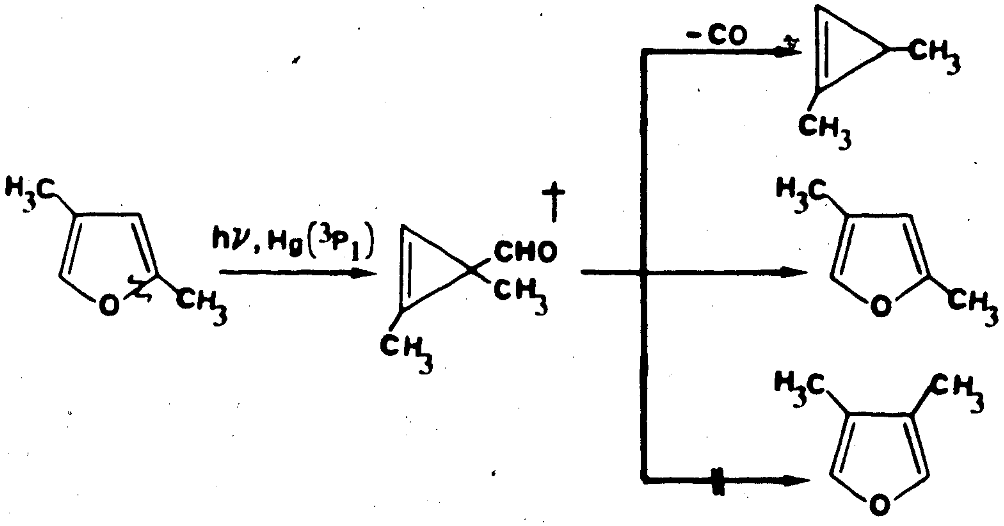
Scheme B

The failure of 3-methylfuran to rearrange to 2-methylfuran in the photosensitized reaction implies a singlet precursor to the intermediate responsible for this rearrangement. That 2-methylfuran will produce 3-methylfuran either upon direct photolysis or triplet sensitization probably suggests a triplet precursor to this same intermediate.

2,5-Dimethylfuran isomerized to the 2,4 isomer on direct irradiation [37], but not in the photosensitized reaction [38] despite the reported isolation of (2-methyl-2-cyclopropenyl) methyl ketone, **9**, from the photosensitized system [34]. To be consistent with Schemes A and B, compound **9** should be the intermediate responsible for the rearrangement of 2,5-dimethyl- to 2,4-

dimethylfuran [35,37].

Sensitization of 2,4-dimethylfuran yielded CO and 1,3-dimethylcyclopropene. The suggested intermediate did not generate 3,4-dimethylfuran, but no reason for this behaviour was provided (Scheme C). Unfortunately, the direct photolysis of 2,4-dimethylfuran has not been reported so it is not known whether positional photoisomerization via a singlet precursor can occur for this molecule. The furan ring contractions observed experimentally have, in at least some cases, been supported by Hückel type MO calculations which



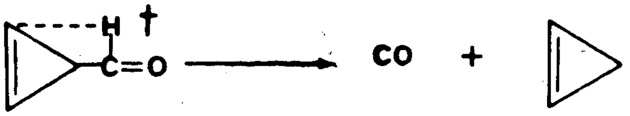
Scheme C

indicate the weakest C-O bond in the first excited state, assuming that it is selectively cleaved [39].

Hiraoka and Srinivasan [36] have suggested that the difference in the behaviour of furan on direct irradiation and $Hg(^3P_1)$ photosensitization indicates inefficient intersystem crossing for the excited singlet state of furan, and that cyclopropene formation is a significant test for the presence of triplet furan. In an attempt to exclude the possibility that the different behaviour resulted from a difference in the energetics of the two excitation techniques, two direct irradiation experiments, employing a filter system which isolated light from the range λ ~ 260-280 nm, were performed. Even under these conditions cyclopropene was at best only a trace product [36]. However, the thermal decomposition of cyclopropene to propyne is known [40] and a dramatic influence of furan pressure on the cyclopropene/propyne ratio was found in the photosensitized case [34].

The effect of O_2 on furan photochemistry has often been reported [34,36,37]. Even a large excess of O_2 did not arrest photoisomerization or decarbonylation although the efficiency of both was reduced. The presence of O_2 was intended as a test for free radical processes. It was concluded that with limited exceptions, relating to the formation of some minor products [38], free radical processes were unimportant.

Decarbonylation of cyclopropenyl intermediates was envisioned to proceed by an intramolecular route. The inability of O_2 to eliminate fragmentation products precluded a free radical mechanism for their formation.



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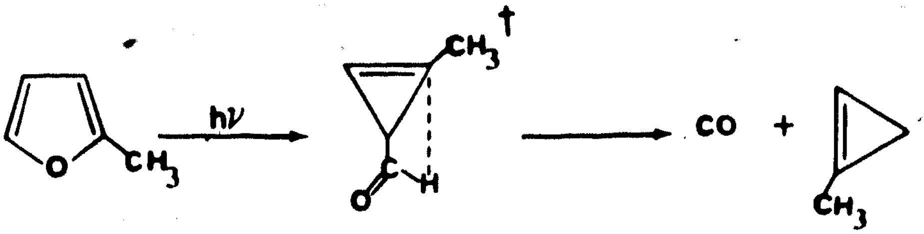
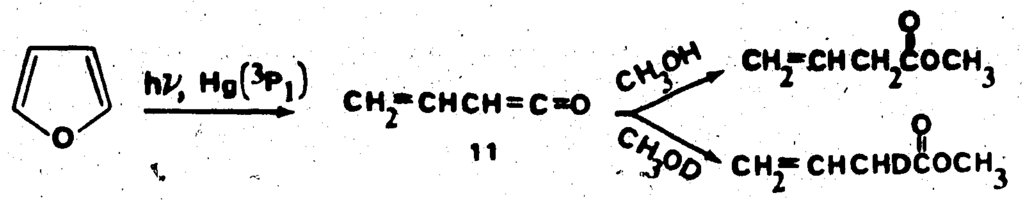


(8)

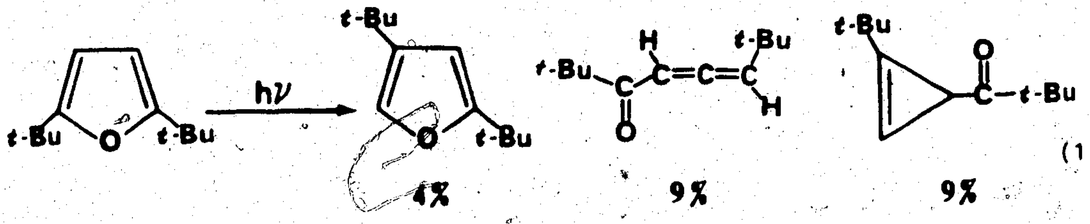
Little quantum yield data for the photoisomerization and decarbonylation are available. A significant complication, only occasionally acknowledged [34], was polymer formation. The polymer complicates quantitative experimants by coating the cell walls, thereby reducing the incident light intensity. Due to its insolubility very little information was gathered about the nature of the polymer. The infrared spectrum of the polymer obtained from the photolysis of furan solutions displayed a strong broad carbonyl absorption centred near 1715 cm^{-1}. The total absence of any aldehyde C-H stretching absorptions suggested that the carbonyl group was not incorporated in an aldehyde functionality. In general, product quantum yields in furan photochemistry were pressure dependent. For the $Hg(^3P_1)$ sensitization of furan itself ϕ_{CO} can be as large as 0.4 [33,39] but decreases at higher substrate pressure. The quantum yields for positional photoisomerization of substituted furans are not reported directly but can be estimated to be roughly an order of magnitude smaller than ϕ_{CO} at low pressure, increasing slightly with increasing pressure [39].

Another interesting species apparently formed during the $Hg(^3P_1)$ sensitization of furan was 1,3-butadienone (vinylketene), **11**. In the presence of CH_3OH or CH_3OD methyl esters of 3-butenoic acid were isolated. The esters were presumed to arise from methanol addition to **11**.



(9)

Nearly coincident with the earliest gas phase results on furan and the methylfurans, van Tamelen and Whitesides published similar results for t-butylfurans [41,42]. Direct irradiation (λ > 220 nm) of 2,5-di-t-butylfuran, **12**, in deoxygenated pentane solution induced photoisomerization to the 2,4 isomer. 50% of **12** was consumed in 1 h and three isomeric products were isolated, **13-15**. The product yields, based on consumed **12**, showed that 78% of the furan which



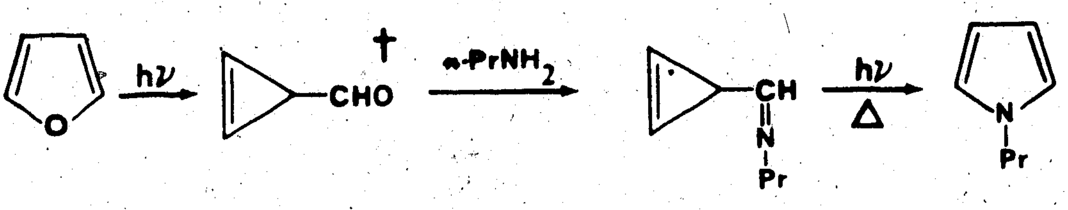
(10)

12 **13** **14** **15**

reacted was converted to insoluble products. On direct irradiation of **15** under similar conditions 84% was consumed in 0.25 h giving a mixture of **12** (9%), **13** (14%) and **14** (23%). Again, polymer formation presumably accounted for the remaining mass balance. The authors concluded that **15** was a true intermediate in the photoisomerization of **12**. A time study of the product ratios **13/15**, **14/15** and **13/14** designed to prove that **15** was the photoisomerization intermediate, unfortunately did not demonstrate that **13** and **14** are both formed from

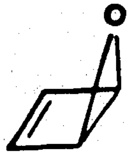
15 as opposed to some other intermediate.

Lablache-Combier <u>et al.</u> [43,44] have carried out the direct irradiation (185, 254 nm) of furans in deoxygenated n-propylamine. They isolated 1-propylpyrroles which they claimed were derived from the reaction of a cyclopropenyl intermediate with the solvent.



(11)

Table 1 summarizes the pyrrole products obtained from furan and its mono- and dimethyl derivatives. It is curious that the photolysis of 2-methylfuran leads to the isolation of both possible monomethyl-1-propylpyrrole isomers, while 3-methylfuran generates only 3-methyl-1-propylpyrrole. This result seems contradictory to Hiraoka's finding that the 2→3 transformation is reversible in the direct photolysis of methylfuran [39]. At a later date, Lablache-Combier <u>et al.</u> [44] implicated the bicyclic intermediate, Dewar furan **16**, in

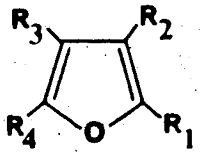
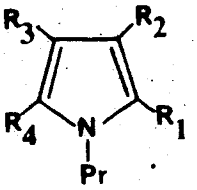


16

rationalizing the recovered pyrroles. The Dewar type structure has its historical roots in benzene photochemistry, already described. The possible involvement of Dewar VB isomers in heterocyclic photorearrangements had sometimes been mentioned, particularly for thiophenes, which will shortly be discussed. Furan researchers had previously given little consideration to a bicyclic intermediate because of the known formation of cyclopropenyl compounds.

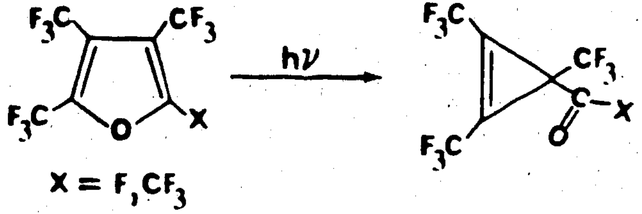
TABLE 1

Pyrrole Products Recovered from the Photolyses of Furans in Propylamine

Initial Furan	Pyrrole Recovered
	
$R_1 = R_2 = R_3 = R_4 = H$	$R_1 = R_2 = R_3 = R_4 = H$
$R_1 = CH_3$, $R_2 = R_3 = R_4 = H$	$R_1 = CH_3$, $R_2 = R_3 = R_4 = H$ + $R_2 = CH_3$, $R_1 = R_3 = R_4 = H$
$R_2 = CH_3$, $R_1 = R_3 = R_4 = H$	$R_2 = CH_3$, $R_1 = R_3 = R_4 = H$
$R_1 = R_4 = CH_3$, $R_2 = R_3 = H$	$R_1 = R_4 = CH_3$, $R_2 = R_3 = H$ + $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$
$R_1 = R_3 = CH_3$, $R_2 = R_4 = H$	$R_1 = R_3 = CH_3$, $R_2 = R_4 = H$

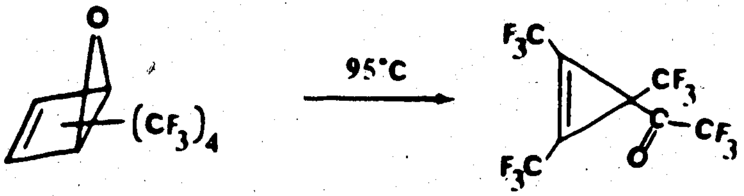
Hiraoka [45,46] also detected a cyclopropenyl carboxaldehyde derivative from 2-cyanofuran. Direct irradiation (254 nm) in methanol led to the formation of solvent adducts with the unsaturated aldehyde. Photoisomerization to 3-cyanofuran was not reported and irradiation of 3-cyanofuran in methanol failed to produce any photoaddition products [46].

Much more recently the photochemical transformations of perfluorotri- and tetramethylfuran were investigated [47]. It was hoped that these furans might generate stable Dewar VB isomers, by analogy to the thiophene systems to be described later. Direct gas phase photolysis of these furans always yielded only the cyclopropenyl derivatives with no evidence of a Dewar furan.



(12)

The very first Dewar furan was recently synthesized by Wirth and Lemal [48]. Perfluorotetramethyl Dewar furan underwent a clean thermal isomerization to the cyclopropenyl ketone ($t_{1/2} \sim 0.3$ h at 95°C) rather than rearomatization. This Dewar furan is a very



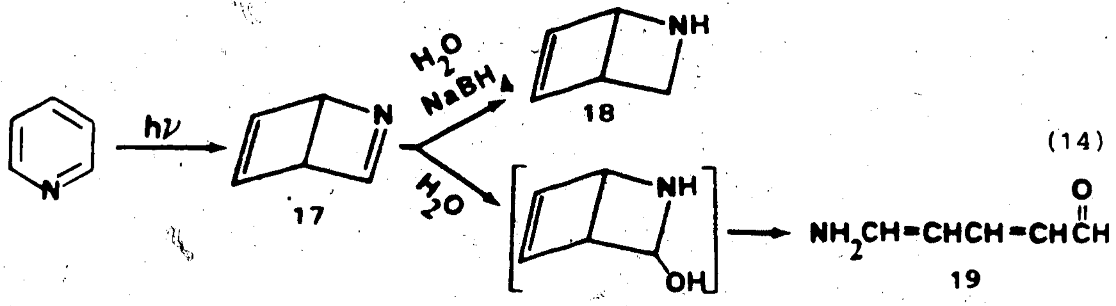
(13)

reactive dienophile, undergoing cycloaddition to furan at 25°C at a rate three orders of magnitude faster than the corresponding Dewar thiophene.

2. Pyridines

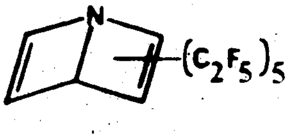
The first pyridine VB isomer was reported by Wilzbach and Rausch

[49] in 1970. They formed the Dewar pyridine, 2-azabicyclo[2.2.0]-hexa-2,5-diene, **17**, in the liquid phase photolysis (254 nm) of pyridine. Both the observed photoreduction to 2-azabicyclo[2.2.0]hex-5-ene, **18**, in aqueous sodium borohydride and the photohydration to 5-amino-2,4-pentadienal, **19**, were proposed to proceed via the Dewar intermediate. A quantum yield of 0.05 at 254 nm was calculated for the formation of **17**. It was thermally unstable, reverting quantitatively to pyridine with $t_{1/2} \sim 2.5$ min at 25°C. At 0°C the half-life increased to 36 min. Photolysis of monomethyl- and dimethylpyridines, known as picolines and lutidines, respectively, also formed thermally unstable isomers which were reduced by $NaBH_4$ and hydrolyzed by H_2O.



(14)

Almost simultaneously Barlow et al. [50] photolyzed pentakis-(pentafluoroethyl)pyridine and isolated not only a Dewar pyridine, **20**, but also the corresponding prismane, **21**. The prismane was found



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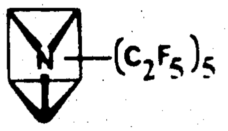

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during shorter wavelength photolysis experiments and was presumed to form by an internal cyclization in the Dewar structure. Both isomers, 1-azabicyclo[2.2.0]hexa-2,5-diene, **20**, and 1-

azatetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane, **21**, display the considerable thermal stability characteristic of perfluoroalkylated VB isomers of benzene and the heteroaromatics. For instance, thermolysis of **20** in hexafluorobenzene at 170°C resulted in pyridine formation with $t_{1/2}$ = 104 h, while under the same conditions **21** had $t_{1/2}$ = 1.1 h and produced a mixture of pyridine, **20**, and a third unidentified component.

The Dewar pyridine isomer described by Wilzbach and Rausch was different from that of Barlow <u>et al.</u> Two Dewar isomers of pyridine can be imagined. If Dewar formation occurs by 2,5-bonding in pyridines a 2-azabicyclo[2.2.0]hexa-2,5-diene, **17**, results, whereas 1,4-bonding produces a 1-azabicyclo[2.2.0]hexa-2,5-diene, **20**. Both CNDO/2 [51] and MNDO [52] MO calculations indicate the 2-aza isomer to be the more stable Dewar form. Thus the calculated energy differences between pyridine and the 1-aza and 2-azabicyclo isomers are roughly 170 and 97 kJ•mol^{-1}, respectively. Therefore the 2,5-bonded isomer, the probable intermediate obtained by Wilzbach and Rausch [49], is more stable by <u>ca.</u> 70 kJ•mol^{-1}. The total energies of these Dewar isomers are minimized when the dihedral angle between the four-membered ring planes, θ, is around 115°. The calculated enthalpies of activation for reversion to pyridine were 128.0 kJ•mol^{-1} for the 1-aza isomer and 124.2 kJ•mol^{-1} for the 2-aza compound. The enthalpy of activation for the reversion of Dewar benzene to benzene was calculated in the same study [52] to be 124 kJ•mol^{-1}.

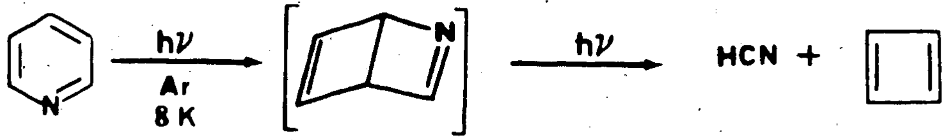
The gas and liquid phase photochemistry of picolines and lutidines were also described by Lablache-Combier <u>et al.</u> in 1970 [53,54]. Gas phase photolysis (254 nm) of picolines produced isomeric picolines, plus lutidenes and pyridine. Lutidenes yielded only other dimethylpyridine isomers on irradiation. The photolytic interconversion of 2- and 4-picoline was actually first reported by Pascual and Tuazon [55], but their work was later repeated and extended [53]. In the gas phase experiments of Caplain and Lablache-Combier [53] polymer formation was extensive. Hg($^3P_1$) sensitization led to the same results as direct photolysis. Lutidene and pyridine formation on picoline photolysis seemed to involve a methylation-demethylation process, while the reversible photoisomerization of 2- and 4-picoline presumably arose by C_2-C_4 interchange in the pyridine ring. The photolytic conversion between lutidene positional isomers was similarly explained, with a more complex set of carbon atom exchanges which involved valence bond isomers similar to those which had just been recently discovered [49,50].

Photolysis (254 nm) of 2-picoline in cyclohexane solution produced, in addition to 4-picoline, two compounds formed by reaction with the solvent: 4- and 6-cyclohexyl-2-methylpyridine [54,56]. 4-Picoline led to 2-picoline and the same substitution products. The cyclohexylpicolines were concluded to be formed by a radical mechanism with a common intermediate involved in both cases. Radical formation during UV photolysis in solution had previously been reported by Wynberg <u>et al.</u> [57] for 3,5-dicarboalkoxy-2,4,6-trimethylpyridines.

The photolysis of polychloropyridines has also been studied. In each case the formation of a pyridyl radical was followed by reactions such as proton abstraction from the solvent or intramolecular cyclization of an appropriately substituted pyridine [58].

Heicklen and Mathias [59] irradiated (214, 229 nm) pyridine vapour at 25 and 260°C. The $Hg(^3P_1)$ sensitized decomposition was also carried out at 25°C. The primary products from the direct photolysis were C_2H_2 and CH_2CHCN. More extensive photolysis produced as additional secondary products: H_2, CH_4, C_2H_4, CH_3CHCH_2, CH_2CCH_2, CH_3CCH, $(CH_3)_2CCH_2$ and polymer. In addition, indirect evidence was obtained for an unknown product concluded to be a short-lived isomer of pyridine. The direct photolysis results were essentially the same at 25 and 260°C but with differences in the amounts of C_2H_2, CH_2CHCN and polymer formed. The sensitized pyridine decomposition proceeded by a different, unspecified, mechanism.

The photodecomposition of pyridine was studied by Chapman *et al.* [60] in a low temperature matrix IR experiment. HCN and cyclobutadiene were produced on secondary photolysis, presumably through a 2-azabicyclo[2.2.0]hexa-2,5-diene intermediate although no absorptions attributable to this intermediate were described.



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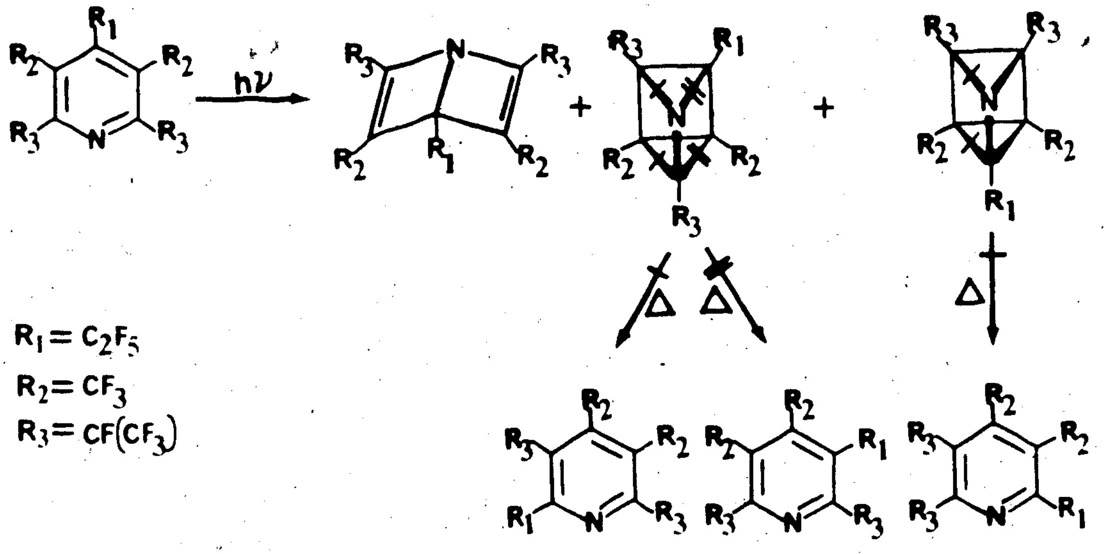
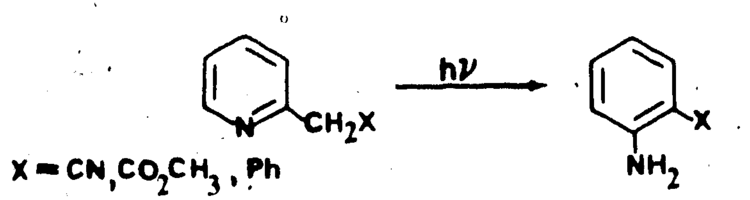
2,4,6-Trimethyl-3,5-bis(trifluoromethyl)-1-azabicyclo[2.2.0]-hexa-2,5-diene forms stable transition metal complexes with Pt(II) and Pd(II) salts. Complex formation was monitored by ^1H and ^{19}F NMR. At room temperature the Dewar pyridine in the complexes slowly rearomatized. The chemical reactivity of this Dewar pyridine, including the kinetics of its thermal rearomatization, have been studied [61].

Chambers and coworkers have photolyzed (254 nm) a symmetrically pentasubstituted perfluoroalkyl pyridine, producing one Dewar and two azaprismane isomers [62]. Thermolysis of the azaprismanes regenerated positional isomers of the initial pyridine (Scheme D). The unsymmetrically substituted azaprismane was assumed to have been formed from the appropriately substituted Dewar isomer, but the latter was not isolated. Irradiation of various perfluorotri- and tetraalkylpyridines produced the first 2-azabicyclo[2.2.0]hexa-2,5-diene derivatives having notable thermal stabilities [63].



Scheme D

The solution phase photorearrangement of substituted 2-methylpyridines to 2-substituted anilines occurred possibly by interchange of the N atom with the adjacent C atom carrying the substituent. The



(16)

intermediacy of Dewar pyridine, azaprismane and azabenzvalene structures was considered [64], and Dewar pyridine derivatives were later isolated [65].

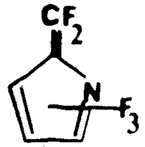
Complexes between cyclobutadienes and $AlCl_3$ reacted with nitriles to yield pyridines, where Dewar pyridines must be the intermediates [66].

A study of the mass spectra of ^{13}C and ^{15}N labelled 2-, 3- and 4-cyanopyridines showed that molecular ions fragmenting during the time frame from 1 to 10 μs displayed positional interchange of C_2, C_4 and C_6 prior to HCN loss. In addition, the labelling revealed that in each cyanopyridine the two N atoms were completely scrambled before HCN expulsion. While the carbon atom scrambling was postulated to occur via a Dewar pyridine$^{+\bullet}$ that of the N atoms was believed to proceed by a 1,4-dicyano-1,3-butadiene intermediate, **22** [67]

$$[CNCH{=}CHCH{=}CHCN]^{+\bullet}$$

22

Rec[illegible]ly, continuous gas phase photolysis and conventional flash photolysis studies have been applied to C_5F_5N [68]. The former produced pentafluoro-2-azabicyclo[2.2.0]hexa-2,5-diene ($t_{1/2}$ = 120 h, ~25°C). Flash photolysis revealed two transient UV absorptions decaying with $t_{1/2}$ = 22 and 3 ms. As the transient absorptions disappeared the pentafluoropyridine signal reappeared. No stable photoproducts were found after flash photolysis. O_2 did not affect the measured decay times, indicating that the transient absorptions were not due to triplet states or to free radicals. When the flash photolysis was monitored by time-of-flight mass spectrometry the presence of a CF_2^+ ion (m/e 50) was revealed [68,69]. This ion was associated with the species responsible for the transient UV absorptions and therefore the fulvene type structures below were assigned to the transients.



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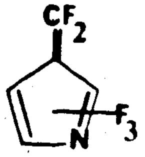

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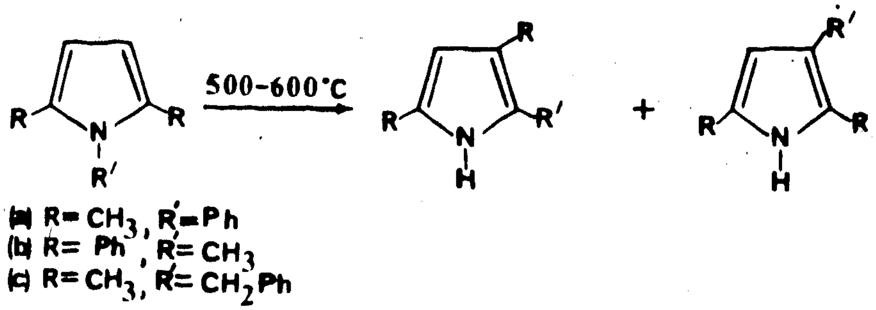
3. Pyrroles

Pyrrole isomerizations are more complex in the sense that both thermal and photochemical rearrangements have been detected, often for the same molecules. For this reason it was decided to include in this presentation a brief account of some thermal isomerizations of pyrroles.

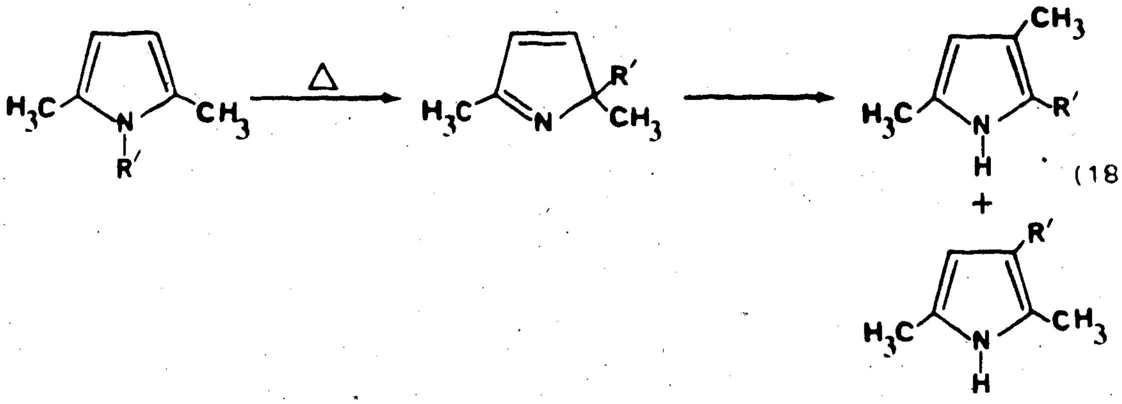
In 1-substituted pyrroles rearrangement occurred thermally at 500-600°C. Alkyl [70] and benzyl [71] substituents at the N atom migrated to the 2 and 3 positions of the pyrrole ring by a unimolecular process. By comparison, 1,2,5-trisubstituted pyrroles rearranged more readily despite blocking of the 2 and 5 positions of the pyrrole ring. Patterson and Soedigdo [72] described the flow pyrolysis of the trisubstituted pyrroles below. The isomeric



(17)

products were formed in equal amounts except in the last case, where the 3-benzyl isomer predominated.

A pyrrolenine or 2-H pyrrole intermediate was postulated for the thermal isomerization of a 1-substituted 2,5-dimethyl pyrrole [72,73]. No pyrrolenine intermediates were isolated from pyrolysis



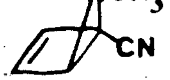
(18)

mixtures but the pyrolysis of 2-benzyl-2,5-dimethyl-2H-pyrrole at different temperatures produced the isomers 3-benzyl-2,5-dimethyl- and 2-benzyl-3,5-dimethylpyrrole in the same ratio as the 1-benzyl-2,5-dimethylpyrrole pyrolysis, thus implicating the pyrrolenine species as an intermediate in the thermal isomerization.

Patterson and Burka [74] were the first to report the photoisomerization of pyrroles. Irradiation (254 nm) of neat 1-benzylpyrrole produced the 2- and 3-substituted isomers in a 5/1 ratio, respectively. Decomposition and polymerization also occurred but was estimated to be less than 5%. The rate of product formation more than doubled in methanol solution. Photolysis of 2- or 3-benzylpyrrole gave only decomposition. Direct photolysis of a 2H-pyrrole did not produce the 3-substituted isomer, suggesting an intermediate different from the thermal isomerizations [72,73]. The authors could not exclude the possibility that the 3-benzylpyrrole formed in the photochemical reaction might have come from thermal isomerization of 2-benzylpyrrole.

The first 2→3 photoisomerization of pyrroles was not reported until 1970 [75]. At least superficially, the results were similar to the photorearrangements already known for furans and thiophenes. Direct irradiation (254 nm) of 2-cyanopyrrole in methanol gave a single photoproduct, 3-cyanopyrrole. 2-Cyanopyrrole thermolysis in methanol at 180°C for 4 h did not produce any 3 isomer showing that, unlike the 1→2 and 1→3 isomerizations of pyrroles, the 2→3 process was exclusively photochemical. The products from the solution photolysis of 1-methyl-2-cyanopyrrole included 1-methyl-3-cyanopyrrole, 2-methyl-2-cyano-2H-pyrrole and a methanol adduct. The methanol adduct **25** was assumed to have been formed by addition of the alcohol to the Dewar structure, **26**. Thermolysis of **25** at 186°C produced methanol and 1-methyl-3-cyanopyrrole, with none of the 2-cyano isomer [76].

25



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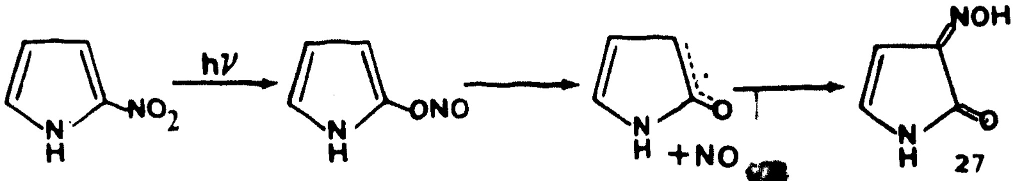
Hunt and Reid [77] have observed a very different behaviour for 2-nitropyrrole as compared with that of 2-cyanopyrrole. Direct irradiation (λ > 280 nm) in acetone produced 3-hydroxyimino-2-oxo-2,3-dihydropyrrole, **27**. The mechanism was suggested to involve rearrangement to the nitrite followed by thermal or photochemical cleavage to NO and a furyloxy radical, and radical recombination at C_3. Precedents for this kind of rearrangement had previously been established by Chapman et al. [78] as well as Reid et al. [79].

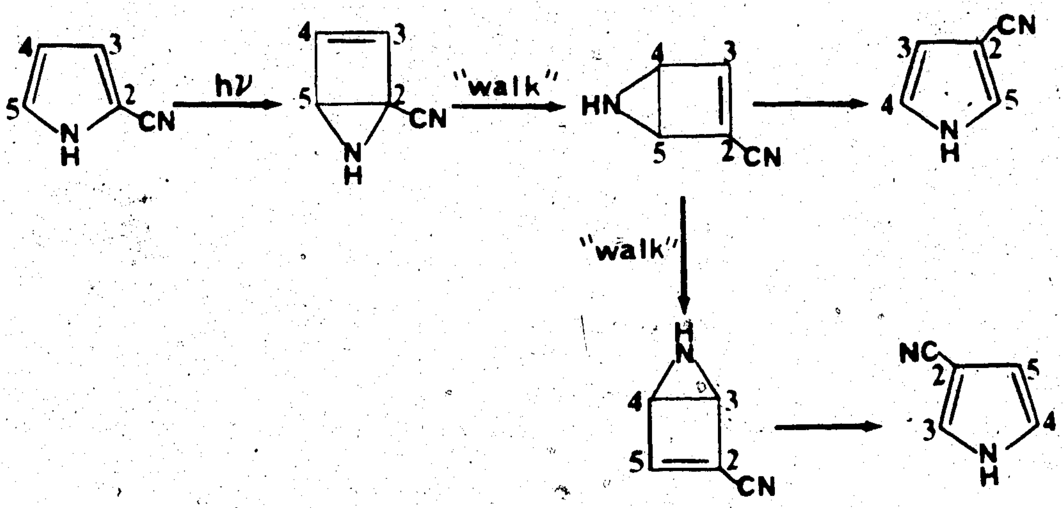


(19)

Wu and Heicklen investigated the vapour phase photolysis of pyrrole [80] and, later, 2,4- and 2,5-dimethylpyrroles [81]. Until then the photochemistry of the parent pyrrole had received almost no attention. One earlier study [82] of its flash photolysis described a transient free radical tentatively assigned as $\bullet CH_2CH{=}CHCN$ based on the similarity of its absorption spectrum with that of the radical produced in the flash photolysis of 3-butenenitrile (allyl nitrile, $CH_2{=}CHCH_2CN$) and 2-butenenitrile (crotyl nitrile, $CH_3CH{=}CHCN$). The vapour phase photolysis of pyrrole (214 nm) and dimethylpyrroles (214, 229 nm) produced many decomposition products. For instance, pyrrole yielded CH_3CCH, CH_2CCH_2, C_2H_2, C_2H_4, H_2, CH_4, CH_3CHCH_2, HCN and polymer. The use of NO or O_2 as free radical scavengers showed that C_2H_4 and most of the H_2 arose from radical precursors. CH_4 and CH_3CHCH_2 were secondary products, also of radical origin, resulting from H atom reactions with C_3H_4 species. Product quantum yields were determined as a function of pressure and a detailed mechanism explaining the formation of all the primary and secondary products was proposed. The quantum yields for ring cleavage products from pyrrole were very small (~0.05-0.001) and it seems, although this was not clearly stated, that polymer formation was a major process.

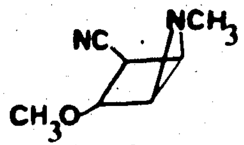
By contrast, dimethylpyrroles gave no ring cleavage products. H_2, CH_4, C_2H_6 and polymer, all of free radical origin, were obtained. Their quantum yields were low (~0.1-0.01) and generally insensitive to changes in substrate pressure, incident light intensity and incident wavelength. No photoisomerization products were detected.

More recently Barltrop et al. investigated the photolysis of cyanopyrroles [83,84]. Solution photolysis of all three possible monomethyl 2-cyanopyrrole isomers produced in each case a monomethyl 3-cyanopyrrole [83]. The authors employed their permutation pattern technique, first introduced to analyze phototransposition reactions of six membered aromatic rings [85], to determine a possible valence bond intermediate consistent with the observed products. The significance of permutation pattern analysis lies in the recognition that during photoisomerization by scrambling of the ring C atoms, only those atoms carrying a unique substituent can definitely be located both before and after rearrangement. Accounting for the different possible locations of "unlabelled" ring C atoms often produces a small set of different permutation patterns consistent with the observed rearrangement. Different patterns may involve different intermediates. Studying all the possible permutation patterns for each monomethyl 2-cyanopyrrole rearrangement and searching for a common pattern, the authors suggested that the initial step was 2,5-bonding in the pyrrole ring to produce a bicyclic Dewar pyrrole like that earlier trapped by Hiraoka [76]. The observed products were stated to be formed by single or double [1,3]-sigmatropic shifts of the N atom, followed by rearomatization. This mechanism involves a stepwise "walking" of the N atom about the cyclobutene ring until the appropriate Dewar precursor to the observed pyrrole product is reached and rearomatization occurs. Scheme E shows the two possible walking steps that can transform 2-cyanopyrrole into 3-cyanopyrrole. Later, solution phase trapping experiments [84] were successful in intercepting the Dewar pyrrole.



Scheme E

Irradiation (254 nm) of 1-methyl-2-cyanopyrrole in methanol produced an adduct, **28**, similar to that reported by Hiraoka [76] except that Barltrop et al. assigned it a structure having the cyano substituent at C_3. In furan solution 1-methyl-2-cyanopyrrole gave two furan DAa



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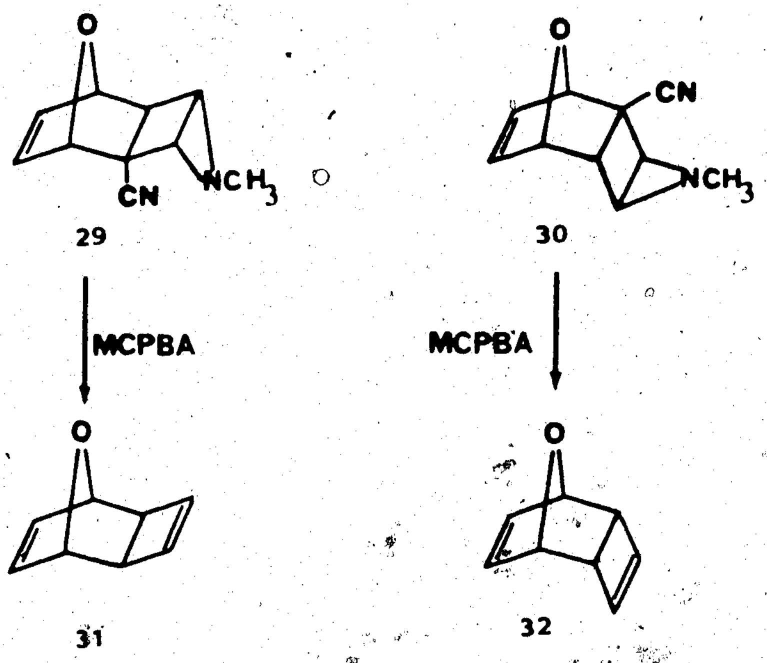
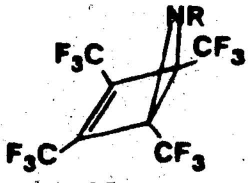
with a 3-cyano Dewar pyrrole, **29** and **30**. These structures were assigned on the basis of the ^1H NMR spectra of the adducts and the corresponding tricyclic dienes, **31** and **32**, obtained by treatment with m-chloroperoxybenzoic acid (MCPBA). The stereochemistry of **29** and **30** was presumably decided in part from steric considerations since the reported NMR data [84] were probably insufficient to permit the stereochemistry to be determined. Evidence that the trapped Dewar



pyrroles were intermediates in the photoisomerization of 2-cyano-pyrroles was obtained by pyrolysis of a furan photoadduct with 2-cyano-5-methylpyrrole. When heated at 175°C for 3 h this adduct generated furan and four isomeric pyrroles. The two major pyrroles were the 2-cyano-5-methyl and 3-cyano-2-methyl isomers. The latter had been previously reported [83] as the major photolysis product from 2-cyano-5-methylpyrrole. Of the two pyrroles found as minor pyrolysis products, one was previously identified [83] as a minor product of the photolysis of 2-cyano-5-methylpyrrole. In order to explain the appearance of four disubstituted pyrrole isomers in the pyrolysis experiment it was suggested that the first bicyclic intermediate formed in the Diels-Alder retrogression could undergo one or more "nitrogen walking" steps before aromatization occurred. The aromatization process presumably competes with the "nitrogen walking". However, although the authors do not comment on this, it is obvious that if all the pyrrole products arise from the same initial Dewar pyrrole formed in the Diels-Alder reversion then the ratios of the disubstituted pyrrole products obtained are not clearly consistent with the number of walking steps required to attain the correct isomer. In any case, Barltrop <u>et al.</u> concluded that pyrrole photoisomerization occurs by interconversion and rearomatization of bicyclic intermediates which are primary photoproducts.

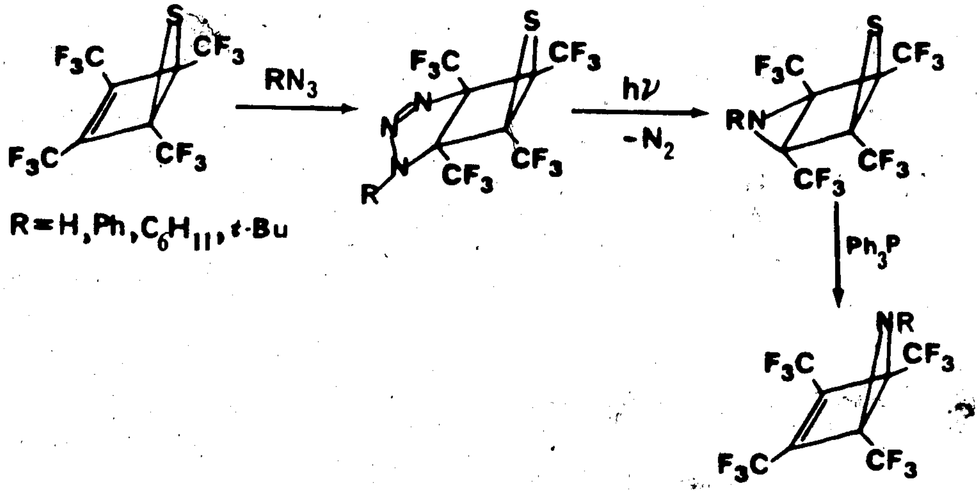
Kobayashi <u>et al.</u> [86] have studied some 1-substituted Dewar pyrroles. All were perfluorotetramethyl derivatives prepared from perfluorotetramethyl Dewar thiophene. Initial reaction of the thiophene with the appropriate azide formed a triazoline derivative,



R = H, Ph, C_6H_{11}, t-Bu

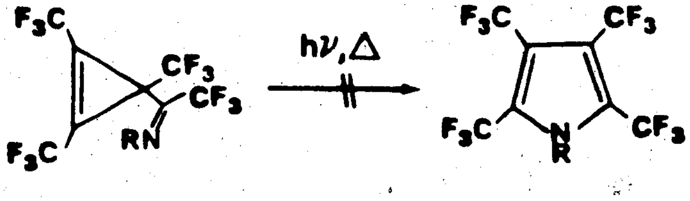
33

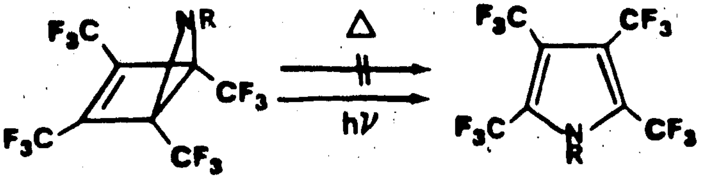
which was then photolyzed to cause N_2 elimination and finally desulfurized to the pyrrole (Scheme F). These Dewar pyrroles underwent Diels-Alder cycloaddition with a variety of dienes including furan, 2,5-dimethylfuran, pyrrole, cyclopentadiene, 1,3-butadiene and 2,3-dimethylbutadiene.



Scheme F

Recently Kobayashi et al. [87] prepared Dewar pyrroles and cyclopropenyl imines stabilized by trifluoromethyl substituents. Neither thermolysis nor photolysis of the cyclopropenyl imines converted them to pyrroles, and photolysis, but not thermolysis, of the Dewar compounds produced pyrroles. Consequently, the authors concluded that neither Dewar pyrroles nor cyclopropenyl imines are intermediates in the photoisomerizations of pyrroles (Scheme G).

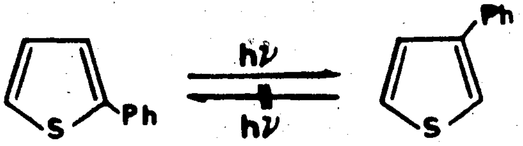




Scheme G

4. Thiophenes

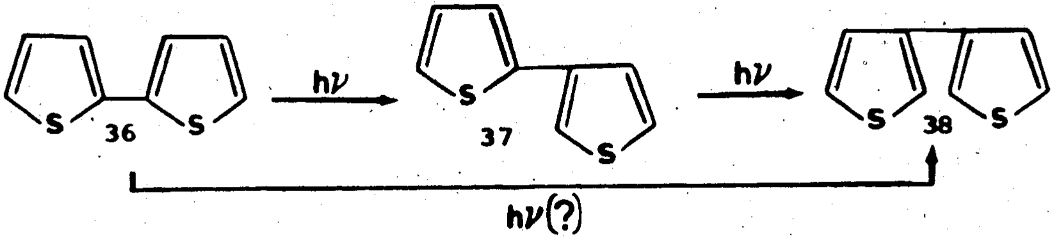
The photochemical rearrangement of substituted thiophenes was initially detected during photolytic arylation experiments with iodothiophenes. The first direct study was reported in 1965 by Wynberg and van Driel [88]. UV photolysis of 2-phenylthiophene produced 3-phenylthiophene irreversibly. Irradiation of 2,2'-dithienyl produced 2,3'-dithienyl and 3,3'-dithienyl in a 2:1 ratio.



34 35

(20)

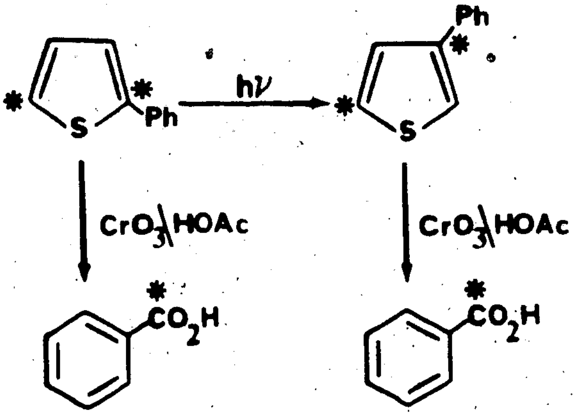
2,3'-Dithienyl gave only the 3,3'-isomer, which yielded no detectable rearrangement when photolyzed. Each photolysis was performed in benzene at ca. 60-80°C using a high pressure Hg arc. Typical photolysis times were 10-38 h and polymer formation occurred in every case. The possible involvement of Dewar or prismane intermediates was suggested on the basis of benzene results.



(21)

Both 2- and 3-phenylthiophene were observed to phosphoresce in a

2-propanol glass at 77 K. Irradiation of **34** under these conditions also produced **35**, as indicated by changes in its phosphorescence spectrum. The phosphorescence decay times were 20 and 300 ms respectively, with a phosphorescence yield for **35** about 13 times that of **34**. Emulating the mesitylene ^{14}C labelling experiment [20], Wynberg and van Driel [89] photolyzed a 2-phenyl-[2,5-^{14}C]thiophene in ether. The 3-phenylthiophene formed was isolated by preparative GC and samples of each phenylthiophene were separately oxidized to benzoic acid [90]. The ^{14}C activity measured in the benzoic acid from the photorearranged 3-phenyl isomer was the same as that in the benzoic acid from the initial 2-phenylthiophene (Scheme H). From

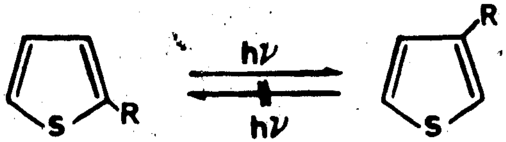


Activity (mC/mol)	0.0310±0.0003	0.0318±0.0007

Scheme H

this result it was concluded that the phenyl substituent remained attached to the same carbon atom during the rearrangement, and therefore photoisomerization must occur by scrambling of the thiophene ring carbons.

Thus far two types of experiments investigating thiophene photorearrangements have been described. The first type [88] examined product mixtures in an attempt to gain insight into the mechanism, while the labelling experiment [89] directly tested the possibility that positional isomers arose via scrambling in the thiophene ring. Returning to their former approach Wynberg and various coworkers published six papers [91-96] relating to many differently substituted thiophenes. The behaviour of monosubstituted thiophenes was deceptively simple. Each 2-substituted thiophene gave the corresponding 3-isomer on photolysis, but the reverse process never occurred.



(22)

R = methyl, t-butyl, neopentyl, thienyl, phenyl, 1- and 2-naphthyl, p-tolyl, mesityl and benzyl.

Investigation of disubstituted thiophenes revealed a more complex photorearrangement behaviour (Table 2). The results for each disubstituted thiophene need not be considered since careful scrutiny of the results on methylphenylthiophenes [94] gives an appreciation of the essential features. Table 3 summarizes the complete results for the methylphenylthiophenes **39-44**. In each instance, all possible positional isomers were detected after photolysis in at least small amounts. The authors stated that time studies with **41**, **43** and **44** showed that the product ratios in Table 3 remained roughly constant with time, indicating that all the products were formed in the primary photochemical act. However, it should be noted that with **41** for example, **44** was the single major product, but significant amounts of **43** were also formed, relative to all other isomers. The major product from the photolysis of **44** is **43**. This observation is

TABLE 2

Disubstituted Thiophenes Investigated by UV Photolysis

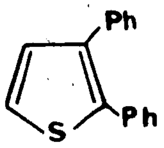
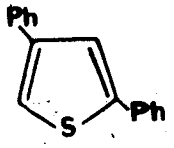
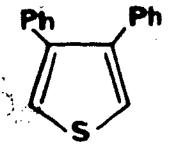
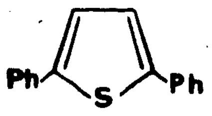
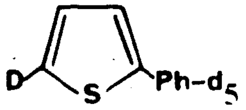
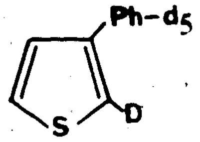
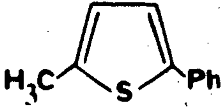
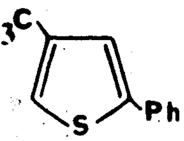
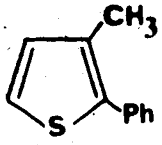
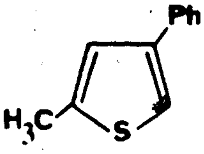
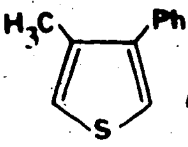
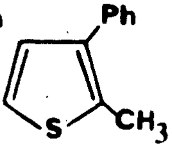
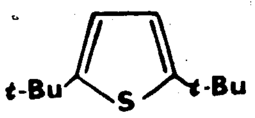
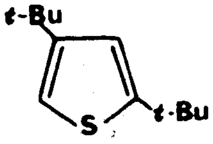
	Ref.
   	91, 92
 	91, 93
 39  40  41  42  43  44	91, 94
 	96

TABLE 3

Relative Percentages of Isomers Formed from Irradiation of the Isomeric Methylphenylthiophenes[a,b]

Starting	Products					
Material	**39**	**40**	**41**	**42**	**43**	**44**
39	80.0	0.8	0.3	**17.1**	1.1	0.7
40	0.5	53.1	1.5	2.9	**37.7**	4.3
41	0.1	0.03	75.6	0.1	2.6	**21.6**
42	0.1	0.6	0.4	95.5	**3.0**	0.4
43	0.8	0.1	**12.1**	0.8	69.9	16.3
44	1.1	0.3	**<4.2**[c]	**4.9**	**19.1**	70.4

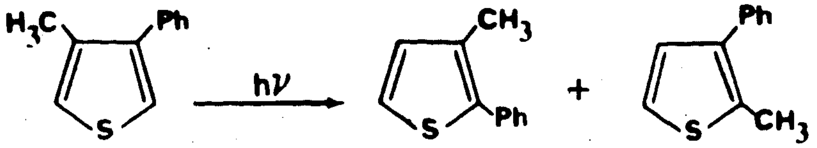
[a] Reproduced from Ref. [94].

[b] Irradiations carried out for 6 h in 1.1×10^{-2} M diethyl ether solution. Yields of recovered isomer mixtures ranged from 42 to 82%.

[c] Absolute maximum value.

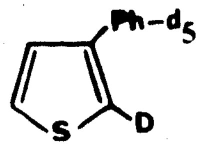
suggestive of secondary photolysis.

More importantly, all methyl-2-phenylthiophene isomers exhibited reasonably selective photoisomerization. The corresponding methyl-3-phenylthiophene isomer obtainable by C_2-C_3 interchange without concomitant C_4-C_5 interchange was always the sole major product. By contrast, the methyl-3-phenyl isomers did not always generate only one major product. For instance, **43** produced roughly equal amounts of **41** and **44**. Clearly, photorearrangements occur in these 3-phenyl substituted thiophenes, resulting in the transposition of thiophene ring carbon atoms other than C_2 and C_3.



43 **41** **44** (23)

Although Wynberg and coworkers did not specifically point this out, it seems evident that disubstituted thiophenes reveal a rearrangement complexity impossible to detect with monosubstituted thiophenes. Proof that this same complexity existed in monosubstituted thiophenes, but was concealed due to the limitation imposed by having only a single carbon atom locator, is found in the photolysis of 2-deutero-3-pentadeuterophenylthiophene, **45**. The deuterium was introduced in order to aid the NMR determination of the product mixture. Substitution of D for H does not alter electronic effects which may influence the reaction path. Following irradiation of **45**, isomers **45-47** were all present in approximately equal amounts. In spite of no change in the location of C_3, bearing the phenyl substituent, photoisomerization had completely scrambled the



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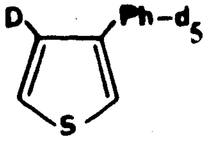

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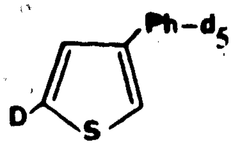

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other thiophene ring carbons. This behaviour was dubbed a photochemical "no-reaction reaction" [95], perhaps an appropriate description for 3-monolabelled thiophenes.

No possible intermediates in the solution phase thiophene photoisomerizations were ever detected by Wynberg in the form of products, and trapping experiments designed to capture such species failed [91]. The rate of 2-phenylthiophene, **34**, disappearance and of 3-phenylthiophene, **35**, appearance was plotted for 2 h. About 40-50% of consumed **34** was found as **35** (Figure 4). The reaction tended to a steady-state after roughly 6 h. The rate of **35** disappearance on photolysis is also shown in Figure 4, but no **34** is formed. The rate for disappearance of **34** was solvent dependent. For the solvent series benzene, cyclohexane, ether, dichloromethane and methanol, the relative extent of disappearance of **34** in 6.4×10^{-3} M solutions irradiated for 2.5 h at 20°C was 1.0/1.7/2.2/5.1/5.9 respectively. The photoisomerization proceeded with equal efficiency regardless of the presence or absence of O_2.

Polymer formation was observed in each thiophene photolysis. Although its yield varied for differently substituted thiophenes, the rate of polymer formation was never studied quantitatively and its intractable nature probably discouraged characterization.

Wynberg _et al._ [92] also reported that phenylthiophenes are luminescent. For the mono- and diphenylthiophene isomers many

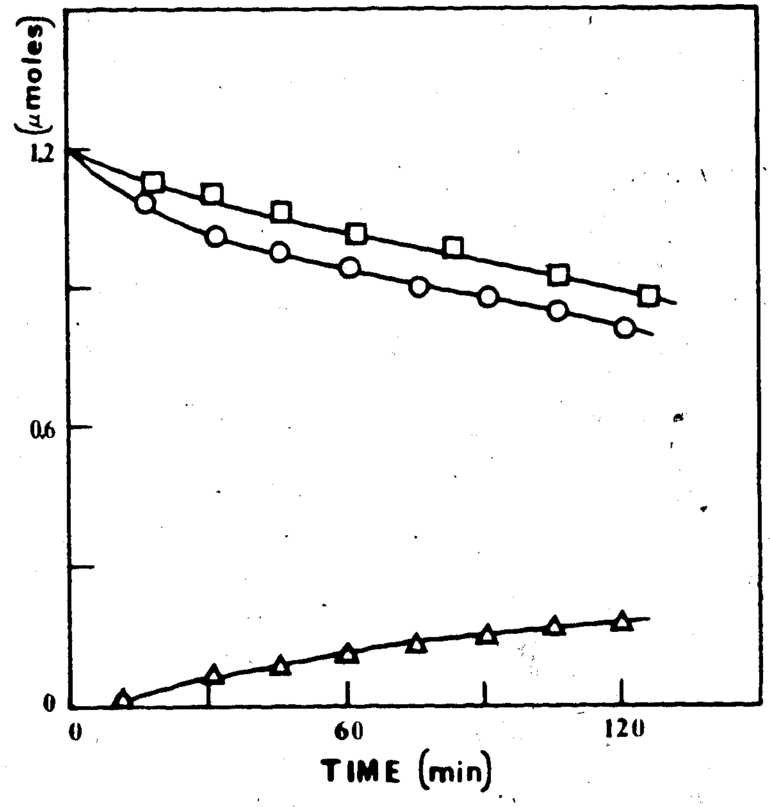


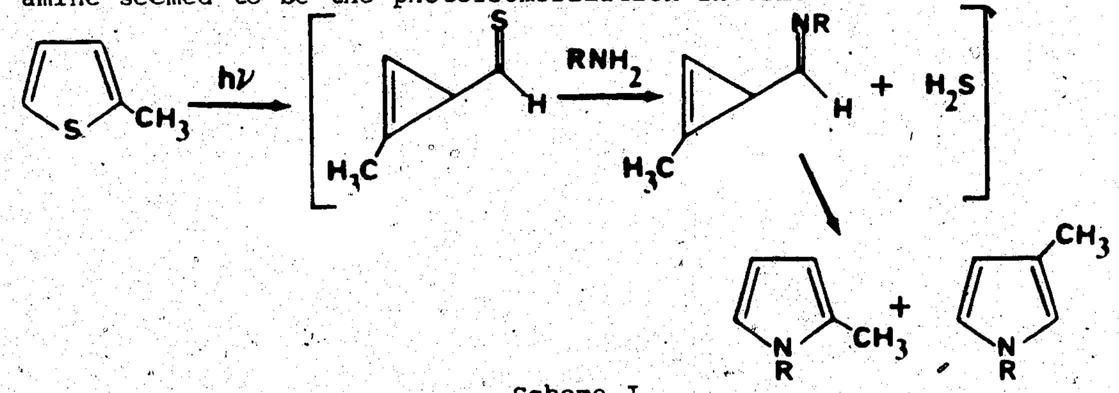
Figure 4. Plots of the disappearance of 2-phenylthiophene, O, and 3-phenylthiophene, □, on UV photolysis (6 × 10^{-3} M solutions in ether). Plot of the formation of 3-phenylthiophene during the UV irradiation of 2-phenylthiophene, Δ. Reproduced from Ref. [92].

fluorescence and phosphorescence maxima were reported, but only the low temperature phosphorescence spectra of **34** and **35** were actually published [88].

Many of Wynberg's early photolysis experiments were performed in benzene solution with a high pressure Hg arc source and no additional wavelength selection. This lamp is a very intense source of UV and visible radiation. The extent of pressure and temperature broadening of the spectral lines generates an emission which is nearly continuous in nature beyond 250 nm [97,98]. The use of benzene as solvent was clearly unwise, although it was probably chosen because the first photorearrangement was detected while photolyzing 2-iodothiophene in benzene, a route to 2-phenylthiophene. Benzene has an absorption band centred near 255 nm ($^1A_{1g} \rightarrow {}^1B_{2u}$, $\varepsilon \sim 200\ M^{-1}cm^{-1}$) and consequently was also photolyzed by the Hg arc. Benzene also has a longer wavelength absorption band with its origin near 340 nm ($^1A_{1g} \rightarrow {}^3B_{1u}$, $\varepsilon \sim 10^{-2}\ M^{-1}cm^{-1}$). This singlet-triplet absorption is weak and for this reason is perhaps of limited concern. For the experimental conditions used in photolyzing 3-phenylthiophene ($\lambda_{max} \sim$ 283 nm, $\varepsilon_{max} \sim 13\ 600\ M^{-1}cm^{-1}$, 6×10^{-3} M) [92] one can readily calculate that only about 5% of the incident light was absorbed by phenylthiophene because of overlap with the absorption spectrum of the solvent. Presumably, such considerations prompted the later switch to a photochemically inert solvent such as diethyl ether.

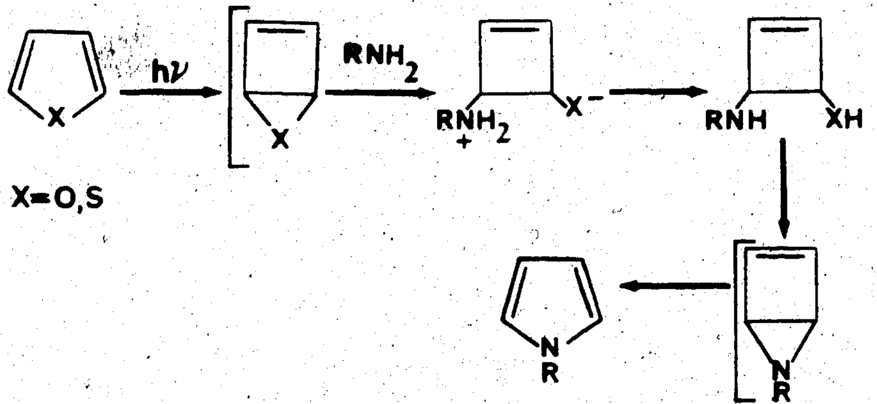
The photorearrangement of 2-phenylthiophene, **34**, in ether solution was investigated in the presence of 1,3-pentadiene (piperylene). This diene quenched the fluorescence of **34** and inhibited its rearrangement to 3-phenylthiophene [99]. In the presence of 1,3-pentadiene **34** was consumed at five times the normal rate and MS indicated the formation of a 1:1 adduct between **34** and the diene ($M^{\overset{+}{\bullet}}$ 228, $C_{15}H_{16}S$). Major fragment ions were observed at M-15 (-CH_3) and M-32 (-S), but no adduct was isolated due to its reportedly unstable nature. Photosensitization of triplet 2-phenylthiophene with benzophenone or acetophenone caused neither consumption of 2-phenylthiophene nor formation of 3-phenylthiophene, although triplet formation was apparently efficient. Thus the photorearrangement of phenylthiophenes proceeded by an excited singlet state and was arrested by the introduction of moderate diene concentrations.

Couture and Lablache-Combier have published a series of papers describing the photolysis of furans and thiophenes in liquid amines [43,44,100,101]. Irradiation (254 nm) of substituted thiophenes as 1% solutions gave the same pyrrole products as previously obtained with comparable furan derivatives. For instance, 2-methylthiophene in 1-propylamine produced both 1-propyl-2- and 1-propyl-3-methylpyrrole. 3-Methylthiophene on the other hand gave only the latter pyrrole product (Scheme I) [42]. The species intercepted by the amine seemed to be the photoisomerization intermediate. These



Scheme I

trapping results, combined with the accepted role of cyclopropenyl aldehydes and ketones in furan photoisomerizations, were concluded to demonstrate the intermediacy of thioaldehydes or thioketo[illegible]thiophene photoisomerizations. Ultimately however, two mecha[illegible]were used to explain pyrrole formation from furans and thiophenes [44]: Scheme I which was just presented, and Scheme J which involves Dewar intermediates. The Dewar type intermediate of Scheme J, as well as the thioaldehyde intermediate in Scheme I, could account for the positional isomerization of 2-methylthiophene.

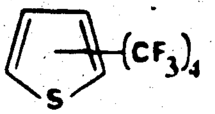


Scheme J

Wiebe and Heicklen [102] subjected thiophene vapour to direct irradiation (214, 229 nm) and Hg($^3P_1$) sensitization at various temperatures, pressures and light intensities. In all cases the products were C_2H_2, CH_2CCH_2, CH_3CCH, CS_2, CH_2CHCCH and polymer. Product quantum yields decreased with increasing pressure. Evidence was given for the presence of an energetic intermediate different from the initially formed thiophene excited state. This intermediate decomposed to allene or was deactivated to thiophene. Presumably it was not a triplet state or a free radical because of the lack of O_2

scavenging, and the absence of cyclopropene from the products was suggested to exclude the possibility of cyclopropenyl thioaldehyde.

The first thiophene valence bond isomer to be isolated was obtained by Heicklen <u>et al.</u> from the direct photolysis (214 nm) and Hg($^3P_1$) sensitization of gas phase 2,3,4,5-tetrakis(trifluoromethyl)-thiophene, **48**. This isomer was initially believed [80,103] to be a cyclopropenyl thioketone, **49**, but the Dewar structure, **50**,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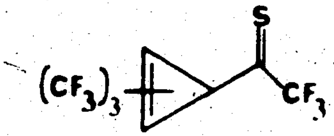
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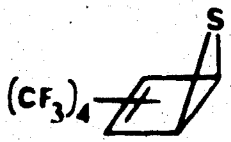
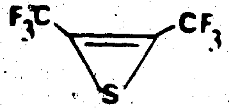

50

was later assigned [104] because the ^{19}F NMR spectrum showed two equal intensity CF_3 absorptions. The other major product was hexafluoro-2-butyne. A minor product detected by MS was assigned the thiirene structure, **51**. An uncharacterized polymer was always formed during photolysis.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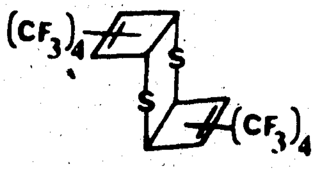
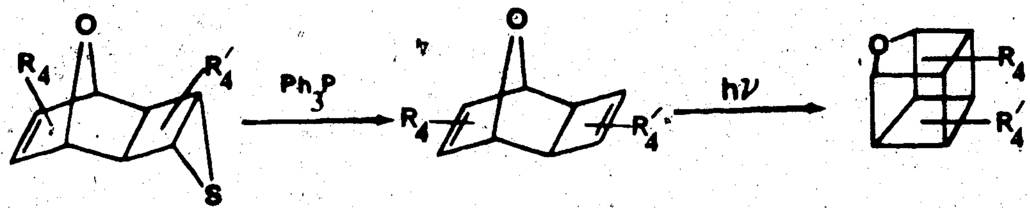
Since Heicklen <u>et al.</u> isolated **50** this compound has been extensively studied. Kobayashi and various coworkers have examined the chemistry of this Dewar thiophene. They generated **50** by direct photolysis (254 nm) of **48** in the gas phase at low pressure, confirming its structure by ^{13}C and ^{19}F NMR. Polymerization, which was substantial in solution phase, was virtually eliminated in the gas phase and **50** was recovered in 58% yield [105]. It reverts thermally to **48** with $t_{1/2}$ = 5.1 h in benzene at 160°C [105,106] and this reversion can be catalyzed by triphenylphosphine. When dissolved in dimethylsulfoxide or dimethylformamide, the crystalline dimer **52** precipitated immediately.



52

The ability of **50** to react as a dienophile has prompted many investigations. Diels-Alder adducts with furan, methylfurans, pyrrole, cyclopentadiene and butadienes have been prepared [107]. **50** behaves as an electron deficient dienophile. An interesting reaction of the furan DAa involves desulfurization to a tricyclic diene, and subsequent solution photolysis (254 nm) in acetonitrile which leads to an oxahomocubane [105,107,108]. For each



(24)

R = H, CH_3 R' = CF_3

Diels-Alder reaction of **50** with a cyclic diene two adducts were generally reported, although in theory four can be imagined. Those obtained were assumed to be the two sterically favoured adducts. For one furan adduct the actual stereochemistry was established by X-ray analysis [109].

More recently, Kobayashi and coworkers have treated **50** with azides, developing a synthetic route to perfluorotetramethyl Dewar pyrrole [110], and also investigated the photolysis of bis- and tris-

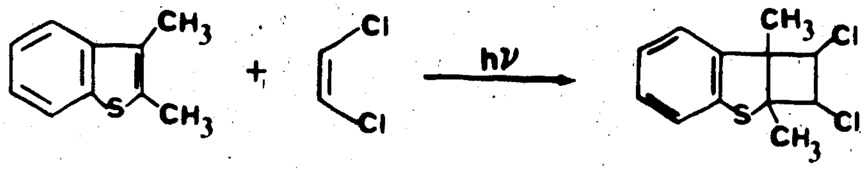
(trifluoromethyl)thiophenes in order to generate Dewar isomers [111].

Verkoczy <u>et al.</u> [112] recently isolated perfluorotetramethyl Dewar thiophene from the gas phase photolysis (>240 nm) of COS in the presence of CF_3CCCF_3. Thiirene, the primary adduct in the reaction of an $S(^1D_2)$ atom with C_4F_6, is sufficiently reactive to add a second C_4F_6 molecule yielding perfluorotetramethylthiophene. Its secondary photolysis produced the Dewar isomer.

Kobayashi and Kumadaki [113] have reviewed the field of valence bond isomers of aromatic compounds stabilized by trifluoromethyl substituents. This stabilizing effect had been recognized earlier by Lemal and Dunlap [114] who designated it as the "perfluoroalkyl (R_f) effect". The stabilizing influence was suggested to be a composite of thermodynamic (steric in origin) and kinetic elements, however these were not fully explained. Stabilization resulting from steric factors, p-π repulsion and hybridization changes in strained carbon frameworks caused by the electronegative character of fluorine have also been discussed [113].

Recent theoretical calculations indicate that CF_3 substituents provide benzene VB isomers with negligible stabilization, relative to the corresponding aromatic structure. The theoretical results supported the contention that some stability might be conferred by removal of steric strain present in the aromatic isomer, but the striking thermal stability of perfluoroalkylated strained rings was concluded to be kinetic in nature [115]. At present the exact reasons for the stabilizing influence of perfluoroalkyl groups seem uncertain.

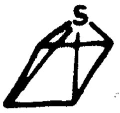
Wynberg et al. [116] studied the photosensitized addition reactions between ethylenes and benzothiophenes. The different stereoisomers of the [2+2] addition product were characterized by ^{1}H NMR.



(25)

In 1971 Wynberg reviewed the chemical, photochemical and spectral properties of thiophenes, including a brief account of his own results on the photorearrangements of mono- and disubstituted thiophenes [117].

Carbon skeletal rearrangements and substituent scrambling in thiophenes have been detected by MS. Isotope distribution in the fragments from ^{13}C or D labelled thiophene provided evidence for carbon skeletal rearrangement and hydrogen scrambling prior to molecular ion fragmentation [118,119]. Although hydrogen scrambling results from carbon skeletal rearrangement, there also seemed to be a mechanism for hydrogen migration independent of carbon scrambling. Carbon and hydrogen scrambling were also found in benzothiophene [120]. While MS studies of aryl substituted furans and thiophenes indicated carbon scrambling in both systems, it was much less efficient in the furans [121]. Initial evidence for scrambling in phenylthiophenes included the similarity of the 2- and 3-phenylthiophene mass spectra and the presence of an $[M-CHS]^+$ ion from 2,5-diphenylthiophene [122]. For 2-phenyl- and 2,5-diphenylthiophene both carbon skeletal rearrangement and phenyl migration without the attached carbon atom occurred in the molecular ion prior to fragmentation [123]. In 3-phenylthiophene, substituent migration predominated over carbon scrambling [124]. No comprehensive explanation has been presented for these MS results, but prismane thiophenes, **53** [118, 119], and cyclopropenyl thioaldehydes, **54** [118,123], have been discussed as possible intermediates. Some authors [118,124] have suggested that a close relationship exists between the mechanisms for photochemical isomerization of thiophenes and their rearrangements observed by MS. These latter rearrangements were all induced by electron impact, with typical beam energies ranging from 15 to 70 eV.



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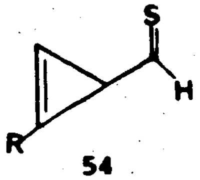

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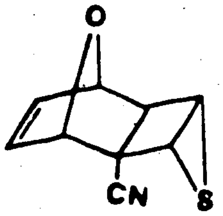
Since 1972 virtually no experimental investigations of thiophene photorearrangements have been performed. Two communications by Barltrop et al. [125,126] report phototranspositions in cyanothiophenes. In a number of solvents at 34°C, irradiation (254 nm) of 2-cyanothiophene, **55**, resulted in the slow formation of 3-cyanothiophene, **56**. Unlike other monosubstituted thiophenes the reaction was reversible. Sensitization with either benzophenone or acetophenone did not cause rearrangement, implying that it occurred via a singlet state precursor.

55 **56**

(26)

The phototranspositions of all six possi[illegible] methyl-2-cyano- and methyl-3-cyanothiophene isomers were examined. These methylated compounds featured a markedly slower rate of transposition, but the rate was enhanced in acetonitrile at 80°C. In each case one major product was obtained with lesser or trace amounts of other isomers. The product distribution was analyzed with the authors' permutation pattern technique [83,85], and it was found that a minimum set of three permutations was required to explain the observed products. These permutations had the common feature of preserving the sequential order of the ring carbon atoms, while changing the position of the sulfur atom within the sequence. This was concluded to be consistent with a mechanism featuring 2,5-bonding in the reactant excited state, giving rise to a set of Dewar thiophene intermediates interconverting by a "walking" of the sulfur atom about the perimeter of the four-membered ring at a rate competitive with rearomatization.

In support of this mechanism, two furan Diels-Alder adducts, 57 and 58, with Dewar thiophenes derived from the photolysis of 55 and 56 were isolated. The adducts' structures were determined by NMR and also by desulfurization to a tricyclic diene. Although not presented, these results were stated to be similar to those described



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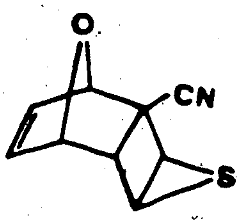
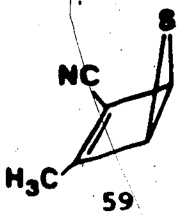


58

earlier for comparable DAa of furan with Dewar cyanopyrroles, **29** and **30**, obtained in the same laboratory [84]. From either 3-cyano-2-methyl- or 3-cyano-4-methylthiophene the same Dewar isomer, **59** was isolated and identified by ^{1}H NMR. **59** undergoes



59

Diels-Alder addition to furan and 2,5-diphenyl-3,4-benzofuran. The photolysis (254, >290 nm) and thermolysis (170°C) of **59** were examined and each produced 3-cyano-4-methylthiophene as the principal product. The presence of other positional isomers indicated that some rearrangement occurred prior to rearomatization. All the observed products retained the sequential order of the carbon atoms in the thiophene ring.

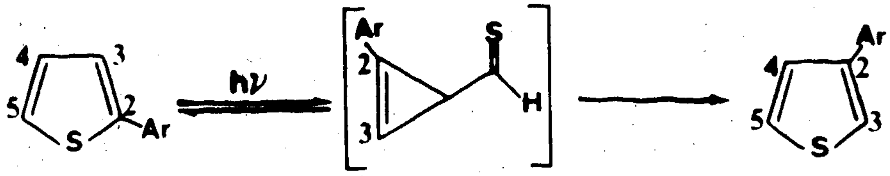
The electronic spectra of thiophene, deuterated thiophenes and the phenylthiophenes have been examined. Di Lonardo et al. [127] recorded the absorption spectra of C_4H_4S, 2-C_4H_3DS, 2,5-$C_4H_2D_2S$ and C_4D_4S vapours. Three electronic transitions between 140 and 250 nm were identified. Abu-Eittah and Hilal [128,129] have performed MO calculations for phenylthiophenes and compared the results of their calculations with the experimental absorption spectra. For 2- and 3-phenylthiophene, it was concluded that excited states arise from extensive interaction betwen the excited states of benzene and thiophene. This same conclusion is easily reached by examining the actual absorption spectra of the compounds. In addition, if planar conformers are assumed for 2- and 3-phenylthiophene, the predicted absorption data lie closer to the experimental spectra than for the case of perpendicular conformers in which the thienyl and phenyl rings are at right angles [128]. Much earlier Elpern and Nachod [130] had examined the UV absorption spectra of these two isomers and attributed the differences to linear conjugation in 2-phenylthiophene as opposed to cross conjugation in 3-phenylthiophene. Galasso and De Alti [131] used extended Hückel MO calculations to determine the conformation of monophenyl furans, pyrroles and thiophenes. Both 2- and 3-phenylthiophene featured an energy minimum for an angle of about 37° between the two rings, a somewhat different result from that of Abu-Eittah and Hilal [128]. It should be mentioned that the experimental phenylthiophene absorption spectra reported by these latter authors do not, in all cases, agree well with the spectra of Elpern and Nachod [130], or, more recently, those of Wynberg et al. [92].

Quite recently Varsányi et al. [132] have examined the lowest energy UV transition of thiophene in the gas phase. Using high resolution spectrometry and by performing temperature dependence studies, the vibronic structure of this absorption was analyzed. Their study was aided by the much earlier work of Rico et al. [133] who obtained infrared spectra of thiophene and all its various deuterated isomers in order to assign the fundamental vibrations.

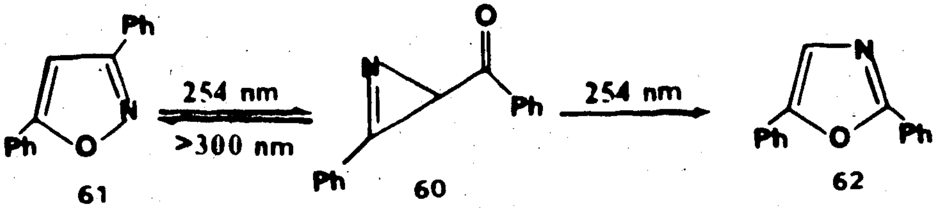
5. Thiophene Photorearrangement Mechanisms

During the preceeding review of the photoisomerizations of benzene and the heteroaromatics, mechanisms involving different intermediates were discussed. In this section those mechanisms offered by various authors to account specifically, although not exclusively, for the photoisomerizations of thiophenes will be briefly summarized.

At an early stage, Wynberg and coworkers suggested a thioaldehyde intermediate to explain the rearrangement of 2-arylthiophenes to 3-arylthiophenes [91] and provide for C_2-C_3 interchange without concomitant C_4-C_5 interchange. This mechanism has subsequently become known as the ring contraction-ring expansion mechanism (Scheme K). A precedent for such intermediates had already been established in other systems. For example, the formation of cyclopropenyl aldehyde in the photolysis of furan had been demonstrated by Srinivasan [34,35], and similar aldehydes and ketones were implicated in alkylfuran photorearrangements [35,37,39]. In addition, the azirine intermediate **60** had been isolated in the photorearrangement of 3,5-diphenylisoxazole, **61**, to 2,5-diphenyloxazole, **62**. Secondary photolysis of **60** produced either **61** or **62** depending on wavelength [134,135].



Scheme K



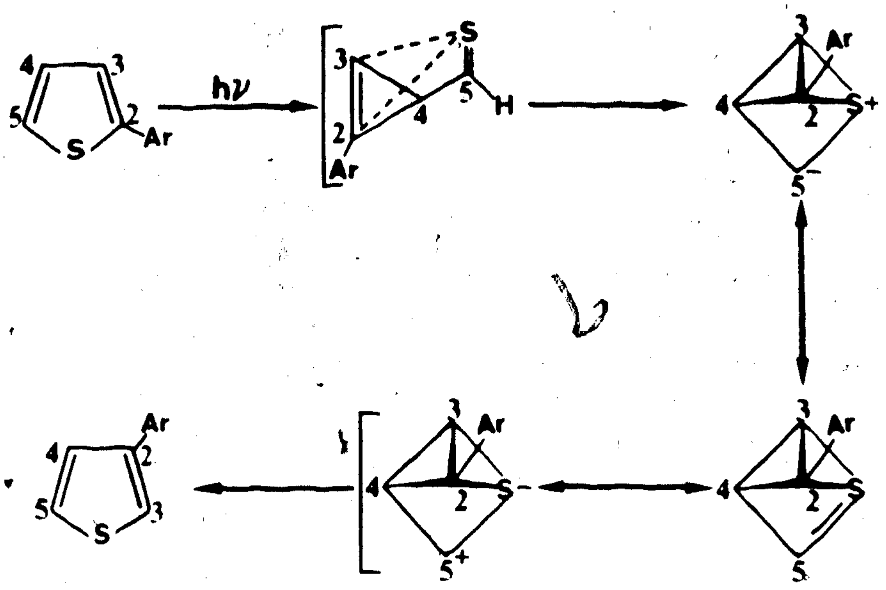
61 60 62 (27)

The trapping of pyrroles from the irradiation of furans and thiophenes in amine solution was initially claimed by Couture and Lablache-Combier as evidence that Scheme K was operative in the photoisomerization reactions of both these systems [43,100,101] although the authors later modified their opinion [44].

A major limitation of Scheme K may be its inability to explain *a priori* the observed irreversibility of monosubstituted thiophene rearrangements. In addition, Wynberg *et al.* [95] criticized Scheme K, suggesting that ring contraction in 2-phenylthiophene would occur preferentially through C_5-S bond cleavage producing a phenyl thioketone, rather than via C_2-S cleavage and subsequent thioaldehyde formation, because of the greater thermodynamic stability of the thioketone. However, Hückel MO calculations of π bond orders in furans supported selective ring contraction in a manner that might explain the irreversible photoisomerization of 2- and 3-methylfuran [37,39].

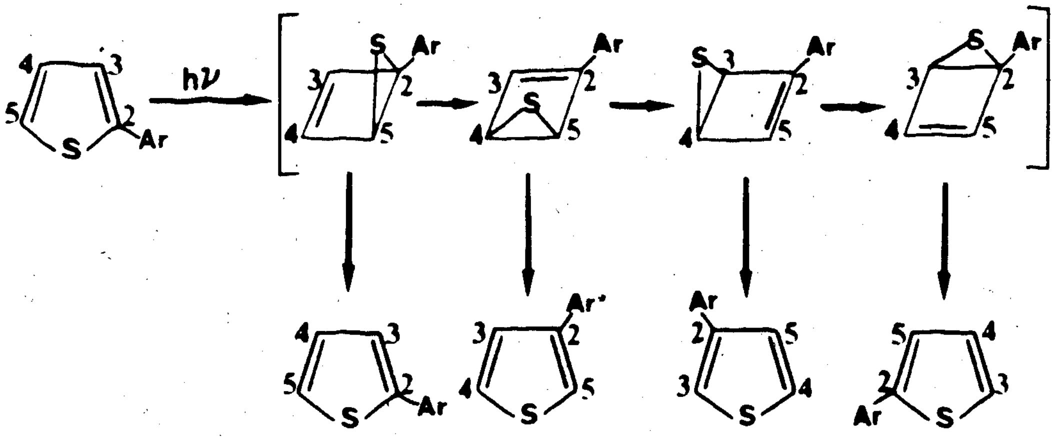
Wynberg *et al.* [95] proposed a mechanism involving a zwitterionic species. This pathway involves valence shell expansion of the S atom, with the formation of a tricyclic intermediate arising from interaction of the sulfur 3d orbitals with the C_2-C_3 double bond in the thioaldehyde. Rearrangement to a thiophene with requisite interchange of the C_2-C_3 atoms can be envisaged. Scheme L fails, however, to explain the features of the deuterium labelled 3-phenylthiophene rearrangements.

The Dewar thiophene intermediate in Scheme M, has been considered by many researchers [44,88,89,95,125,126], and can account for the rearrangement of a 2-substituted thiophene to its correspond-

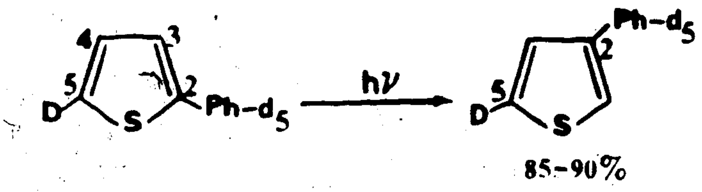


Scheme L

ing 3 isomer. However, the sequential order of the thiophene ring carbon atoms should be preserved regardless of the number of "sulfur walking" steps. While many of the observed thiophene rearrangements meet this criterion some clearly do not conform to this rule; for instance:



Scheme M



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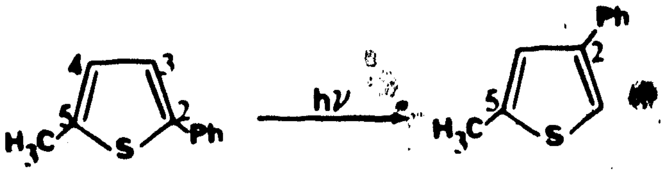


(29)

(30)

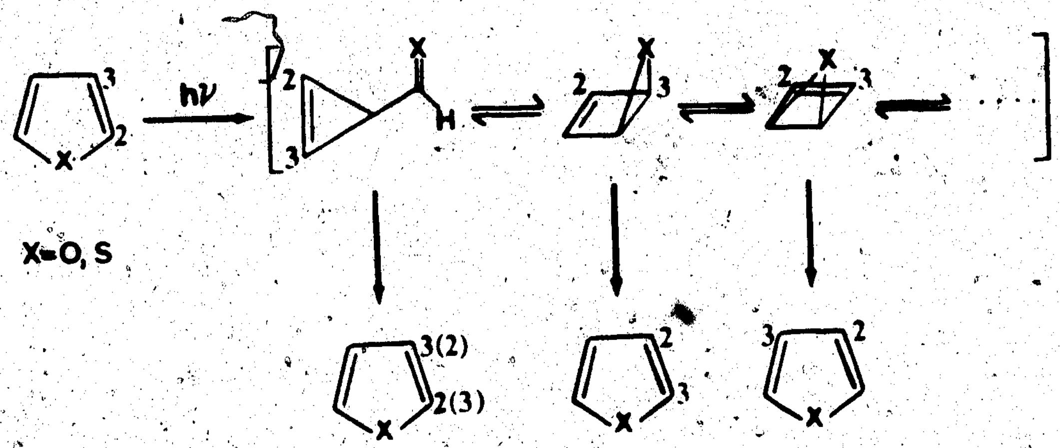
Also the reason that a Dewar intermediate should chose to rearomatize only after the correct number of "sulfur walks" have been executed is not immediately apparent.

Relevant to a "sulfur walking" mechanism are some ^{19}F NMR studies on perfluorotetramethyl Dewar thiophene and its S-oxide [136,137]. The former showed two distinct types of CF_3 resonance at room temperature. These signals coalesced on heating to 190°C. By contrast, the S-oxide displayed four equivalent CF_3 resonances even at -100°C, indicating that dramatic differences must exist in the two compounds for the interchange of CF_3 groups between different environments. This was viewed as occurring by a "sulfur walking" process, although the possibility of a pyramidal intermediate or transition state, **63**, was mentioned. It should be pointed out that

63

the high stability of perfluorotetramethyl Dewar thiophene toward rearomatization, even at 190°C, allowed this phenomenon to be observed. For Dewar structures rearomatizing at much lower temperature however, the competitive ability of this "sulfur walking" process might be reduced.

In an attempt to design a unified photorearrangement mechanism for five-membered aromatic heterocycles, van Tamelen and Whitesides proposed Scheme N. Its essential feature is a fortuitous equilibrium



Scheme N

between Dewar and cyclopropenyl structures. Unfortunately, using appropriate sequences of cyclopropenyl and Dewar intermediates, this mechanism can account for any scrambling pattern of the heterocyclic ring carbon atoms, and thus there is no explanation of the experimentally observed selectivity of many photoisomerizations. In addition, the logic of suggesting a rapid equilibrium between bicyclic and cyclopropenyl intermediates is questionable.

While aldehydes are commonplace in chemistry, thioaldehydes are much less well known. Thioaldehydes are unstable and tend to decompose or oligomerize readily. Some have recently been trapped by Diels-Alder reactions [138,139], and the first conventional synthesis of a thioaldehyde was achieved in 1983. 2,2-Dimethylpropanethial, **64**, survived up to 16 h in solution at 20°C [140].

$$t\text{-BuCH=S}$$

64

OBJECTIVES

Having reviewed the literature concerning the photochemistry of furans, pyridines, pyrroles and thiophenes, it remains to describe how the objectives of the current investigation fit into this framework. In an effort to gain insight into the thiophene photorearrangements Wynberg and coworkers performed the solution phase photolysis of many differently substituted thiophenes, identifying in each case any positional isomers formed by irradiation [88,91-96]. This approach provided some information about the nature of the rearrangements. For instance, it initially revealed that for monolabelled thiophenes the 2→3 photoisomerization appeared to be irreversible, but D labelling experiments later showed that, in a 3-substituted thiophene, other carbon scramblings occur even though the position of the C_3 which bears the substituent remains unchanged.

Hypotheses about the types of mechanism and intermediate species responsible for the thiophene photorearrangements were offered, based on these results. Although many different suggestions were made, direct experimental evidence for the existence of any of the postulated intermediates was presented in only a limited number of cases. Moreover, the existing experimental evidence was, in our opinion, deficient [99,125,126].

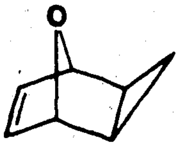
We concluded that only a new approach to this problem would allow us to acquire further insights into the mechanistic pathways of heterocyclic photorearrangements. The fundamental difference in our approach as compared to previous work was that it concentrated on obtaining direct experimental evidence for the existence of short-lived photochemical intermediates generated during the photolysis of thiophenes, as opposed to postulating the existence of such species on the basis of the observed products of many photorearrangement reactions. To this end we devised a plan of attack incorporating three different types of experiments. Thiophenic compounds were chosen for this investigation because they represent the most studied, yet least understood photoisomerizing heteroaromatic system.

A. Solution Phase Photolysis with In-Situ Trapping Reagents

Reflecting on Wynberg's numerous experiments with thiophenes we decided to reconsider the solution phase photolysis of 2-phenylthiophene in piperylene. After irradiating 2-phenylthiophene in piperylene Kellogg and Wynberg [99] found an unstable product identified by MS as a 1:1 adduct of 2-phenylthiophene and the diene. In addition, the rate of conversion of 2-phenylthiophene to 3-phenylthiophene was severely retarded by the presence of piperylene.

The implication of these two observations is that the diene intercepts a photochemically generated intermediate which is responsible for the photoisomerization of 2-phenylthiophene to 3-phenylthiophene. Owing to the apparent instability of the 1:1 adduct it was never more fully characterized, and consequently its structure remained unknown.

We also noted that Srinivasan had trapped two furan adducts with cyclopropene, as well as an adduct of unknown stereochemistry with cyclopropenyl carboxaldehyde, while investigating the gas phase photolysis of furan. The structures of these products suggested that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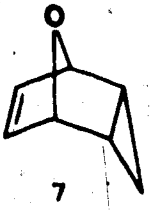
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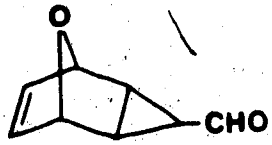
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they were formed by Diels-Alder cycloaddition reactions between excess furan and either cyclopropenyl carboxaldehyde, generated by the photolysis of furan, or cyclopropene, which was formed on decarboxylation of this aldehyde.

Owing to the success of Wynberg's solution phase experiments with 2-phenylthiophene and piperylene we decided to study this same <u>in-situ</u> trapping system and attempt to extend his work by applying this approach to a series of phenylthiophenes. Our initial objective was to determine which phenylthiophenes formed an adduct with piperylene during photolysis. The final objective was to isolate and fully characterize the structure of these adducts so that the nature of the short-lived intermediate species intercepted from the photolysis of the thiophene might be determined.

B. Low Temperature Matrix Isolation

There are at least two approaches to the problem of isolating short-lived intermediates from photochemical reactions. In chemical trapping experiments, such as just described, the short-lived intermediate is intercepted by a second species, with which it reacts chemically to form a stable product. Identification of this product hopefully provides insight into the structure of the short-lived photochemical intermediate.

A second approach involves generating the intermediate under conditions where it has a sufficiently long lifetime to be identified. Low temperature matrix isolation is a technique which has been applied with great success to the study of short-lived intermediates or new unstable species produced in some photoreactions (cf. Experimental). In many cases these species are not sufficiently stable to be examined by more conventional methods.

We decided to investigate the photoly[illegible] thiophene and some substituted thiophenes in a low temperatu[illegible] at ca. 10 K with the hope that the photochemical intermediate[illegible] responsible for the photoisomerization process could be stabilized under these conditions, possibly permitting their identification. For the purpose of comparison with the thiophene system, and also because its photochemistry had already been examined in both the gas and solution phases, we included the photolysis of furan in our low temperature matrix isolation experiments. The application of the matrix isolation technique to the photochemistry of thiophenes has not previously been reported.

C. Photophysical Behaviour

Finally, it was decided that a study of the photophysical behaviour of phenylthiophenes would be a worthwhile endeavour. Wynberg et al. [92] reported emission maxima for many mono- and diphenylthiophenes. It was hoped that a detailed investigation of their fluorescence and phosphorescence characteristics, including the measurement of singlet and triplet lifetimes, might provide a more detailed picture of the photochemistry of these compounds. Thus any similarities or differences in the photophysical behaviour of a series of phenylthiophenes could perhaps be related to their photorearrangement behaviour.

RESULTS AND DISCUSSION

A. Solution Phase In-situ Trapping Experiments

1. Evidence of Trapped Intermediates

a. Photolysis of Tetraphenylthiophene

The first successful solution phase piperylene trapping experiments were performed with tetraphenylthiophene (TPT). This phenylthiophene was selected for two reasons. Firstly, TPT was the only commercially available phenylthiophene. Its use therefore considerably reduced the amount of time expended on the synthesis and purification of materials required for the exploratory testing of different photolysis conditions. Secondly, since high piperylene concentrations are required in the trapping experiments and significant diene absorption begins in the 275-300 nm region (Figure 5), the absorption spectrum of the thiophene should extend to > 300 nm. The longest wavelength UV absorption of TPT is centred around 315 nm ($\varepsilon_{max} \sim 13\ 700\ M^{-1}cm^{-1}$) and consequently there is little spectral overlap between this absorption of TPT and that of the diene solution. Photolysis was performed with the Pyrex filtered radiation of a medium pressure Hg lamp (Figure 5). The photochemically productive Hg emission lines isolated with this experimental arrangement are located about 300 and also 313 nm where the attenuating effect of the Pyrex filter is decreasing rapidly and TPT absorbs strongly. The majority of mono- and diphenylthiophene

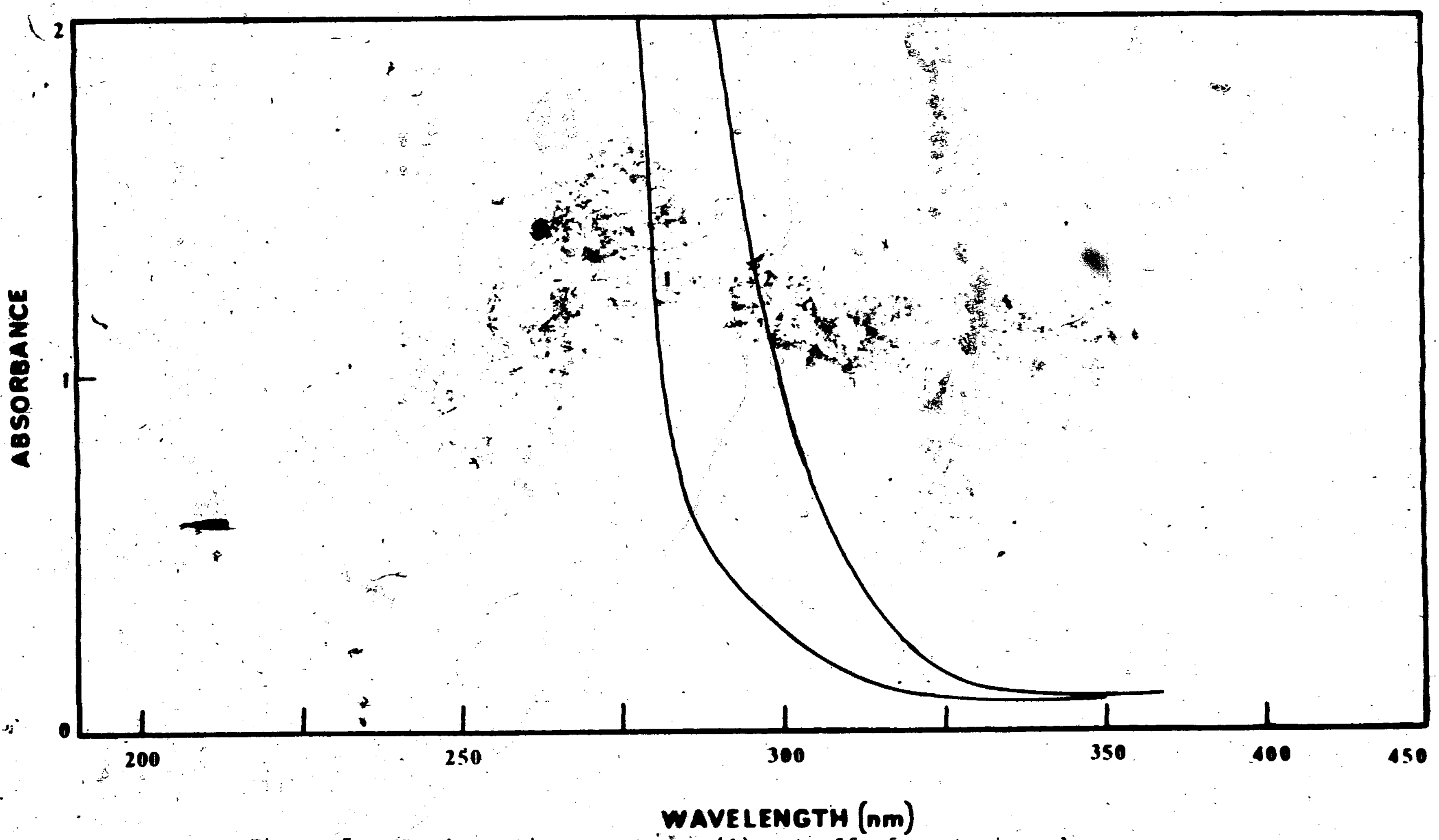


Figure 5. UV absorption spectra: (1) cut-off of neat piperylene, (2) cut-off of a typical Pyrex filter.

isomers show little substantial UV absorption for $\lambda > 300$ nm.

After the photolysis was completed an initial separation of much of the unphotolyzed TPT was effected by recrystallization. The product fraction was examined by chemical ionization MS with NH_3. This fraction contained a peak having the correct mass (m/e 457) for a 1:1 adduct of TPT with piperylene. Like Wynberg's adduct between 2-phenylthiophene (2-PT) and piperylene this new product showed two prominent fragments; $M^{\overset{+}{\cdot}}$ -15 ($-CH_3$) and $M^{\overset{+}{\cdot}}$ -32 (-S) (Table 4). Although a signal at m/e 389 might be expected for the 1:1 adduct, as it could likely undergo a retro-addition in the mass spectrometer, the base peak at this mass, as seen from Table 4, must probably be due to the presence of a large excess of unreacted TPT in the product containing fraction. Comparable mass spectral evidence for adduct formation with TPT was reproduced a number of times. Although sample ionization was usually achieved by electron impact (EI) the chemical ionization (CI) technique was occasionally employed as this latter "softer" ionization method provided MS data with a stronger molecular ion signal for the adduct. This probably enhances the sensitivity of MS as a simple diagnostic test for adduct formation in different photolysis systems. In some product fractions, evidence for a 2:1 adduct (i.e. two units of piperylene, m/e 524) was observed by MS.

Due to the comparatively high mass of TPT and its adducts, as well as the presumed instability of the latter, it was regarded as unfeasible to attempt their separation by GC. Instead, silica gel TLC was attempted. Fluorescent plates aided in locating product zones, although the fluorescence of TPT itself was suitable for its

TABLE 4

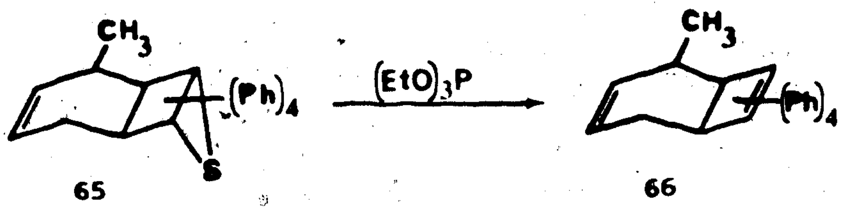
Chemical Ionization Mass Spectrometry[a] (NH_3) of the Product Fraction from the TPT/Piperylene System

m/e	Relative Intensity	Fragment
457	0.9%	1:1 adduct
442	7.9	$-CH_3$
425	3.9	-S
389	100	TPT

[a] AEI MS12

detection. Although many solvent combinations were tested, effective product separation was never achieved. Consequently, a different approach was then used to gain some information about the structure of the TPT-piperylene adduct.

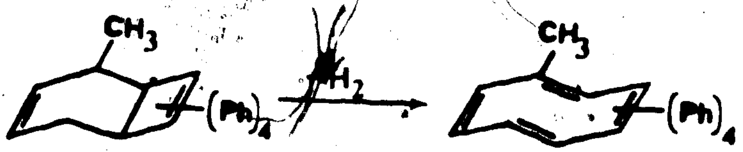
Recalling that Day et al. [125] had recently reported the isolation of furan adducts with a Dewar cyanothiophene following the photolysis of 3-cyanothiophene we suspected that Wynberg's unidentified piperylene-2-PT adduct and our piperylene-TPT adduct might have structures analogous to the Dewar cyanothiophene adduct. To investigate this latter possibility desulfurization of the TPT adduct was attempted using $(EtO)_3P$. This reagent has been utilized in other studies for the desulfurization of thiirane rings to generate an olefin [141]. If the TPT adduct was the trapped Dewar thiophene, **65** it should be desulfurized by the $(EtO)_3P$ resulting in the formation of the bicyclic diene, **66**. Hence, the occurrence



65 66 (31)

of desulfurization would provide some indirect evidence about the structure of the adduct.

TLC of a desulfurized sample of the photolysis mixture revealed one partially resolved new product. A fraction enriched in this component was isolated by column chromatography (silica gel, 5:1 hexane/$CHCl_3$ v/v). Its high resolution mass spectrum showed a substantial peak at m/e 424 ($C_{33}H_{28}$) corresponding to the exact mass for the bicyclic diene **66** expected from successful desulfurization. The diene fragmented in the mass spectrometer by two successive H atom losses producing a peak at m/e 422. Further fragmentation occurred by the loss of a CH_3 or Ph group. From this fragmentation pattern it appeared that the bicyclic diene formed by desulfurization initially undergoes ring expansion in the mass spectrometer to produce a cyclooctatetraene, doubtless relieving the strain of the bicyclic ring structure.



(32)

m/e 424 m/e 422

Wynberg claimed that the piperylene-2-PT adduct was thermally unstable and we therefore expected the piperylene-TPT adduct to be even less so; on the other hand, the bicyclic diene should be considerably more stable than either adduct. Consequently a second sample of desulfurized product was analyzed by GC (10%, SE-30, ~3 mm × 2 m). At 275°C a very small shoulder on the rising edge of the TPT peak was resolved. GC/MS analysis of this shoulder indicated a molecular ion at m/e 422, which fragmented by loss of CH_3 or Ph (Table 5).

Although these combined results did not provide conclusive structural evidence for the adduct, the occurrence of adduct formation during the photolysis of TPT in piperylene was definitely established. Moreover, the fact that the adduct seemed to be desulfurized by $(EtO)_3P$ was consistent with the proposal of a

TABLE 5

GC/MS[a] Analysis of the Product Formed by Desulfurization of **65**

m/e	Relative Intensity	Fragment
423	35%	$^{13}C\ ^{12}C_{32}H_{26}$
422	100%	$C_{33}H_{26}$
407	31%	$-CH_3$
345	13%	-Ph

[a] 10% SE-30, ~3 mm × 2 m, AEI MS12.

piperylene-Dewar thiophene structure for the 1:1 adduct. In spite of the possibility that a sufficient amount of desulfurized adduct might eventually have been isolated to enable its structural determination by ^{1}H and ^{13}C NMR, these spectra would have been complicated by the presence of the four aromatic rings. Also, the isolation of the actual Dewar thiophene adduct, **65**, would be a more elegant proof of its existence. As a result it was decided to initially examine the scope of the adduct formation reaction by irradiating other phenylthiophenes under conditions similar to those successfully employed for TPT, rather than immediately concentrating on the TPT system.

b. Photolysis of the Mono- and Diphenylthiophenes in Piperylene

Solution phase in-situ trapping experiments were next tried using 2-PT, 3-PT, 2,3-DPT and 2,5-DPT. Low resolution MS of the product mixtures clearly showed the formation of both 1:1 and 2:1 adducts between piperylene and both of the monophenylthiophene isomers. Irradiated 2,3-DPT also led to the formation of 1:1 and 2:1 adducts, although the signals attributed to these adducts were very weak by comparison to those for the monophenylthiophenes. By contrast, MS analysis did not reveal any adduct formation for the case of 2,5-DPT. Its irradiation was continued for a very long time (260 h) because this DPT seemed particularly resistant to photolysis, as evident from the absence of any polymerization or substantial change in solution colour during irradiation. It was decided that if piperylene adduct formation occurs with 2,5-DPT it must be much less efficient than adduct formation with the monophenylthiophenes. An observation made by Wynberg et al. [92], which is pertinent to this result, was that even after irradiating 2,5-DPT for 260 h no photorearranged isomers could be positively detected.

As frequently mentioned, Wynberg stated that his 2-PT-piperylene adduct was thermally unstable. By contrast, in the current investigation, MS data on product fractions containing phenylthiophene-piperylene adducts showed no evidence of aging effects, even after several weeks of storage in the dark at ~ -5°C. Consequently, it was suspected that these adducts might possess greater thermal stability than previously believed, and we decided to examine the adduct-containing photolysis products by GC. The monophenylthiophenes were investigated first because the MS results indicated that adduct formation was more efficient with these compounds. In addition, the lower mass monophenylthiophene adducts could be eluted at much lower column temperatures.

Figures 6 and 7 show the chromatograms obtained for the products of photolysis (254 nm) of 2- and 3-PT in piperylene, respectively. In both cases numerous products of mass greater than the initial PT were observed. In Figure 6 the presence of 3-PT is noteworthy. The identity of this component was verified by coinjection with a small quantity of the authentic material. In addition to the occurrence of trapping by the diene, photorearrangement of 2-PT to 3-PT has taken place. Unfortunately this experiment was designed to yield only qualitative information about adduct formation with piperylene, and therefore no estimate of the efficiency of the rearrangement process under these conditions, as compared with its rate in the absence of

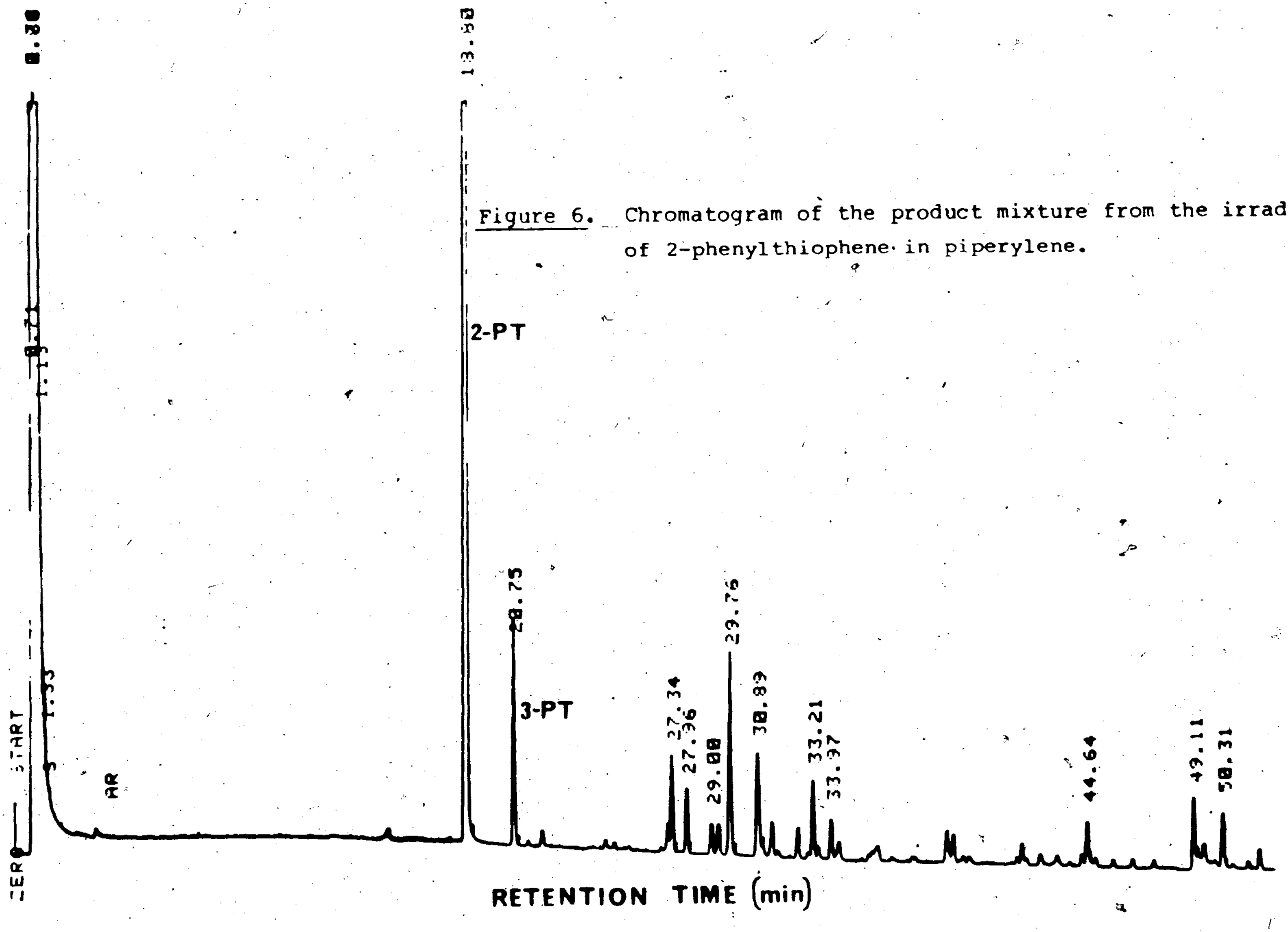


Figure 6. Chromatogram of the product mixture from the irradiation of 2-phenylthiophene in piperylene.

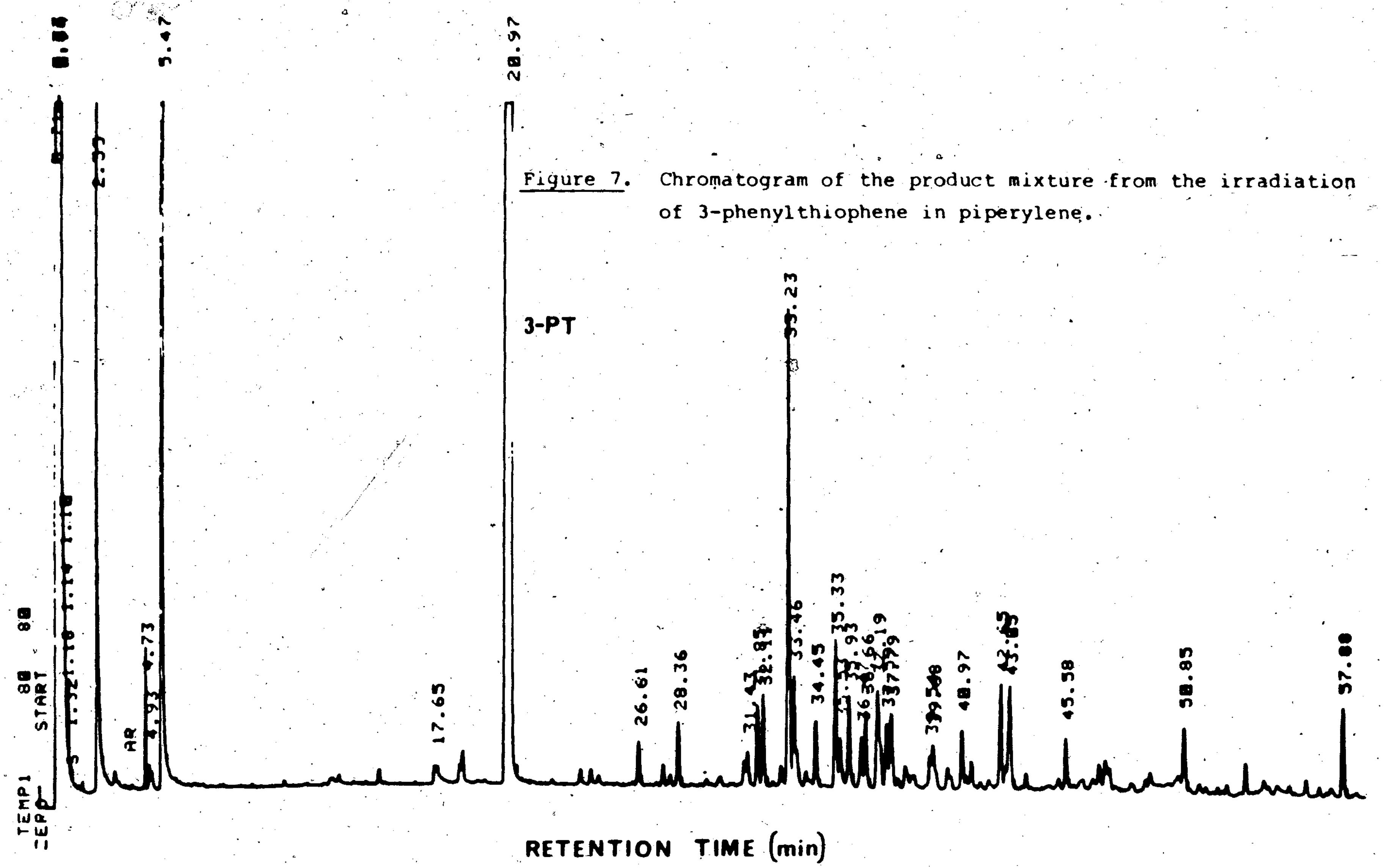
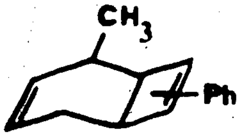


Figure 7. Chromatogram of the product mixture from the irradiation of 3-phenylthiophene in piperylene.

the diene, was gained. By contrast, the product mixture obtained from the photolysis of 3-PT (Figure 7) revealed no trace of 2-PT. This observation was consistent with the well documented, though not understood, irreversibility of the photoisomerization of 2-arylthiophenes to their 3-substituted counterparts.

The 3-PT product mixture was the first to be analyzed using capillary GC/MS to investigate some of the major products having retention times longer than the PT. Only the portion of the chromatogram beginning with 3-PT and including the higher mass products is shown in Figure 8. Mass spectra were obtained for each of the peaks indicated. Following 3-PT ($M^{+\cdot}$ 160) a minor product eluted which had a molecular ion at m/e 196. This corresponds to the mass for a desulfurized 1:1 PT-piperylene adduct of (m/e 228 -S). The fragmentation pattern of this product gave little further structural insight, but by analogy to the TPT results described earlier a bicyclic diene structure, **67**, might be suspected. After a small retention time interval (Figure 8) a cluster of product peaks was observed. Since these products were present in differing amounts twelve of the most abundant were selected for examination by MS. All twelve mass spectra were similar. Each displayed a molecular ion at m/e 228, corresponding to a 1:1 adduct between the diene and PT. In addition, the base peak was always located at m/e 160, which is the



67

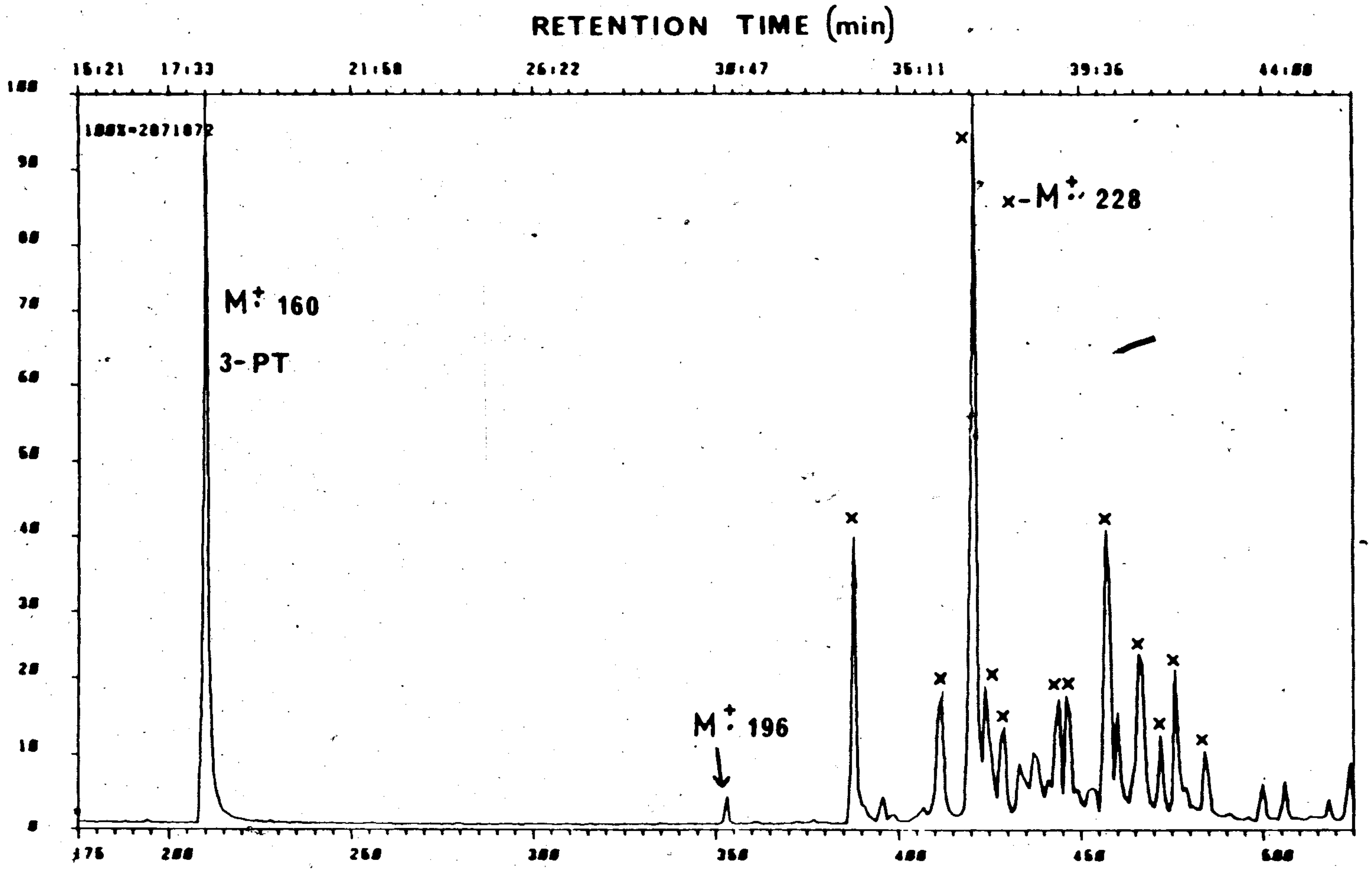


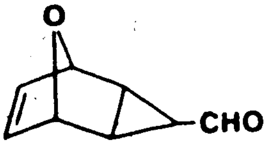
Figure 8. GC/MS analysis of the product mixture from the irradiation of 3-phenylthiophene in piperylene.

mass of PT. This implied that the major fragmentation pathway for each adduct involved a retro-addition process which regenerated PT and piperylene. Comparison of all twelve mass spectra provided no apparent clues about possible structural differences between the many isomeric 1:1 adducts.

It was assumed that the numerous products from the photolysis of 2-PT in piperylene (Figure 6) were also isomeric 1:1 adducts, and this mixture was not analyzed by capillary GC/MS. Clearly, the separation and characterization of so many isomeric products would be an arduous task.

The above results clearly demonstrate the possibility of trapping photochemically generated thiophene intermediates with an added diene. Upon consideration of the hypothetical mechanism for the trapping process however, it became apparent that in the cycloaddition of piperylene to an unsymmetrical dienophile generated by photolysis, the formation of a large number of isomers was possible. For instance, the tricyclic ring structure of an adduct such as 67 introduces four different stereochemical possibilities. The total number of isomers is even larger because of the unsymmetrical nature of the monosubstituted diene and dienophile, as well as the possibility that scrambling of the phenyl substituent might occur prior to the trapping step. Thus, it is possible to imagine 32 distinct isomeric compounds arising from the cycloaddition of piperylene to a Dewar thiophene generated by the photolysis of 2-PT.

Moreover, if other isomeric forms of 2-PT, capable of acting as dienophiles, were generated by irradiation and trapped with piperylene, then even more 1:1 adducts could be observed. For instance, with furans the results of many photolysis experiments have provided evidence for a ring contraction-ring expansion mechanism which generates cyclopropenyl aldehydes or ketones. Srinivasan reported the trapping of cyclopropene-3-carboxaldehyde via its cycloaddition to furan to produce 8. Comparable thioaldehydes or thioketones might conceivably be trapped during PT photolysis experiments.



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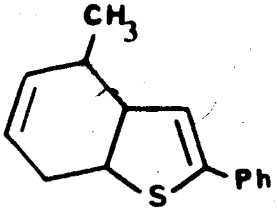
Further complexities to the mechanism of adduct formation can be envisaged. For example, the possibility that PT itself may also participate in cycloadditions must at least be recognized [142]. A Diels-Alder reaction with piperylene could yield a bicyclic structure such as 68. If the PT participated in a photochemical [2+2] cycloaddition with one double bond in the diene molecule then products similar to 69 might result.



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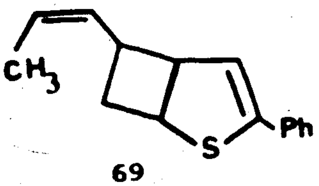

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The total number of 1:1 adducts that can be imagined is indeed quite large. Certainly not all of these adducts will be formed. In addition, the product ratios may be so widely diverse for different types of adducts that, to at least some extent, the number of adducts observed will depend on the technique used for their detection. Guidelines, which can help to predict the relative likelihood of certain cycloadditions, do exist. For example, the Woodward-Hoffmann rules utilize symmetry considerations about the MO's of the starting materials and products in analyzing the progress of different types of pericyclic reactions, including cycloaddition. However, there are many factors which can influence the course of a cycloaddition reaction, and theoretical predictions on unknown systems serve a very limited purpose, especially when the products are not isolated and characterized.

In view of the preceeding discussion the large number of 1:1 adducts observed for the 2- and 3-PT trapping experiments with piperylene is not unreasonable. These results confirm and broaden Wynberg's earlier success in trapping a 2-PT isomer with piperylene. In fact, he presumably trapped a mixture of many 1:1 adducts although this was not realized because the product was only analyzed by MS with no technique of fractionation. We have clearly established that photolysis of both monophenylthiophenes in piperylene leads to the formation of several 1:1 adducts. The implications of this simple observation regarding the photorearrangement mechanism of arylthiophenes will be dicussed later. These adducts had sufficient thermal stability to be observed by GC, contrary to Wynberg's finding.

Our next objective was to isolate and characterize the 1:1 adducts. It seemed unreasonable to attempt the isolation and characterization of each of the 1:1 adducts between piperylene and one of the monophenylthiophenes without first trying to simplify the adduct system to be separated. It was therefore decided to replace piperylene with a symmetrical diene in order to reduce the total number of 1:1 adducts possible, and 2,3-dimethylbutadiene (DMBD) was selected.

c. Photolysis of the Monophenylthiophenes in DMBD

Both 2-PT and 3-PT were photolyzed (254 nm) in DMBD and in each case the formation of 1:1 (m/e 242) and 2:1 (m/e 324) adducts between the diene and the PT was indicated by MS. Capillary GC analysis revealed much simpler product mixtures than were obtained using piperylene as the trapping agent, but the number of apparent 1:1 adducts was still approximately ten in both the 2-PT and 3-PT systems. Separate capillary GC/MS examinations of each product mixture revealed, in addition to the 1:1 adducts (m/e 242), two other compounds each having their molecular ion located at exactly three times the diene mass ($M^{\overset{+}{\cdot}}$ 246) and a base peak at m/e 82. These compounds had retention times very similar to those of the 1:1 adducts and were concluded to be trimers of DMBD. Under the experimental conditions employed in the DMBD trapping experiments, some of the incident radiation was directly absorbed by the diene. Owing to the small spectral overlap of the UV absorption of the diene with those for the phenylthiophenes, combined with the use of a large excess of diene, such a situation was unavoidable. The chromatograms and MS data from the 2-PT and 3-PT trapping experiments with DMBD are illustrated in Figures 9 and 10, repectively.

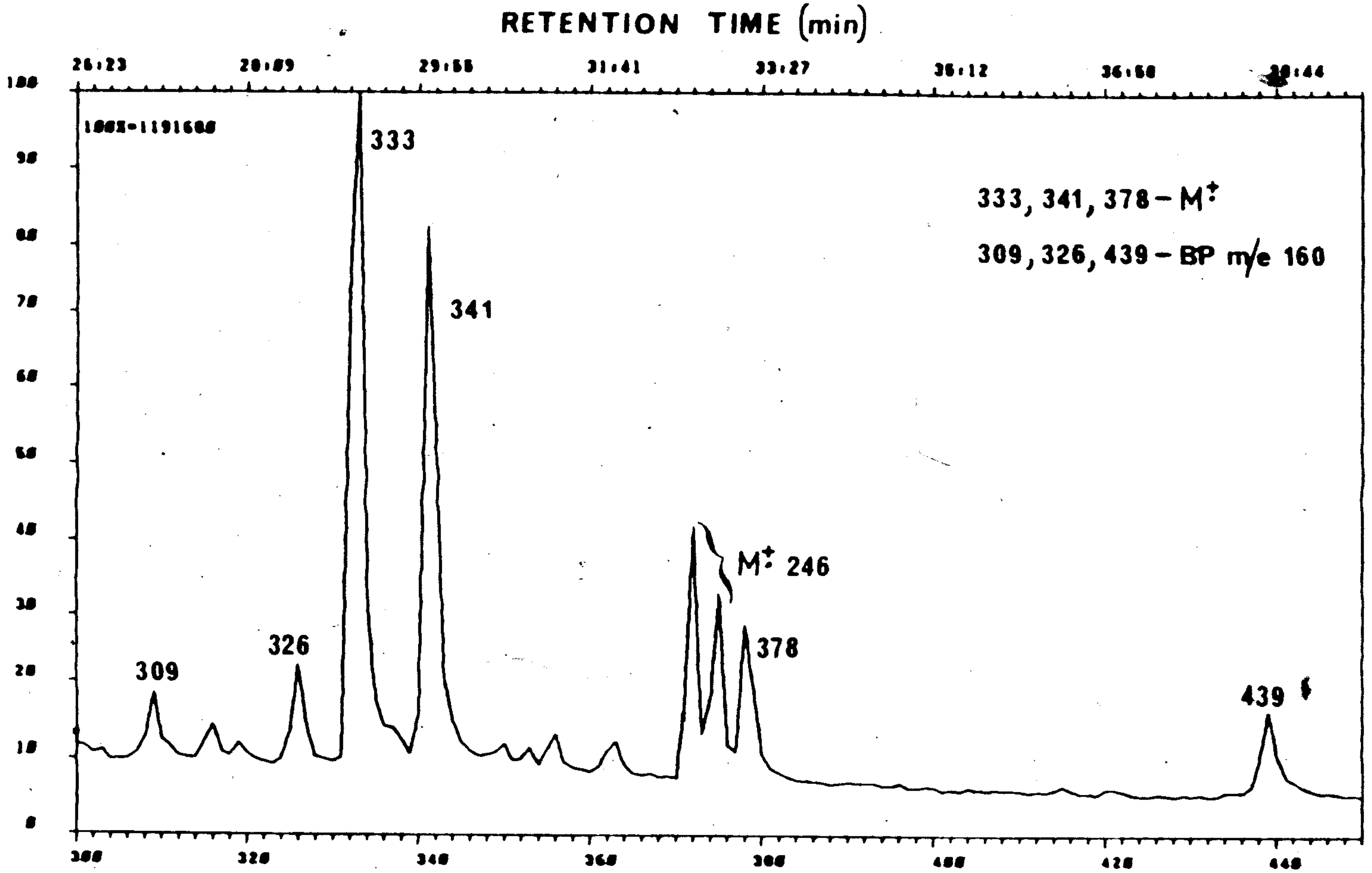


Figure 9. GC/MS analysis of the product mixture from the irradiation of 2-phenylthiophene in DMBD.

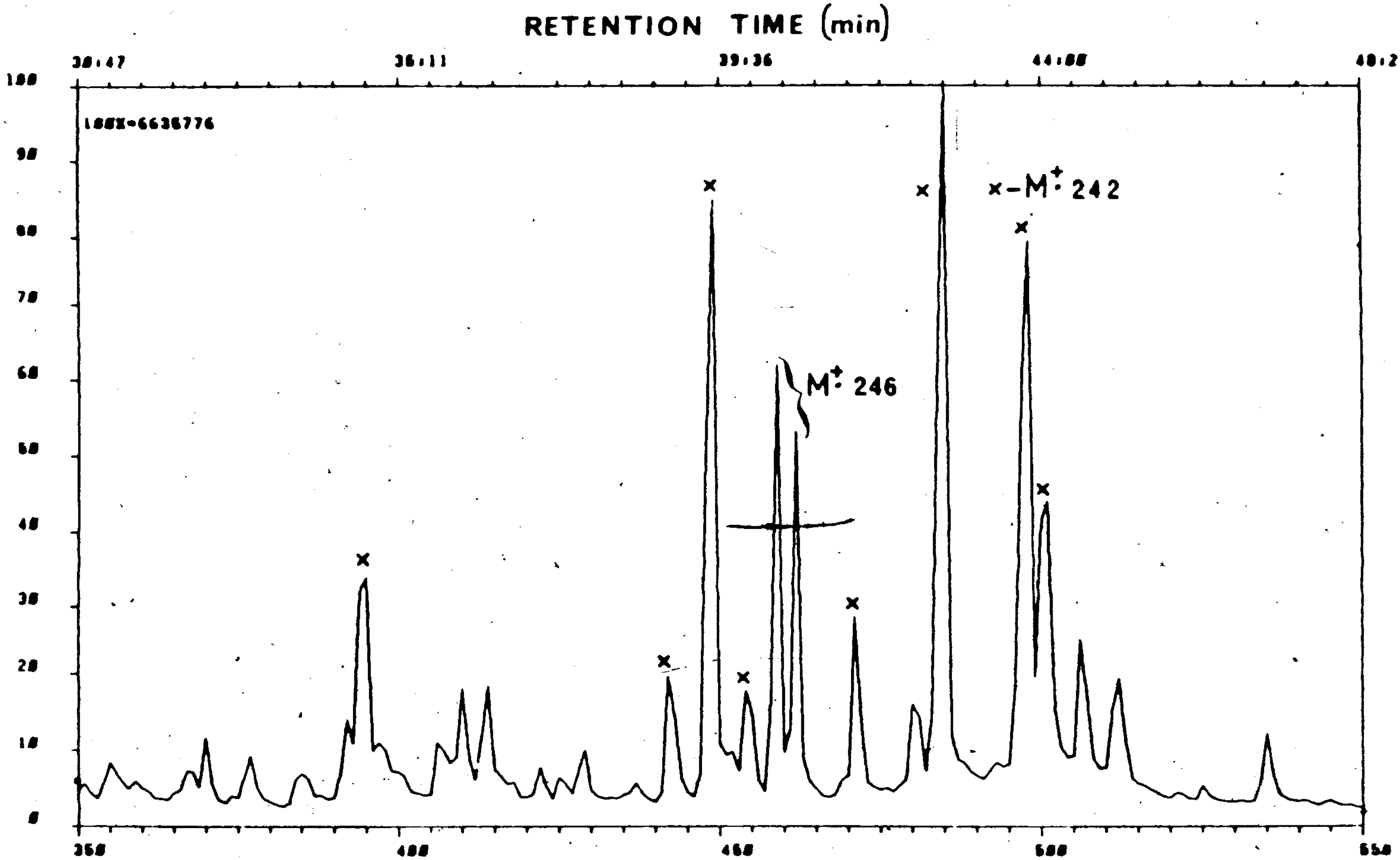


Figure 10. GC/MS analysis of the product mixture from the irradiation of 3-phenylthiophene in DMBD.

For the 2-PT-DMBD system three 1:1 adducts (peaks #333, 341, 378) were clearly identified from their mass spectra. In addition to the two DMBD trimers three other products (peaks #309, 326, 439) were also examined by MS. Although a weak molecular ion at m/e 242 was detected in only one of the three compounds (peak #326), each had a base peak at the PT mass (m/e 160) similar to the three 1:1 adducts (peaks #333, 341, 378) which did produce strong molecular ion peaks. This was considered to suggest that these three products might also be 1:1 adducts.

The GC/MS results for the 3-PT-DMBD system (Figure 10) revealed a total of eight 1:1 adducts. Each adduct produced a molecular ion signal at m/e 242, but again the relative intensity of these molecular ion peaks varied considerably between the different adducts. The two products assigned as DMBD trimers were also observed, eluting in the middle of the various 1:1 adduct products.

d. Photolysis of Thiophene in Furan

Concurrent with our solution phase trapping experiments with the monophenylthiophenes and DMBD an in-situ solution phase trapping experiment with a symmetrical thiophene, specifically parent C_4H_4S, was designed. In addition to reducing the total possible number of trapped isomeric products, the use of parent thiophene would simplify the task of product characterization by NMR, as compared with adducts containing phenyl substituents. Reports of thiophene ring scrambling in isotopically labelled parent thiophenes were described earlier in the Introduction. Although no comparable photoinduced scrambling in the parent thiophene was known, it seemed likely that the mechanism of carbon atom scrambling in the thiophene ring, which is responsible for converting 2-substituted thiophenes to their corresponding 3-substituted derivatives, also operates in the parent molecule. However, in the absence of isotopic labelling, the difference between the initial thiophene and a scrambled thiophene cannot be detected.

The short-lived species generated during the photolysis of thiophenes have lifetimes that are dependent not only on their structure and the experimental conditions but also on the nature of any substituents. In the PT trapping experiments cycloaddition to the diene must be competing with other processes which consume the short-lived intermediates. For the parent thiophene the analogous intermediates, if formed, may have significantly different lifetimes. In particular any stabilizing influence imparted by the presence of the aromatic chromophores would be absent in the unsubstituted case. This could dramatically alter the trapping efficiency.

Acknowledging these considerations, it remained to attempt a solution phase trapping experiment with thiophene, C_4H_4S. Owing to the very short wavelength UV absorption of thiophene ($\lambda_{max} \sim 230$ nm), as compared to the phenylthiophenes, it was evident that with the typical diene/thiophene ratios used in the PT experiments nearly all of the incident radiation would be absorbed by the diene. Consequently, substituted butadienes such as piperylene or DMBD were unsuitable as trapping reagents for solution phase photolysis experiments with thiophene. Instead, furan was selected for this purpose. The successful use of furan to intercept short-lived intermediates during photolysis of cyanopyrroles and cyanothiophenes was reported by Day et al. [84,125]. Srinivasan also discovered the diene properties of furan by trapping cyclopropenyl carboxaldehyde in the gas phase [34,35]. The UV absorption spectrum of furan in solution has a maximum near 215 nm. Consequently the Cd($^1P_1$) resonance radiation (229 nm) used for these experiments was mostly (ca. 85%) absorbed by the thiophene, even in the presence of a large molar excess of furan. Moreover, furan has the advantage of being a symmetrical diene, and therefore the total number of isomeric products generated by its cycloaddition reaction with a particular dienophile should be less than for the same reaction with piperylene as the diene.

The irradiation (229 nm) of a solution of thiophene in furan (mole ratio ~ 1/10) at ca. 25°C produced five principal products detected by capillary GC. Analysis by capillary GC/MS (OV-101, 0.3 mm × 50 m, T_1 = 115°C, rate 2°C/min) revealed that the first three products were likely furan dimers, $M^{+\cdot}$ 136, while the last two were 1:1 adducts of thiophene and furan, $M^{+\cdot}$ 152. These capillary GC/MS results are presented in Figure 11.

2. Isolation and Structural Identification of Trapped Intermediates

a. Furan/Thiophene Adducts

The present work, together with earlier literature reports, has clearly shown that solution phase photolysis of thiophene and various substituted thiophenes in the presence of a diene generates 1:1 thiophene/diene adducts, readily detected by MS. Our trapping

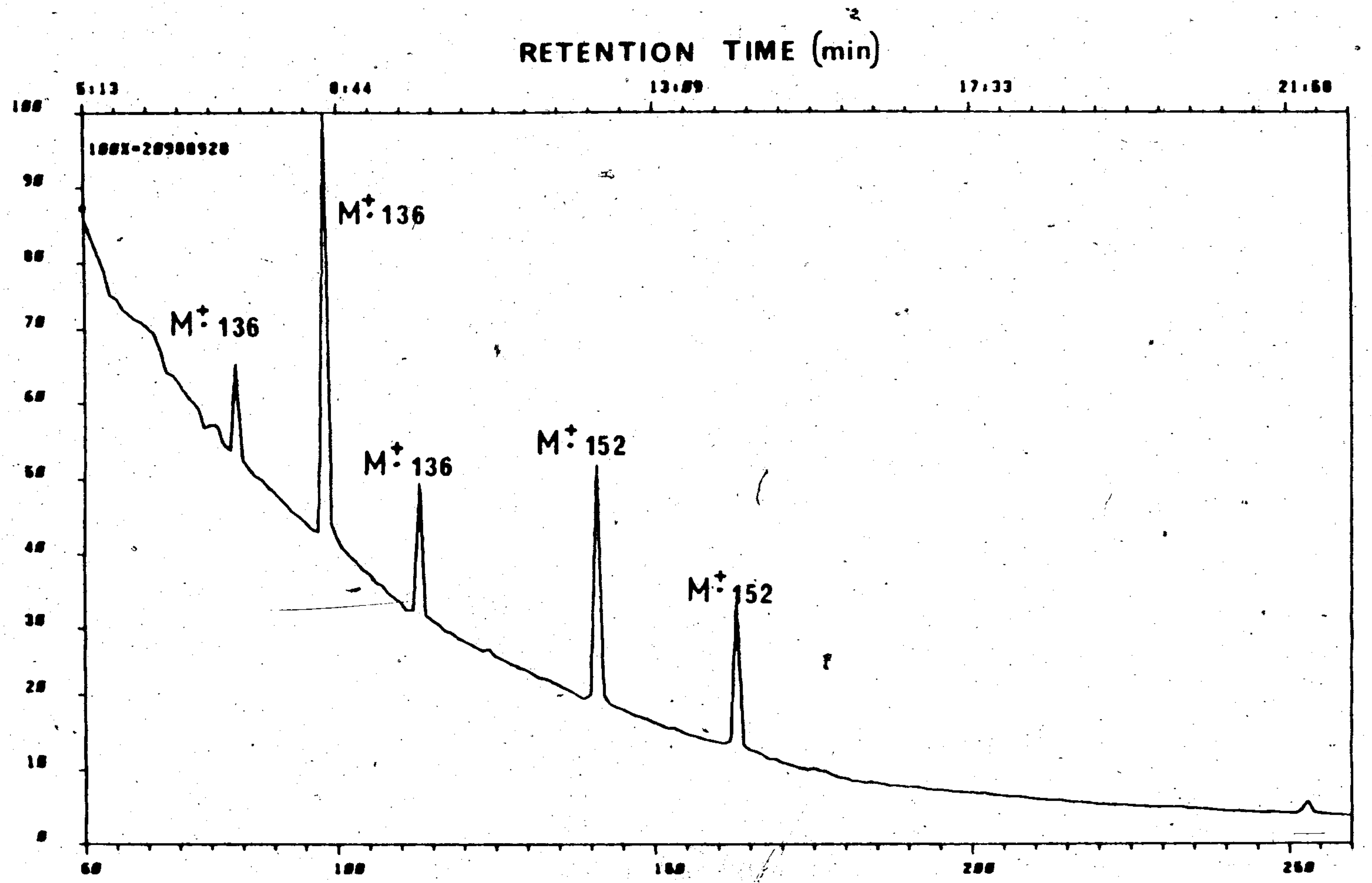


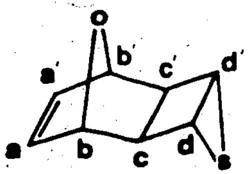
Figure 11. GC/MS analysis of the product mixture from the irradiation of thiophene in furan.

results with piperylene confirmed and extended Wynberg's earlier findings, but also revealed a previously unappreciated complexity in the product distribution. Except for the results of the desulfurization experiments on the trapped adducts obtained from the photolysis of TPT, which suggested a Dewar structure for the thiophene moiety, little information about the actual structure of any of the trapped species has been provided. However, the photolysis of thiophene in furan seemed to produce only two adducts, thereby simplifying their isolation and characterization.

A number of furan/furan adducts were also obtained, providing the additional possibility of obtaining information on the types of intermediates formed during the photolysis of furan. Although these aspects were not of primary interest in the solution phase trapping experiments with furan, knowledge of these intermediates is important for at least two reasons. Firstly, Srinivasan had reported the trapping of cyclopropene and cyclopropenyl carboxaldehyde by furan during the gas phase photosensitization of furan. Secondly, as stated amongst the objectives of the current investigation we wished to perform low temperature matrix isolation experiments with furan and hence the unexpected furan dimer products from the solution phase experiments might provide an important connection between the low temperature matrix and the room temperature solution phase experiments.

On completing the irradiation of thiophene in furan the polymer which formed was separated by filtration, and excess furan and thiophene were removed by distillation. A small quantity of yellow oil remained. In order to check whether any of the products might be the cyclopropenyl aldehyde trapped by Srinivasan, a GC/FTIR experiment (10% SE-52, ~3 mm × 3 m, 145°C) was performed. GC/FTIR confirmed the presence of an aldehyde in each of the first three (Figure 11) principal photolysis products, by the characteristic C=O and C-H stretching absorptions. The two furan/thiophene adducts definitely were not aldehydes. This latter result virtually negated the possibility that the five principal products consisted only of photolytically generated isomeric C_4H_4O species, trapped by either furan or thiophene. Since the initial focus of the current investigation was thiophene photochemistry, it was decided to first pursue the complete characterization of the two heavier molecular weight products, which hopefully would be thiophene photolysis products trapped by furan.

The IR spectra of these two compounds, **70** and **71** (Figures 12 and 13) were very similar, consistent with the possibility that these adducts might be stereoisomers. Compounds **70** and **71** were separated by preparative GC (15% SE-30, ~6 mm × 2 m, 130°C) and each was assigned the structure of a furan DAa with Dewar thiophene on the basis of their MS, and ^{1}H and ^{13}C NMR spectra, to be described now.



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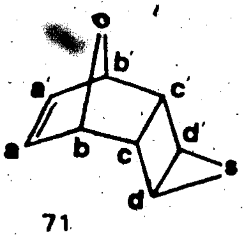

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Exact mass measurements on the separated adducts gave an $M^{+\bullet}$

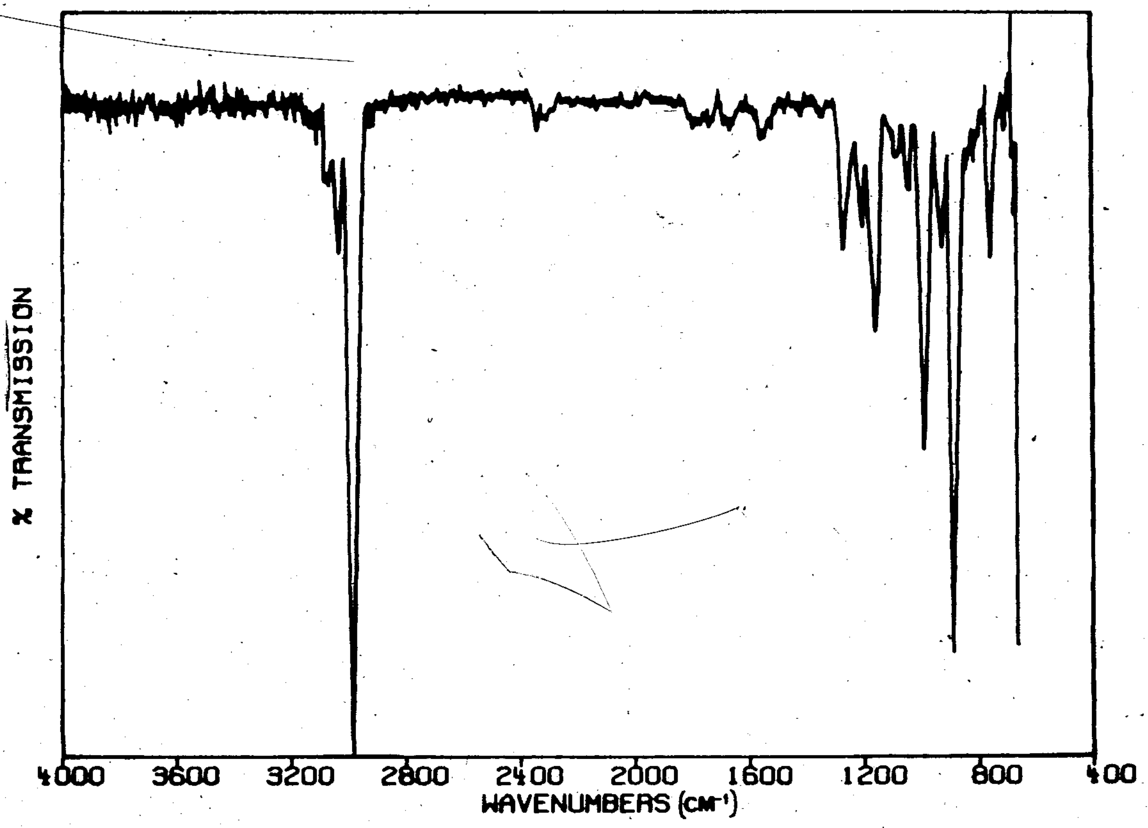


Figure 12. IR spectrum of **70** obtained by GC/FTIR.

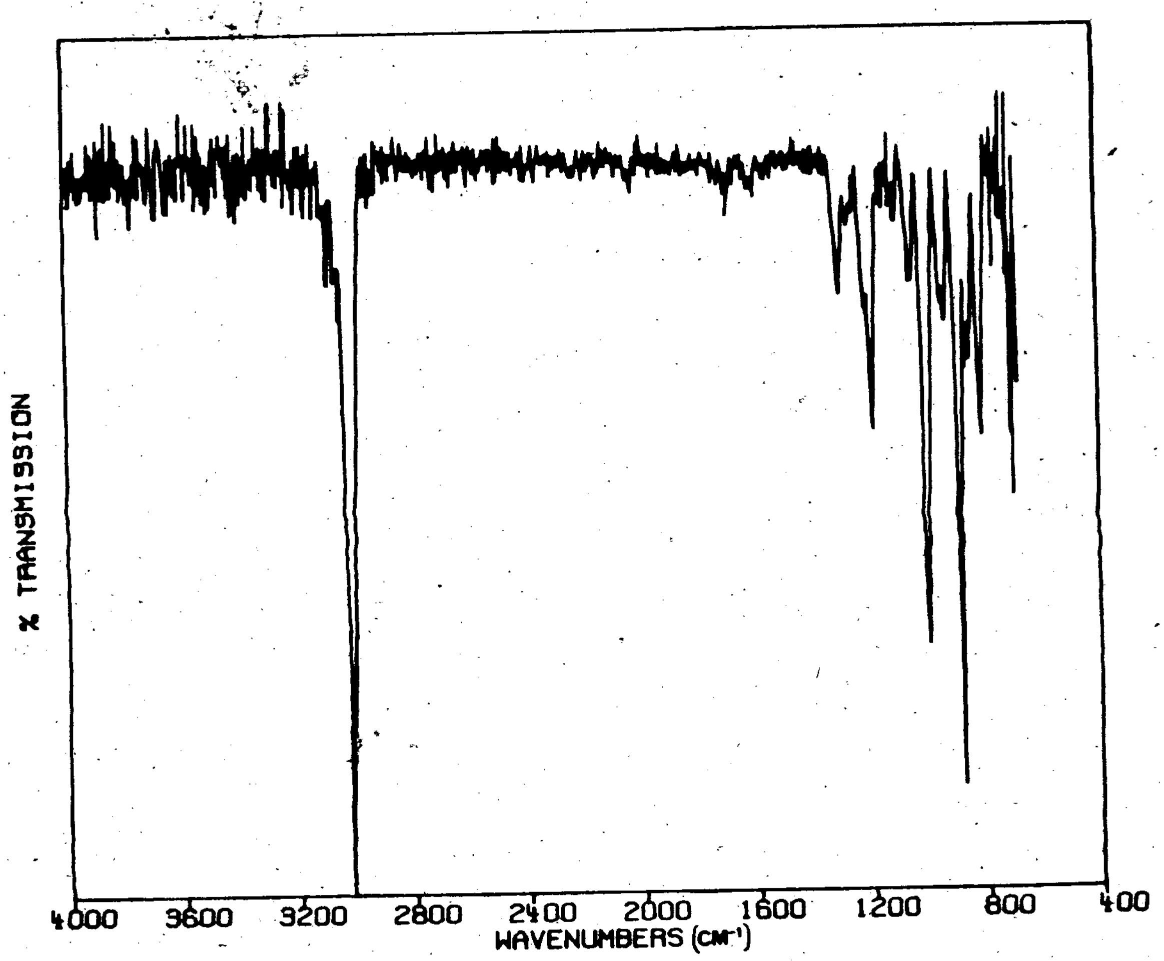
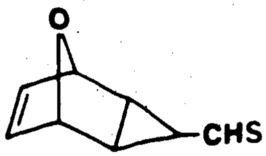


Figure 13. IR spectrum of **71** obtained by GC/FTIR.

corresponding to the molecular formula C_8H_8OS. MS also revealed that the formation of C_4H_4S and C_4H_4O was a major fragmentation process for each adduct (**70**, m/e 152(90%), 123(78%), 107(63%), 84(100%), 68(84%); **71**, m/e 152(51%), 123(77%), 107(43%), 84(100%), 68(66%)). The presence, in each isomer, of a base peak at m/e 84 as well as a large peak at m/e 68 is consistent with the known tendency of cyclic olefins to undergo a Diels-Alder retrogression in the mass spectrometer [143]. As with the McLafferty rearrangement, either fragment in the Diels-Alder retrogression may retain the charge. By contrast, an adduct such as **72**, formed by furan trapping of a cyclopropenyl thioaldehyde, would probably not be expected to produce a strong signal at m/e 84.



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The structures of **70** and **71** were decisively established by the ^1H and ^{13}C NMR results. In each case the ^1H NMR showed four sets of two chemically equivalent protons and the ^{13}C NMR, four sets of two identical carbon atoms, in agreement with the C_s symmetry of the structures. The ^1H NMR spectra of **70** and **71** are shown in Figures 14 and 15. These spectra also include the frequency expansions and selective ^1H decoupling results used to confirm the adducts' structures and assign their stereochemistry. The ^{13}C NMR spectra of these same products are illustrated in Figures 16-18. The symmetries of the adducts, witnessed in the NMR spectra, alone provided strong qualitative evidence for structures **70** and **71**. The NMR data for the

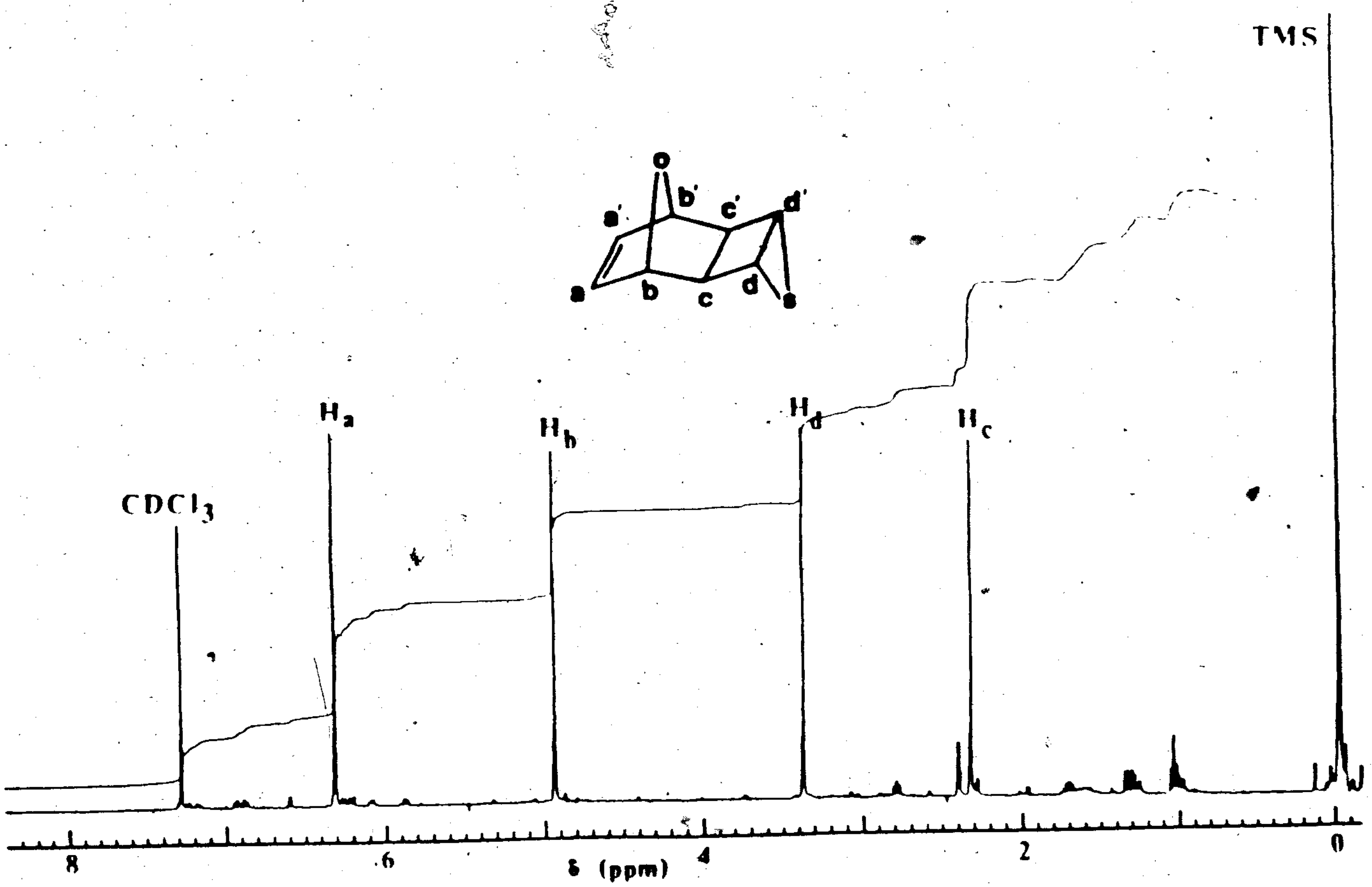


Figure 14a. 400 MHz ^1H NMR spectrum of 70.

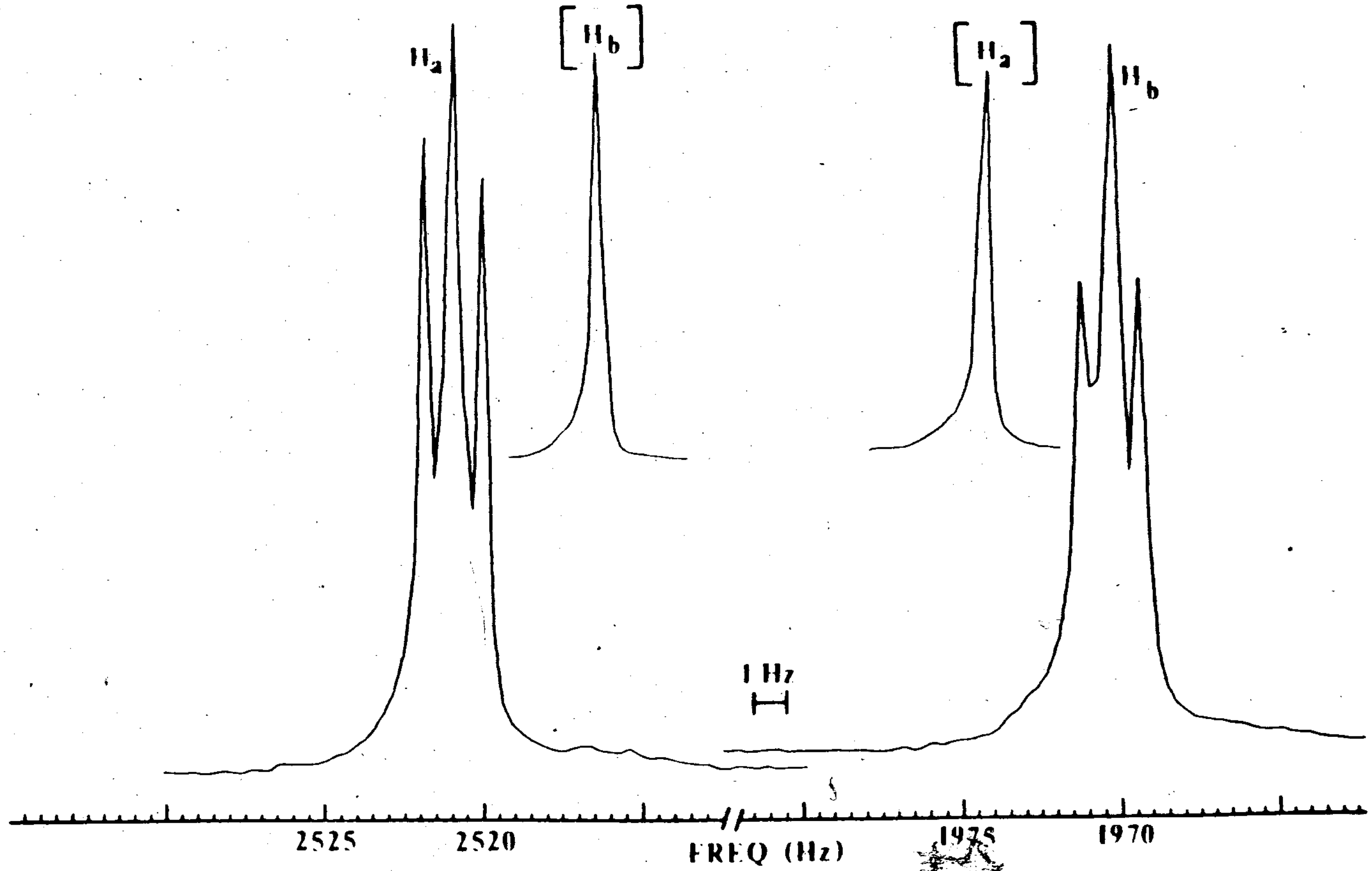


Figure 14b. Frequency expansion and selective ^{1}H decoupling at ca. 2524 and 1972 Hz.

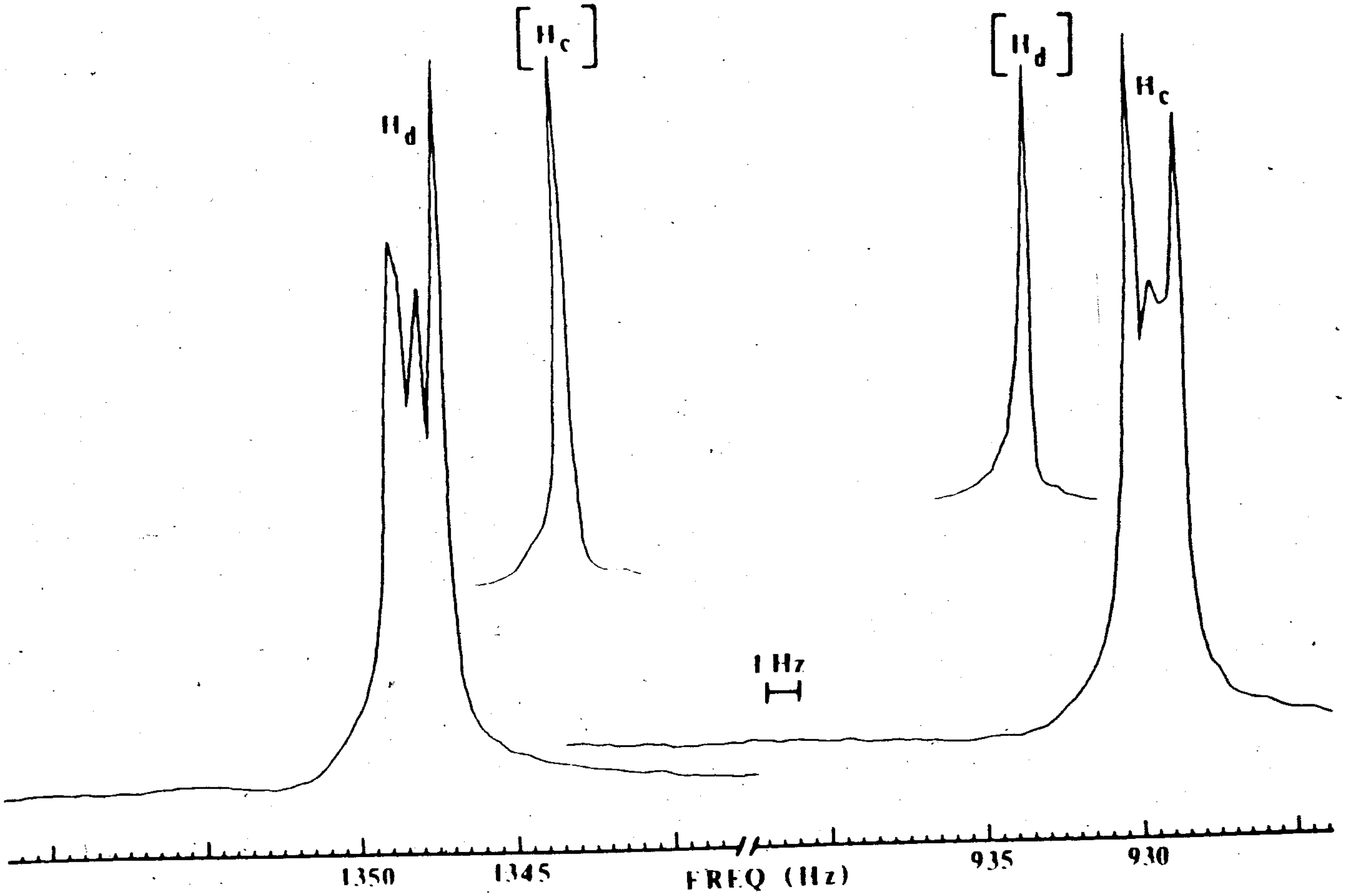


Figure 14c. Frequency expansion and selective ^{1}H decoupling at ca. 1348 and 928 Hz.

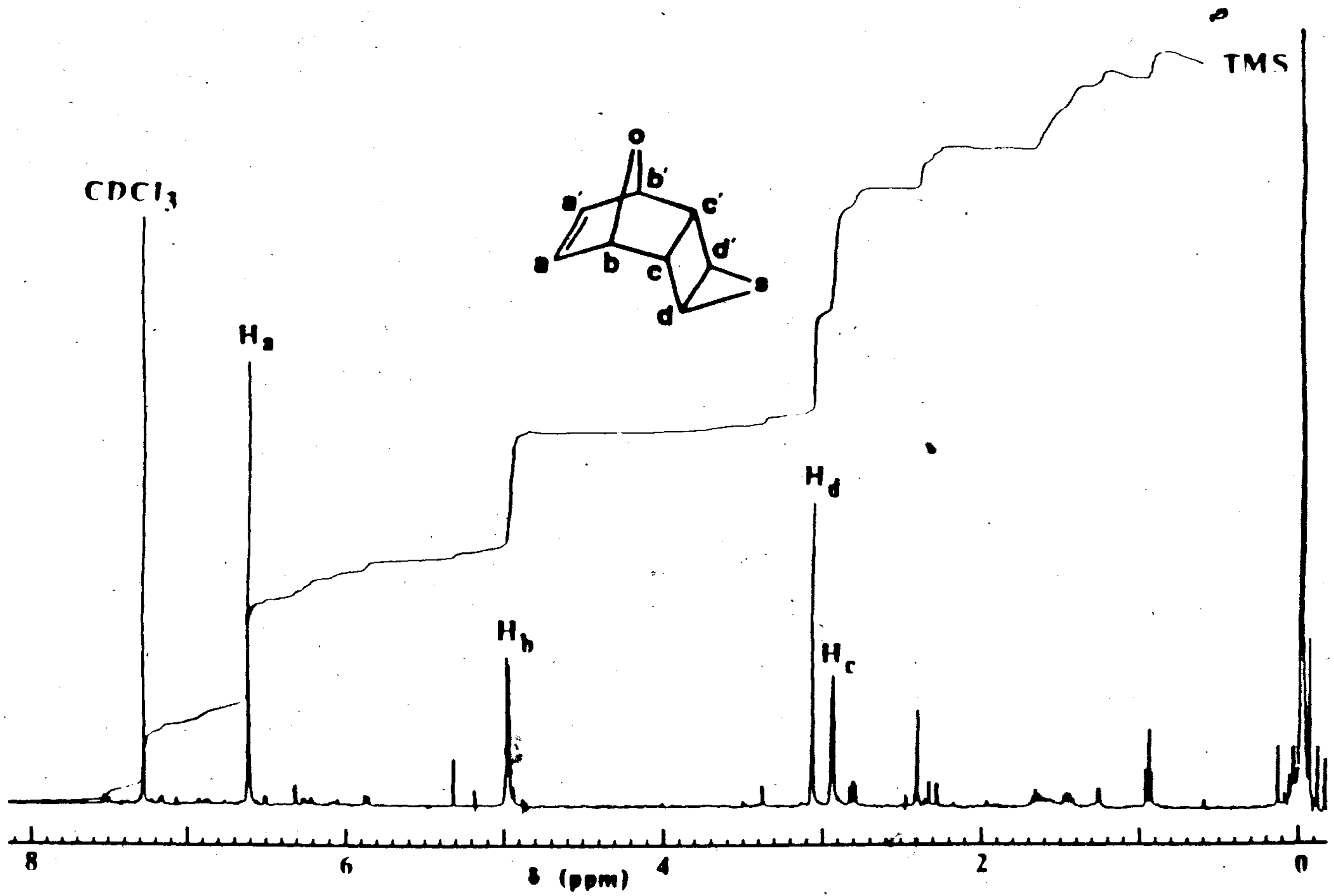


Figure 15a. 400 MHz ^{1}H NMR spectrum of 71.

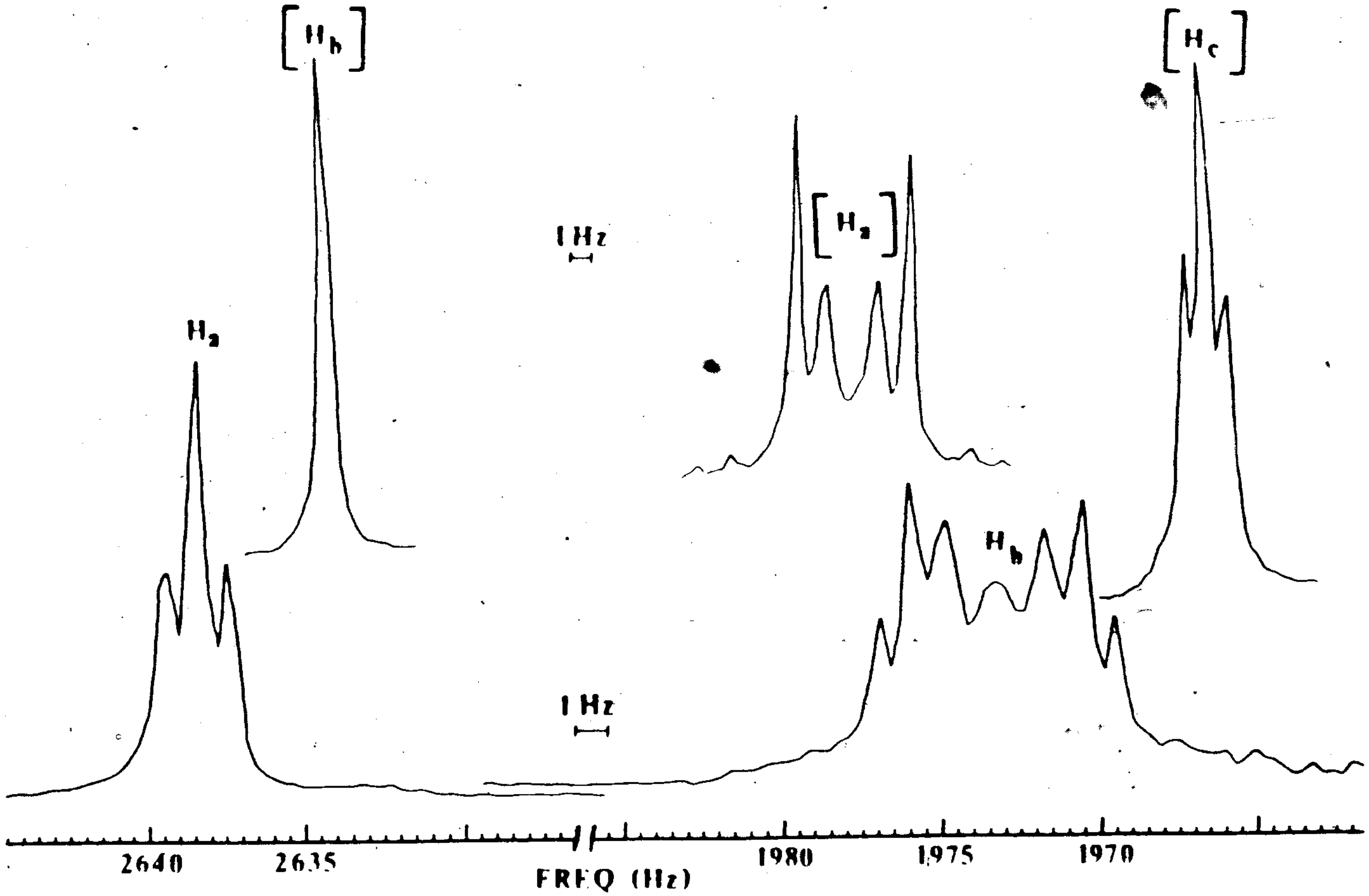


Figure 15b. Frequency expansion and selective ^{1}H decoupling at *ca.* 2640, 1988 and 1172 Hz.

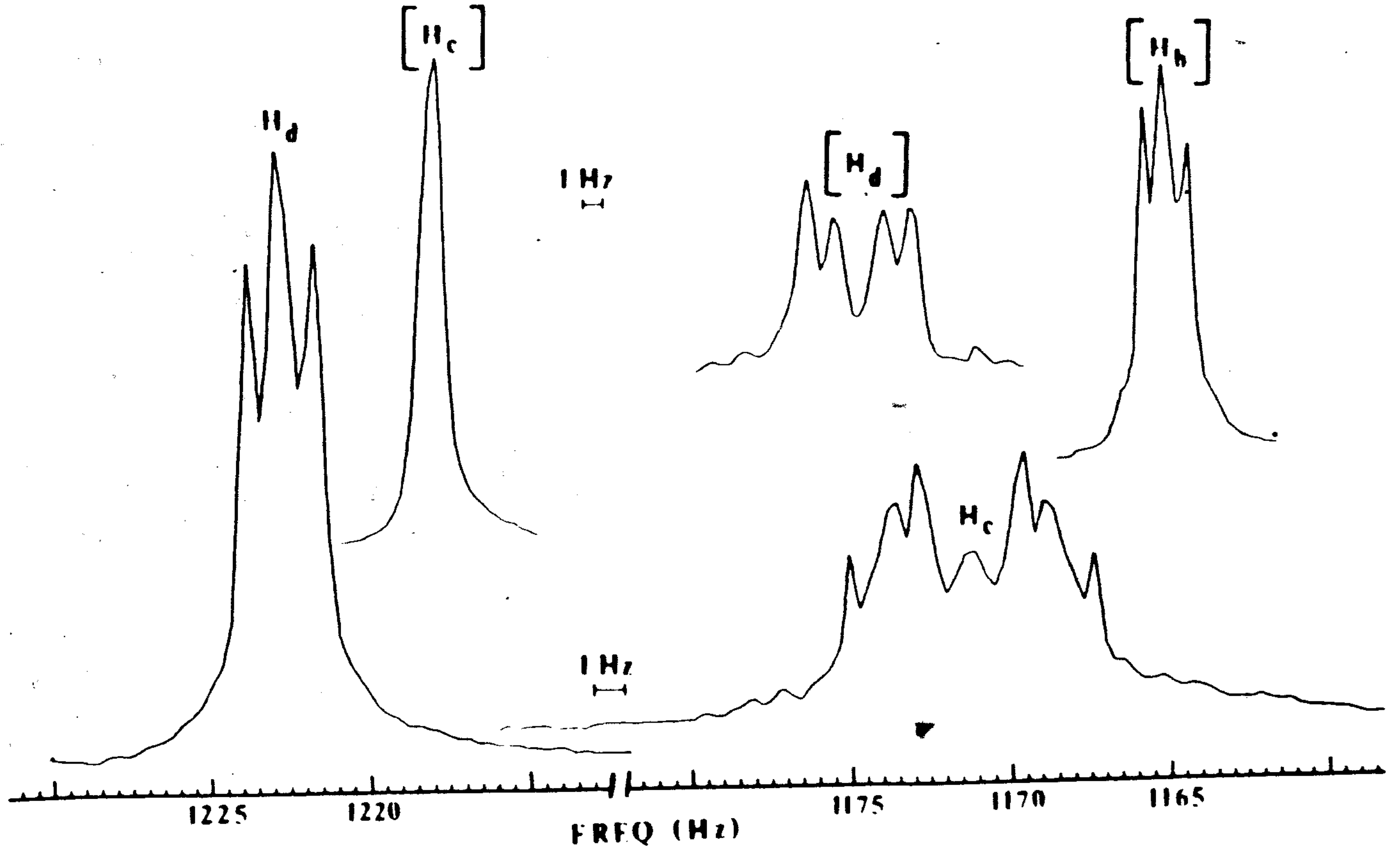


Figure 15c. Frequency expansion and selective ^{1}H decoupling at ca. 1988, 1224 and 1172 Hz.

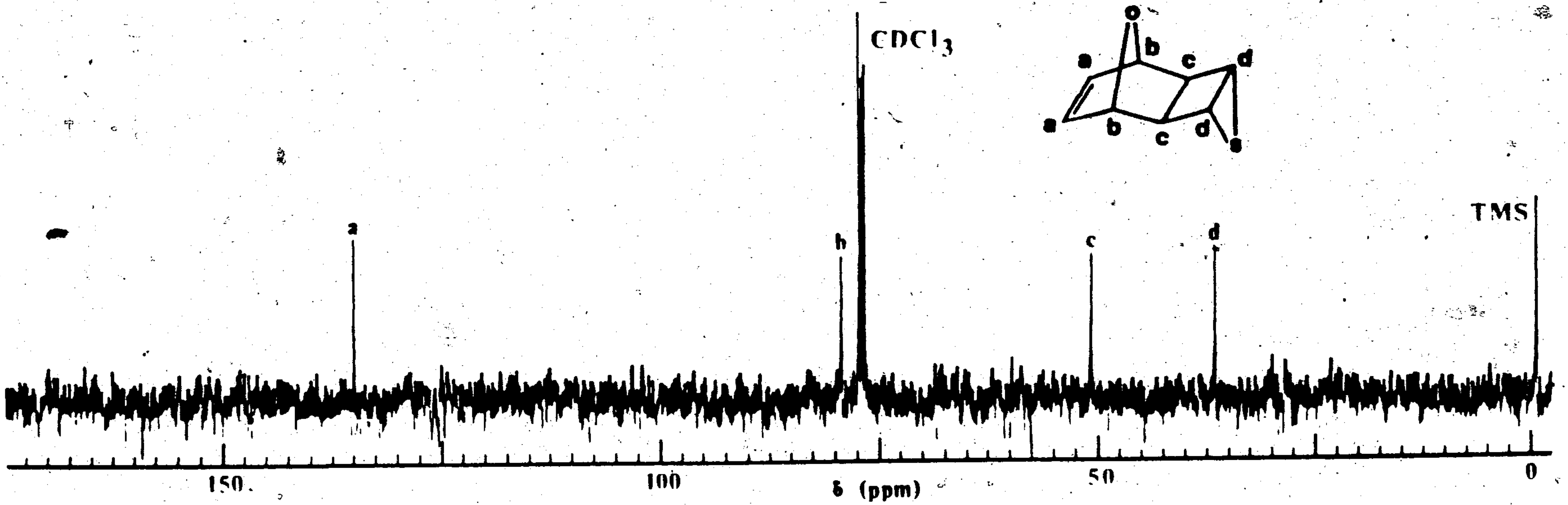


Figure 16. 100 MHz ^{13}C NMR spectrum of **70** (7000 scans).

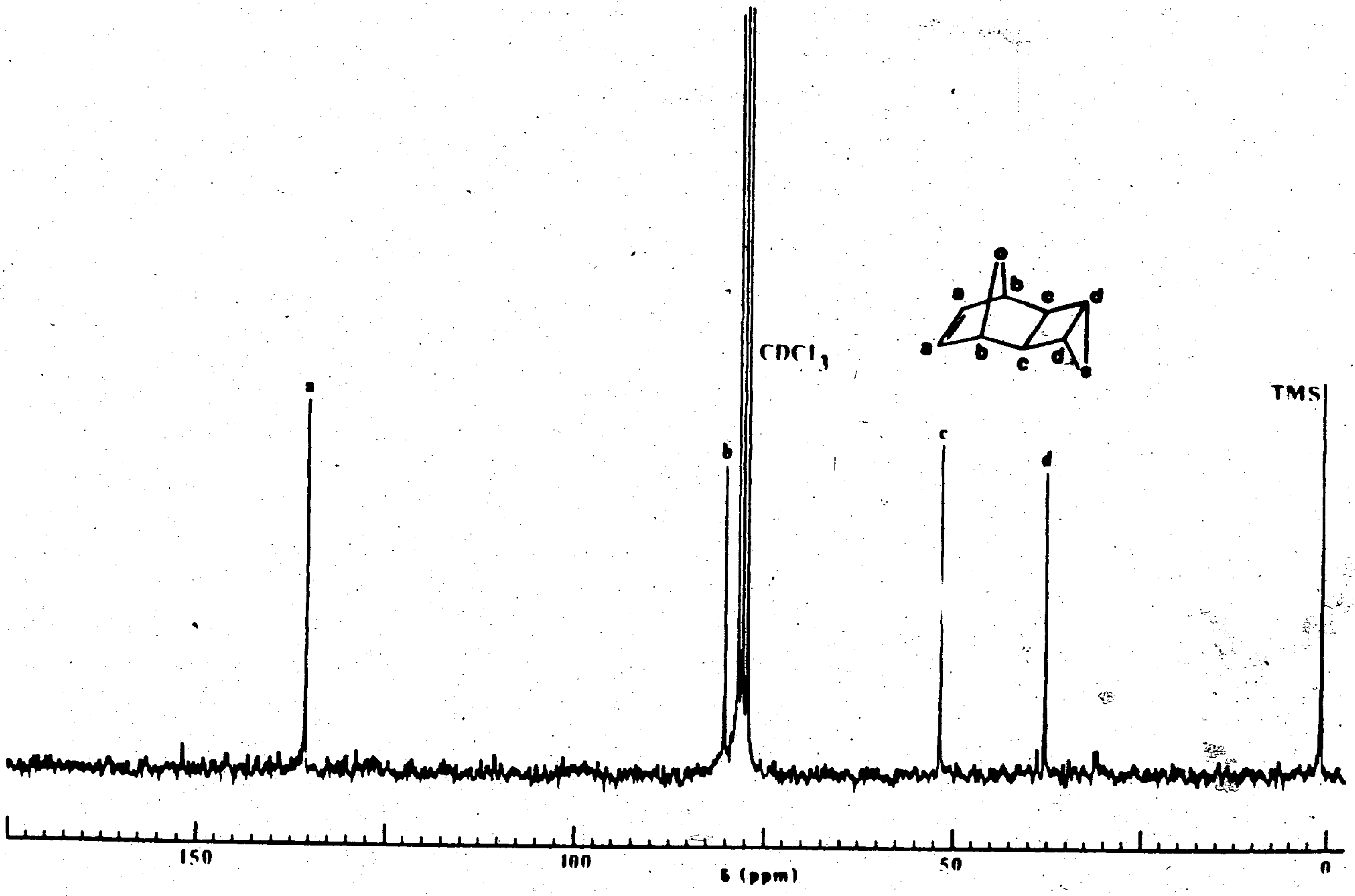


Figure 17. 50 MHz ^{13}C NMR spectrum of 70 (91 000 scans).

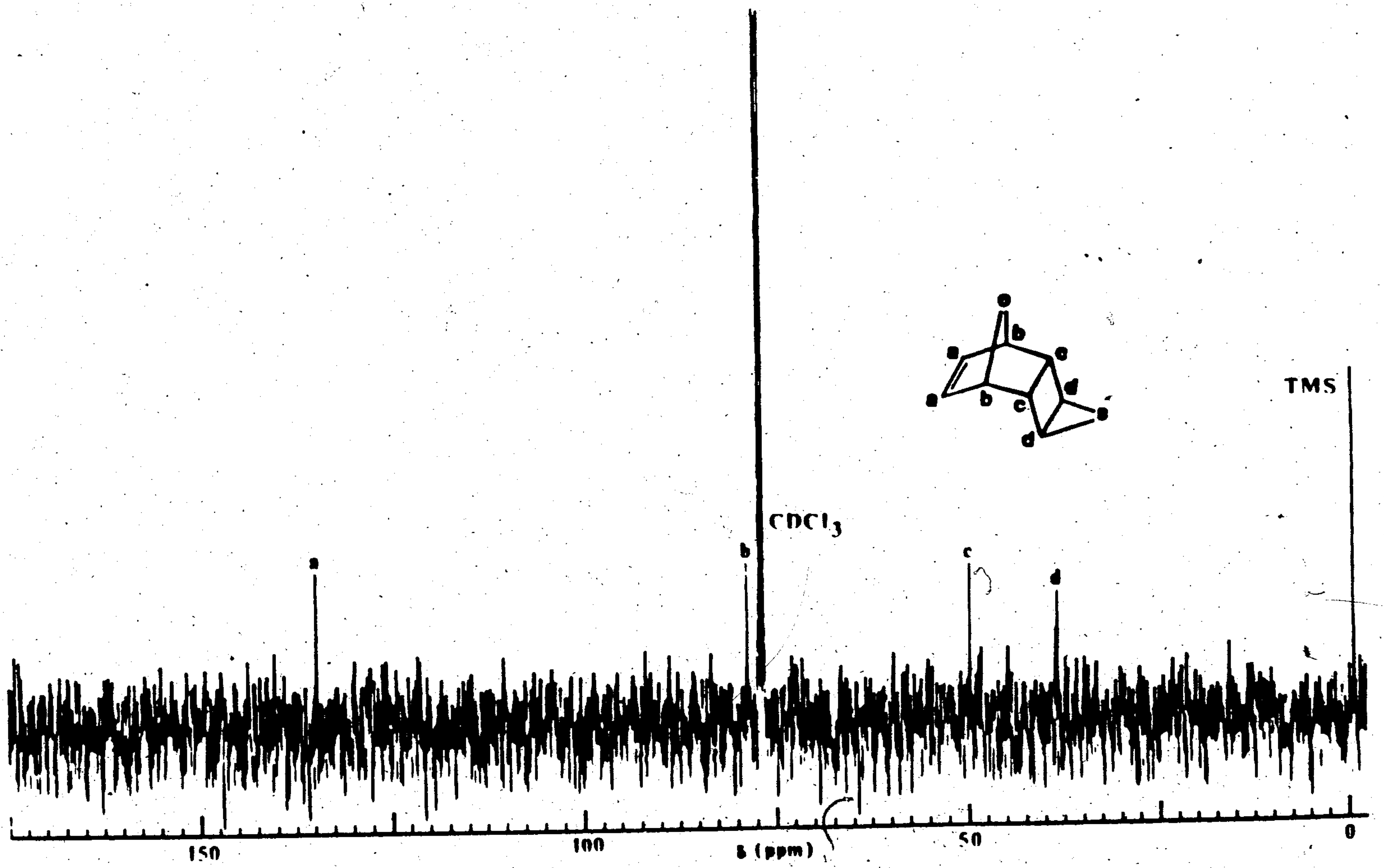
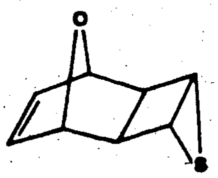


Figure 18. 100 MHz ^{13}C NMR spectrum of 71 (6800 scans).

two Dewar thiophene adducts with furan are summarized in Table 6. The ^{1}H and ^{13}C chemical shifts are entirely consistent with the assigned structures. The carbon and hydrogen connectivities for the assignments made in Table 6 have been experimentally verified for the case of **70** by selective ^{1}H decoupling results in the ^{13}C NMR. These decoupling results are presented in Figure 19.

Some elaboration on the NMR data is required in order to demonstrate the method for determining the stereochemistry of the adducts. In principle the Diels-Alder cycloaddition between Dewar thiophene and furan could produce four different stereoisomers. This is most easily realized by recognizing that two possible configurations exist for the cyclobutane ring, either <u>exo</u> or <u>endo</u>, relative to the olefinic end of the molecule. In addition, there are two possible configurations of the thiirane ring for each configuration of the four-membered ring. The structures of all four possible stereoisomers are illustrated below. Structures **70** and **71**



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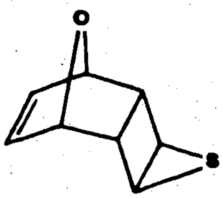

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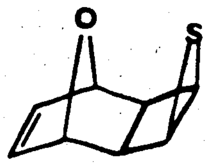

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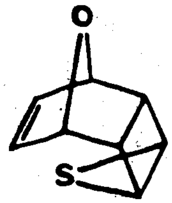

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were already assigned to the experimentally observed products, while stereoisomers **73** and **74** were not detected.

Although the symmetry of these molecules gives rise to magnetically nonequivalent protons and renders their ^{1}H NMR spectra higher than first order, selective decouplings in the ^{1}H NMR spectra

TABLE 6

400 MHz ^{1}H and 100 MHz ^{13}C NMR Data for **70** and **71**

Adduct	Chemical Shifts (ppm)[a]		Assignment[b]
	δ_H	δ_C	
70	6.31	134.9	a,a'
	4.93	79.4	b,b'
	3.37	36.9	d,d'
	2.32	51.0	c,c'
71	6.60	134.8	a,a'
	4.97	78.8	b,b'
	3.06	38.6	d,d'
	2.93	50.0	c,c'

[a] Chemical shifts in $CDCl_3$ relative to TMS.

[b] The prime notation is introduced to account for the magnetic nonequivalence within each set of chemically equivalent atoms.

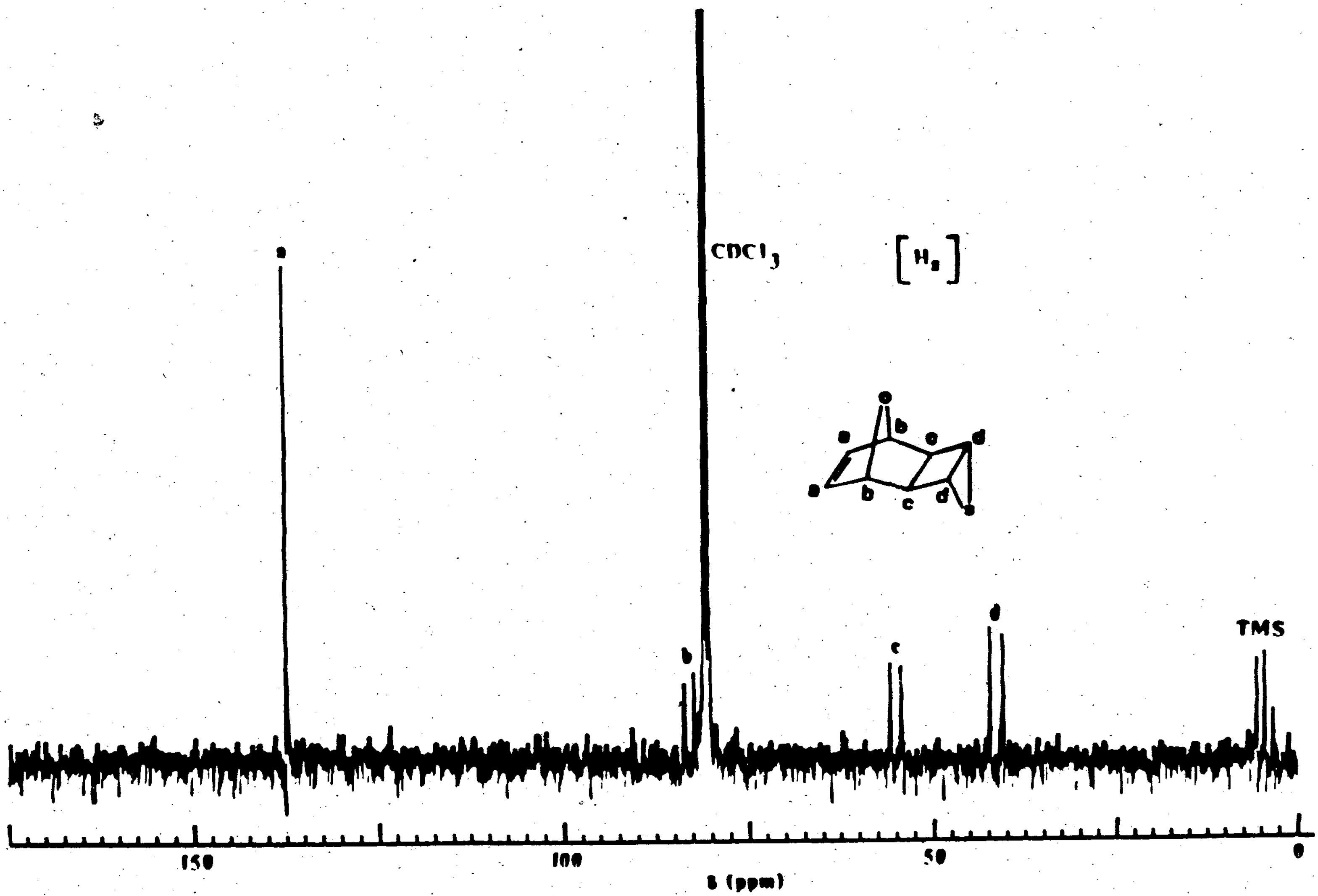


Figure 19a. Selective ^{1}H decoupling in the 100 MHz ^{13}C NMR of 70. Decoupling protons H$_a$, δ_H = 6.31 ppm.

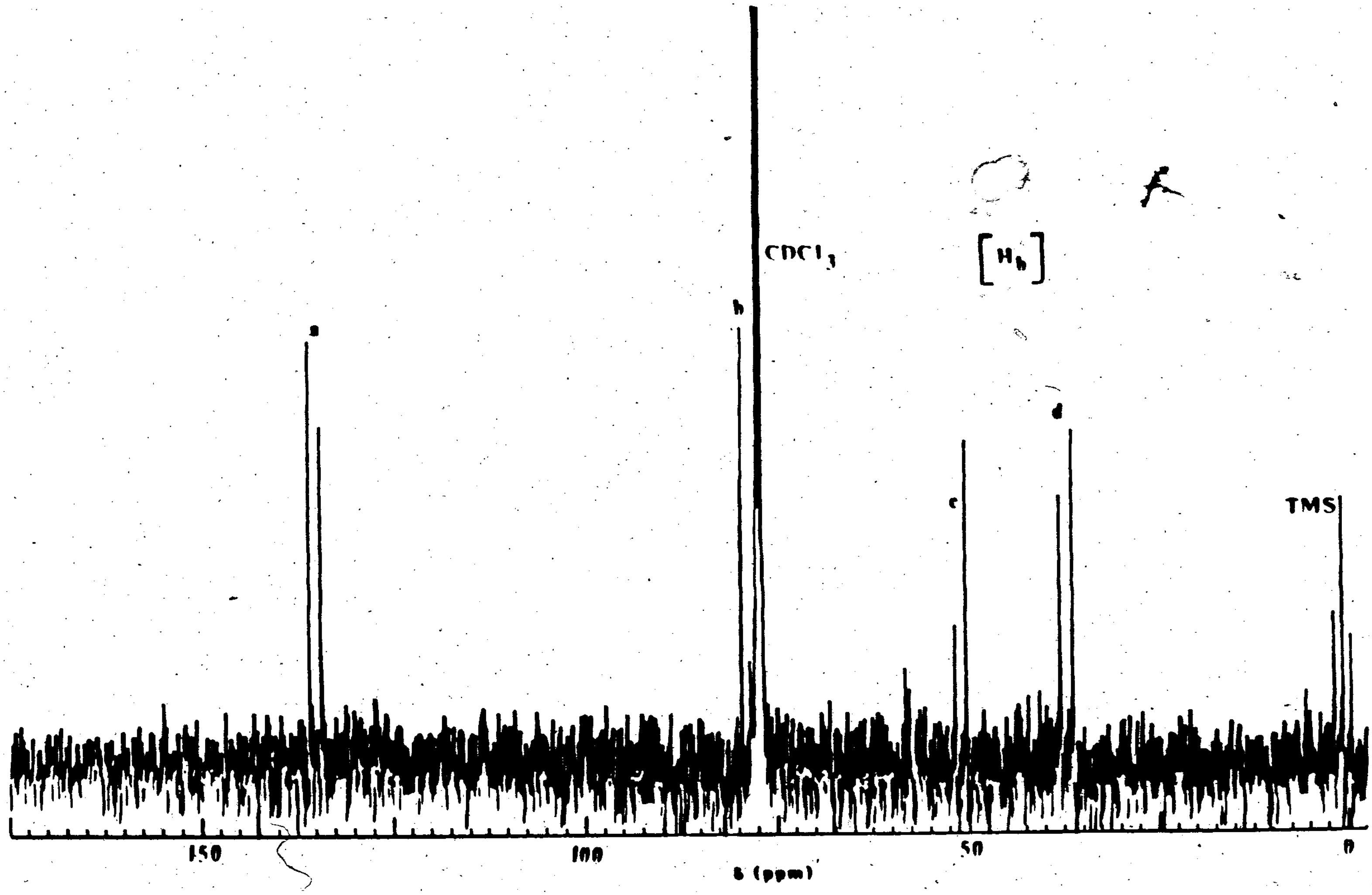


Figure 19b. Decoupling protons H_b, δ_H = 4.93 ppm.

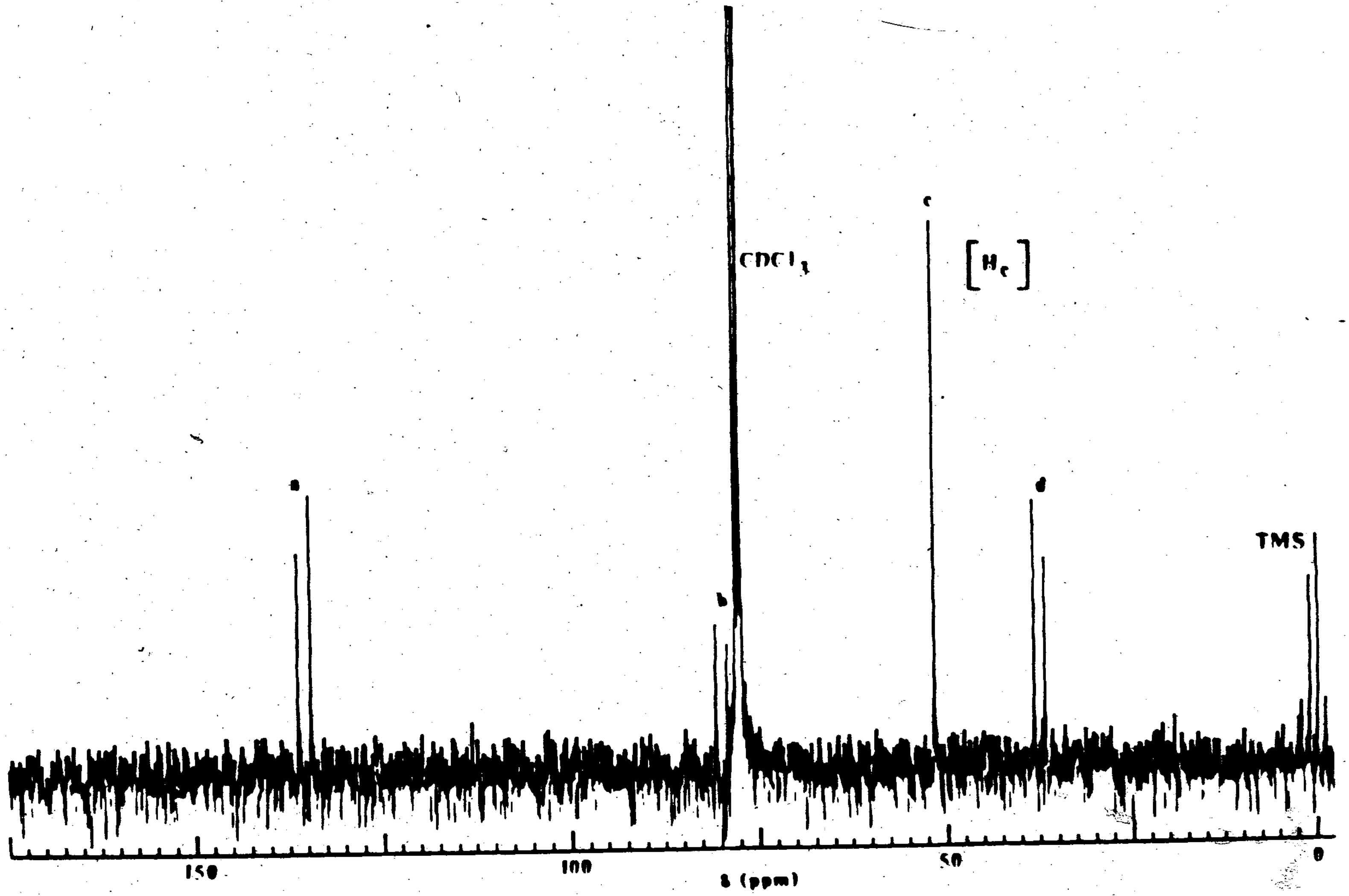


Figure 19c. Decoupling protons H_C, δ_H = 2.32 ppm.

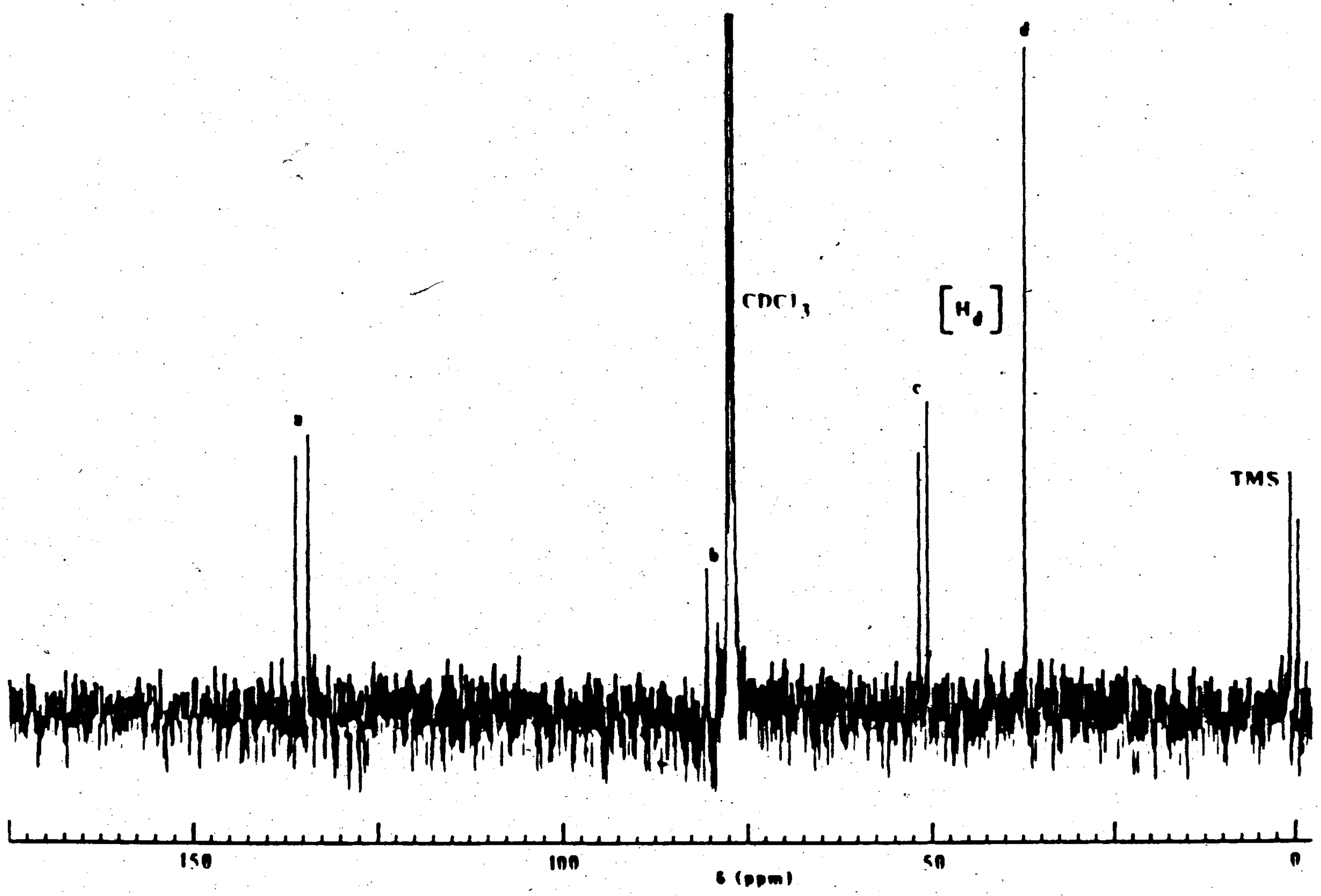
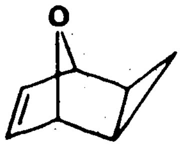


Figure 19d. Decoupling protons H_d, δ_H = 3.37 ppm.

of **70** and **71** permitted their stereochemistry to be determined. An exo configuration of the four-membered ring, as in structure **70**, produces a dihedral angle of nearly 90° between protons H_b and H_c and consequently a very small J_{b-c} coupling constant would be expected. In the alternative endo configuration of the four-membered ring, as in structure **71**, the corresponding dihedral angle is much smaller and therefore the coupling constant should be closer to a normal value. Selective proton decoupling experiments revealed that the adduct assigned structure **70** had no discernible coupling between its H_b and H_c protons, while in the other adduct a significant J_{b-c} coupling was observed. These decoupling differences can be seen by comparing Figures 14b and 14c with Figures 15b and 15c. The decoupling results for **70**, presented in Figures 14b and 14c, clearly illustrate that no discernible coupling exists between the H_b and H_c protons in this compound. The dramatic contrast in Figures 15b and 15c is evident. With selective irradiation of the H_a protons (δ 6.60 ppm) for instance, the residual splitting pattern for the H_b protons demonstrates their significant coupling to the H_c protons in this stereoisomer.

This technique of determining the stereochemistry in such ring systems has been briefly described by LaRochelle and Trost, who distinguished the exo and endo DAa of cyclopropene with furan in this manner [144]. It is indeed an extremely useful tool for this purpose; one which we will utilize again when examining our furan trapped, furan photolysis products.

The chemical shifts of the H_c protons in **70** and **71** also provide a clue to the stereochemistry of these compounds. It is known that the magnetically anisotropic double bond in bicyclic DAa exerts a paramagnetic effect on protons in the exo position and a diamagnetic effect on protons in the endo configuration. Consequently the endo protons are more shielded than the corresponding exo protons [145]. For instance, in the tricyclooctene isomers, **75** and **76**, the endo protons are more shielded by 0.35 ppm [146]. In **70** and **71** a difference of 0.61 ppm exists for the H_c protons, with the protons in compound **70**, which have the endo configuration, being more shielded. This is consistent with the anisotropic effect of the double bond and provides further proof of the stereochemical assignment. The much larger chemical shift difference in **70** and **71** as compared with **75** and **76** may be indicative of an additional deshielding effect on the H_c protons in **71** as a result of their proximity to the O atom. A chemical shift difference is also observed for the H_d protons in **70** and **71**. In the configuration where the H_d protons are closer to the O atom, **70**, they are comparatively deshielded by 0.31 ppm.



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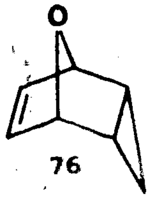

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As stated earlier, in each adduct there are two possibilities for the stereochemistry of the thiirane ring segment, thereby completing the set of four possible stereoisomers that can be obtained from the Diels-Alder addition between furan and Dewar thiophene. In two stereoisomers, the H_c and H_d protons are cis, while in the other two, these protons must be trans. Within each pair of cis or trans isomers the dihedral angle between the H_c and H_d protons is the same; however, the dihedral angle in the trans isomers is much larger as compared with the cis isomers. A simple inspection of the H_c-H_d splitting patterns aids in assigning the actual stereochemistry in **70** and **71**. In the two adducts these couplings are very similar, suggesting that protons H_c and H_d bear the same relationship in the two compounds. Typically, ^1H-^1H coupling constants for hydrogen atoms on a cyclobutane ring range from 6.1-11.4 Hz for cis hydrogens and 2.2-10.7 Hz for trans hydrogens [147]. In the Dewar thiophene adducts with furan the strained thiirane ring changes the dihedral angles from those expected for cyclobutane, however the decoupling results presented in Figures 14c and 15c clearly reveal that the H_c-H_d coupling in both adducts is of the order 1.5-2 Hz. Thus it was concluded that in both **70** and **71** the H_c and H_d protons were trans.

It is noteworthy that these adducts, where protons H_c and H_d are trans, should be, for steric reasons, the favoured Diels-Alder products in relation to their counterparts with the opposite stereochemistry at the thiirane ring. Clearly, steric hindrance is caused by the sulfur atom in the transition states of **73** and **74**. Consequently, these adducts are not formed. Moreover, the experimental **70**/**71** adduct ratio of 5/3 is consistent with transition state considerations which show that no significant preference should exist for the formation of either stereoisomer, **70** or **71**.

The combined chemical yield of **70** and **71** from the solution phase trapping was approximately 1.2% based on consumed thiophene. This relatively low yield can be explained in terms of the occurrence of primary steps other than isomerization to the Dewar form, incomplete trapping of the Dewar thiophene by furan, destruction of the adducts by free radical attack and secondary photolysis. That secondary photolysis of **70** occurs was demonstrated in an auxiliary experiment using the vycor 7900 (4 mm) filtered radiation ($\gtrsim$ 235 nm) of a Cd resonance lamp. Under these conditions the principal effective wavelength from a Cd lamp is the Cd($^3P_1$) resonance line located at 326 nm. Thiophene does not absorb this wavelength, but **70** and **71** do ($\lambda_{max} \sim$ 287 nm, onset of absorption $\lambda \sim$ 350 nm, Figure 20). Since the actual purity of these adducts was not known no attempt was made to calculate molar extinction coefficients based on the UV absorption spectra in Figure 20. The photolytic destruction of adduct **70** was followed in one trial by ^{1}H NMR, and in a second, by its UV absorption. For the NMR experiment the quantity of adduct was monitored in comparison to a small amount of $CHCl_3$ added as an internal reference. The $CHCl_3$/adduct ratios observed as a function of photolysis time are summarized in Table 7. Although the uncertainty associated with each individual ratio was fairly large compared to the absolute changes in the ratios as a function of time, a definite decreasing trend was observed for the relative amount of adduct. After 10 h about 16% of the adduct had been destroyed. The data for the UV experiment are listed in Table 8. After 17 h, 14% of the adduct had been consumed.

Detailed speculation regarding the quantitative relationship of

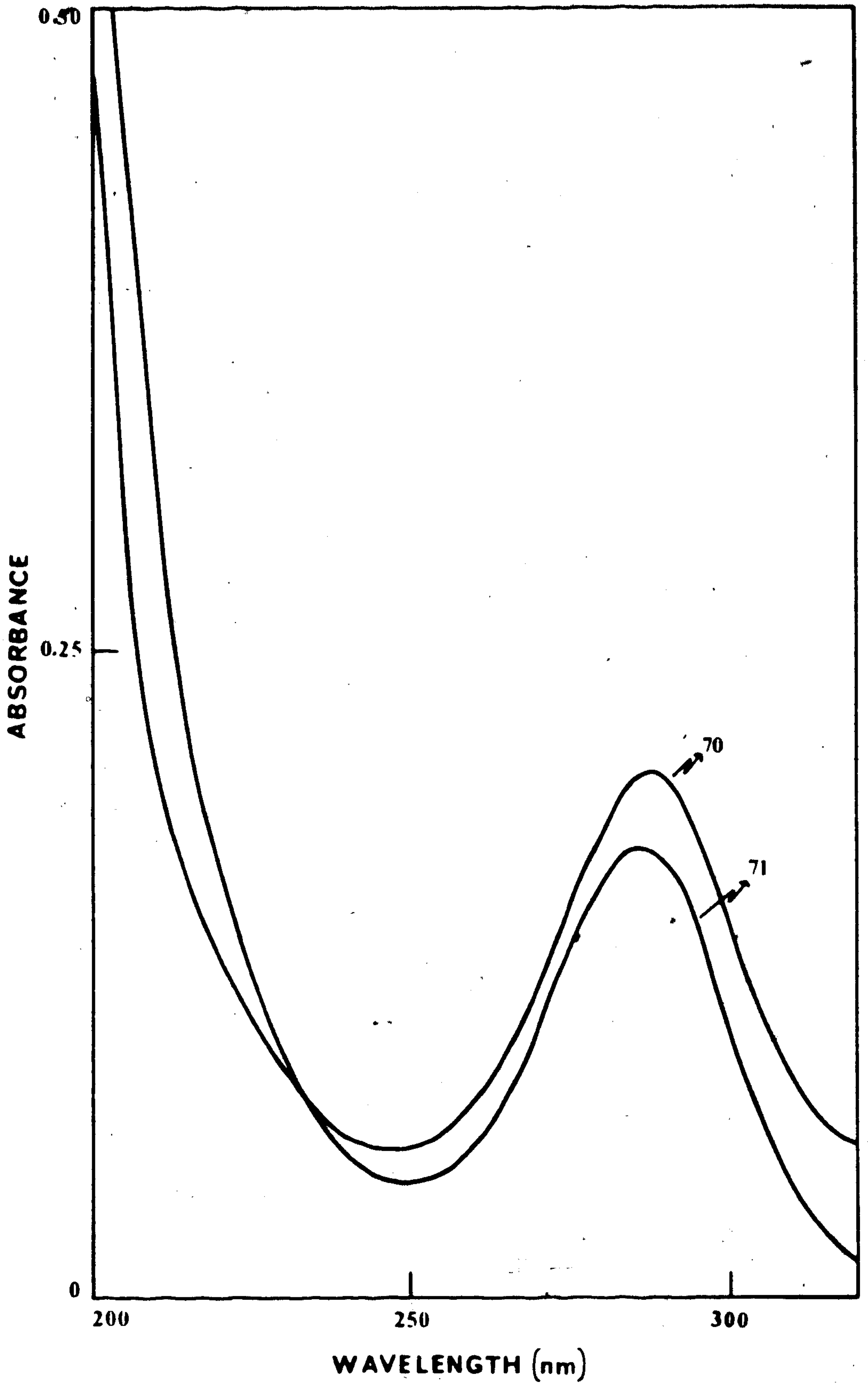


Figure 20. UV absorption spectra of **70** and **71** in hexanes (~10^{-3} M).

D

TABLE 7

Photostability of **70**: NMR Experiment[a]

Photolysis Time (h)	$CHCl_3$/**70** Ratio
0	2.37
1.25	2.52
5.25	2.73
10	2.76

[a] NMR data recorded in ether-d_{10} on a Bruker WP-80 spectrometer.

TABLE 8

Photostability of **70**: UV Experiment[a]

Photolysis Times (h)	$A_{287\ nm}$
0	0.21
17	0.18

[a] Adduct sample dissolved in spectroscopic grade hexanes.

these experiments to the actual photolysis conditions where the adducts are formed is not possible because of the unknown role of many factors, such as the formation of polymer and other absorbing photoproducts which attenuate the incident light. However, a correction of the combined primary chemical yield of **70** and **71** based on the observed rate of photodecomposition of **70** would suggest that the actual yield was larger by a factor of 2-2.5, increasing its value to ca. 2.5-3%.

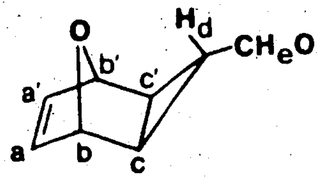
b. Furan/Furan Adducts

The furan dimer products mentioned earlier were first observed by GC/FTIR following the irradiation of a solution of thiophene in furan. However, for the purpose of their isolation and characterization these adducts were generated in larger quantities by the photolysis of liquid furan.

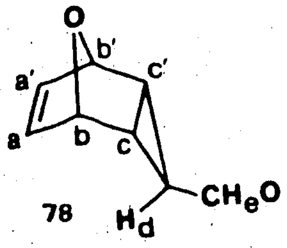
Photolysis of neat furan at about 25°C was performed using conventional steady-state photolysis and also in a cyclic photolysis reactor (cf. Experimental). The design of the latter improved the efficiency of the trapping process for two reasons. Firstly, the periodic circulation of the photolyzate washed the insoluble solid products out of the photolysis zone. In conventional steady-state photolysis, polymer accumulation seriously attenuates the incident radiation. Secondly, because trapped products were removed from the photolysis zone long irradiation times, equivalent to high conversion in a conventional photolysis, could be used with reduced chance of secondary photolysis.

On completion of irradiation the polymer formed was separated by filtration and excess furan was removed by distillation. A small quantity of yellow oil remained. As found earlier, GC/MS analysis indicated the presence of three principal products. Each of them was a furan dimer as indicated by their mass spectra ($M^{+\cdot}$ 136) and showed -CHO loss (m/e 29) as an important fragmentation process. GC/FTIR confirmed the presence of an aldehyde group in all three products, by the characteristic C=O and C-H stretching absorptions.

The three products were separated by preparative GC (15% SE-30, ~ 6 mm × 2 m, 112°C) and examined by ^1H and ^{13}C NMR. **77** and **78** were more readily identified. They were each assigned the structure of a furan DAa with cyclopropene-3-carboxaldehyde. Exact mass measurement



77



78

by MS on the separated adducts, **77** and **78**, gave an $M^{+\cdot}$ corresponding to $C_8H_8O_2$ and showed successive loss of -CHO then -CO as the major fragmentation route. A second important fragmentation pathway was a Diels-Alder retrogression to generate C_4H_4O (**77**, m/e 136(2%), 107(33%), 79(100%), 68(28%); **78**, m/e 136(9%), 107(52%), 79(100%), 68(36%)). The IR spectra of **77** and **78** (Figures 21 and 22) showed carbonyl absorptions at 1708 and 1711 cm^{-1} respectively, as well as aldehyde C-H stretching absorptions near 2730 and 2835 cm^{-1}.. In addition each IR revealed a very weak C=C stretching absorption near 1560 cm^{-1}. Due to the symmetric nature of **77** and **78** (vide supra) this double bond absorption was expected to be weak. The observed

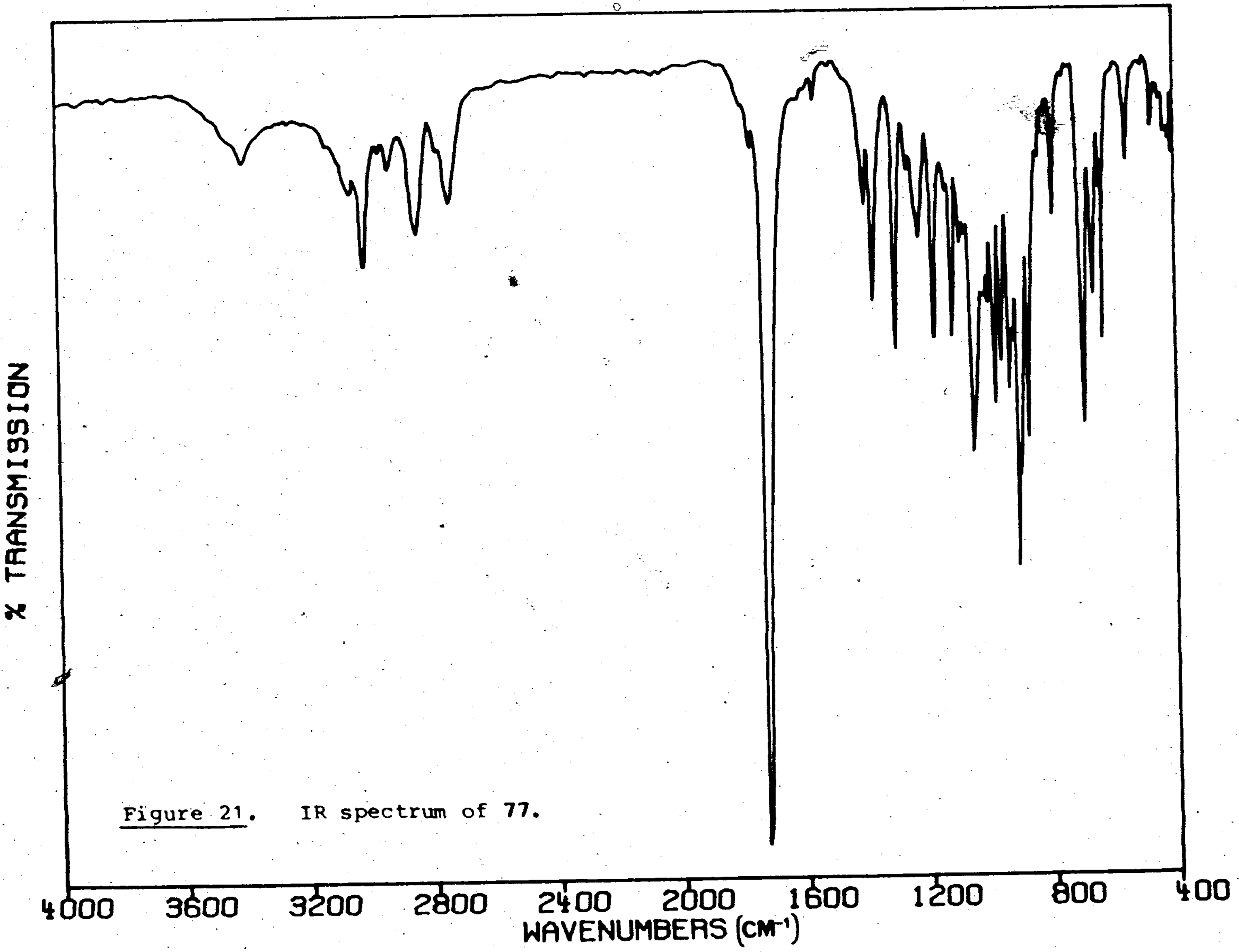


Figure 21. IR spectrum of 77.

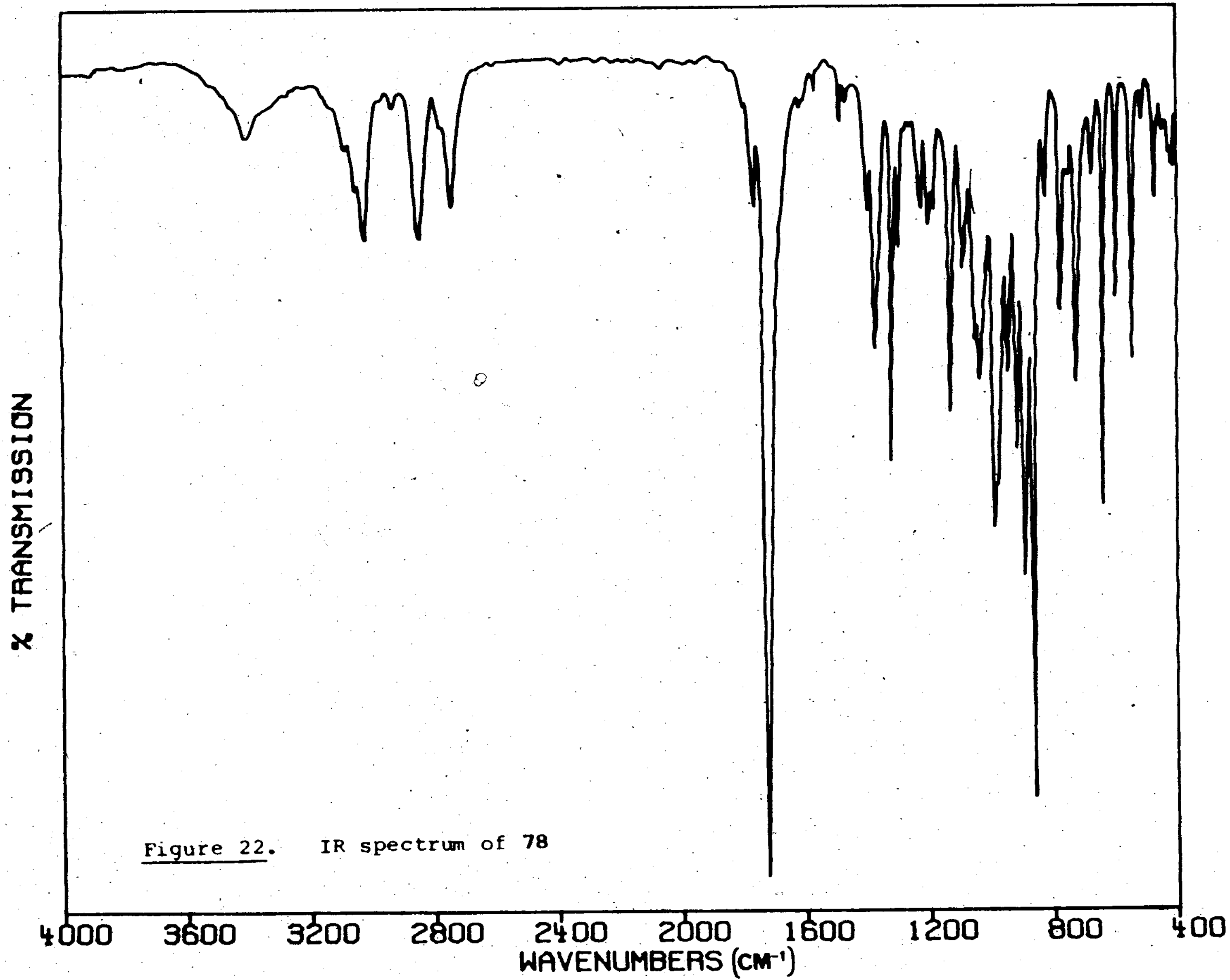


Figure 22. IR spectrum of 78

position is similar to that reported for norbornene, 1575 cm^{-1} [148]. For both **77** and **78** the ^1H NMR showed three sets of two chemically equivalent protons and the ^{13}C NMR three sets of two identical carbon atoms in agreement with the C_S symmetry of the structures. The NMR data for **77** and **78** are summarized in Tables 9 and 10. The NMR chemical shifts are entirely consistent with the assigned structures. The ^1H NMR spectra of **77** and **78** are shown in Figures 23 and 24. These spectra also include the frequency expansions and selective ^1H decoupling results used to confirm the adducts' structures and assign their stereochemistry. The ^{13}C NMR spectra of these same products are illustrated in Figures 25 and 26.

Although the symmetry in **77** and **78** gives rise to three sets of magnetically nonequivalent protons and renders their ^1H NMR spectra higher than first order, selective decouplings in the ^1H NMR spectra of **77** and **78** permitted their stereochemistry to be determined. An _exo_ configuration of the three-membered ring, as in **77**, produces a dihedral angle of nearly 90° between protons H_b and H_c. Consequently a very small J_{b-c} coupling constant would be expected. In the alternative _endo_ configuration of the three-membered ring, as in **78**, this dihedral angle is much smaller and therefore the coupling constant should be closer to a normal value. Selective proton decoupling experiments revealed that the adduct assigned structure **77** had no discernible coupling between its H_b and H_c protons, while in the other adduct a significant J_{b-c} coupling was observed. This is consistent with the results reported by LaRochelle and Trost [144] for the _exo_ and _endo_ DAa of cyclopropene with furan, **6** and **7**,

TABLE 9

400 MHz ^{1}H NMR Data for **77** and **78**

Adduct	Chemical Shift[a] δ_H (ppm)	Integration	Coupling Constant[b] J (Hz)	Assignment[c]
77	9.40 d	1	4.1	e
	6.58 m	2	-	a,a'
	4.85 m	2	-	b,b'
	2.88 dt	1	4.1, 2.7	d
	1.96 d	2	2.7	c,c'
78	9.27 d	1	4.1	e
	6.18 m	2	-	a,a'
	5.05 m	2	-	b,b'
	2.57 m	2	-	c,c'
	2.01 dt	1	4.1, 2.5	d

[a] Chemical shifts in $CDCl_3$ relative to TMS.

[b] The magnetic nonequivalence of certain protons complicates the analysis of their coupling constants.

[c] The prime notation is introduced to account for the magnetic nonequivalence within each set of chemically equivalent atoms.

TABLE 10

100 MHz ^{13}C NMR Data for **77** and **78**

Adduct	Chemical Shift[a] δ_C (ppm)	Assignment[b]	
77	197.5	e	$>\underline{C}=O$
	138.4	a,a'	$=\underline{C}H$
	77.4	b,b'	$H>\underline{C}-O$
	40.8	d	$H>\underline{C}-CHO$
	30.1	c,c'	$H>\underline{C}-C$
78	195.6	e	$>\underline{C}=O$
	131.5	a,a'	$=\underline{C}H$
	78.8	b,b'	$H>\underline{C}-O$
	46.5	d	$H>\underline{C}-CHO$
	24.8	c,c'	$H>\underline{C}-C$

[a] Chemical shifts in $CDCl_3$ relative to TMS.

[b] The prime notation is introduced to account for the magnetic nonequivalence within each set of chemically equivalent atoms.

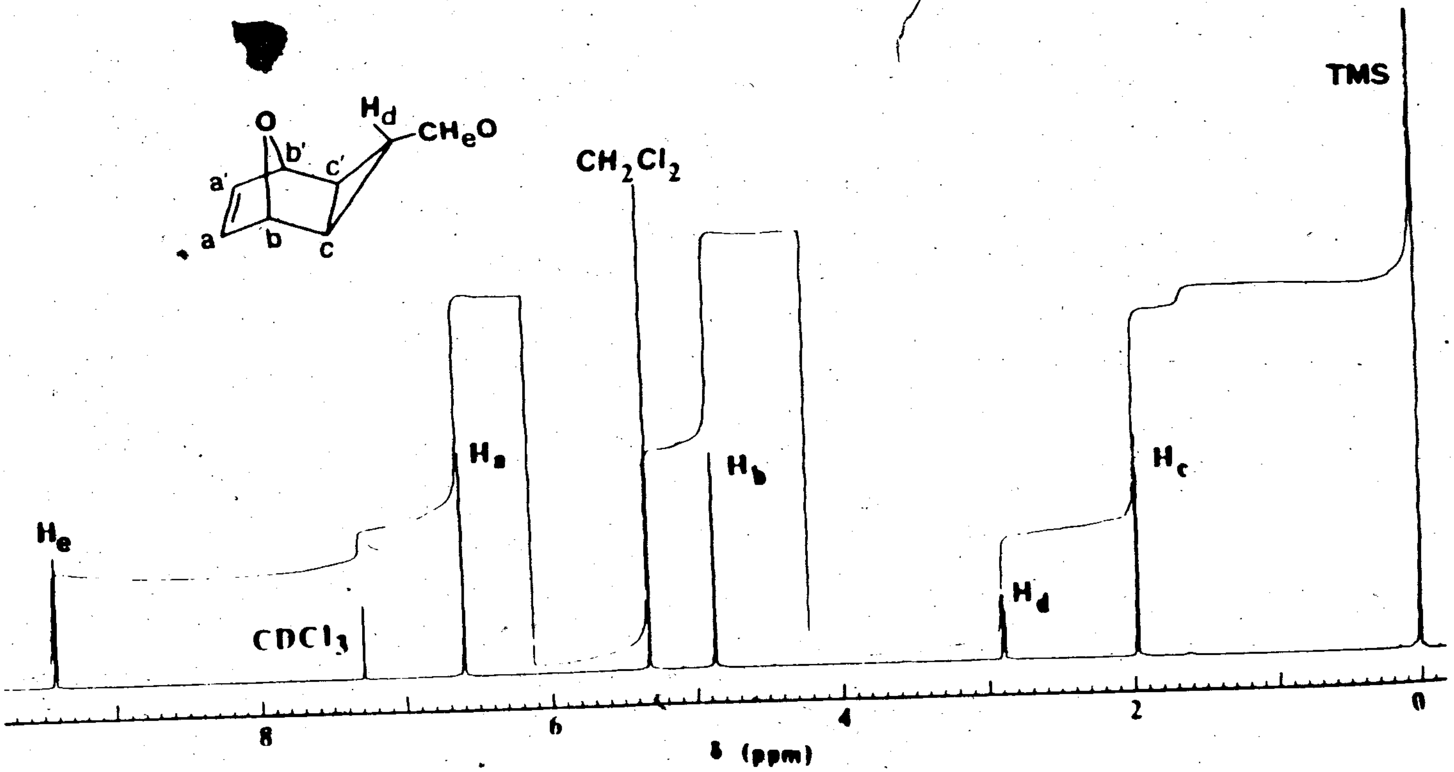


Figure 23a. 400 MHz ^{1}H NMR spectrum of 77.

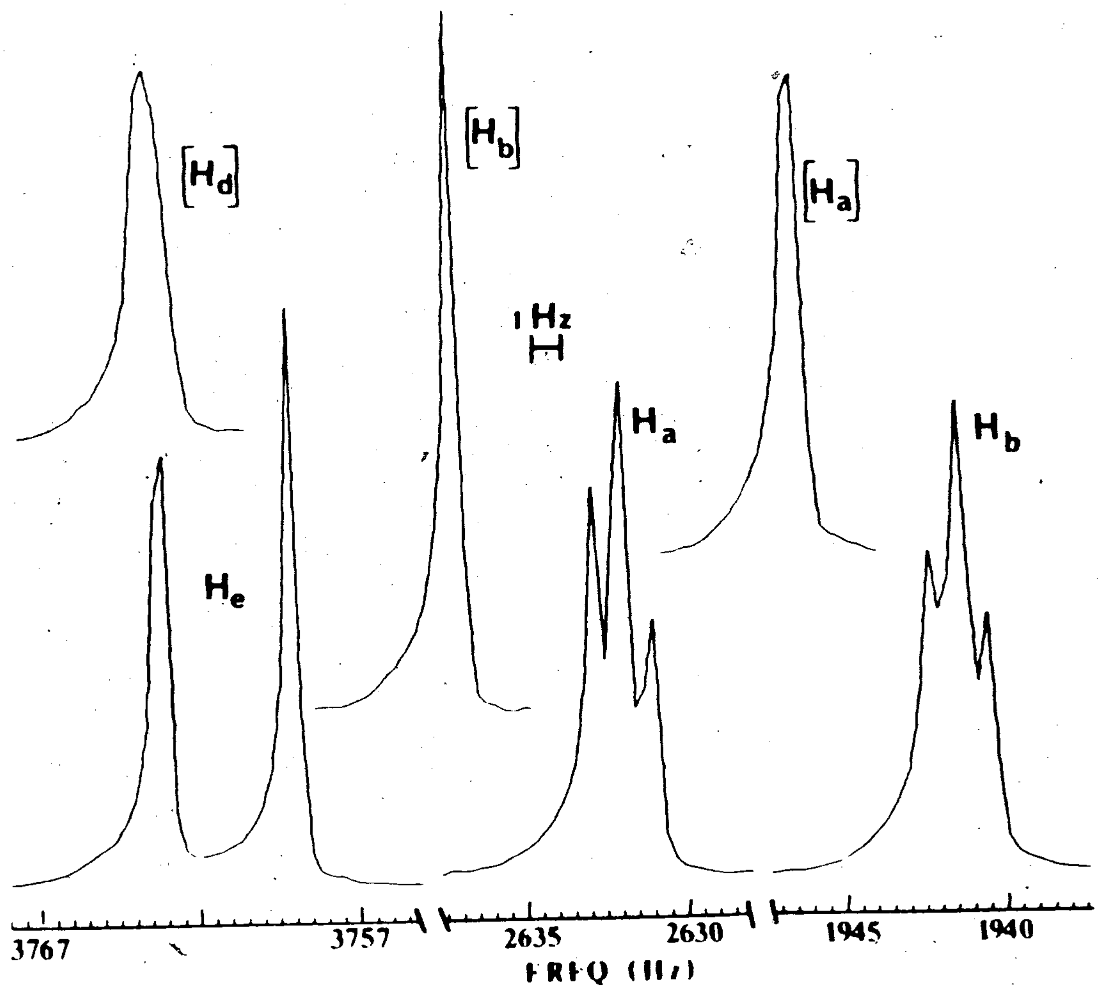


Figure 23b. Frequency expansion and selective ^{1}H decoupling at *ca.* 2632, 1940 and 1152 Hz.

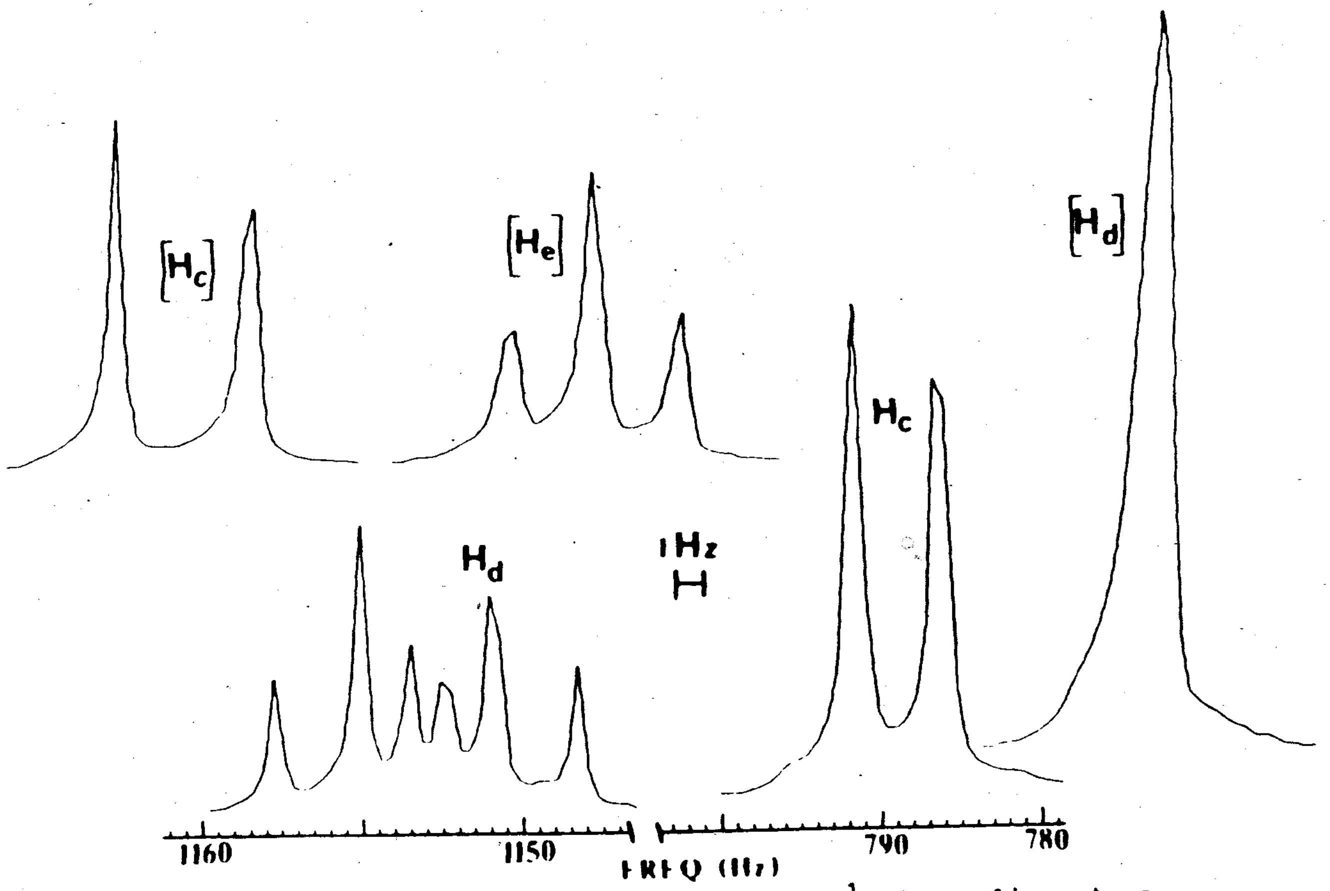


Figure 23c. Frequency expansion and selective ^1H decoupling at *ca.* 3760, 1152 and 784 Hz.

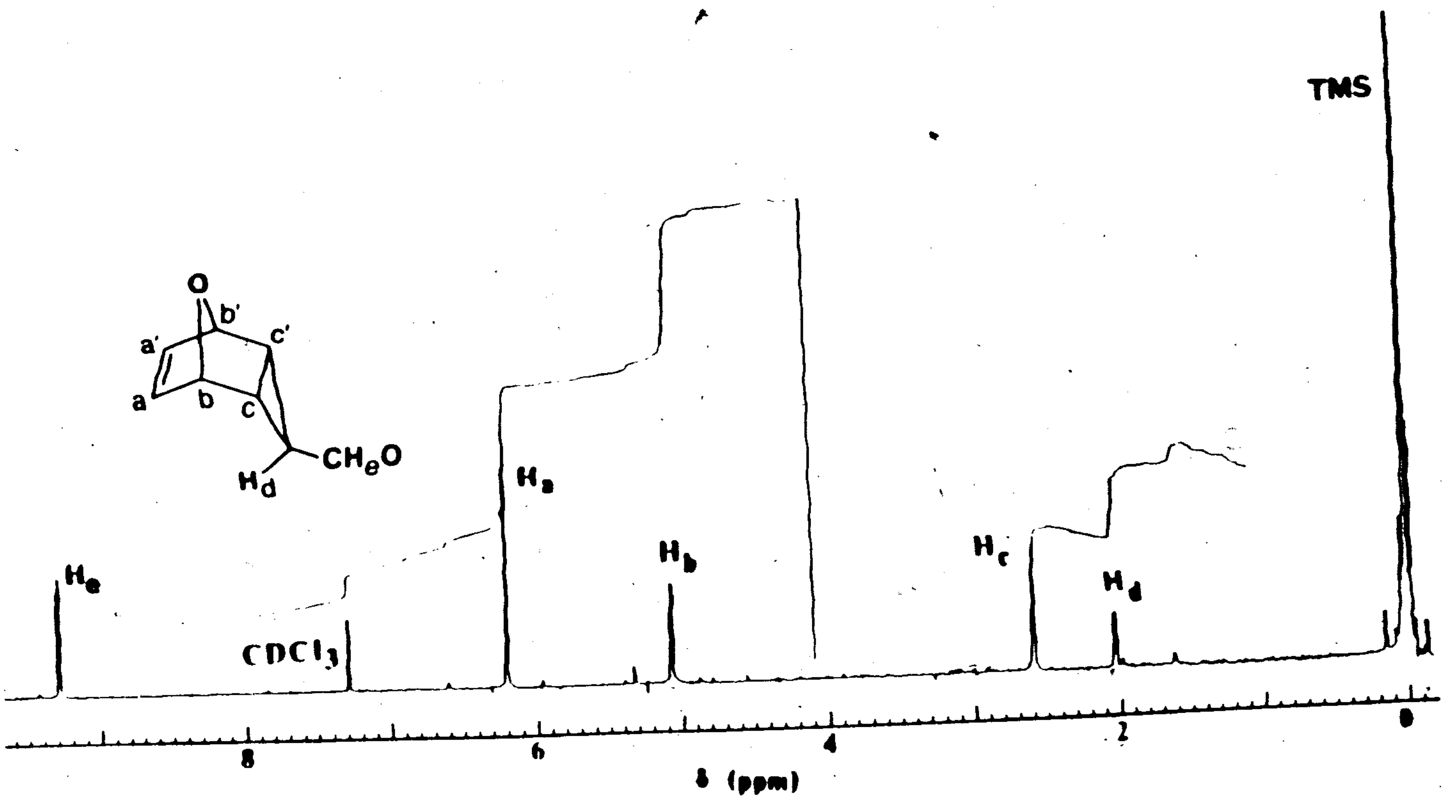


Figure 24a. 400 MHz ^1H NMR spectrum of 78.

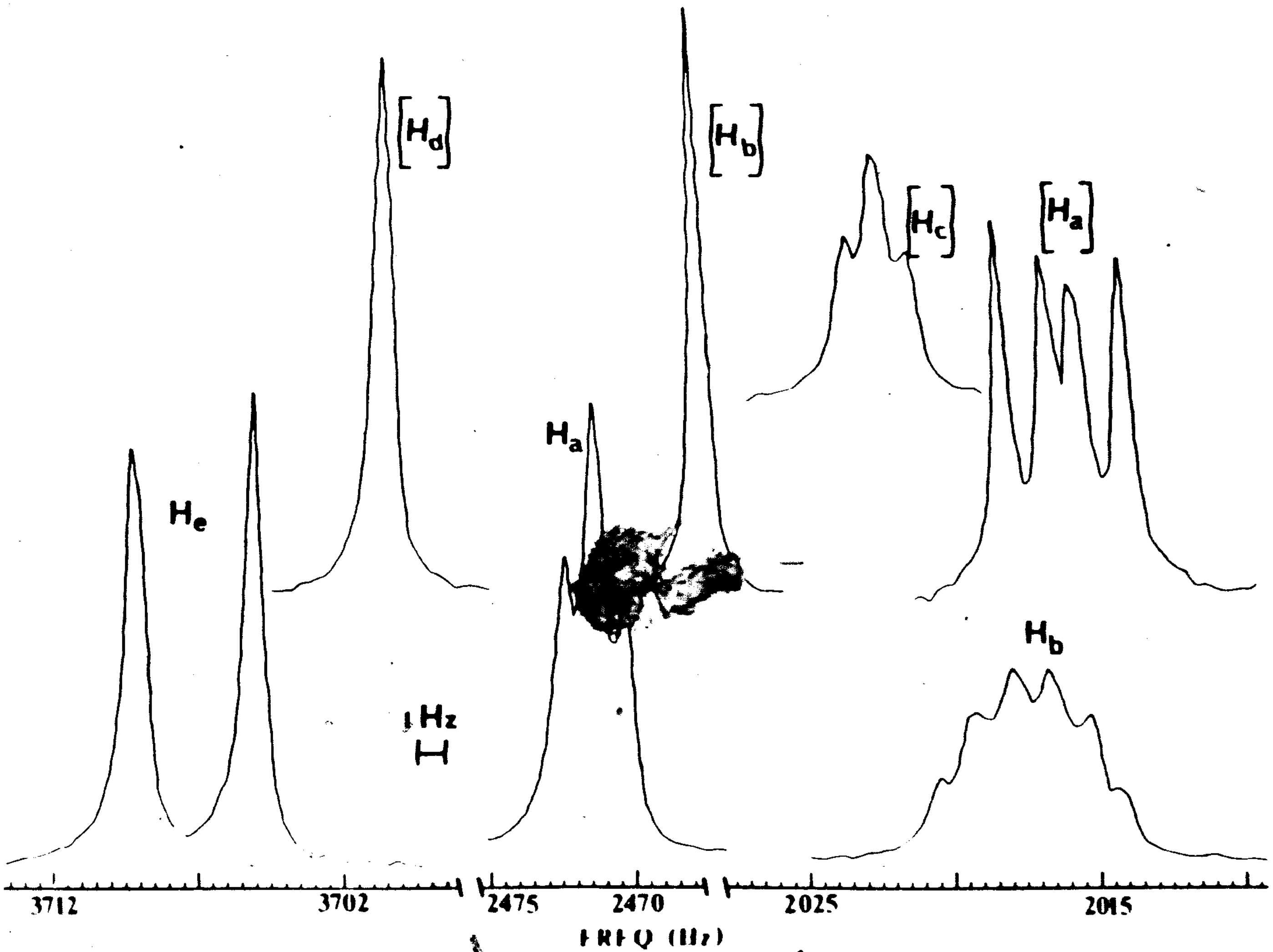


Figure 24b. Frequency expansion and selective ^1H decoupling at ca. 2472, 2020, 1028 and 804 Hz.

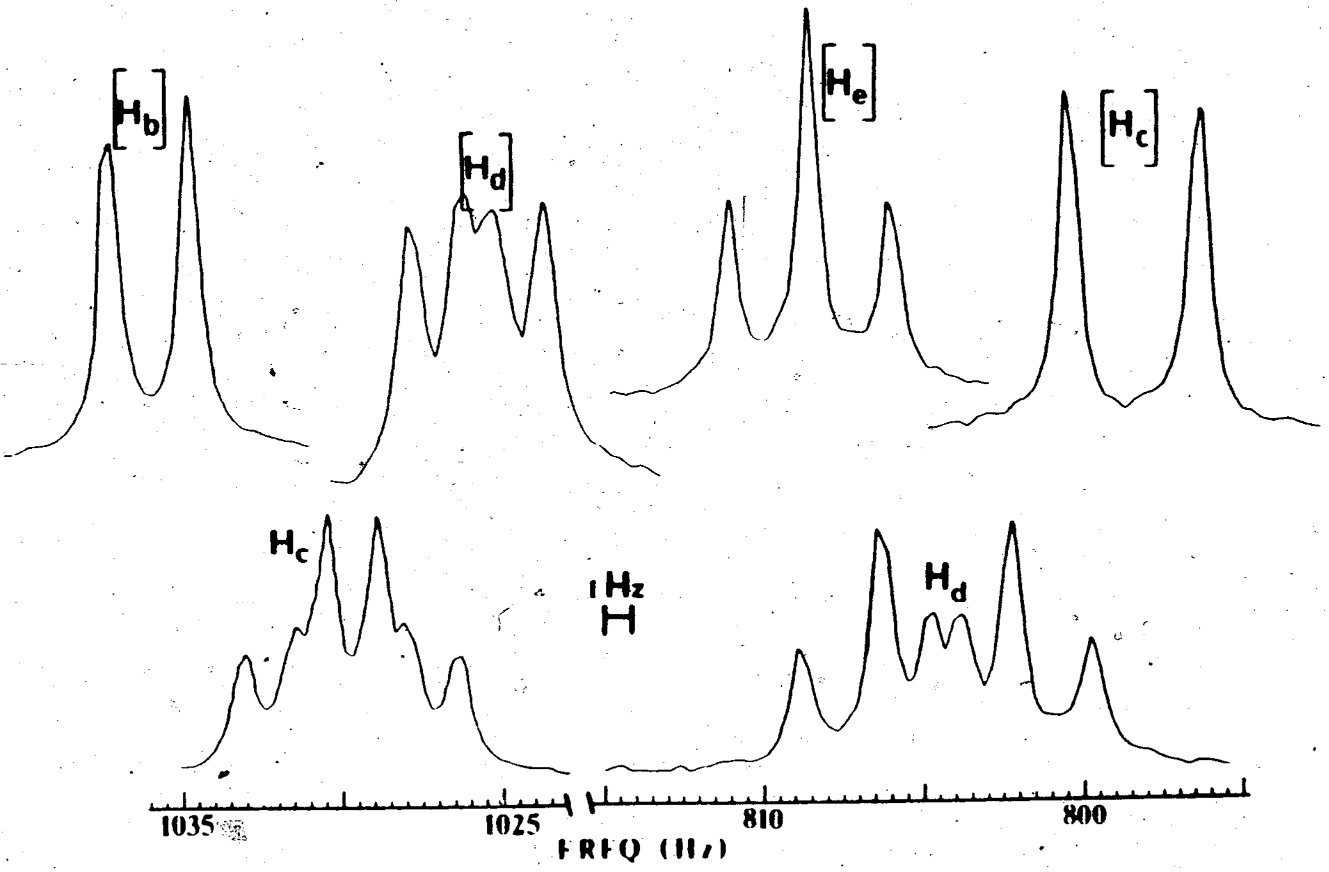


Figure 24c. Frequency expansion and selective ^{1}H decoupling at *ca.* 3708, 2472, 2020 and 1028 Hz.

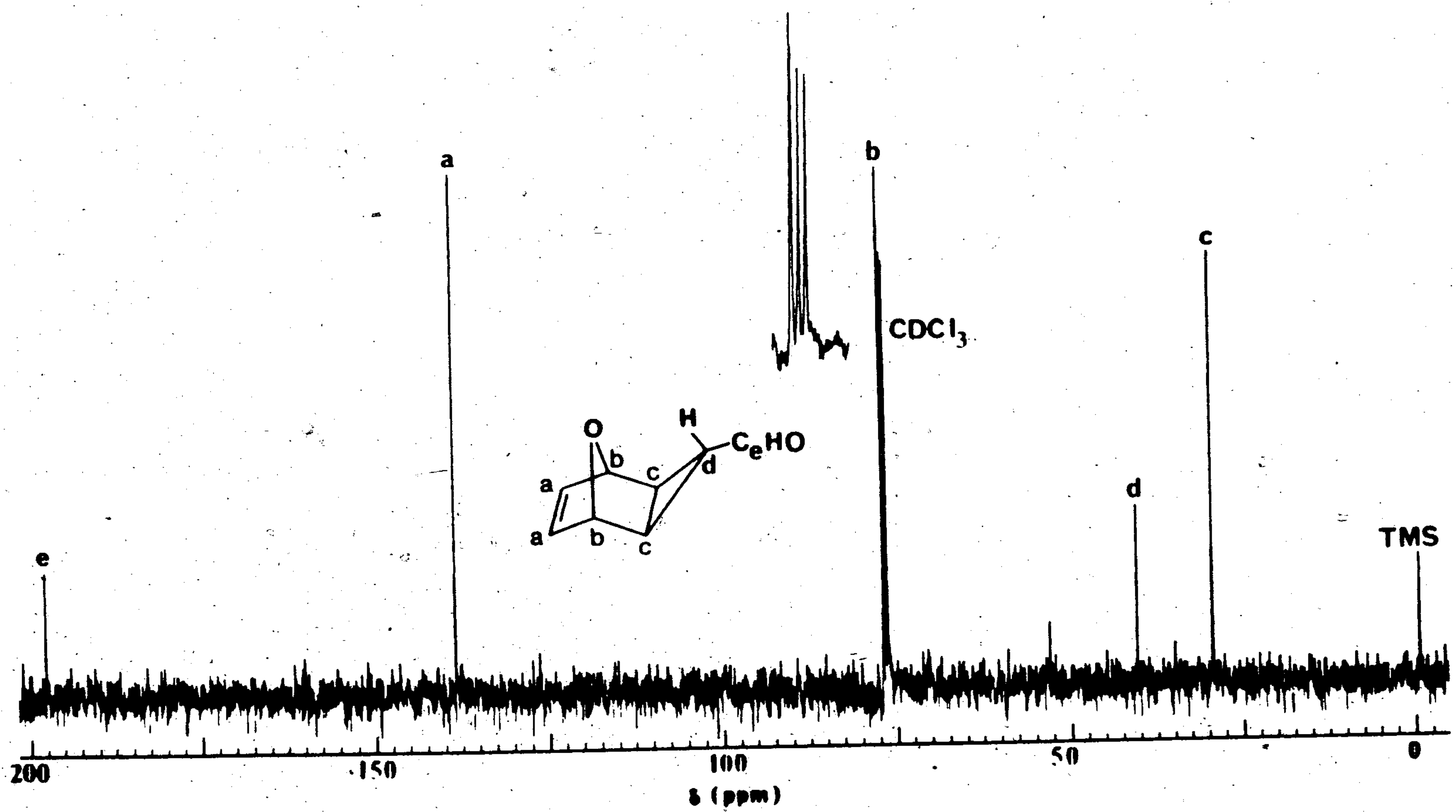


Figure 25. 100 MHz ^{13}C NMR spectrum of 77.

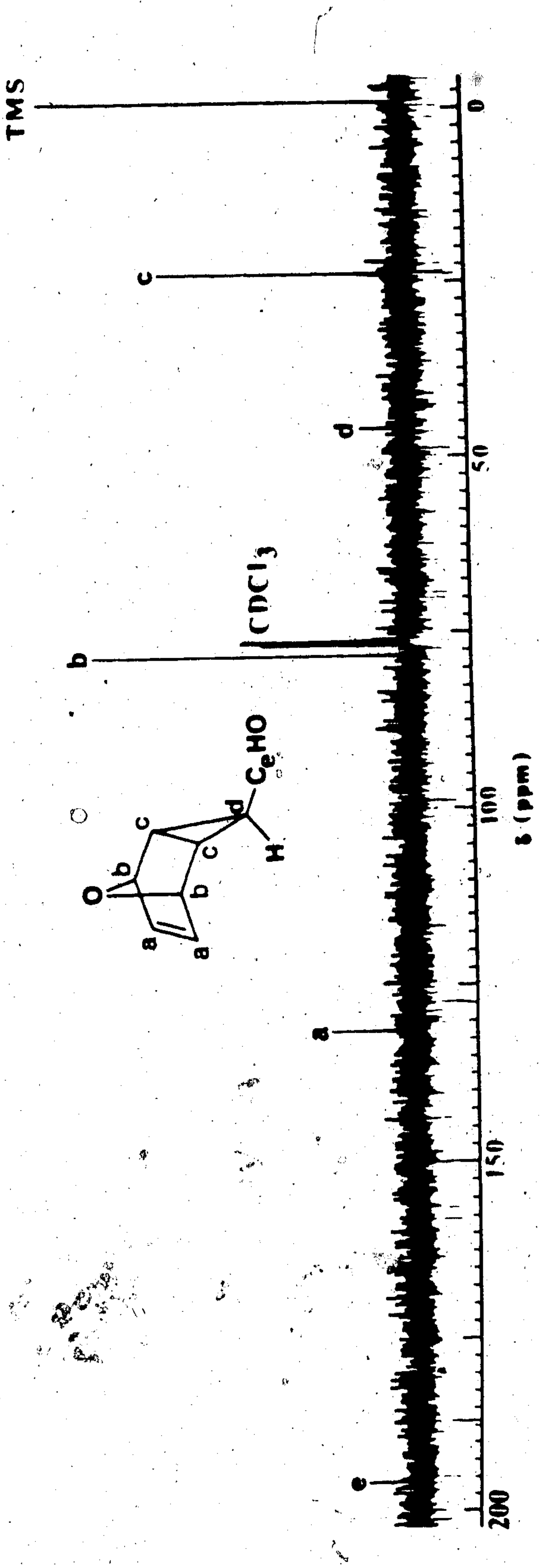


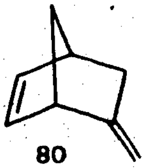
Figure 26. 100 MHz ^{13}C NMR spectrum of 78.

respectively.

The same effect of the magnetically anisotropic double bond described for the Dewar thiophene DAa with furan, **70** and **71**, was again observed in **77** and **78**. In **77** and **78** a difference of 0.61 ppm exists for the H_c protons, with the protons in compound **77**, which have the *endo* configuration, being more shielded. This is consistent with the stereochemical assignment. Again, a much larger chemical shift difference was seen in **77** and **78** as compared with **75** and **76**. This may be indicative of an additional deshielding effect on the H_c protons in **78** as a result of their proximity to the O atom. A large chemical shift difference was also observed for the H_d protons in **77** and **78** with the H_d proton in the latter isomer being more shielded by [illegible].87 ppm.

That the aldehyde substituent is *exo* to the three-membered ring in both **77** and **78** was determined from the magnitude of the J_{c-d} coupling. Selective proton decoupling experiments allowed this coupling to be measured. Values of J_{c-d} ~2.7 and 2.5 Hz were found in **77** and **78**, respectively. Typical coupling constants between such protons on a cyclopropane ring are of the order 6.6-8.0 Hz when the protons are *cis* and 3.6-4.6 Hz if *trans* [149]. Thus, it was concluded that in both **77** and **78**, proton d was *trans* to the c protons. The angles imposed by the tricyclic ring structure probably account for the smaller *trans* coupling constant as compared with cyclopropanes. It is noteworthy that these DAa with the *exo* configuration of the -CHO group should, for steric reasons, be preferred to those with the opposite stereochemistry, thus lending further support to the structure assigned by NMR.

Exact mass measurement by MS showed that **79** had molecular formula $C_8H_8O_2$ ($M^{+\cdot}$ 136). The major fragmentation process was a Diels-Alder retrogression forming C_4H_4O (**79**, m/e 136(10%), 107(33%), 79(66%), 68(100%)). The IR spectrum of **79** (Figure 27) showed a carbonyl absorption at 1721 cm^{-1} and characteristic aldehyde absorptions near 2730 and 2820 cm^{-1}. A weak double bond absorption was evident at 1563 cm^{-1}, very similar in position and of somewhat greater intensity than the double bond absorptions of **77** and **78**. A much stronger double bond absorption near 1665 cm^{-1} as well as a strong absorption near 895 cm^{-1} are consistent with an exocyclic methylene (vide infra). The norbornene structure, **80**, has double



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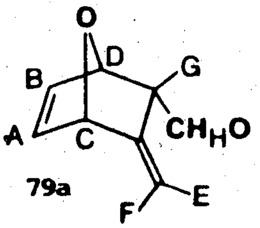
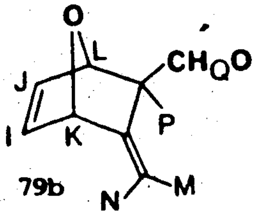
bond absorptions at 1575(w) and 1667(m) cm^{-1} as well as a strong absorption located at 876 cm^{-1} [150]. The ^{1}H NMR spectrum of **79** isolated by preparative GC clearly indicated the presence of two separate aldehyde compounds, each having a total of eight protons. Based on their ^{1}H and ^{13}C NMR spectra the compounds were each assigned the structure of a furan DAa with 2,3-butadienal. From the ^{1}H NMR integrations the concentration ratio of **79a** to **79b** was 2.8/1. The ^{1}H and ^{13}C NMR data for **79a** and **79b** are reported in Tables 11 and 12, respectively. Owing to the very complicated nature



79a



79b

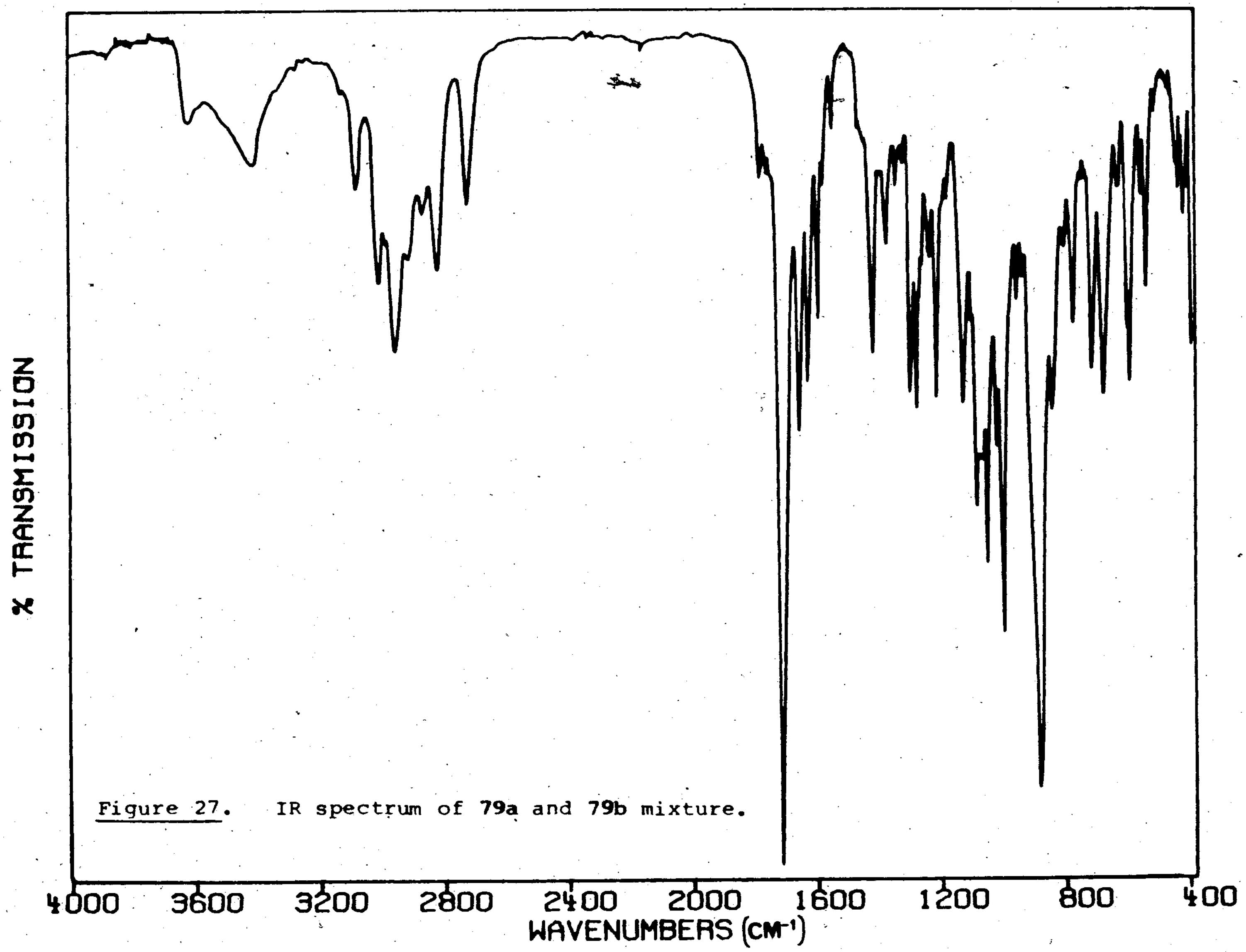


Figure 27. IR spectrum of **79a** and **79b** mixture.

TABLE 11

400 MHz ^{1}H NMR Data for **79a** and **79b**

Adduct	Chemical Shift[a] δ_H (ppm)	Assignment
79a	9.08	H
	3.47	G
	5.02	F
	5.24	E
	5.21	D
	5.17	C
	6.51	B
	6.51	A
79b	9.49	Q
	2.81	P
	5.06	N
	5.33	M
	5.15	L
	5.29	K
	6.41	J
	6.52	[illegible]

[a] Chemical shifts in $CDCl_3$ relative to TMS.

TABLE 12

50 MHz ^{13}C NMR Data for **79a** and **79b**

Adduct	Chemical Shift[a] δ_C (ppm)	Assignment
79a	199.7	$>\underline{C}=O$
	141.4	$=\underline{C}H_2$
	135.2	$=\underline{C}H_A{}^b$
	133.0	$=\underline{C}H_B{}^b$
	107.5	$>\underline{C}=$
	82.6	$H>\underline{C}-O$
	79.8	
	57.1	$H>\underline{C}-CHO$
79b	199.7	$>\underline{C}=O$
	144.7	$=\underline{C}H_2$
	136.2	$=\underline{C}H_J{}^b$
	134.5	$=\underline{C}H_I{}^b$
	109.0	$>\underline{C}=$
	81.9	$H>\underline{C}-O$
	80.2	
	56.0	$H>\underline{C}-CHO$

[a] Chemical shifts in $CDCl_3$ relative to TMS.

[b] Tentative assignments based on the well known γ-gauche steric interaction [151,152].

of the proton couplings in these adducts the complete decoupling experiments will not be presented in the interest of brevity. A complete decoupling series was performed as part of the assignment of each compound. These decoupling results as well as the NMR chemical shifts reported in Tables 11 and 12 are entirely consistent with the assigned structures **79a** and **79b**. The high field ^1H and ^{13}C NMR spectra obtained for the mixture of **79a** and **79b** are presented in Figure 28 and 29, respectively.

Although many of the ^1H chemical shifts were located between about 5 and 6.5 ppm, with the aid of the 400 MHz NMR spectrometer, the various signals were assigned by selective ^1H decoupling. The NMR integrations and self-consistency of the selective decoupling series clearly separated the proton resonances into two sets, one belonging to **79a** and the other to **79b**. The assignment of **79a** as the endo isomer and **79b** as the exo isomer was readily determined from the ^1H NMR spectra. In **79a** proton G couples to proton D, α to the O atom with a coupling constant J_{DG} ~4.6 Hz. By contrast, in **79b** proton P reveals no discernible coupling to proton L. These differences are attributable to the differences in the dihedral angle between **79a** and **79b**, analogous to the situation already described for **77** and **78**.

The effects on chemical shift of the magnetically anisotropic double bond are also manifested in the ^1H NMR data of DAa **79a** and **79b**. Proton P in **79b** has an endo configuration and is more shielded than proton G in **79a** by 0.66 ppm. Once again the observed chemical

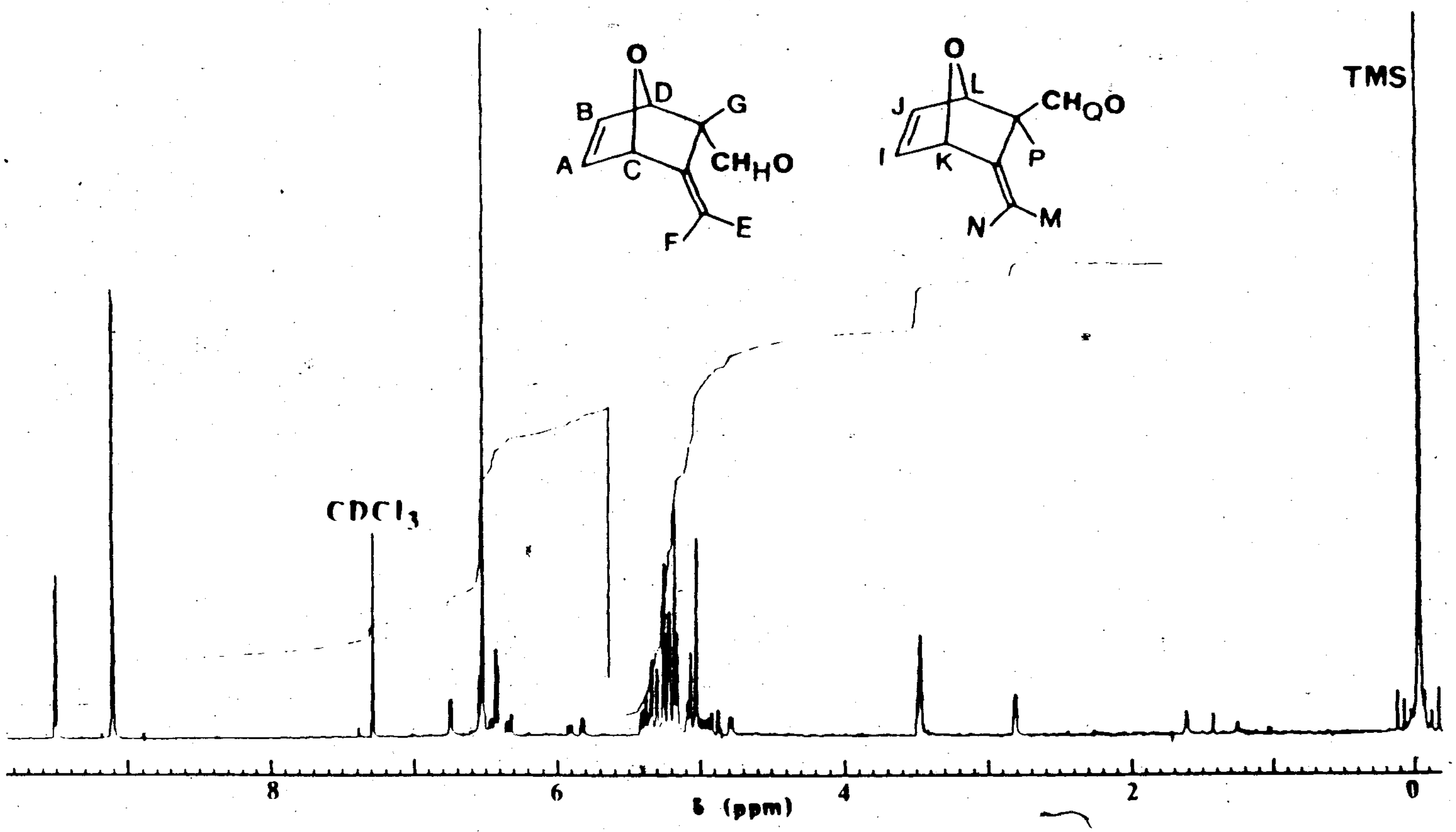


Figure 28. 400 MHz ^{1}H NMR spectrum of **79a** and **79b** mixture.

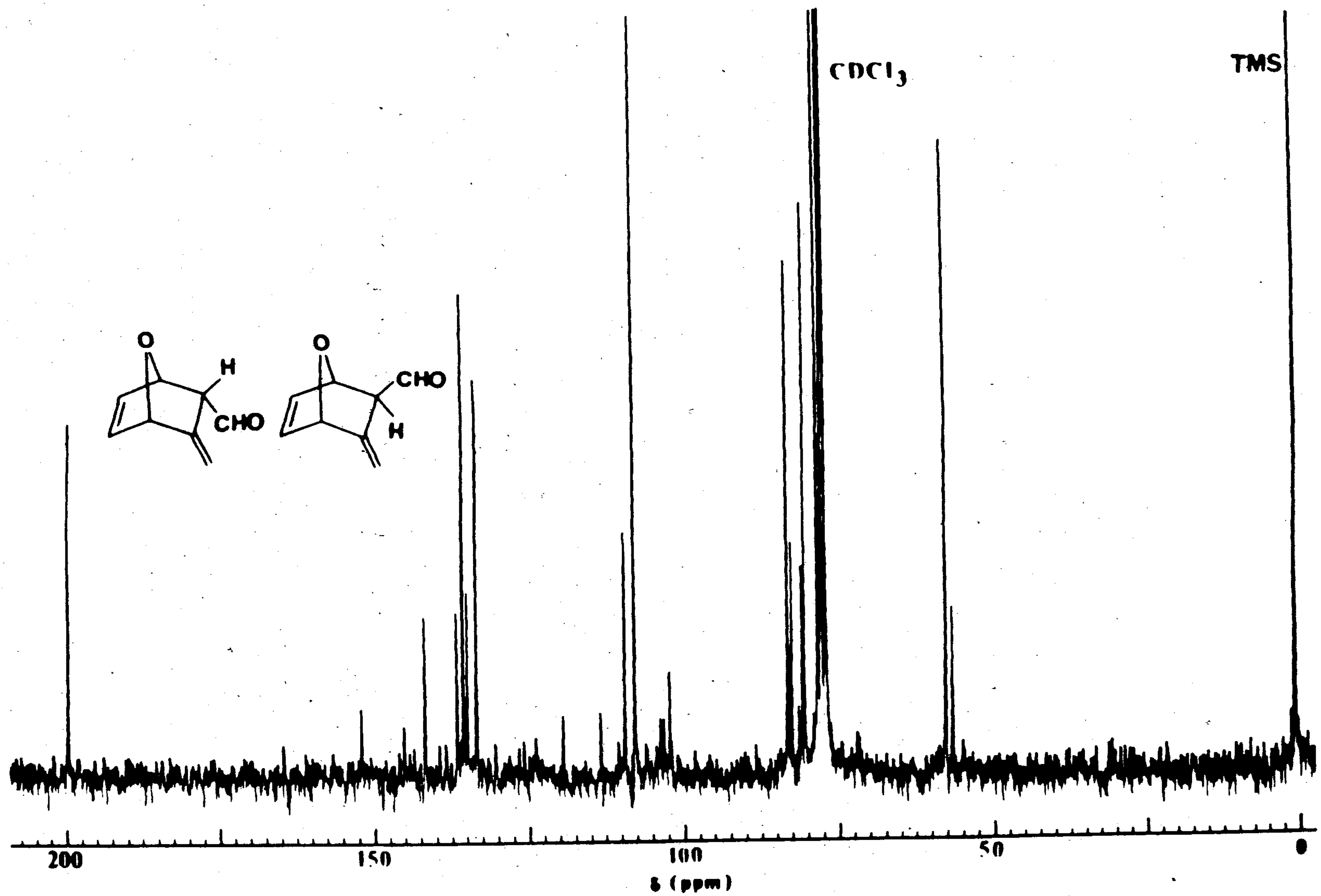


Figure 29. 50 MHz ^{13}C NMR spectrum of **79a** and **79b** mixture.

shift difference is larger than in the tricyclooctenes, **75** and **76.** In addition, the aldehyde proton in **79b** is 0.41 ppm downfield with respect to its counterpart in **79a.** The exact interpretation of these chemical shift data is complicated by the presence in each of these adducts of so many magnetically anisotropic groups in the vicinity of the protons concerned.

As seen in Table 12 only one carbonyl carbon resonance was detected (δ 199.7 ppm) for the mixture of trapped butadienal adducts with furan. To prove that the carbonyl absorptions in **79a** and **79b** were fortuitously identical, the ^{13}C spectrum was remeasured with selective irradiation of proton Q (δ 9.49 ppm). In this way the carbonyl signal for **79a** was split into a doublet by its coupling with H and the weaker carbonyl resonance for **79b** at δ 199.7 ppm was clearly uncovered and confirmed. The same experiment was also performed in reverse with selective irradiation of proton H (δ 9.08 ppm). These results are shown in Figure 30.

In the absence of a proton coupled spectrum, or alternatively, a series of selective ^{1}H decoupling experiments, an experimental assignment of the olefinic and bridgehead carbons in the ^{13}C NMR spectra of adducts **79a** and **79b** was not possible. However, a tentative assignment of the olefinic carbons has been made based on the γ-gauche effect [151,152]. It has been shown that monomethyl substitution at the C_5 position in norbornene causes an upfield shift on the γ carbon signal when the methyl group is endo. The corresponding exo-methyl substitution caused a slight downfield shift [153]. Moreover, the magnitude of the chemical shift difference is

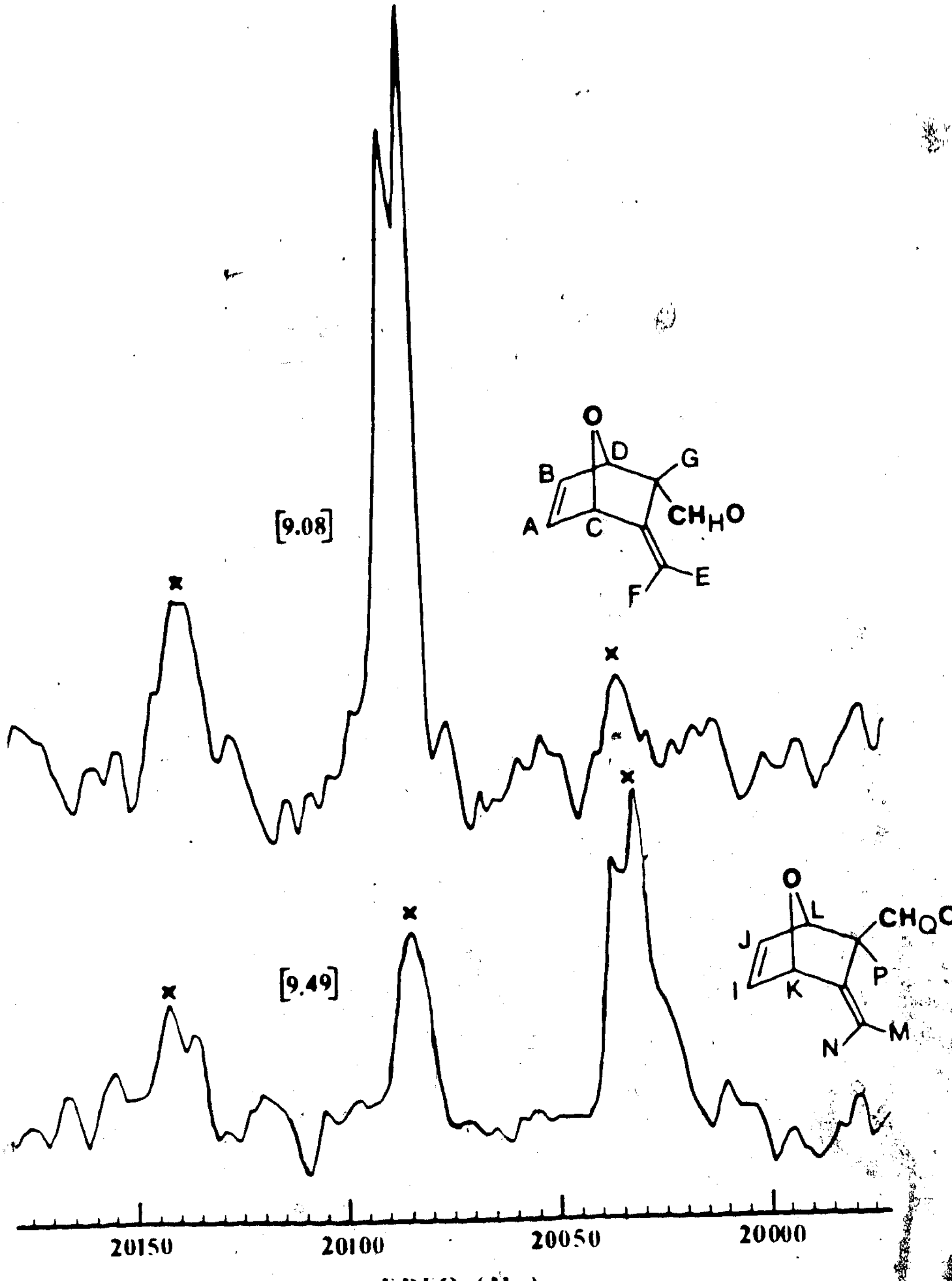
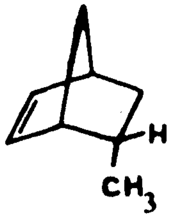
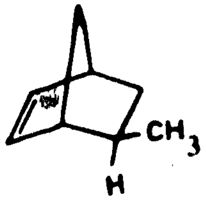


Figure 30. Selective ^{1}H decoupling in the 100 MHz ^{13}C NMR of **79a** and **79b** mixture.



81



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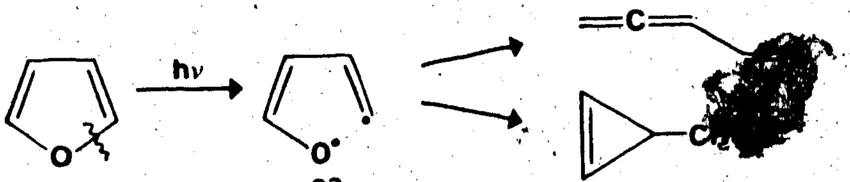
substituent independent. These effects are due to the γ-gauche steric interaction and have been exploited in making our tentative ^{13}C assignments. Chemical shift differences in norbornenes have also been reported for carbon atoms α and β to the substitution site [153]. Since the magnitude of these effects was much smaller, no attempt has been made to assign the carbon atoms in **79a** and **79b** based on such effects.

GC of the **79a** and **79b** adduct mixture on Carbowax 20M successfully resolved the components, and a concentration ratio of 2.7/1, respectively, was determined from the GC peak areas.

The furan DAa with 2,3-butadienal described here represent the first reported trapping of this parent aldehyde as a photolysis product from furan. Van Tamelen and Whitesides [41,42] previously found the corresponding t-butyl ketone, **14**, as a stable product of 2,5-di-t-butylfuran photolysis. It was not definitely established that **14** was a primary photolysis product, although the authors preferred a mechanism in which secondary photolysis of the cyclopropenyl ketone, **15**, produced **14**. Direct irradiation of **15** did indeed generate a mixture of **12-14**. Photolysis of 2,3,5-tri-t-butylfuran also produced a cyclopropenyl ketone but as a minor product.

In the present study, photolysis wavelengths of 214 and 229 nm were employed. The π systems of the C=O and C=C chromophores in **15** are not conjugated and so it is unlikely that the π-π* absorptions in this molecule have any significant extinction from 215-230 nm. The n-π* carbonyl absorption is located at much longer wavelength than we have used for photolysis. For instance, with **15** van Tamelen and Whitesides reported the following UV data in pentane solution: λ_{max} ~ 293 nm, ε ~ 50 $M^{-1}cm^{-1}$ [42]. In addition, the present investigation included both conventional steady-state and cyclic photolyses. The chemical yields of **77**, **78** and **79** were estimated to be approximately 6%, 12% and 8%, respectively, in steady-state photolysis experiments where the furan conversion was ~1%. Regardless of the different experimental conditions, the adducts **77**, **78** and **79** were always formed in the same ratio. This would indicate that in the current experiments the 2,3-butadienal was not formed by secondary photolysis of the cyclopropenyl aldehyde. Whether it might arise by a 1,2-H migration in a 1,5-diradical such as **83**, or by the dark reaction of a vibrationally excited cyclopropenyl aldehyde, cannot be decided at present. The initial step in furan photolysis is widely accepted to be C-O bond cleavage to produce a diradical such as **83**.

We have employed the direct photolysis of furan (214, 229 nm) in generating the cyclopropenyl aldehyde-furan DAa, **8**. Srinivasan [34,35] has isolated **8** from the gas phase triplet mercury

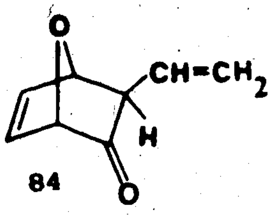


83

(33)

photosensitized reaction of furan, implicating the intermediacy of a triplet state. In the present solution phase study, two DAa between furan and the cyclopropenyl aldehyde were formed and isolated, however, no evidence was found for the formation of the cyclopropene adducts **6** or **7**. Hiraoka and Srinivasan [36] consider "the formation of cyclopropene" and therefore presumably its DAa with furan in the neat solution phase "a significant test for the present of triplet state furan". Consequently the absence of **6** and **7** in our products would seem to suggest that the triplet state of furan is not implicated in the liquid phase direct photolysis.

In addition to the principal furan photolysis products characterized in this work GC/MS (10% Carbowax 20M, ~ 3 mm × 2 m, 150°C) indicated the presence of two additional furan dimers, $M^{+\cdot}$ 136. GC/FTIR (10% Carbowax 20M, ~ 3 mm × 2 m, 150°C) analysis of these two compounds revealed intense C=O absorptions at 1808 and 1818 cm^{-1}. The low yield of these minor products has hampered their isolation and characterization by NMR. The IR data are suggestive of a cyclic ketone, possibly derived from trapping of the 1,3-butadienone. As mentioned previously this species was trapped by Srinivasan following furan photosensitization [35].



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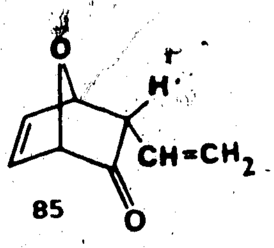

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c. <u>Thiophene Photolysis at Low Temperature with Post-Photolysis Trapping by Furan</u>

From the solution phase photolysis of thiophene in furan we have obtained two adducts which were concluded to arise via Diels-Alder cycloaddition between furan, the <u>in-situ</u> trapping agent, and Dewar thiophene which is formed during thiophene irradiation. For two reasons the low temperature photolysis of thiophene employing post-photolysis trapping with furan was investigated. Firstly, a major objective of the low temperature matrix isolation experiments, to be discussed later, was to generate, stabilize and identify intermediates in the photolysis of thiophene. The low temperature photolysis system about to be described formed a vital link between the very low temperature regime of the matrix isolation experiments and the room temperature trapping studies already presented. In an earlier attempt to detect Dewar thiophene, we photolyzed thiophene at low temperature and examined the high field ^{1}H NMR of the photolyzed mixture, still maintained at low temperature. This experiment was unsuccessful, indicating that either no detectable amount of Dewar thiophene was formed under these conditions or that it was sufficiently reactive in the cold, but fluid, NMR solution that its lifetime was too short to permit detection. Secondly, using <u>in-situ</u> furan trapping at room temperature, it was impossible to exclude the possibility that the observed thiophene/furan adducts resulted from the interception by furan of a thiophene excited state. In this regard Wynberg's results on the trapping of 2-PT by piperylene should be recalled [99]. Photolysis of 2-PT in the presence of the diene resulted in both 1:1 adduct formation and quenching of the 2-PT fluorescence. It was concluded that piperylene reacted directly with an excited state of 2-PT, rather than with a photochemically generated ground state intermediate. Certainly a successful post-photolysis trapping experiment would prove that ground state Dewar thiophene was being generated and subsequently captured by the furan.

Therefore, in order to ascertain that the trapped species was indeed an intermediate, and not a short-lived excited state of thiophene, the photolysis of thiophene was performed at ca. -175°C in a glassy matrix (10% thiophene in diethyl ether, v/v). At the conclusion of irradiation (229 nm, 8 h) furan was slowly distilled under vacuum and deposited on top of the frozen glass. The mixture was allowed to warm up to the temperature of a dry ice/acetone bath (-78°C), and the resulting solution was stirred rapidly. This temperature was maintained for several hours after which the solution was allowed to gradually warm to 25°C. The formation of the same two adducts **70** and **71** was established on the basis of capillary GC retention time, coinjection with a sample of the authentic adducts isolated from the liquid phase photolysis, and capillary GC/MS. The adducts formed at low temperature had mass spectra much like those for the adducts previously isolated from liquid phase photolysis (Table 13).

TABLE 13

Comparison of the MS Data from the GC/MS[a] Analyses for **70** and **71** Produced in the Solution Phase and Low Temperature Photolyses of Thiophene

Adduct	*m/e*	Relative Intensity		Fragment
		Solution Phase	Low Temperature	
70	152	~50%	~50%	$M^{\overset{+}{\bullet}}$
	123	65	70	-CHO
	84	100	100	$-C_4H_4O$
	68	65	65	$-C_4H_4S$
71	152	~25%	~25%	$M^{\overset{+}{\bullet}}$
	123	75	80	-CHO
	84	100	100	$-C_4H_4O$
	68	65	60	$-C_4H_4S$

[a] DB-1, 70-150°C @ 2°C/min, VG 7070E.

The product ratio, **70/71**, in the low temperature photolysis was exactly the same, 5/3, as was observed in the liquid phase photolysis suggesting that the nature of the intermediate trapped was the same in the two cases. Since in the low temperature experiment only ground state Dewar thiophene could have been trapped, it is unlikely that in the room temperature system there could have been any contribution to the adducts as a result of the interception of excited states. Presumably an excited state of thiophene, or even Dewar thiophene itself, would have a different geometry from the ground state of Dewar thiophene. This geometry difference would be expected to influence the ratio of exo and endo stereoisomers produced.

The combined adduct yield was not determined in the low temperature photolysis. Although the irradiation time was much shorter than in the room temperature trapping experiments, and only a thin surface layer of thiophene was actually irradiated due to the experimental arrangement for the low temperature photolysis, Dewar thiophene was still generated and trapped. In addition, only a small quantity of polymer was formed in the low temperature trapping experiment by comparison to the low temperature NMR experiment which employed very similar conditions for the generation of intermediates (10% thiophene in diethyl ether, 229 nm, 2.5 h). This observation may be evidence that Dewar thiophene decomposes or polymerizes unless trapped.

Consequently, we have demonstrated that thiophene photolysis results in the formation of Dewar thiophene and that this reactive valence bond isomer can be trapped by a Diels-Alder cycloaddition with furan. The quantum yield of Dewar formation has not been determined. Owing to the tendency for the Dewar to rearomatize, or undergo other processes all of which compete with the trapping reaction it may be possible that the actual quantum yield for Dewar formation is much larger than might be inferred from the corrected combined chemical yield of **70** and **71** in the liquid phase photolysis. Therefore, this yield of 2.5-3% must be regarded as a lower limit to the quantum yield.

B. Low Temperature Matrix Isolation (LTMI) Experiments

1. Methodology

A brief description of the strategy employed in analyzing the photochemistry observed in the LTMI system is required at this point. Our MI apparatus is routinely coupled with IR spectroscopy as a means of following the progress of a photochemical reaction.

One of the most challenging problems encountered in a MI experiment can be the determination of the number of different species formed from the in-situ photolysis of the chosen substrate or precursor. When the substrate is irradiated, a number of new IR absorptions are frequently observed. An important simplification in the process of their assignment to distinct species is gained if the absorptions can be separated into groups, for which each absorption in one group arises from the same single compound. This separation process is considerably more difficult when there is no prior knowledge about the species that might be generated by the photolysis.

Frequently, the grouping of new IR absorptions is accomplished by means of time studies which monitor the intensity change of each IR absorption as a function of photolysis time, thereby identifying groups of peaks having the same growth rate, and thus presumably attributable to a common species. However, in our experiments we have found a more discriminating approach, involving the use of different UV photolysis wavelengths. This technique should be particularly well suited to photochemical reactions which produce many low intensity IR absorptions, because such absorptions are more difficult to monitor reliably in a time study. The photolysis wavelength technique relies on the fact that different species formed in the matrix will have different UV absorption spectra. Probing the matrix with a number of photolysis wavelengths ultimately reveals conditions where the rates of formation or consumption of different species differ dramatically. In this manner the new IR absorptions can be separated into groups arising from single compounds.

In a conventional MI experiment the substrate, if it is a gas at room temperature, is firstly mixed with a large excess pressure (<u>ca.</u> 200-1000 fold) of an inert gas, most frequently Ar. The mixture is stirred for a time considered to be sufficient to guarantee its homogeneity, and then admitted at a regulated flow rate to the cold (10 K) sample window of the MI apparatus. The deposition process is continued until the desired amount of substrate has been introduced. The IR spectrum of the substrate isolated in the matrix is recorded before photolysis, and then the irradiation can be commenced. At any desired intervals the progress of the photolysis can be checked by IR, and irradiation resumed with the same or a different wavelength, as required. We will hereafter refer to this type of MI experiment as a single layer experiment because all of the substrate is introduced in one deposit step.

During the irradiation of a matrix isolated compound, photochemical reaction is first initiated in the substrate molecules situated at, or near, the surface of the matrix in relation to the incident light. As the photolysis proceeds substrate molecules located at progressively greater depths inside the matrix are photolyzed. From this viewpoint one can envisage the potential for certain experimental problems in MI, depending in particular on the nature of the substrate and the new species generated by its photolysis. For instance, in our single layer experiments with thiophenes only a small amount of substrate could easily be converted to primary photolysis products. Only a very slow disappearance of substrate and the gradual growth of secondary photolysis products continued on further irradiation. This same situation was also encountered, but to a lesser degree, with furan. Unfortunately, many of the products isomeric to furan and thiophene, that might be generated during the matrix photolysis of these two heteroaromatic compounds, contain chromophores which absorb in the same UV region as the substrate. While furan has a UV absorption maximum centred near 215 nm, thiophene and its alkyl substituted derivatives have maxima located near 230 nm. Generally, MI experiments on furan and thiophenes were performed with photolysis wavelengths of 185, 214, 229 and 254 nm. As a result, only weak IR spectra of many of the new primary photolysis products were ever generated using the single layer deposit method.

In view of this limitation of the single layer MI experiments in their application to heteroaromatic compounds, one conceivable solution was to replace the single deposit layer with a number of thinner layers, each photolyzed separately. Although seemingly obvious, such a modification of the MI method, which we have called the "multilayer technique", has never to the best of our knowledge been reported in the literature. This does not mean that other laboratories may not have used such a sample deposition technique but the systems examined to date by MI may not have required this technique since the location of a wavelength suitable for selective irradiation of the substrate, without interference from absorption by the photolysis products, does not usually present problems.

The application of our multilayer deposit technique to the MI studies of furan and thiophene enhanced the relative concentrations of primary photolysis products generated, as compared with the single layer results. Consequently, this new approach to sample deposition and photolysis was frequently employed in our MI experiments. As an example of the success of the multilayer technique the IR spectra (Figures 31 and 32) obtained after the photolysis of matrix isolated furan can be compared. Figure 31 was obtained by the single layer method, while Figure 32 was a multilayer experiment. In addition to identifying the IR bands of the substrate in Figures 31 and 32, those attributable to primary and secondary photolysis products have also

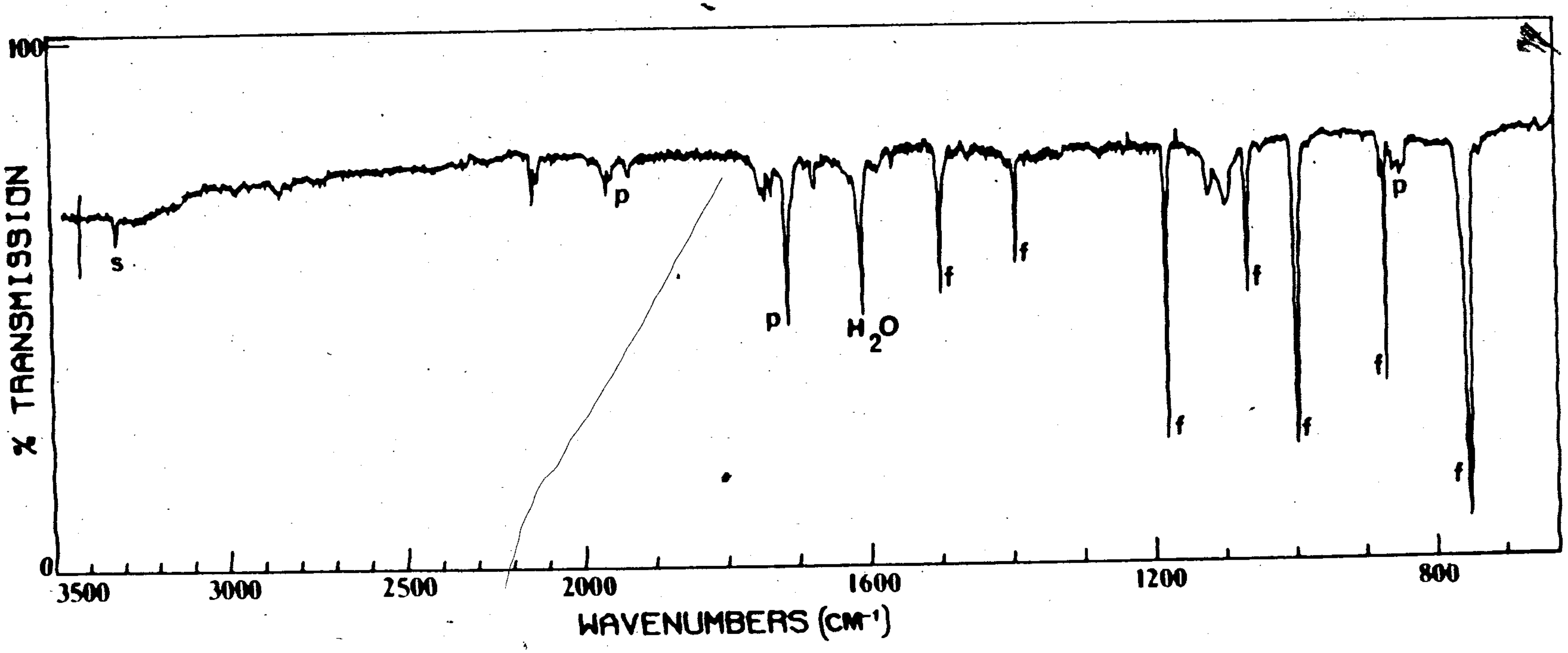


Figure 31. Typical single layer furan matrix isolation experiment; f-furan, p-primary photolysis product, s-secondary photolysis product.

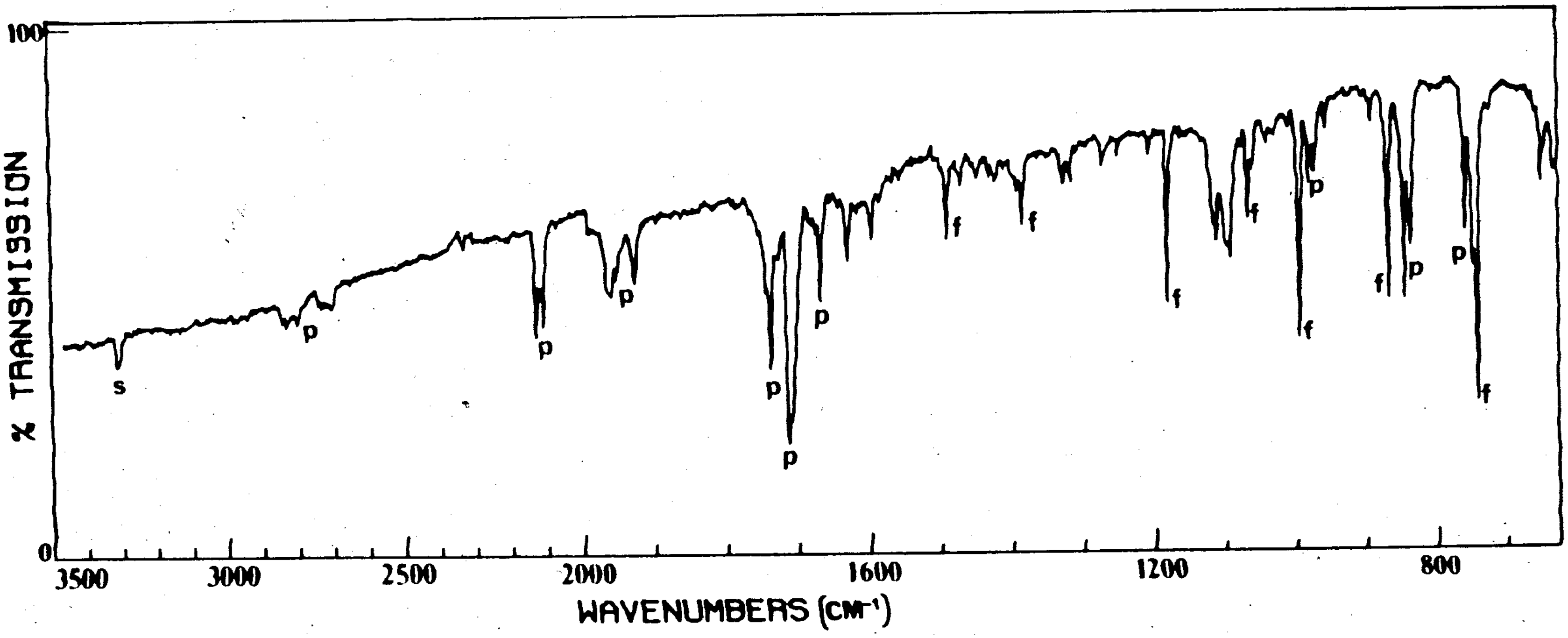


Figure 32. Typical multilayer furan matrix isolation experiment; f-furan, p-primary photolysis product, s-secondary photolysis product.

been indicated. Another dramatic demonstration of the value of the multilayer technique is revealed for the case of thiophene in Figures 33 and 34.

Having presented a brief introduction to the strategy of our MI studies we can now begin to consider some of the experimental results. The MI results for furan will be described first. Since the gas and solution phase photolyses of furan have been previously investigated by Srinivasan [33-35], and because we have identified several additional products from the photolysis of neat liquid furan, it was considered that a substantial amount of information was already available about the species which might be formed in the matrix.

2. Furan Matrix Isolation Experiments

In his gas phase photolysis experiments with furan Srinivasan detected CO and three different C_3H_4 fragmentation products [33,34], cyclopropene, methylacetylene and allene. In addition, at higher furan pressures, two furan DAa with cyclopropene, and one with cyclopropenyl aldehyde were reported [34,35]. According to Srinivasan the solution phase photolysis of furan did not produce any evidence for these products [34], although 1,3-butadienone (vinylketene) was trapped [35].

When we irradiated neat liquid furan we isolated and fully characterized four DAa of furan, **77-79b**. In addition, IR and MS evidence for structure **84** and **85**, derived from the furan trapping of vinylketene, was obtained.

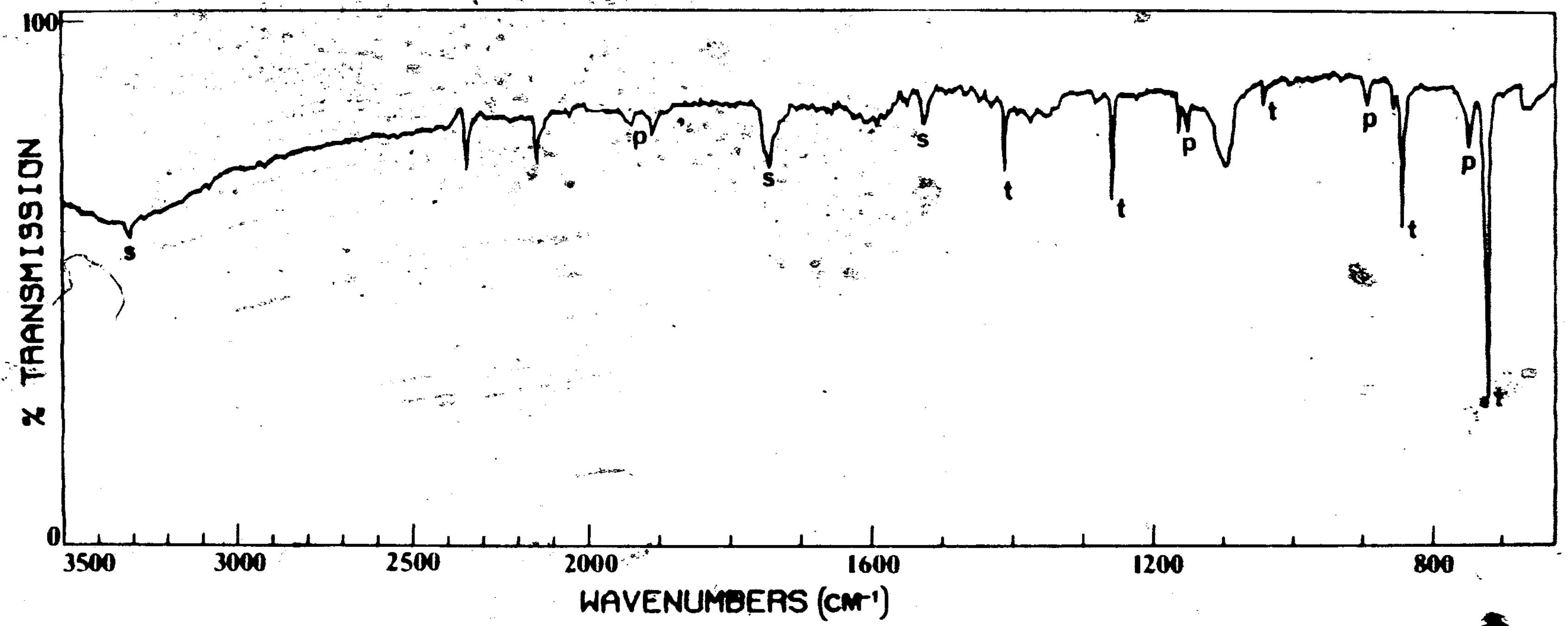


Figure 33. Typical single layer thiophene matrix isolation experiment; t-thiophene, p-primary photolysis product, s-secondary photolysis product.

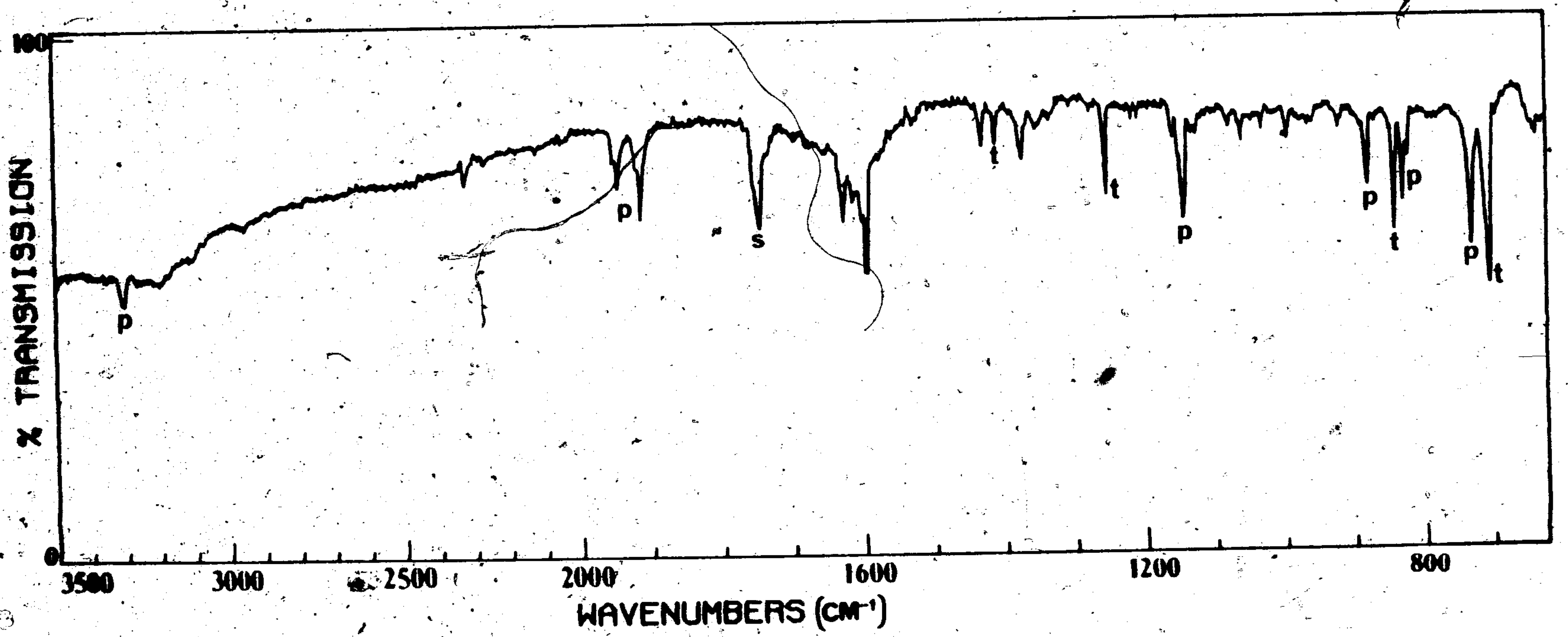
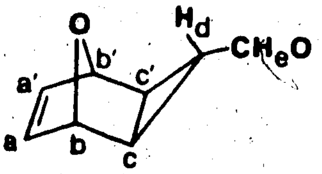


Figure 34. Typical multilayer thiophene matrix isolation experiment; t-thiophene, p-primary photolysis product, s-secondary photolysis product.



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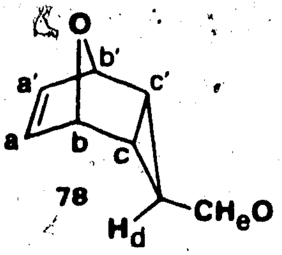

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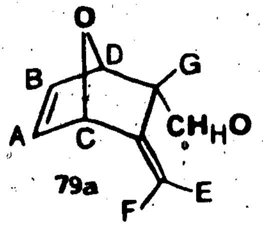
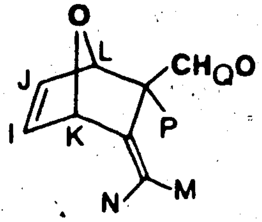
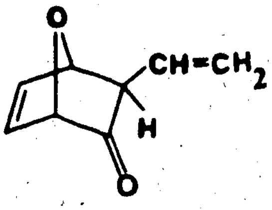


79a



79b



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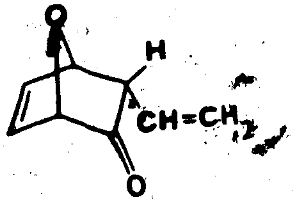


85

a. Identification of the Fragmentation Products

Single layer photolyses (185, 214 nm) of furan produced substantial amounts of CO, CH_2CCH_2 and CH_3CCH, especially at longer photolysis times. These products were identified based on their characteristic absorptions summarized in Table 14. The positions of the actual absorptions in the low temperature matrix are usually shifted slightly. For instance, CH_2CCH_2 had one absorption at 1951 cm^{-1} and a second absorption at 839 cm^{-1}, which is due to the $-CH_2$ out-of-plane deformation. The best confirmation of the identity of a matrix isolated species is provided by comparison of its spectrum with that of a matrix isolated sample of the authentic compound. When commercial methylacetylene and allene were introduced into an Ar matrix at approximately 10 K they produced spectra which matched the IR spectra of the CH_3CCH and CH_2CCH_2 formed by the photolysis of furan with regard to both the positions and the relative intensities of the absorptions. Since, in a single layer MI experiment, little

TABLE 14

Characteristic IR Absorptions of CO, Monosubstituted Acetylenes and CH_2CCH_2

Compound	Approximate Description	Vibrational Frequency (cm^{-1})	Relative Intensity
CO	C═O stretch	2150	–
RCCH[a]	≡CH stretch	3310-3320	s
	C≡C stretch	2100-2140	w
	≡CH bend o.o.p.	610-680	s
CH_2CCH_2[b]	═CH stretch	3005	m
	C═C═C asymm. str.	1957	s
	CH_2 scissoring	1398	s
	CH_2 bend i.p.	1033.5	m
	CH_2 bend o.o.p.	841	vs

[a] Data taken from Ref. [154].

[b] Gas phase data taken from Ref. [155].

or no CH_3CCH or CH_2CCH_2 was usually observed at short photolysis times (~2 h), but their quantities became substantial with long irradiations (~10-20 h), it was concluded that these hydrocarbons must be arising primarily by secondary photolysis of other primary photoproducts.

In our MI experiments with furan, cyclopropene was never observed even at long irradiation times. Mitchell et al. [156] have recorded the IR spectrum of cyclopropene in a Xe matrix. A very short, partial list of the characteristic absorptions most valuable in detecting matrix isolated cyclopropene, is given in Table 15. Although in our MI studies the 1600-1700 cm^{-1} region was often complicated due to the presence of different types of carbonyl absorptions, as well as an H_2O absorption (~1600 cm^{-1}) which was often large, the region from 1000-1050 cm^{-1} clearly contained no absorptions. If cyclopropene were generated in the matrix its 1011 and 1044 cm^{-1} bands would have been detectable. The former is the most intense IR absorption of cyclopropene [156].

The absence of cyclopropene in the matrix photolysis of furan was an interesting result for two reasons. Firstly, Hiraoka and Srinivasan discovered that direct irradiation of furan in the gas phase did not produce cyclopropene, while its $Hg(^3P_1)$ photosensitization produced large, pressure dependent, yields of cyclopropene. As a result, they suggested [36] that cyclopropene formation was a significant test for the presence of triplet furan. This is consistent with the matrix results since direct photolysis at either 185 or 214 nm was employed for these experiments. By

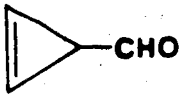
TABLE 15

Some Characteristic Fundamental IR Absorptions of Cyclopropene in a Xe Matrix[a]

Approximate Description	Vibrational Frequency (cm^{-1})	Relative Intensity
CH bend o.o.p.	584	s
CH bend i.p.	1011	vs
C[illegible] wag.	1044	s
C=C stretch	1643	m-s

[a] Data are taken from Ref. [156].

contrast, Chapman has published a review article on the low temperature photochemistry of many compounds [157]. In this publication it was stated that the irradiation of furan in a matrix (8 K) produces cyclopropenyl carboxaldehyde, 86, which on secondary photolysis, can produce 2,3-butadienal, 87, 2-butynone, 88, and cyclopropene plus carbon monoxide. The formation of cyclopropene



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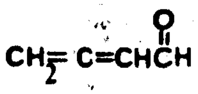


$CH_2{=}C{=}CH\overset{\overset{\displaystyle O}{\|}}{C}H$

87

claimed in this review article has [illegible] the best of our knowledge, been supported by any pu[illegible] describing the experimental details of this study.

[illegible] have trapped both **86** and **87** in the liquid phase photolysis of neat furan. Their role in our matrix experiments will be dicussed shortly. On the basis of the known IR spectrum of **88** [150] however, it was concluded that **88** is not a product of the MI photolysis of furan.

b. Identification of Ketenes

As mentioned earlier Srinivasan successfully trapped vinylketene, **11**, during the photosensitization of furan in the

$$CH_2{=}CHCH{=}C{=}O$$

11

presence of methanol [35]. The gas phase IR spectrum of **11** was reported by Bjarnov in 1979 [158], and is shown in Figure 35. The

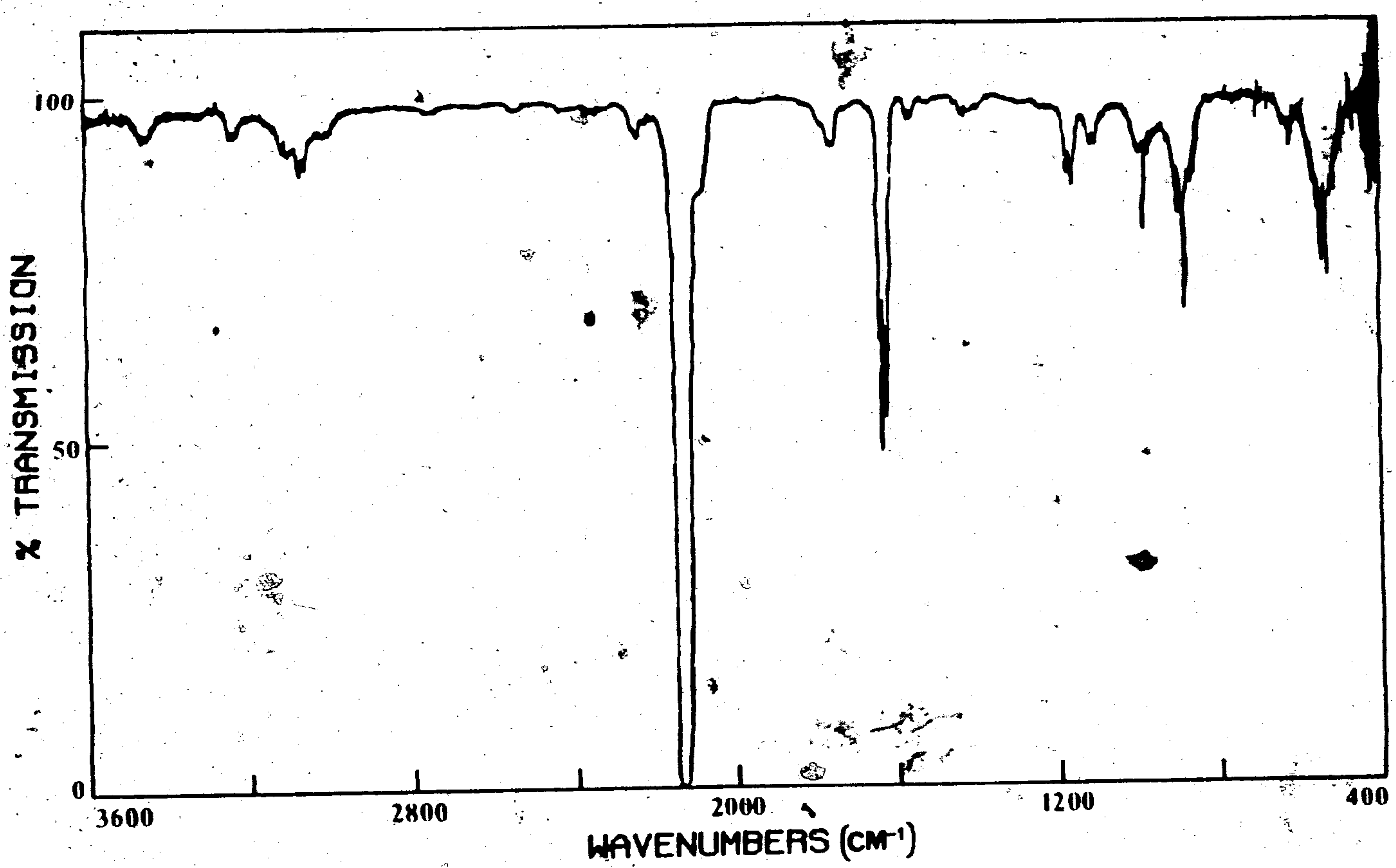


Figure 35. IR spectrum of gaseous 11. Reproduced from Ref. [158].

extremely strong absorption at 2137 cm^{-1} is characteristic of a ketene moiety. The presence of the vinyl moiety is indicated by bands near 976 and 875 cm^{-1}. The 2137 cm^{-1} absorption is, however, about an order of magnitude stronger than the vinylic absorptions. Vinylketene can have two planar rotamers, as illustrated below. The room temperature spectrum of gaseous **11** was concluded to show only bands due to the trans-rotamer.

cis

11

trans

In both single and multilayer photolyses of furan CO, which absorbs at ca. 2140 cm^{-1}, was observed as a fragmentation product. The rapid growth of the CO absorption was always accompanied by increases in the absorptions of CH_3CCH and CH_2CCH_2. However, in addition to CO there were two other IR absorptions located near 2140 cm^{-1}. For instance, lengthy irradiation of furan at 185 nm produced absorptions at 2120 and 2130 cm^{-1}, as shown in Figure 36. Secondary irradiation of these new absorptions, at 254 nm, resulted in the disappearance of the 2120 cm^{-1} absorption, while the 2130 cm^{-1} band increased. These two absorptions were also generated by the MI photolysis of furan at 214 nm, however, under this condition the 2120 cm^{-1} peak produced was considerably larger than that at 2130 cm^{-1}. Once again secondary irradiation at 254 nm caused the disappearance of the 2120 cm^{-1} absorption while that at 2130 cm^{-1} was considerably enhanced (Figure 36).

For this region of the IR spectrum only two types of absorptions

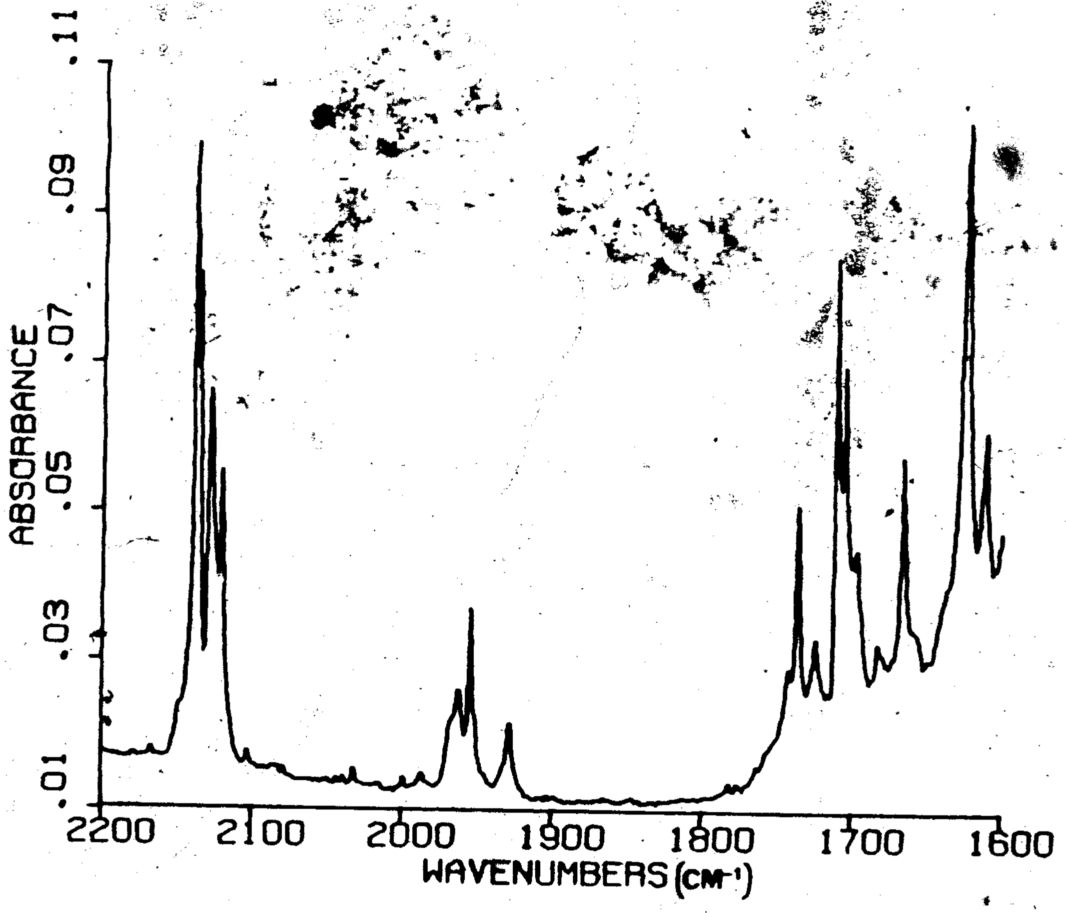


Figure 36a. Matrix isolation of furan, after ~16 h of irradiation at 185 nm.

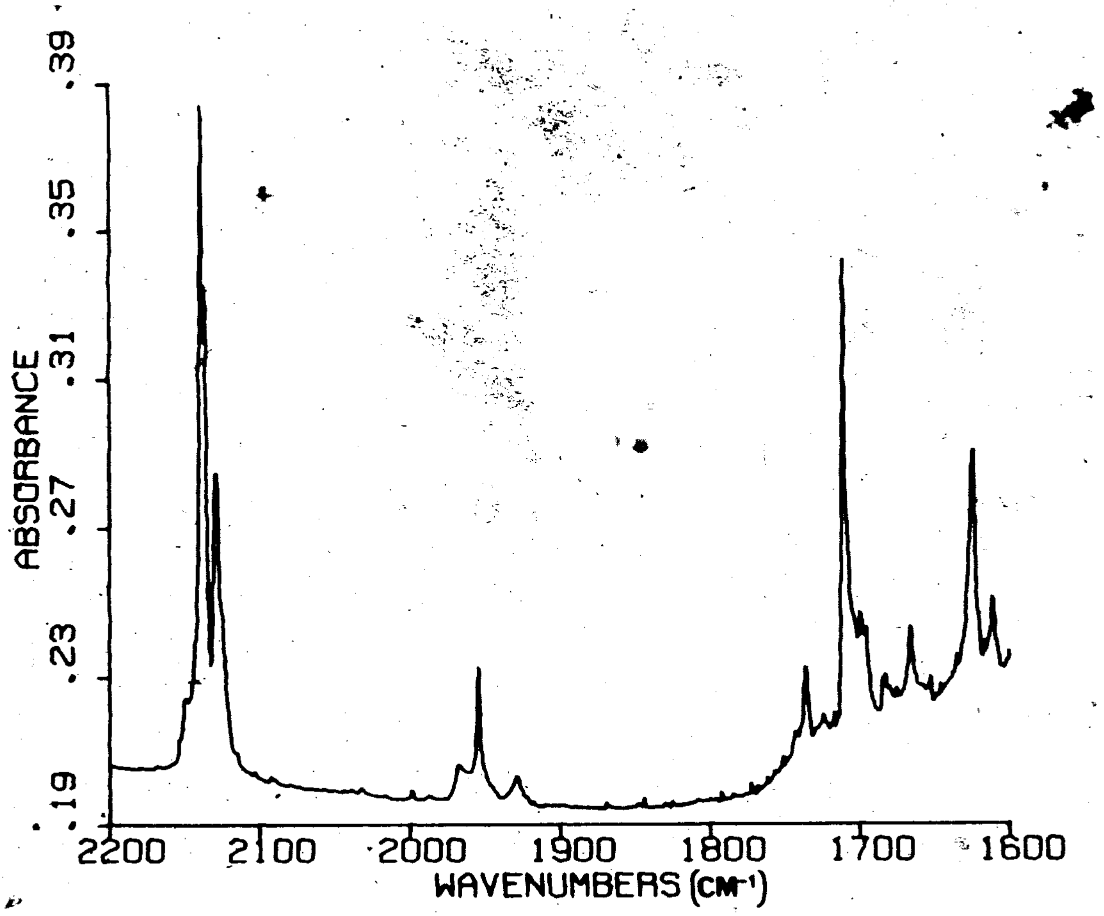


Figure 36b. Same matrix after 4.75 h of secondary photolysis at 254 nm.

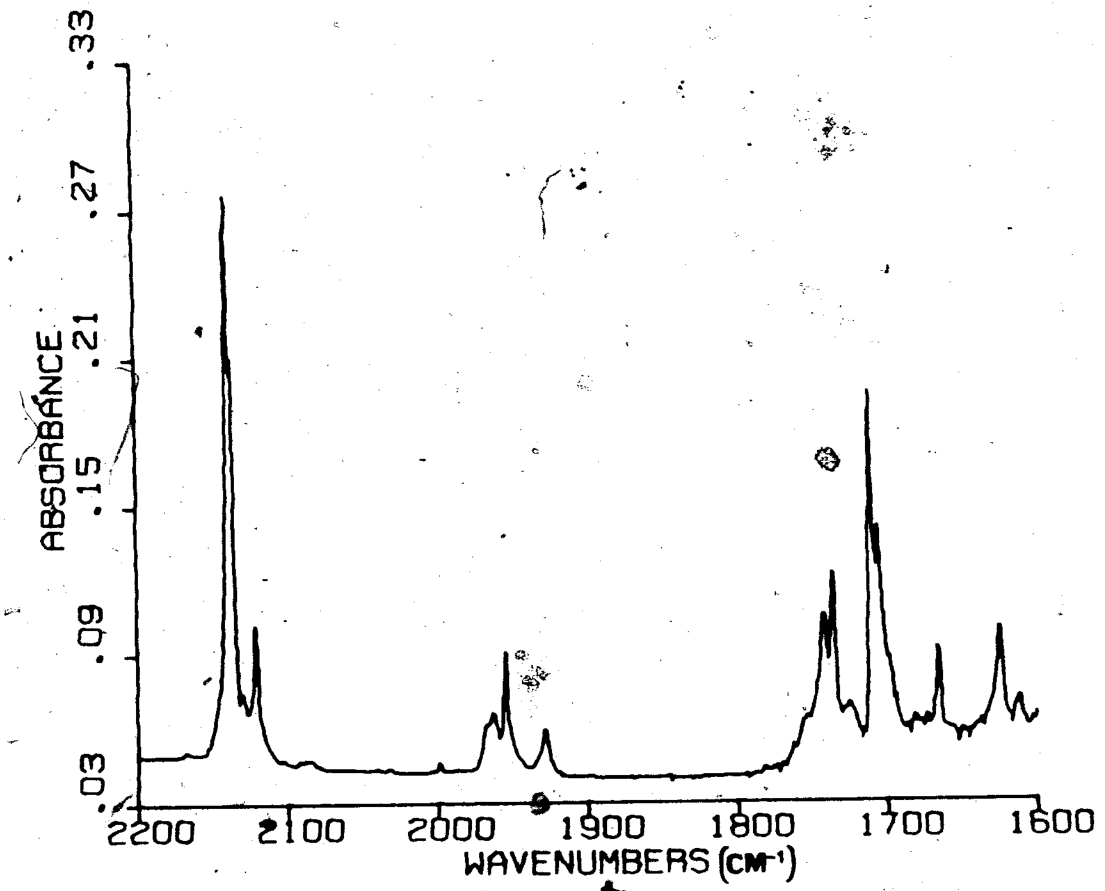


Figure 36c. Matrix isolation of [illegible] after 12 h of irradiation at 214 nm.

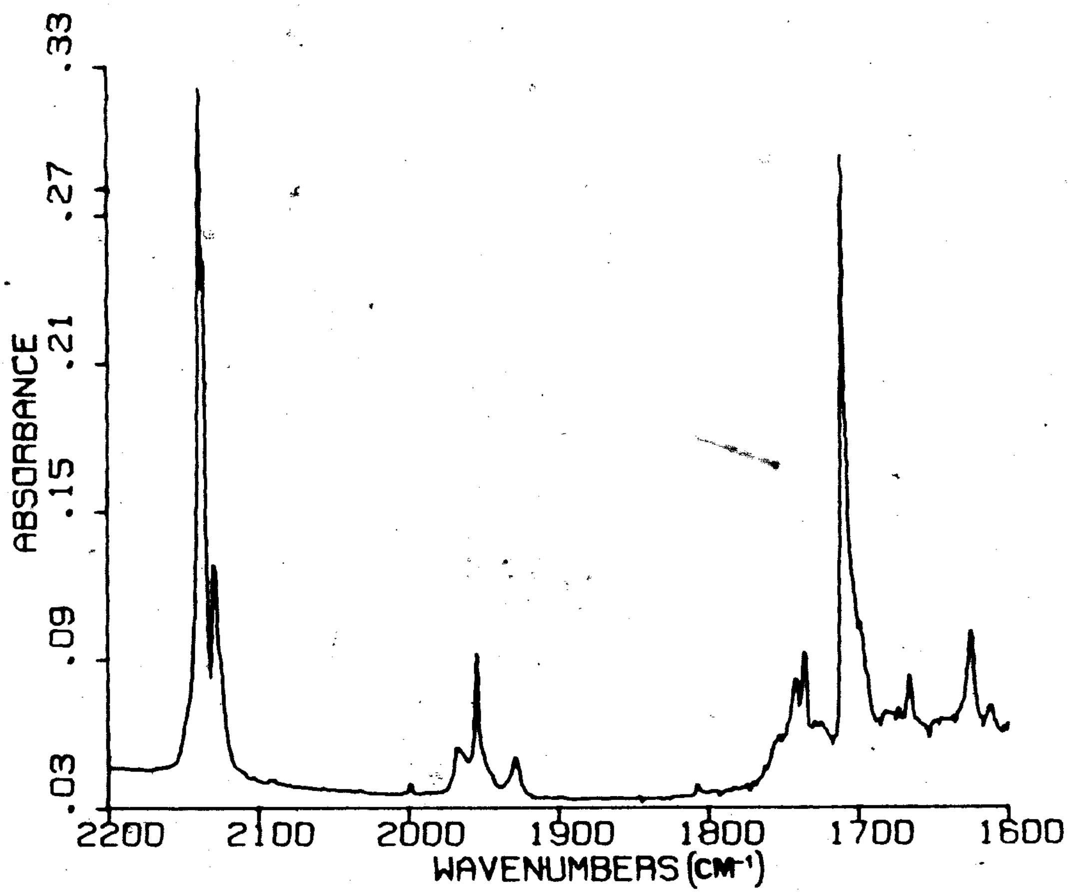


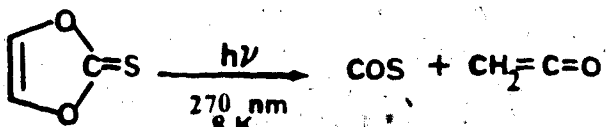
Figure 36d. Same matrix after 12 h of secondary photolysis at 254 nm.

can easily be imagined (in addition to that of CO) which are compatible with possible furan photoproducts. Firstly, alkyl monosubstituted alkynes such as CH_3CCH show a triple bond stretching absorption around 2100-2150 cm^{-1} [154]. Secondly, as noted above, ketenes display very characteristic, intense absorptions at this location. The alkyne absorption tends to be of rather low intensity, and thus for the small amount of CH_3CCH formed in the matrix photolysis of furan, it would not likely be observable. This conclusion was supported by the fact that neither the 2130 cm^{-1} absorption nor the 2120 cm^{-1} absorption behaved in unison with the 3320 cm^{-1} peak of CH_3CCH. CH_3CCH was a secondary photolysis product, while the 2120 and 2130 cm^{-1} absorptions are due to primary photolysis products. Therefore, it was concluded that both of these absorptions are attributable to ketene species. The possibility that the parent ketene, **89**, might be present was considered.

$$CH_2{=}C{=}O$$

89

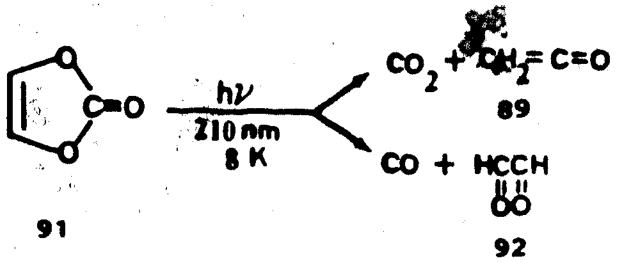
Torres et al. [159] have generated **89** by the Ar matrix photolysis of two different precursors. Irradiation of vinylene thioxocarbonate, **90**, at 270 nm resulted in the production of COS and **89**.



(34)

90 **89**

The characteristic ketene absorption was located at 2140 cm^{-1}. Other absorptions due to **89** were at least ten times weaker. Photolysis of vinylene carbonate, 91, resulted in the formation of CO, CO_2, 89, and glyoxal, 92. The IR spectrum of the product mixture revealed only a



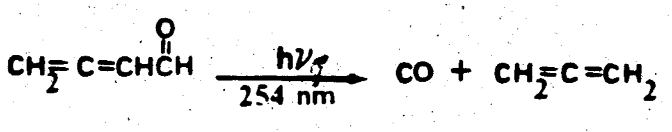
(35)

single absorption at 2140 cm^{-1}, indicating that the C=O absorptions from CO and CH_2CO were not resolvable on the Nicolet 7199 FTIR at a nominal resolution of 1 cm^{-1}. This indicated that neither the 2130 nor the 2120 cm^{-1} absorption detected in the matrix photolysis of furan could be assigned to 89. It did however, raise the possibility that 89 may be present, yet hidden by the CO absorption. No definite conclusion regarding this possibility can be made at the present time, although the absence of C_2H_2 (3287, 729 cm^{-1} [160]), which would presumably be the other fragmentation product formed if furan photolysis produced 89, was considered as evidence against the significant production of 89.

Consequently, the 2130 and 2120 cm^{-1} absorptions were tentatively assigned to the two rotamers of 11 illustrated earlier. The distribution of these rotamers was dependent on the photolysis wavelength, and secondary photolysis (254 nm) resulted in the conversion of one rotamer to the other. Although no characteristic vinylic absorptions, 976 and 875 cm^{-1}, were observed these absorptions were likely too weak, in comparison to the 2137 cm^{-1} absorption, to be seen. This considerable difference in intensity was already noted in Figure 35.

c. Identification of 2,3-Butadienal

The results of our furan MI experiments will now be considered with respect to the products trapped in solution by DA cycloaddition. In solution we found the DAa of furan with both cyclopropene-3-carboxaldehyde, **86**, and 2,3-butadienal, **87**, generated by the photolysis of furan. Owing to the cumulative nature of the double bonds in allenes, **87** should have very characteristic IR absorptions in the region 1915-1980 cm^{-1} [161]. The photolysis of matrix isolated furan (185, 214 nm) generated three absorptions in this vicinity. One absorption was due to the parent allene. The other two allene-type absorptions, near 1925 and 1965 cm^{-1}, always increased and disappeared in unison, and also seemed to be associated with a somewhat stronger absorption at 1665 cm^{-1} (Figure 37). These absorptions were assigned to **87**. IR data on some allenyl ketones reveal similar absorptions. For instance, $CH_2CCHCOCH_3$ has absorptions at 1951, 1931 and 1680 cm^{-1}, while $CH_2CCHCOC_2H_5$ absorbs at 1955, 1935 and 1685 cm^{-1} [162]. The conjugation of the carbonyl group with the cumulative double bond system lowers the carbonyl stretching frequencies in these compounds. The 254 nm photolysis of **87** led to its slow destruction, accompanied by a slow growth of the parent allene and CO.



$$CH_2{=}C{=}CH\overset{\overset{O}{\|}}{C}H \xrightarrow[254\ nm]{h\nu} CO + CH_2{=}C{=}CH_2 \qquad (36)$$

d. Identification of Cyclopropene-3-Carboxaldehyde

The cyclopropenyl aldehyde, **86**, trapped in solution experiments,

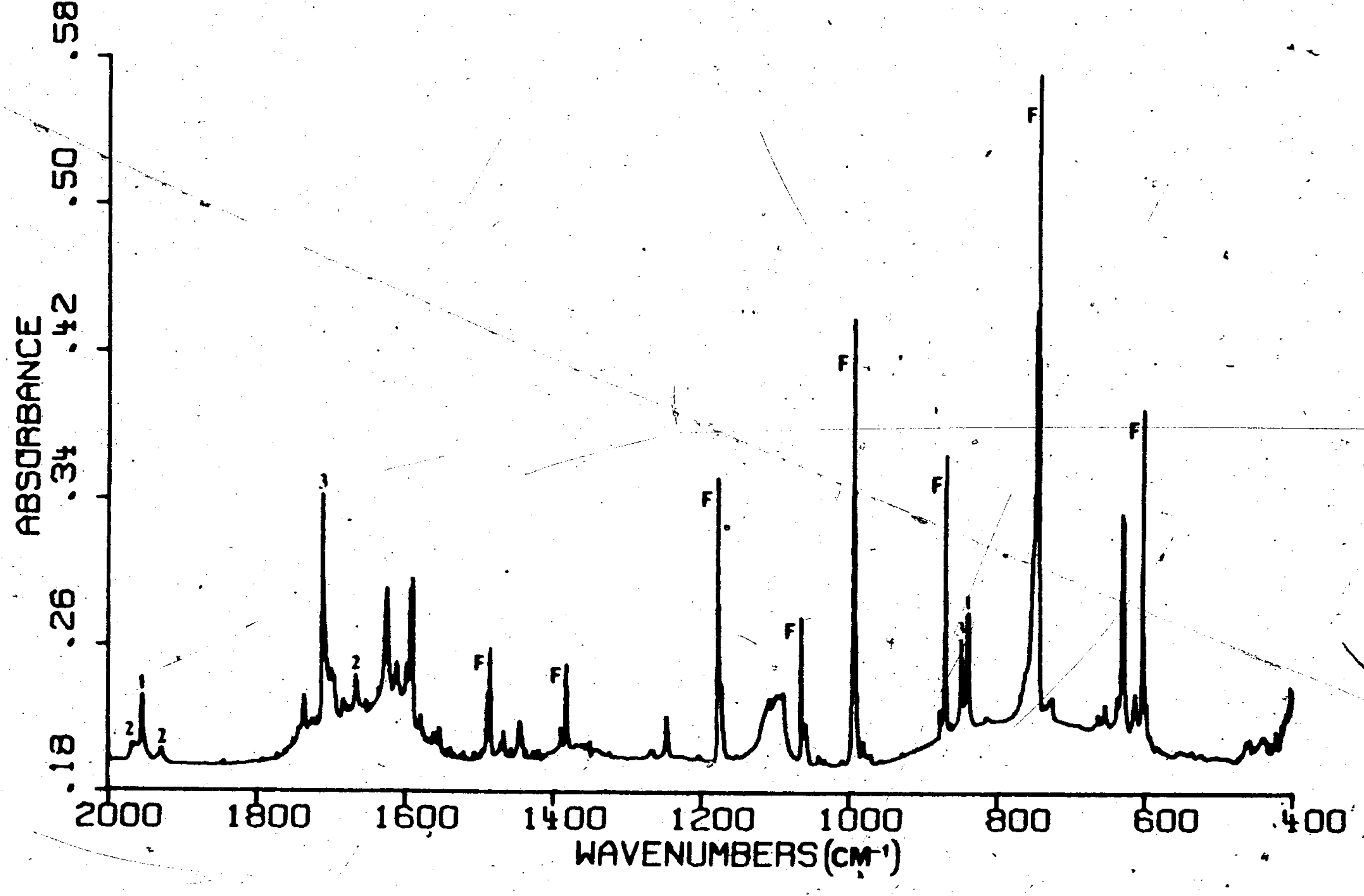
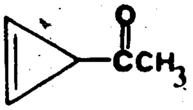


Figure 37. IR spectrum showing absorptions assigned to furan (F), CH_2CCH_2 (1), **87** (2) and **86** (3).

has also been identified as a primary photolysis product in the matrix photolysis of furan. Srinivasan previously reported the trapping of a DAa of unknown stereochemistry between furan and this aldehyde. With respect to their carbonyl groups, the structure of the DAa is quite similar to **86**. Although the complete IR spectrum of this DAa was not given, a strong absorption at 1710 cm^{-1}, as well as a weak absorption at 2750 cm^{-1}, were described. In our MI experiments (185, 214, 229 nm) two correlated IR absorptions have been assigned to this species, a strong absorption near 1705-1710 cm^{-1}, and another one situated near 848 cm^{-1} (Figure 37).

86 was detected by Tsuchiya et al. [163] in the solution phase photolysis of pyridazine N-oxides. Unfortunately, only a carbonyl absorption at 1720 cm^{-1} was reported for the liquid aldehyde, and no further details of its IR spectrum have been provided. Limited IR data have also been described for the cyclopropenyl compounds, **93** and **94** [163,164], but again no C-H bending vibrations were included so that comparison with the 848 cm^{-1} absorption observed in the present work is not possible.



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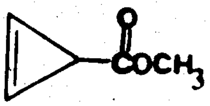


94

We have attempted to examine the secondary photolysis of **86**. A number of different wavelengths were employed (185, 229, > 280, > 305 nm) in separate experiments, but **86** was quite resistant to photolysis under any of these conditions. Irradiation at λ > 305 nm seemed to cause small decreases in the amount of **86**, however the formation of **87**, **88** and cyclopropene, as claimed by Chapman [157], was not observed.

Only two additional absorptions, belonging to a single primary photoproduct (185, 214 nm), remained to be assigned. These absorptions were located near 760 and 890 cm^{-1} and the conclusion that they belonged to the same species was reached in the usual manner, using many different photolysis wavelengths. Further description of the behaviour of these absorptions, as well as their assignment to a specific species, will be deferred until later in this section for reasons that will soon become evident.

3. Thiophene Matrix Isolation Experiments

We have examined the photolysis of thiophene in our LTMI apparatus. Wiebe and Heicklen [102] have previously irradiated (214, 229 nm) thiophene vapour identifying C_2H_2, CH_2CCH_2, CH_3CCH, CH_2CHCCH and CS_2 as products of thiophene fragmentation. Utilizing information from this gas phase study, as well as our MI experiments with furan, the IR spectra from the matrix experiments with thiophene were analyzed.

The production of CS_2 upon UV photolysis (214, 229 nm) of matrix isolated thiophene was quickly established. The identification of CS_2 was based upon the observation of its characteristic C=S stretching absorption near 1522 cm^{-1} [154]. Since the amount of CS_2 produced became most significant after long irradiations, and because it was produced during the secondary photolysis of the primary photoproducts derived from the irradiation of thiophene, CS_2 was judged to be primarily a secondary photolysis product. The irradiation of thiophene in the matrix also resulted in the formation of a brown, presumably sulfur-containing, polymer.

In the previous gas phase investigation [102] the reported quantum yield of CH_2CCH_2 formation was ~0.1. By comparison, the quantum yields for the formation of C_2H_2, CH_2CHCCH and CH_3CCH, which were the other hydrocarbon products detected, were ~0.25, 0.25 and 0.05, respectively. The quantum yield for formation of 1-buten-3-yne (vinylacetylene), **95**, was time dependent. For the longest

$$CH_2{=}CHC{\equiv}CH$$

95

irradiation times reported this quantum yield had decreased by a factor of 2-3 as compared with its maximum measured value, indicating that this species was susceptible to secondary photolysis at both 214 and 229 nm. The quantum yield for CH_2CCH_2 also decreased slightly at longer irradiation times, declining to roughly 70-75% of the maximum value reported at shorter irradiation times. The quantum yields of the other products found by Wiebe and Heicklen were essentially time independent.

Allene, CH_2CCH_2, was not detected as a product from the photolysis of matrix isolated thiophene. If CH_2CCH_2 were present it would have been readily recognized due to its cumulative double bond stretching absorption at 1950 cm^{-1}, as well as a stronger $=CH_2$ out-of-plane bending vibration near 845 cm^{-1}. As previously mentioned, these IR data for CH_2CCH_2 were verified by depositing the commercial compound in a low temperature Ar matrix.

a. Identification of Vinylacetylene

In the matrix photolysis of thiophene a primary photoproduct possessing an acetylenic C-H stretching absorption near 3320 cm^{-1} was observed. This absorption was readily correlated with a typically acetylenic C-H bending absorption near 630 cm^{-1}. These IR spectral features were considered to be appropriate for CH_3CCH (Table 14). On the other hand, **95** could be expected to have similar acetylenic absorptions, and might, in addition, show a terminal $=CH_2$ absorption (ca. 900 cm^{-1}) which is characteristic of vinyl groups. In fact, a strong absorption at 890 cm^{-1} was observed. The growth rate of this absorption correlated well with those for the two acetylenic absorptions just described, however on secondary photolysis (254 nm) the 890 cm^{-1} absorption disappeared significantly more rapidly than the 3320 cm^{-1} absorption, which underwent a noticeable change in band contour. The shapes of the broad absorptions in the 630-650 cm^{-1} region were also observed to change upon irradiation at 254 nm. The available literature data for gaseous **95** [165] describes three characteristic IR absorptions. Bands located near 3335 and 920 cm^{-1} were the strongest and of similar intensity, and the absorption centred near 920 cm^{-1} was very broad, ranging from 870-970 cm^{-1}. The third distinctive absorption of this compound had a maximum near 630 cm^{-1}.

Based on these results we concluded that both CH_2CHCCH and CH_3CCH were probably formed in the matrix photolysis of thiophene.

The former was a primary photolysis product, and could be destroyed by secondary photolysis at 254 nm. The 254 nm photolysis also seemed to simultaneously generate CH_3CCH, by a process which we have not identified but which presumably cannot involve CH_2CHCCH, and thus the other acetylenic absorptions were affected by secondary photolysis without actually showing much change in their intensities.

C_2H_2 was a major product of the gas phase photolysis of thiophene. In the matrix photolysis of thiophene the strongest IR absorption of the substrate would obscure the characteristic 730 cm^{-1} absorption of any C_2H_2 which could have been formed. A weak absorption around 3280 cm^{-1} may be the C-H stretching band of some C_2H_2 formed in the matrix [160].

b. Identification of Thio-2,3-butadienal

In the IR region from 1900-1950 cm^{-1}, where allenes show characteristic absorptions, two new absorptions at 1950 and 1920 cm^{-1} were produced by the photolysis (214, 229, > 230 nm) of matrix isolated thiophene. Both of these absorptions were doublets, the splittings presumably resulting from matrix site effects. The magnitude of each splitting was of the order of ~5 cm^{-1} (Figure 38). Growth curves for these absorptions demonstrated that they were attributable to primary photolysis products (Figure 39). Secondary photolysis (254 nm) caused the disappearance of both absorptions, although the 1950 cm^{-1} absorption, which was always of lower intensity, did not initially respond to secondary photolysis as rapidly as the 1920 cm^{-1} absorption.

This behaviour is somewhat similar to that already described for

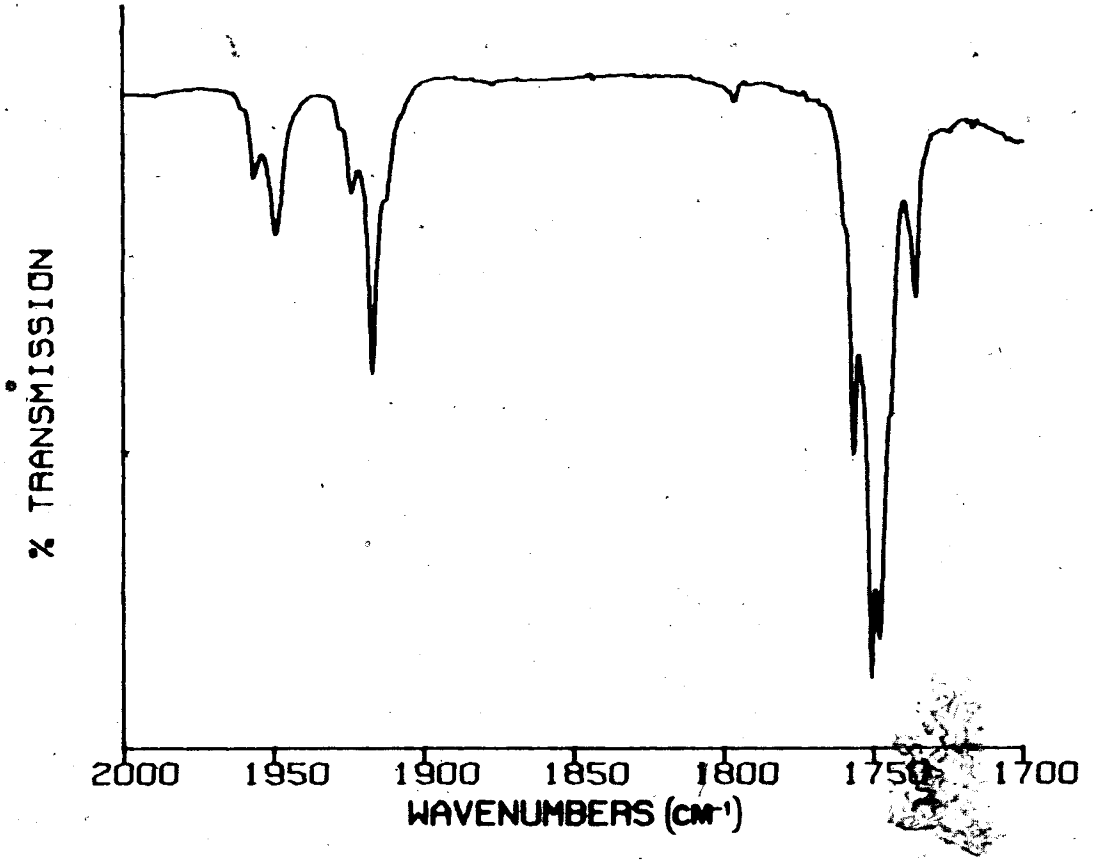


Figure 38. IR spectrum showing some absorptions assigned to **96** and **97**.

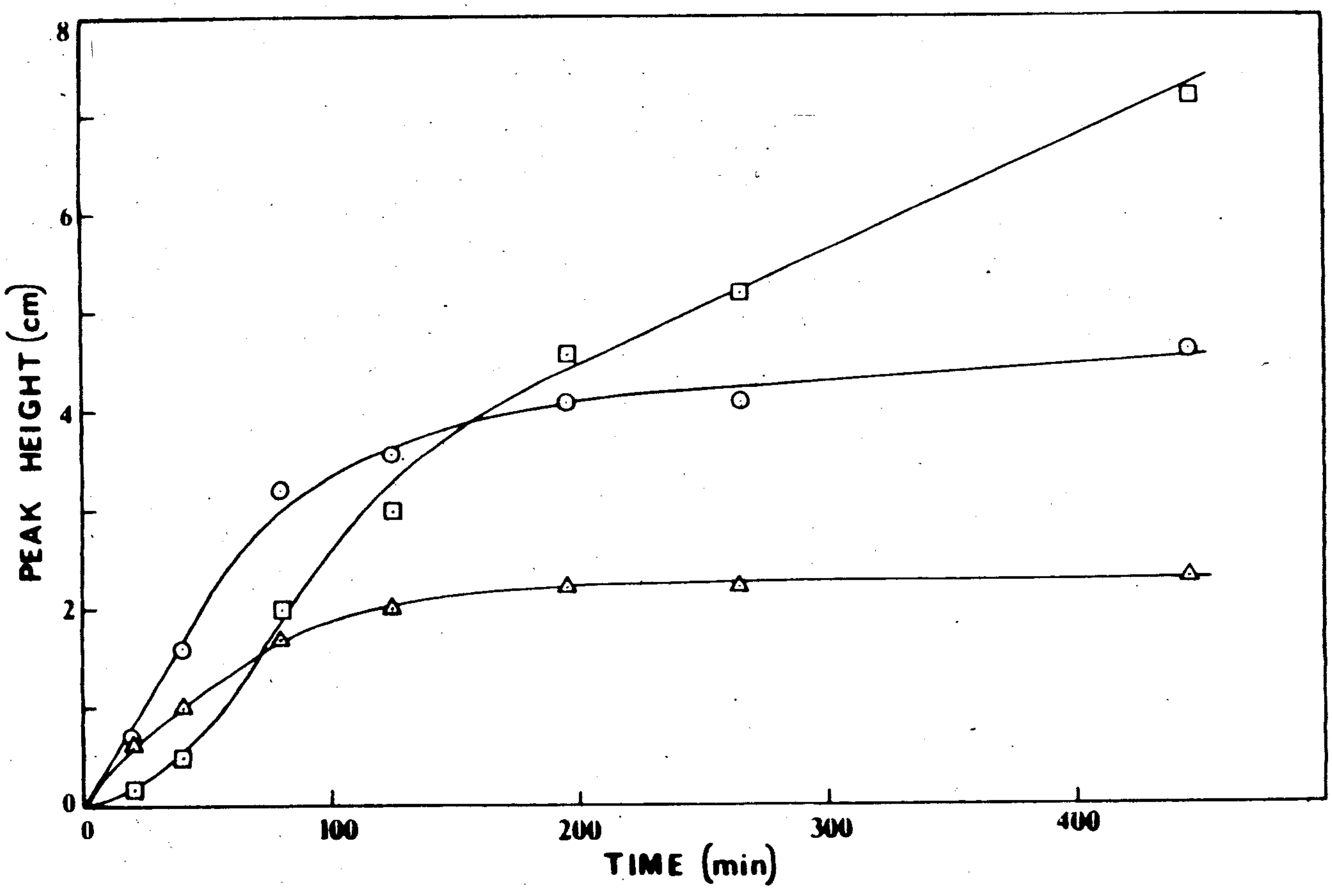


Figure 39. Growth curves for some IR absorptions formed by the 229 nm irradiation of a single thiophene layer, (○) 1920 cm^{-1}, (Δ) 1950 cm^{-1} and (□) 1750 cm^{-1}.

one of the products identified in the photolysis of matrix isolated furan. It will be recalled that two C=C=C stretching absorptions were generated and were assigned to 2,3-butadienal.

By analogy to the furan system the above two C=C=C stretching absorptions produced by the matrix photolysis of thiophene have been assigned to thio-2,3-butadienal, **96**. The thiocarbonyl stretching

$$CH_2{=}C{=}CHCH{=}S$$

96

absorption from this species could not be identified, however such absorptions are usually of low intensity and thus it was concluded that on the basis of the magnitude of the C=C=C stretching bands observed, no significant thiocarbonyl absorption should be expected.

It is interesting to note that Wiebe and Heicklen found CH_2CCH_2 as a primary product of the gas phase photolysis of thiophene [102], whereas we have not observed it in the matrix and instead obtained **96** which was not reported in the gas phase study. Perhaps CH_2CCH_2 forms in the gas phase by the decomposition of vibrationally excited **96**, which is a primary photolysis product of thiophene.

c. Identification of Thioketenes

Another interesting species observed in the matrix photolysis of furan was 1,3-butadienone. The analogous sulfur-containing compound, which might be produced in the matrix photolysis of thiophene, is vinyl thioketene, **97**. **97** has never been isolated, and thus no IR data are available for this compound.

$CH_2=CHCH=C=S$

97

Thioketenes show a characteristic C=C stretching absorption near 1750 cm^{-1} [166]. Photolysis (229 nm) of matrix isolated thiophene generated a substantial absorption in this region. This absorption was usually broad and showed at least four splittings (Figure 38). In the matrix photolysis of furan two ketene absorptions were observed and ultimately assigned to different rotamers of the vinyl ketene. Vinyl thioketene can also exist as two different rotamers. In addition, the possibility that the parent ketene was also present after furan irradiation could not be excluded. Torres et al. [167] have recently described the IR spectra of parent thioketene, CH_2CS, as well as its two deuterated isomers, each isolated in a low temperature matrix. CH_2CS gives rise to a strong, and sometimes broad, absorption at 1755 cm^{-1}. Thus, it is evident that the absorption around 1750 cm^{-1} in the matrix photolysis of thiophene could be quite complex, due to the possibility that a mixture of thioketene products might have been generated. Some experimental evidence, which may help to partially unravel this 1750 cm^{-1} absorption, will now be described.

The growth curves presented in Figure 39 also include a plot of the peak height of the 1750 cm^{-1} absorption as a function of irradiation time. This curve clearly reveals an induction period for the appearance of this absorption on the time scale examined. Since the time study was performed with the single layer depositional technique the most substantial growth in the IR peaks attributable to primary photolysis products occurred in the initial 2 h of irradiation. After roughly 3 h of photolysis plateaus had been attained in most of the growth curves. However, the curve for the 1750 cm^{-1} absorption, in addition to showing a distinct induction period, continued to increase significantly between 2 h and 7.5 h, at which time the experiment was terminated. These results indicated that the 1750 cm^{-1} absorption was attributable to a secondary photolysis product. Since vinyl thioketene, if formed, was expected to arise as a primary photolysis product of thiophene, the secondary nature of the 1750 cm^{-1} absorption was taken as an indication that this band was due to the parent thioketene.

Torres et al. [167] assigned many of the vibrations of CH_2CS. A C-H in-plane bending vibration at 1323 cm^{-1} was the second most characteristic IR absorption of CH_2CS in their MI study and was roughly an order of magnitude less intense than the 1750 cm^{-1} peak, thereby making its observation more difficult. A weak absorption at 1333 cm^{-1} was observed in the present system. Although its growth rate was difficult to assess, it appeared to be consistent with that of the 1750 cm^{-1} absorption, and both absorptions responded in the same manner to secondary photolysis at 254 nm.

We have also investigated the matrix photolysis (229 nm) of perdeuterothiophene, C_4D_4S. With this substrate the position of the resulting thioketene absorption shifted slightly. A broad split peak centred around 1740 cm^{-1} was observed. This agrees very well with the results of Torres et al. [167], who found that the C=C stretching absorption of matrix isolated CD_2CS was located at 1738 cm^{-1}.

In some instances, secondary photolysis (254 nm) caused a noticeable change in the shape of the 1750 cm^{-1} absorption. This change resulted in decreased intensities of the two outermost splittings, seen on the shoulders of this peak (Figure 38), and a small increase in the peak height at the centre of the absorption band. It was difficult to judge whether these changes were evidence for the existence of more than one distinct thioketene species in the matrix, or, alternatively, simply the outcome of matrix relaxation effects.

To summarize, it has been concluded that CH_2CS was formed in the matrix photolysis of thiophene. The presence of some vinyl thioketene in the matrix cannot be ruled out, although no strong experimental evidence for its existence can be offered.

d. Identification of Cyclopropenyl Thioaldehyde, Dewar Thiophene and Dewar Furan

Now only a small number of prominent new IR absorptions, generated by the matrix photolysis of thiophene, remain to be assigned. These absorptions were located at 740, 855 and 1150 cm^{-1}. The 1150 cm^{-1} absorption was broad and split, while the other two absorptions were sharp bands. The intensity of each of these three absorptions decreased upon secondary photolysis at 254 nm, and these reversals were accompanied by an increase in the IR absorptions of the substrate (Figure 40). Thus, secondary photolysis of some primary photolysis product responsible for one or more of these three absorptions, resulted in the regeneration of thiophene. The positions of at least two of these unassigned IR bands were

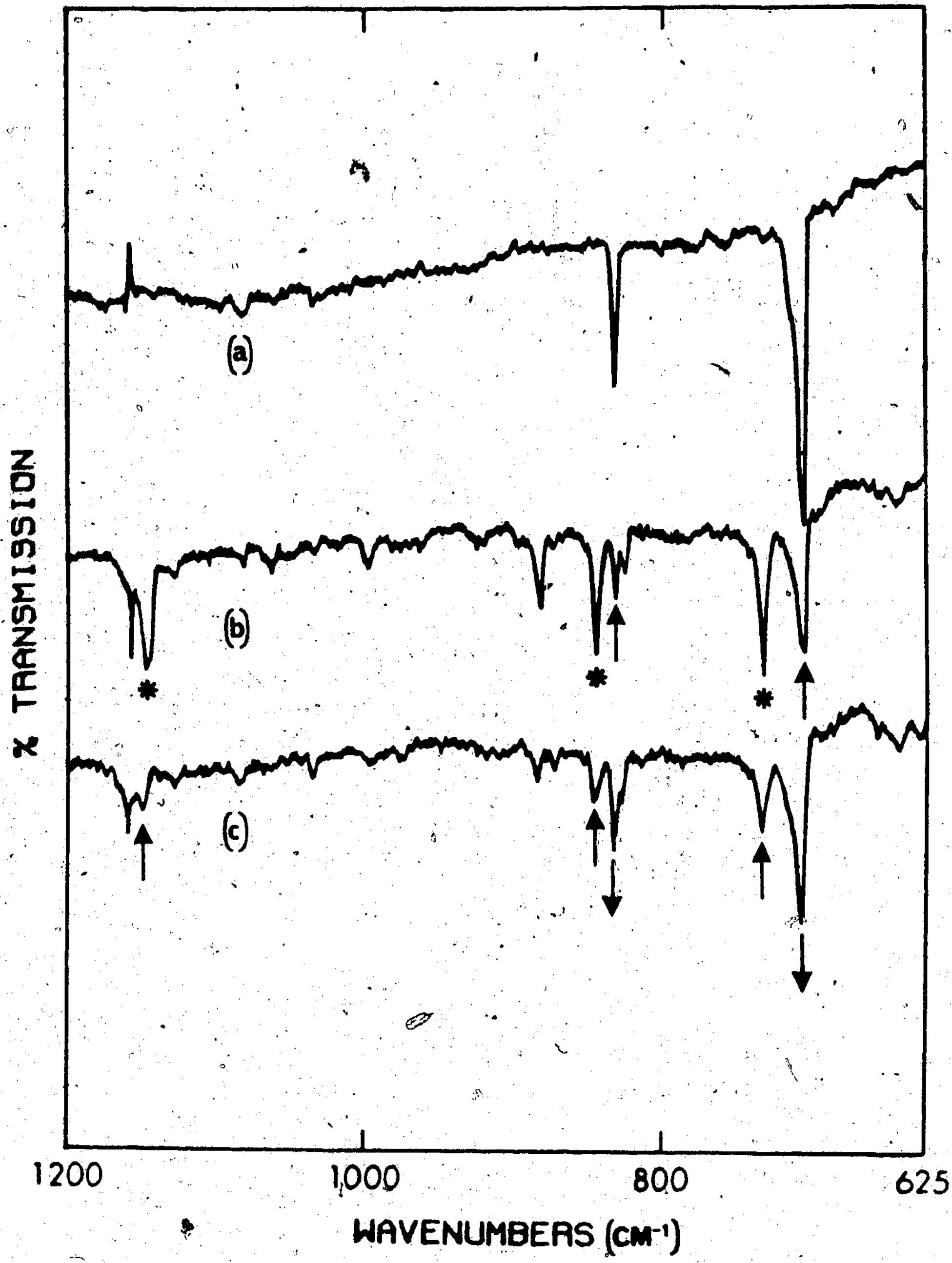


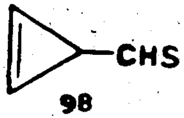
Figure 40. Matrix isolation of thiophene (layered method) - secondary photolysis at 254 nm (a) thiophene deposit, (b) after 8.6 h of irradiation at 229 nm, (c) after 2.5 h of secondary photolysis at 254 nm; * -740, 855 and 1150 cm^{-1} absorptions.

consistent with those expected for olefinic C-H out-of-plane bending vibrations in small rings. For the purpose of comparison, consider the vibrational spectra reported by Griffith et al. [168] for two VB isomers of benzene, benzvalene and Dewar benzene. Benzvalene had a very strong =C-H bending vibration situated around 740-745 cm^{-1} in Ar and N_2 matrices, while Dewar benzene revealed two very intense =C-H bending vibrations in an Ar matrix, the lower frequency absorption being located near 705 cm^{-1} and the other occurring at roughly 795 cm^{-1}. No helpful IR data are available for the Dewar isomers of the five-membered heteroaromatics, furan, pyrrole and thiophene, or their derivatives.

Visual inspection of the relative rates of disappearance of the 740, 855 and 1150 cm^{-1} absorptions upon secondary photolysis at 254 nm clearly indicated a difference between the absorption at 740 cm^{-1}, and those at 855 and 1150 cm^{-1}. In some experiments a moderately strong absorption band at 740 cm^{-1} still remained, even after the other two absorptions had completely disappeared. On the other hand, while employing a variety of different photolysis wavelengths (185, 214, 229, > 230, 254 nm) the absorptions at 855 and 1150 cm^{-1} always behaved the same way. On the basis of this observation these two absorptions were attributed to a common species, while the 740 cm^{-1} band was clearly due to a second compound. The fact that at least one of these species was capable of regenerating thiophene when photolyzed, suggested that it must be isomeric with thiophene, and possess a structure that would be able to readily rearrange to thiophene. Although some of the other compounds identified in the matrix photolysis of thiophene, for instance 95 and 96, also disappeared upon secondary photolysis, the acetylene 95 is a fragmentation product and clearly cannot regenerate thiophene; and while the allene thioaldehyde is an open-chain C_4H_4S isomer it is difficult to visualize how it could rearrange to its heteroaromatic precursor on photolysis.

At this point it is worthwhile to briefly note some results presented previously pertaining to our solution phase photolysis of thiophene and the matrix photolysis of furan. We have trapped Dewar thiophene generated in the solution phase photolysis of thiophene. Therefore, it seemed reasonable to suspect that Dewar thiophene might be present in the matrix. With furan, the isomeric cyclopropenyl aldehyde was identified in the matrix; in addition, we noted two IR absorptions, located at 760 and 890 cm^{-1}, presumably belonging to a single species.

Matrix isolated cyclopropenyl aldehyde featured two absorptions, 1710 and 848 cm^{-1}. If the comparable sulfur-containing species, cyclopropenyl thioaldehyde, 98, was formed during the matrix photolysis of thiophene, it would also be expected to have an absorption near 850 cm^{-1}. Rather than displaying the typically strong carbonyl absorption, however, 98 would possess a thiocarbonyl absorption which is much less intense and occurs at lower frequencies. Bellamy [159] quotes the IR region from 1020-1250 cm^{-1}



98

as being appropriate for C=S vibrations. 2,2-Dimethylpropanethial, **64**, was recently isolated and reported to show a thiocarbonyl absorption at 1085 cm^{-1} [140].

$t\text{-BuCH=S}$

64

In view of these considerations we have assigned the 855 and 1150 cm^{-1} absorptions generated by the matrix photolysis of thiophene to cyclopropenyl thioaldehyde, **98**.

In order to substantiate this assignment, a single layer of perdeuterothiophene, C_4D_4S, was photolyzed (229 nm) in an Ar matrix. Several new IR absorptions appeared, and upon secondary photolysis (254 nm) three of the most prominent new absorptions, located at 665, 675 and 1145-1150 cm^{-1}, decreased. For any IR absorption, the frequency shift that should be expected as a result of deuteration is dependent on the nature of the vibration responsible for the absorption. Vibrational modes which directly involve the displacement of H atoms (i.e. C-H stretching and bending vibrations) show the largest isotopic shifts. Experimentally determined frequency ratios are often smaller than the D/H reduced mass ratio (i.e. $\sqrt{2}= 1.414$), with values around 1.3-1.35 being common for such C-H absorptions [167]. The 665 and 675 cm^{-1} absorptions formed by the photolysis of C_4D_4S probably corresponded to the 855 and 890 cm^{-1} bands from the photolysis of C_4H_4S. Here, the frequency ratios observed on deuteration were roughly 1.3. If a similar shift in the 740 cm^{-1} absorption, from the matrix photolysis of C_4H_4S, occurred on deuteration then the resultant peak could possibly be hidden beneath the strongest absorption of C_4D_4S (ca. 550 cm^{-1}), thus accounting for the experimentally observed absence of any new absorption in this IR region following irradiation of C_4D_4S. The observation that deuteration did not cause a substantial shift in the position of the 1150 cm^{-1} absorption was consistent with its assignment to the C=S vibration in **98**, although a small deuterium shift would have been expected by comparison with IR data for the positions of the carbonyl absorptions in some labelled ketones [155].

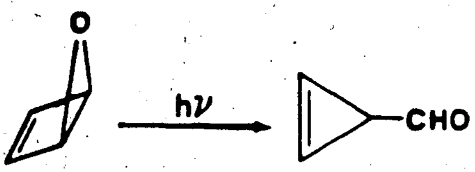
Proof of the presence of a thioaldehyde compound in the matrix might be gained not only by coupling the LTMI technique with IR spectroscopy, but also by probing the electronic absorptions of species generated in the matrix. Thiocarbonyl compounds possess a long wavelength $\pi^* \leftarrow n$ absorption band, often located between 500 and 600 nm. Unfortunately, these absorptions are weak ($\varepsilon_{max} \sim$ 10-100 $M^{-1}cm^{-1}$) [140,169,170]. We have attempted to photolyze matrix isolated **98**, by irradiation of its long wavelength $\pi^* \leftarrow n$ absorption band. Monitoring the progress of this matrix photolysis by IR spectroscopy, it was found that the absorptions assigned to **98** did not decrease, even after extended photolysis at $\lambda > 500$ nm. Moreover, matrix experiments using a UV/VIS spectrophotometer in an effort to directly observe the growth of a thiocarbonyl absorption band (500-600 nm) during the UV photolysis of thiophene in various matrix materials (Ar, N_2, $C_2H_5OC_2H_5$), failed to produce evidence for such an absorption. Our lack of success in these experiments was not, however, considered to be strong evidence against the assignment of **98** as a photolysis product in the matrix.

The position (740 cm^{-1}) of the one remaining unassigned IR absorption generated by the photolysis of matrix isolated thiophene, was very similar to the position (760 cm^{-1}) of one of the as yet unassigned absorptions described earlier for the matrix photolysis of furan. In view of all that has been presented earlier, these absorptions, as well as the 890 cm^{-1} absorption observed in the furan case, were assigned to the Dewar isomers of furan and thiophene.

e. <u>Some interesting observations about secondary photolysis of some matrix isolated species</u>

During the secondary photolysis (254 nm) of Dewar thiophene, thiophene itself was regenerated. However, as discussed previously, the cyclopropenyl thioaldehyde, the thioketene and the allenyl thioaldehyde absorptions also decreased under these conditions. Since the photofragmentation products of thiophene cannot regenerate thiophene, and if we accept the hypothesis that open-chain C_4H_4S isomers such as vinyl thioketene or allene thioaldehyde are unlikely to reform a heteroaromatic ring structure when irradiated, then cyclopropenyl thioaldehyde and Dewar thiophene are the only logical precursors to the photolytic regeneration of thiophene in the matrix. Unfortunately, the exact role of these two species in this regard cannot be determined from the present results. Nevertheless, the observation of both of these possible photoisomerization intermediates in the matrix, plus the discovery that at least one of them can be photolytically reconverted to thiophene, is an important finding.

In the MI experiments with furan secondary photolysis (254 nm) of the Dewar species produced a dramatic change. After only short periods of irradiation (~2 h) a considerable amount of Dewar furan was destroyed and only those IR absorptions attributed to cyclopropenyl aldehyde, **86**, had increased. The growth of the aldehyde was readily observed due to the change in its characteristic carbonyl absorption (Figure 41).



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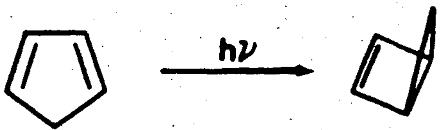
4. Cyclopentadiene Matrix Isolation Experiments

In search of additional evidence to support our assignments of the Dewar furan and thiophene isomers in the matrix photolysis of furan and thiophene, respectively, the LTMI of cyclopentadiene was examined.

The Dewar isomer of cyclopentadiene was first isolated by van Tamelen et al. [171]. UV irradiation of cyclopentadiene solutions yielded a single product which was assigned as the valence isomer. Bicyclo[2.1.0]pent-2-ene, **99**, was characterized by 100 MHz ^{1}H NMR, but no IR data were reported. Owing to its reactivity as a dienophile **99** readily reacted with excess cyclopentadiene to produce DAa [172].



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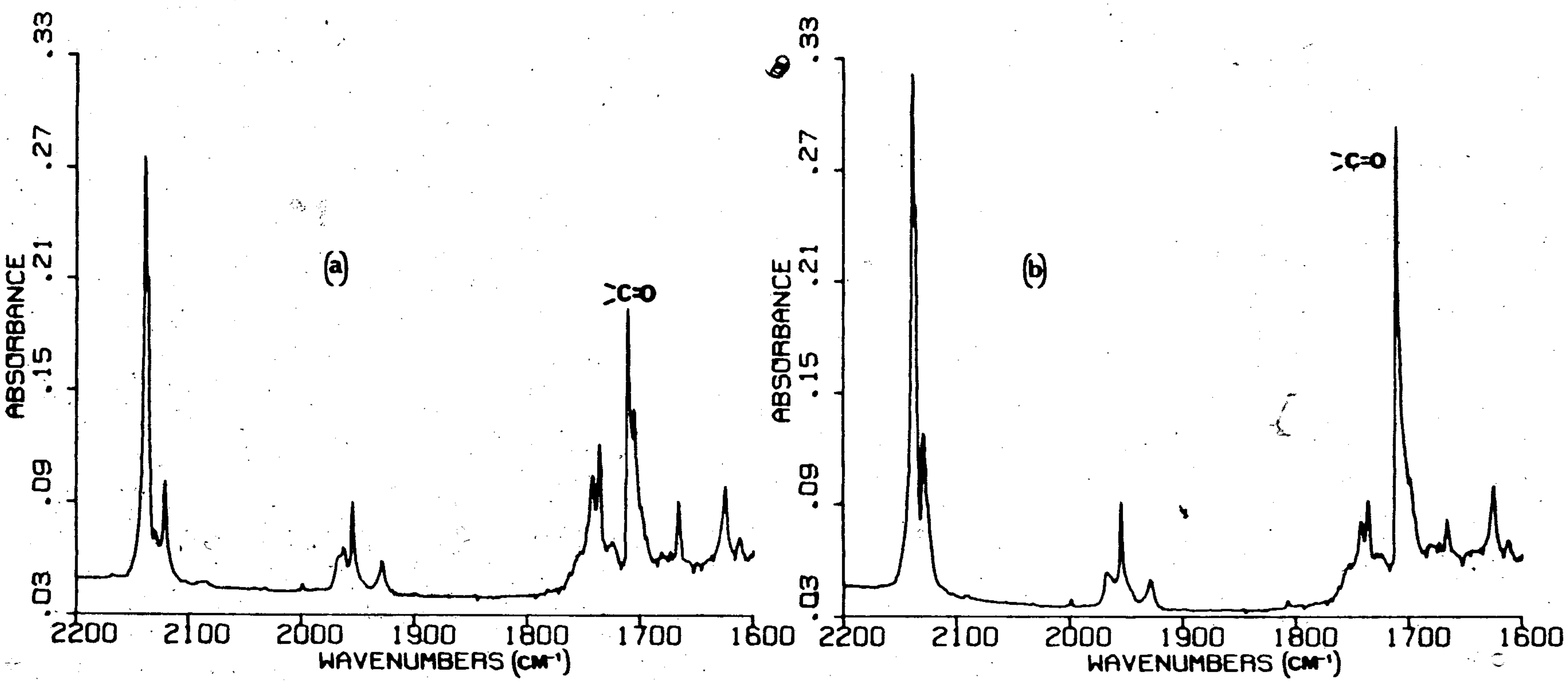
(38)



<u>Figure 41.</u> Growth of the C=O absorption of **86** on secondary photolysis (a) IR spectrum of matrix isolated furan after 12 h of irradiation at 214 nm, (b) IR spectrum of the same matrix after 12 h of secondary photolysis at 254 nm.

We have investigated the photolysis of matrix isolated cyclopentadiene in the hope that the IR spectrum of its Dewar isomer in the matrix could provide a useful model for some of the analogous Dewar furan and Dewar thiophene absorptions. When a single deposit layer of cyclopentadiene was irradiated (254 nm) for only 1.5 h, a substantial portion of the substrate was destroyed and several new IR absorptions appeared (Figure 42). Although many new IR peaks are present in Figure 42, only a small number are prominent. Of particular interest were the absorptions located at 720, 770, 860 and 945 cm^{-1} as the positions of these absorptions were similar to those observed for the Dewar species of furan and thiophene. In addition, a C=C stretching absorption was observed near 1530 cm^{-1}. This position is very similar to that of the C=C absorption for cyclobutene, which is located at 1566 cm^{-1} [154]. Each of the new peaks generated by the photolysis of cyclopentadiene seemed to belong to the same species, as indicated by secondary photolyses at a number of different wavelengths. The matrix photolysis of cyclopentadiene thus generated a single photoproduct, presumably the Dewar isomer, the same as in the solution phase [171].

In an attempt to demonstrate beyond any doubt that the photoproduct of cyclopentadiene formed in the matrix was **99**, the matrix photolysis of cyclopentadiene was repeated several times, and the mixtures of substrate and photoproduct generated in each photolysis were collected in an NMR tube for examination by high

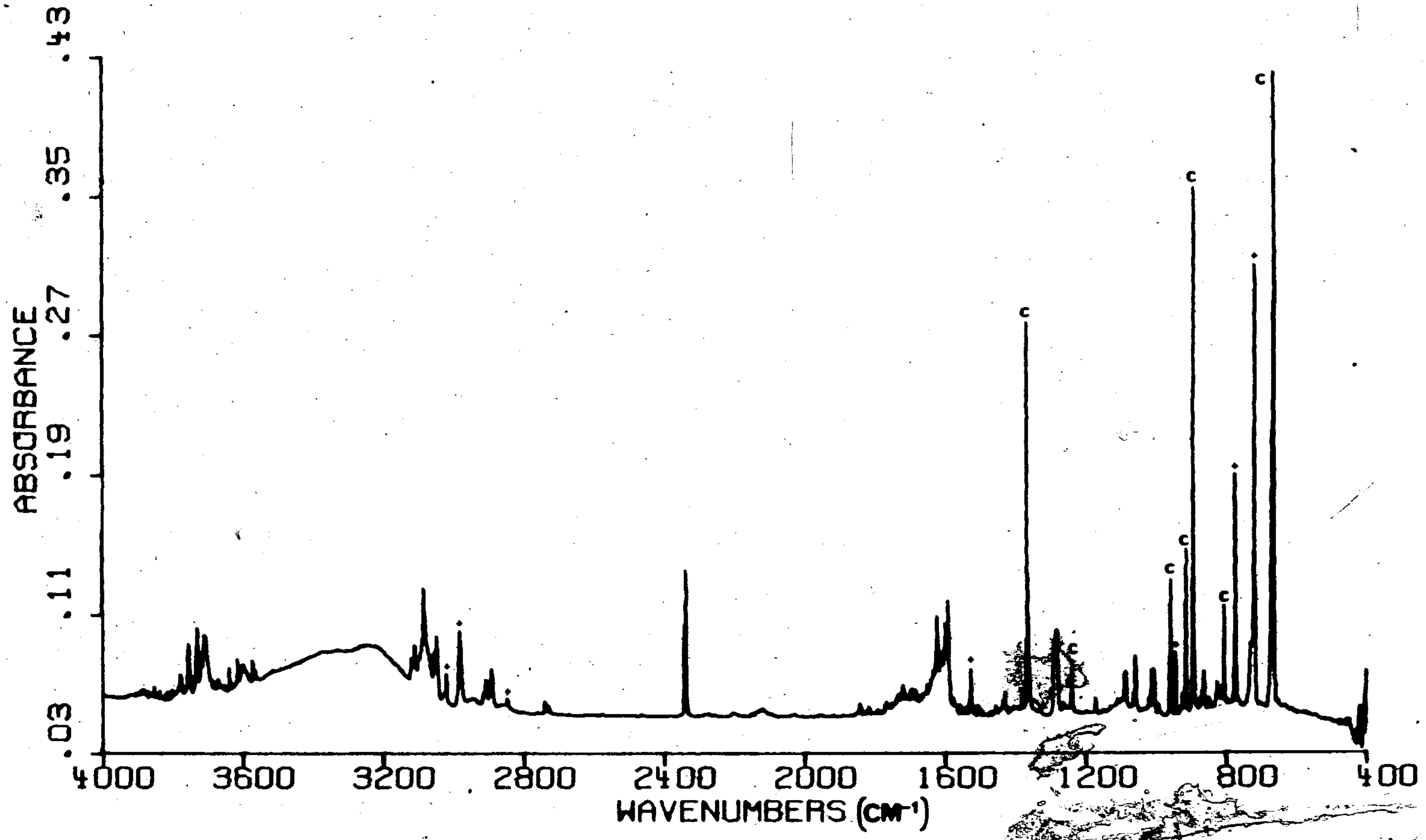


Figure 42. IR spectrum recorded after 254 nm irradiation of matrix isolated cyclopentadiene (c-cyclopentadiene absorptions, +-some of the more prominent new absorptions generated by the photolysis).

field ^1H NMR at low temperature. Van Tamelen et al. [171] reported that purified **99** had a half life of about 2 h in dilute CCl_4 solution at room temperature. The most serious losses of **99** would probably result from its facile DA reaction with any cyclopentadiene present.

The thermal stability of the photoproduct was tested by distilling it from the matrix to a liquid N_2 trap (-196°C), and then redepositing the trapped sample in the low temperature matrix. The photoproducts survived these manipulations, being successfully redeposited in the matrix, however NMR spectra obtained on the species distilled from the matrix failed to reveal the presence of any compound other than unphotolyzed cyclopentadiene. Since the writing of this manuscript the bicyclopentene has been successfully removed from the low temperature matrix and identified by NMR. These results are found in Appendix II at the end of the thesis. Initially, in the absence of the NMR results an alternative method of demonstrating that the photoproduct detected in the matrix was probably **99**, was employed. Moreover, this alternative method yielded great dividends for the cases of furan and thiophene as well.

The UV absorption spectrum of bicyclopentene was measured in the gas phase by Baldwin and Andrist [173], and an unusually low energy transition was observed ($\lambda_{max} \sim 263$ nm, $\varepsilon_{max} \sim 440$ $M^{-1}cm^{-1}$). Similarly, both Heicklen et al. [104] and Verkoczy et al. [112] have examined the UV absorption spectrum of gaseous perfluorotetramethyl Dewar thiophene, also finding a long wavelength absorption ($\lambda_{max} \sim 337$ nm, $\varepsilon_{max} \sim 50$ $M^{-1}cm^{-1}$).

Consequently, secondary photolyses of the cyclopentadiene photolyzate were performed at various wavelengths. At λ > 280 nm the cyclopentadiene photoproduct was very slowly consumed (~20 h). At λ > 260 nm however the rate of its disappearance was much more rapid (~3 h). For thiophene, secondary photolysis at λ > 320 nm resulted in a very slow disappearance (~5 h) of the 740 cm^{-1} absorption. For λ > 280 nm however the rate of disappearance of this peak increased dramatically (2 h). These findings were consistent with the known UV absorption spectra for bicyclopentene and Dewar thiophene, and therefore were concluded to be strong evidence for the assignment of these parent Dewar structures to the IR absorptions in question.

For the case of Dewar furan, only 4 h of irradiation (λ > 320 nm) produced detectable decreases in the IR absorptions located at 760 and 890 cm^{-1}. No other IR absorptions were significantly affected. Thus Dewar furan also has a long wavelength UV absorption.

C. Dewar Thiophene - Mechanistic Implications

We have detected and identified the parent Dewar thiophene in both the solution and matrix photolyses of thiophene. This does not, however, prove that this valence bond isomer is involved in the photoinduced scrambling which results in positional isomerization of substituted thiophenes. Since our interest in the photoisomerization of substituted thiophenes inspired the current investigation, we carried out additional experiments with the aim of elucidating the possible role of the Dewar isomer in the photorearrangement process.

If Dewar thiophene is an intermediate in the photorearrangement of thiophenes, then the carbon atom scrambling responsible for this rearrangement may have occurred prior to the DA cycloaddition which yields trapped Dewar thiophenes. This could result in the observation of common Dewar thiophene adducts from the solution phase photolyses of 2- and 3-monosubstituted thiophenes in a suitable diene. In search of such evidence we began by reviewing our results from the photolyses of 2-PT and 3-PT in DMBD. A comparison of the chromatograms showing the 1:1 adducts formed in each system (Figures 9 and 10) suggested that no common products were present. This conclusion was verified by making a mixed injection into the gas chromatograph.

Since the 2-PT and 3-PT trapping experiments with DMBD yielded a rather large number of 1:1 adducts, and because we were anxious to detect common adducts, thereby demonstrating a vital role for Dewar thiophene in the photorearrangement process, an additional trapping experiment was performed using the lower molecular weight 2- and 3-methylthiophenes (MT) in order to simplify the interpretation of the NMR data.

The UV absorption spectra of the methylthiophenes are very similar to that of thiophene itself, and thus furan was employed as the trapping agent. The photolyses of 2-MT and 3-MT in furan solutions were carried out under conditions similar to those employed for the parent thiophene. In comparison with the case of thiophene, the photolysis of its monomethyl derivatives produced adducts at a much slower rate. Thus the photolysis of thiophene in furan solution had yielded furan-trapped furan photolysis products, and trapped Dewar thiophene, in roughly equal amounts. By contrast, the photolysis of the methylthiophenes generated these same furan dimers in yields estimated to be at least twenty times greater than any of the 1:1 adducts formed.

GC comparison of the photolyzed 2-MT and 3-MT mixtures did not reveal any common products with retention times appropriate for 1:1 adducts. Analysis by GC/MS definitely established the presence of two 1:1 adducts in each photolyzed sample. These adducts had molecular ions at $M^{+\cdot}$ 166 and fragmented via a Diels-Alder retrogression. The MS results are summarized in Table 16. A mixed injection into the GC/MS system, revealed four distinct 1:1 adducts, indicating that none of these trapped products were the same.

The monomethylthiophenes were also examined in the low temperature matrix, where a rather different behaviour was observed as compared to the solution phase thiophene. Initial photolysis of either compound at 229 nm generated several new IR absorptions, many of which were bleached upon secondary photolysis at 254 nm. Some of these absorptions obviously belonged to allenic compounds, presumably similar to those already identified during the matrix photolysis of parent thiophene. In addition, absorptions similar to those for the cyclopropenyl thioaldehyde and Dewar thiophene formed during thiophene photolysis, were among those which disappeared at 254 nm. For instance, with 2-MT these absorptions were located near 740, 795, 845 and 1180 cm^{-1}. For 3-MT, absorptions at 740, 795 and 845 cm^{-1} were again present, but the peak at 1180 cm^{-1} was absent. The observation of these common IR absorptions, particularly one which is similar to that assigned to the parent Dewar thiophene in the matrix,

TABLE 16

GC/MS[a] Data for the 1:1 Adducts Formed by Photolysis of 2-MT and 3-MT in Furan

Thiophene Derivative	Adduct Retention Time (min)	m/e	Relative Intensity	Fragment
2-MT	18.2	166	~15%	$M^{+\cdot}$
		137	40	-CHO
		98	15	$-C_4H_4O$
		68	15	$-C_5H_6S$
		59	100	
2-MT	19.1	166	~15%	$M^{+\cdot}$
		137	20	-CHO
		98	100	$-C_4H_4O$
		68	35	$-C_5H_6S$
3-MT	15.5	166	~10%	$M^{+\cdot}$
		137	50	-CHO
		121	30	-CHS
		98	100	$-C_4H_4O$
		83	95	$-C_5H_7O$
		68	75	$-C_5H_6S$
3-MT	16.5	166	~25%	$M^{+\cdot}$
		137	100	-CHO
		121	<10%	-CHS
		98	100	$-C_4H_4O$
		83	<10%	$-C_5H_7O$
		68	50	$-C_5H_6S$

[a] DB-1, 70-150°C @ 2°C/min, VG 7070E.

was of considerable significance since it suggested that both monomethylthiophenes formed a common Dewar species when photolyzed in the matrix. This of course was in disagreement with the solution phase results, which indicated that the major Dewar adducts detected in each case were different. These were assumed to be the exo and endo furan DAa of 2-methyl Dewar thiophene and 3-methyl Dewar thiophene, derived from 2-MT and 3-MT, respectively.

Owing to the slow rate of photolysis of the monomethylthiophenes, as compared with thiophene itself, all of the new IR absorptions observed were very small, and thus any changes occurring in the concentration of these species during their secondary photolysis were difficult to assess. It was, however, of interest to know whether secondary photolysis of these primary products could result in the formation of the other MT positional isomer. The regrowth of the parent thiophene resulting from photolysis of its primary photoproducts isolated in the matrix has already been described.

As a result, the layered technique was applied to the careful examination of the effects of secondary photolysis of the methylthiophene primary products (254 nm). The substrate of interest was deposited in several small layers, and both primary photolysis (229 nm) and secondary photolysis (254 nm) were performed on each layer individually. This optimized the conditions for determining whether 3-MT was produced by the photoinduced reaction of the primary photoproducts derived from 2-MT photolysis, and vice versa. After accumulating 45 individually reversed layers of 2-MT it was observed that 3-MT was being formed, based on the appearance of four weak absorptions corresponding to the four most prominent bands of 3-MT. The same experiment, when performed with 3-MT, did not show any convincing evidence for the formation of 2-MT, even after a total of 43 matrix layers. The duration of such matrix experiments was always limited by environmental factors such as the accumulation of moisture which lead to a deterioration of the matrix with time, and consequently, also the IR spectra obtained. It was concluded that a 2→3 isomerization was induced by secondary photolysis of a matrix isolated intermediate, but the reverse rearrangement process did not occur. It was strongly suspected that the observed irreversibility of the monomethylthiophene rearrangements in the matrix arises from a substituent-controlled preference for the selective formation of 3-MT from the intermediate involved. In solution, photorearrangement is, of course, not induced by secondary photolysis, but occurs in a dark reaction which follows the initial excitation. Thus there is no clearly definable relationship between the matrix and solution experiments. Nevertheless, our matrix results, if correct, provide the first evidence to the effect that the observed irreversibility may be simply a consequence of a substituent-directed process.

At this point it is still not possible to form a definite conclusion about the involvement of Dewar thiophene in the photorearrangement process; however, the secondary photolysis of Dewar thiophenes in the matrix leads to the regeneration of thiophenes, with a selectivity being expressed in the case of substituted thiophenes. The discrepancies between the matrix results and the solution phase trapping experiments, regarding the formation of common Dewar intermediates, may result from the drastic difference in the experimental conditions employed. Low temperature photolysis experiments with post-photolysis trapping might yield further insight. As mentioned, a serious drawback encountered when investigating the monomethylthiophenes was their slow rate of photolysis. Wynberg <u>et al.</u> [95] reported that the rate of rearrangement of 2-alkylthiophenes was very much slower than that of 2-arylthiophenes. In future mechanistic information might be gained more readily using monodeuterated thiophenes, as these compounds will likely yield adducts at a greater rate, and possess positional labels which are inert in the sense that they do not introduce steric or electronic effects capable of directing the course of a reaction.

D. Photophysical Characterization of the Phenylthiophenes

The photophysics of seven phenylthiophenes were investigated. Although both steady-state and time resolved emission studies were performed, no obvious connection between the photophysical and photochemical behaviour (i.e. photoinduced positional isomerization) of phenylthiophenes could be discovered. Consequently, the photophysical results presented here should be considered <u>per se</u>, and we hope they will be of value for future work concerned with the photochemistry of thiophenes.

The UV absorption spectra of the phenylthiophenes examined are given in Figure 43. The UV data are summarized in Table 17, and are in agreement with data reported some time ago by Wynberg et al. [92]. The steady-state fluorescence spectra of all the phenylthiophenes were recorded in fluid solution at room temperature (Figures 44-50). Excitation spectra are not presented here, but they were recorded in solution at room temperature and showed no detectable difference from the UV absorption spectra already given. Owing to the weak output from the Xe lamp in the steady-state spectrofluorimeter at wavelengths below 250 nm, the recording of accurate excitation spectra in the 200-250 nm region was difficult.

In addition, phosphorescence spectra were measured for the phenylthiophenes in EPA glasses at 77 K. Only 2,5-DPT failed to show any phosphorescence. Fluorescence spectra were also recorded at 77 K, and the possibility of delayed fluorescence from the rigid solutions was always checked, although none was ever observed. The fluorescence and phosphorescence spectra of 2-PT and 3-PT, in EPA at 77 K, are shown in Figures 51 and 52, respectively. From these emission spectra the first excited singlet states of these molecules, $E_{S_1^o}$, were estimated to lie approximately 370 ± 2 and 414 ± 2 $kJ{\cdot}mol^{-1}$ above the zeroth vibrational level of the ground electronic state, $E_{S_0^o}$. The corresponding triplet energies, $E_{T_1^o}$ were 238 ± 2 and 270 ± 2 $kJ{\cdot}mol^{-1}$ for 2-PT and 3-PT, respectively. Thus, the singlet-triplet energy separations, $\Delta E_{S_1^o-T_1^o}$, were quite similar for the two monophenylthiophenes, having values of 132 ± 4 $kJ{\cdot}mol^{-1}$ for 2-PT and 144 ± 4 $kJ{\cdot}mol^{-1}$ for 3-PT.

Some steady-state emission characteristics for the

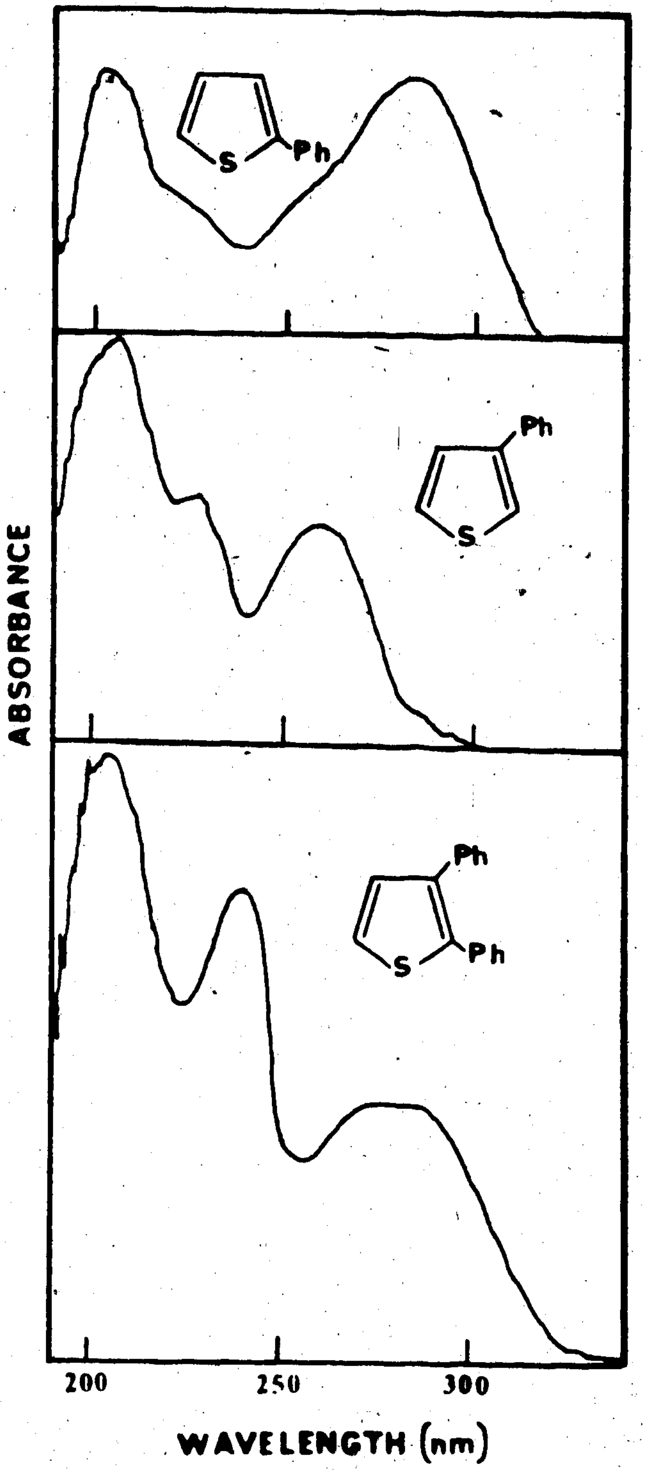


Figure 43a. UV absorption spectra of phenylthiophenes; 2-PT, 3-PT and 2,3-DPT.

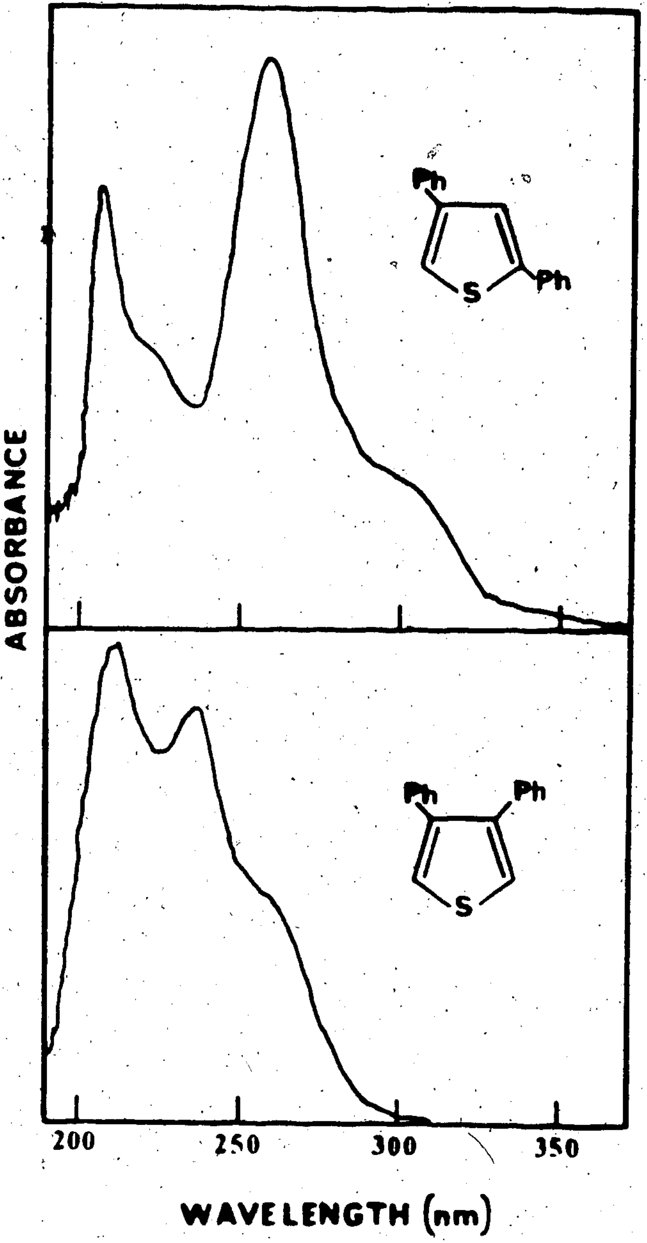


Figure 43b. 2,4-DPT and 3,4-DPT.

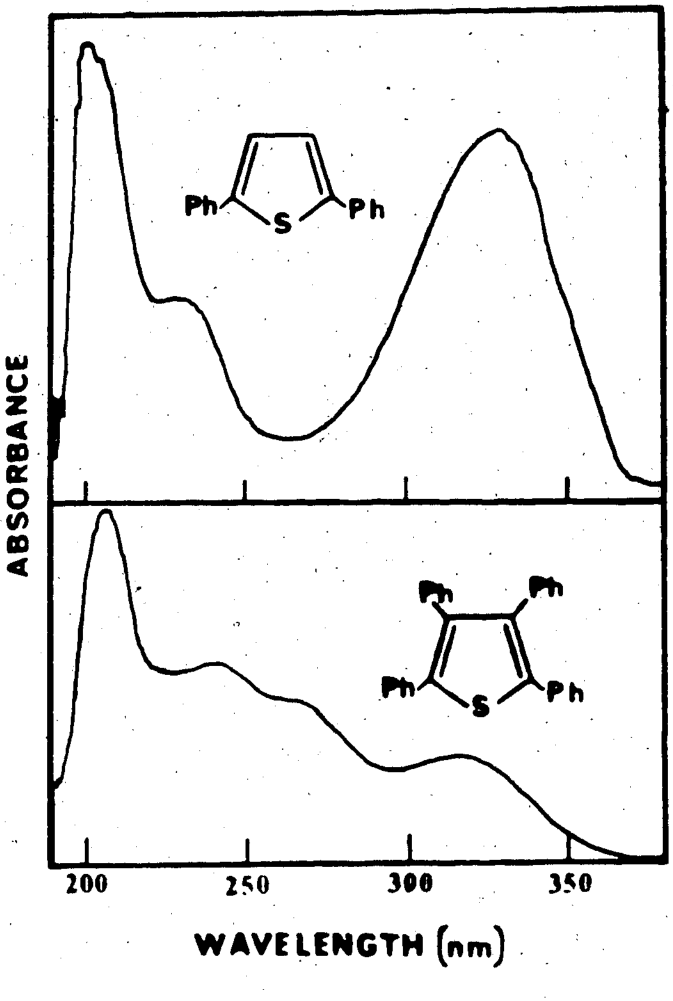


Figure 43c. 2,5-DPT and TPT.

TABLE 17

UV Absorption Data of Phenylthiophenes

Compound	λ_{max}, (nm)		ε_{max}, $(M^{-1}cm^{-1})$	
	a	b	a	b
2-phenylthiophene	283 225(sh)	283 222	14 000 5900	18 300 7800
3-phenylthiophene	259 227	259 227	13 600 14 500	12 000 12 800
2,3-diphenylthiophene	280 239	278 238	12 100 22 400	11 400 20 300
2,4-diphenylthiophene	305(sh) 259 224(sh)	305(sh) 258 224(sh)	7900 32 900 14 700	9400 33 800 16 000
2,5-diphenylthiophene	324 231	324 230	27 500 11 100	28 400 11 900
3,4-diphenylthiophene	260(sh) 236	260(sh) 234	12 500 23 200	12 300 24 500
tetraphenylthiophene	315 270(sh) 242	n.d.[c]	13 700 20 000 25 000	n.d.[c]

[a] This work. Solvent: spectroscopic grade hexanes.

[b] Wynberg et al. [92]. Solvent: 96% ethanol.

[c] Not determined.

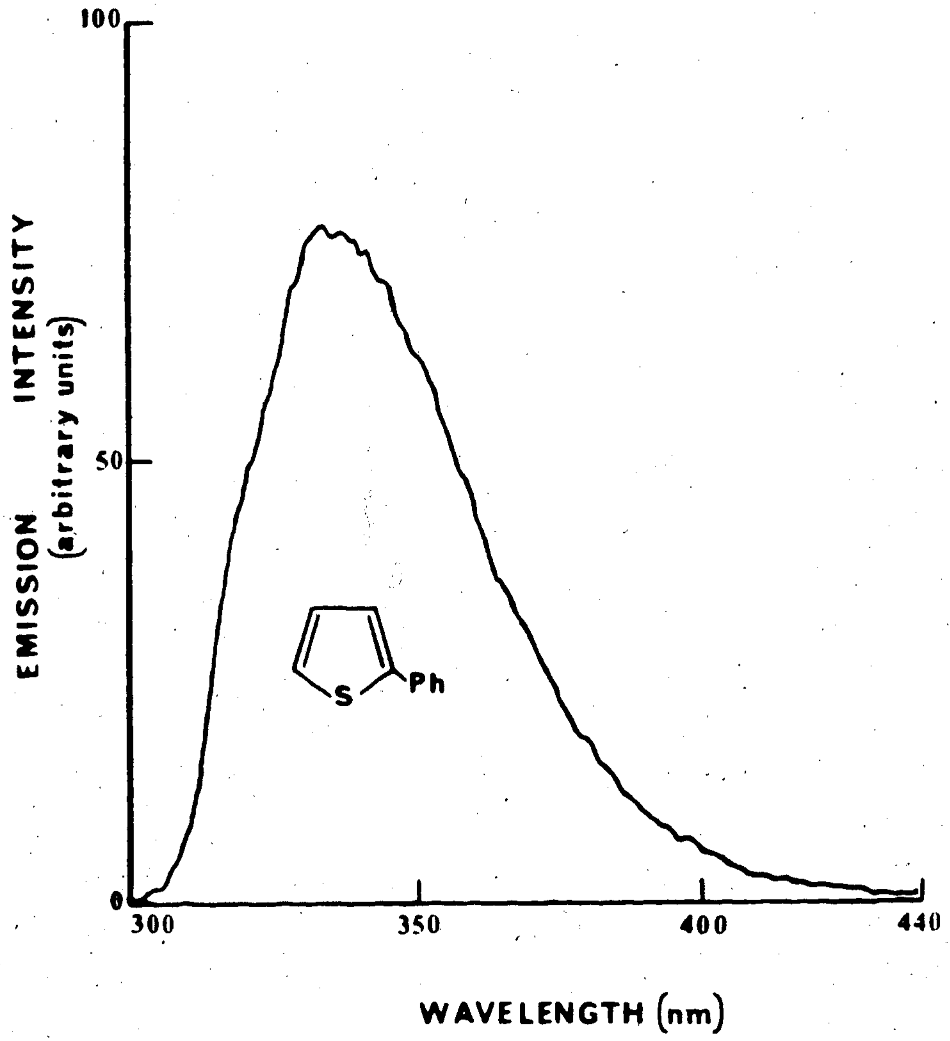


Figure 44. Emission spectrum of 2-phenylthiophene (methanol, 5 × 10^{-5} M, λ_{exc} 280 nm).

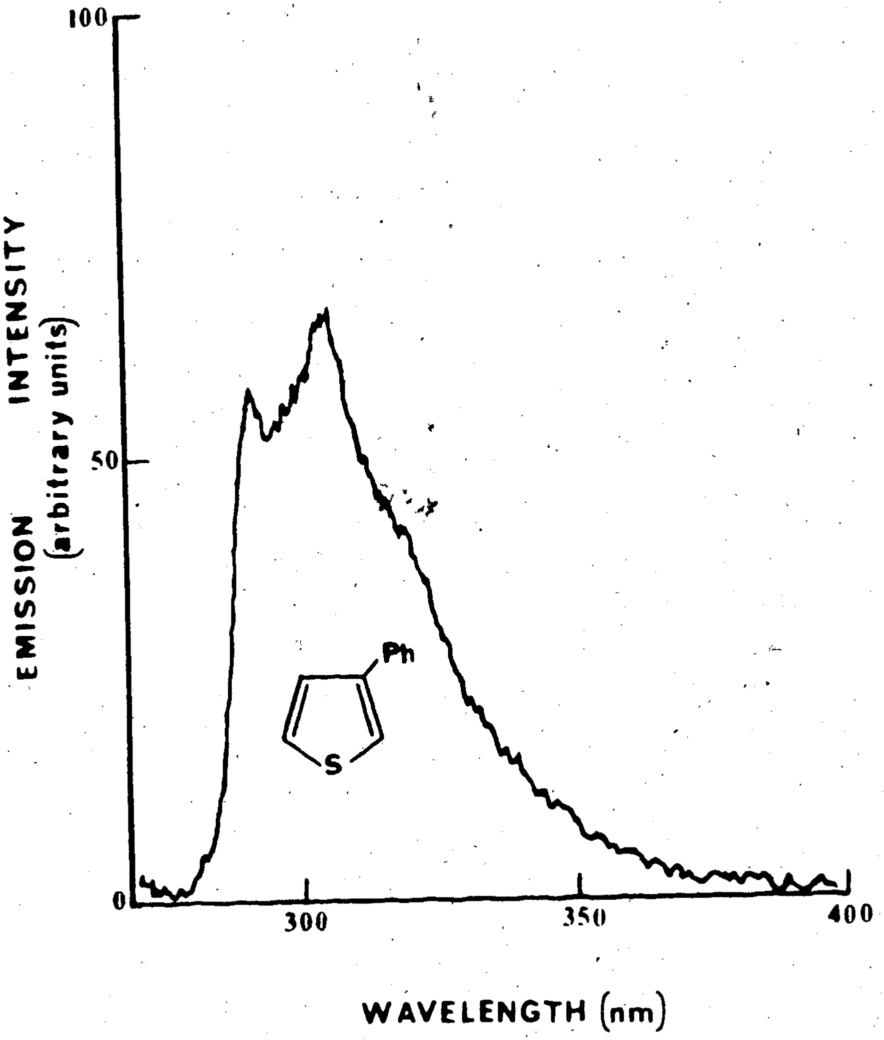


Figure 45. Emission spectrum of 3-phenylthiophene (methanol, 3×10^{-5} M, λ_{exc} 265 nm).

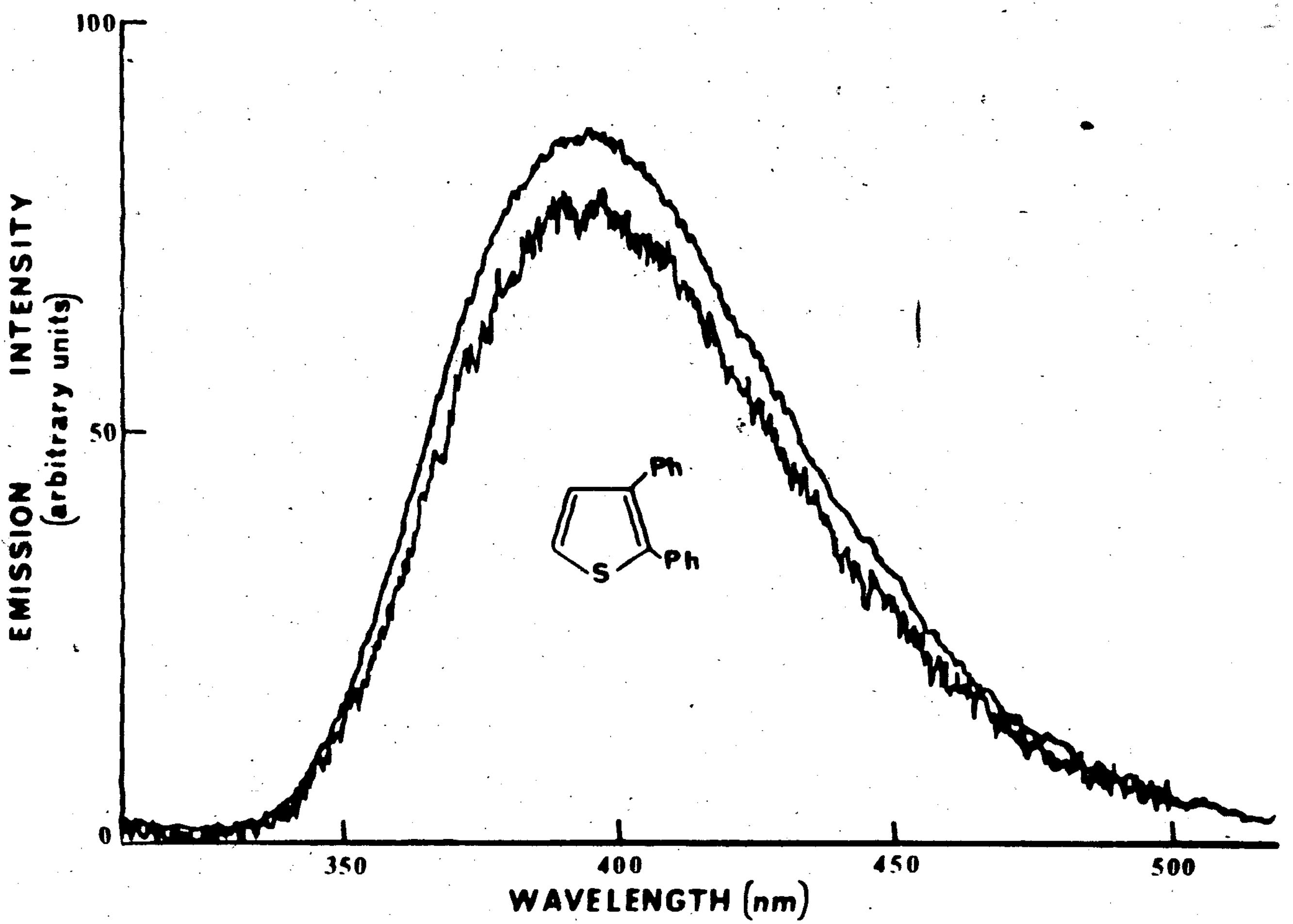


Figure 46. *Emission spectrum of 2,3-diphenylthiophene (methanol,* 2 × 10^{-5} M, λ_{exc} 275 nm, the two emission profiles were recorded with slightly different instrumental attenuation settings).

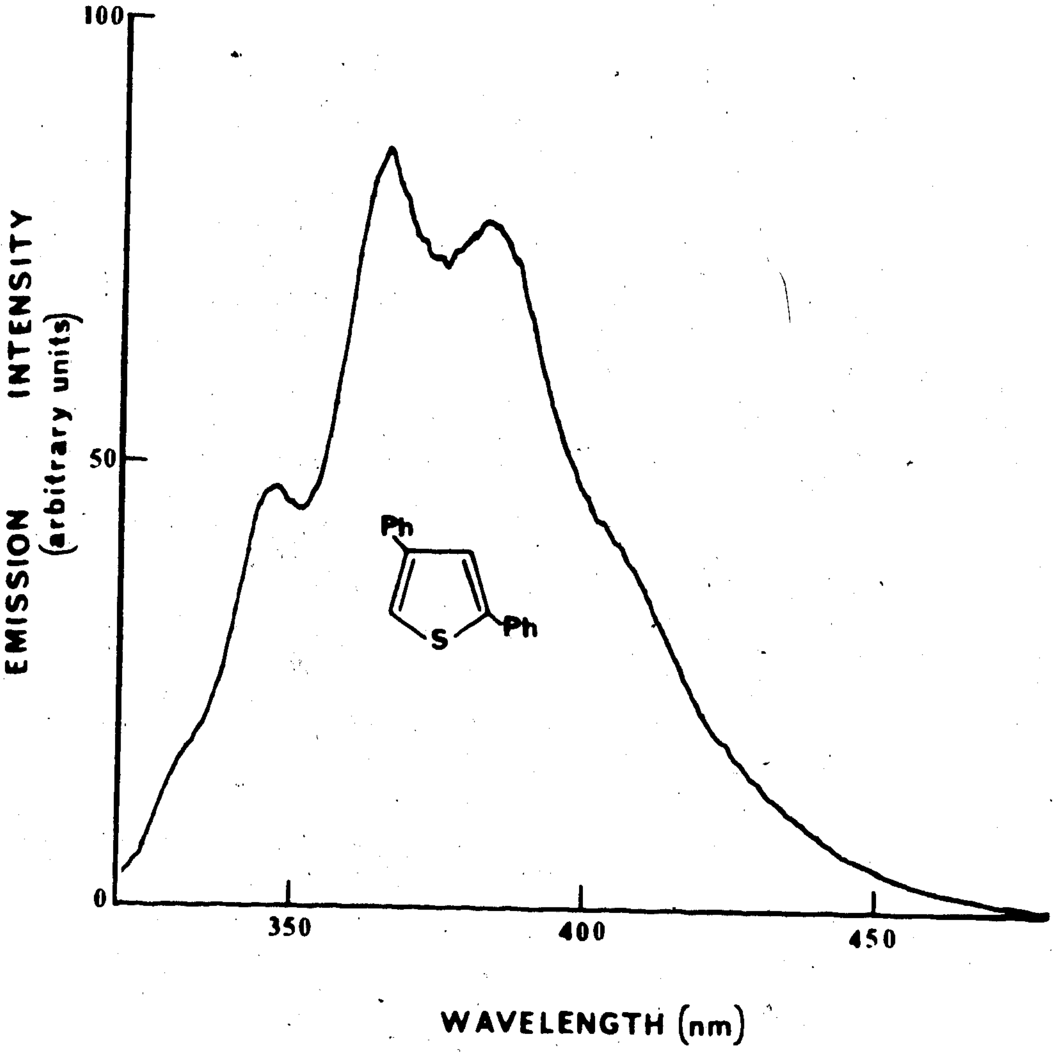


Figure 47. Emission spectrum of 2,4-diphenylthiophene (hexanes, 3 × 10^{-4} M, λ_{exc} 320 nm).

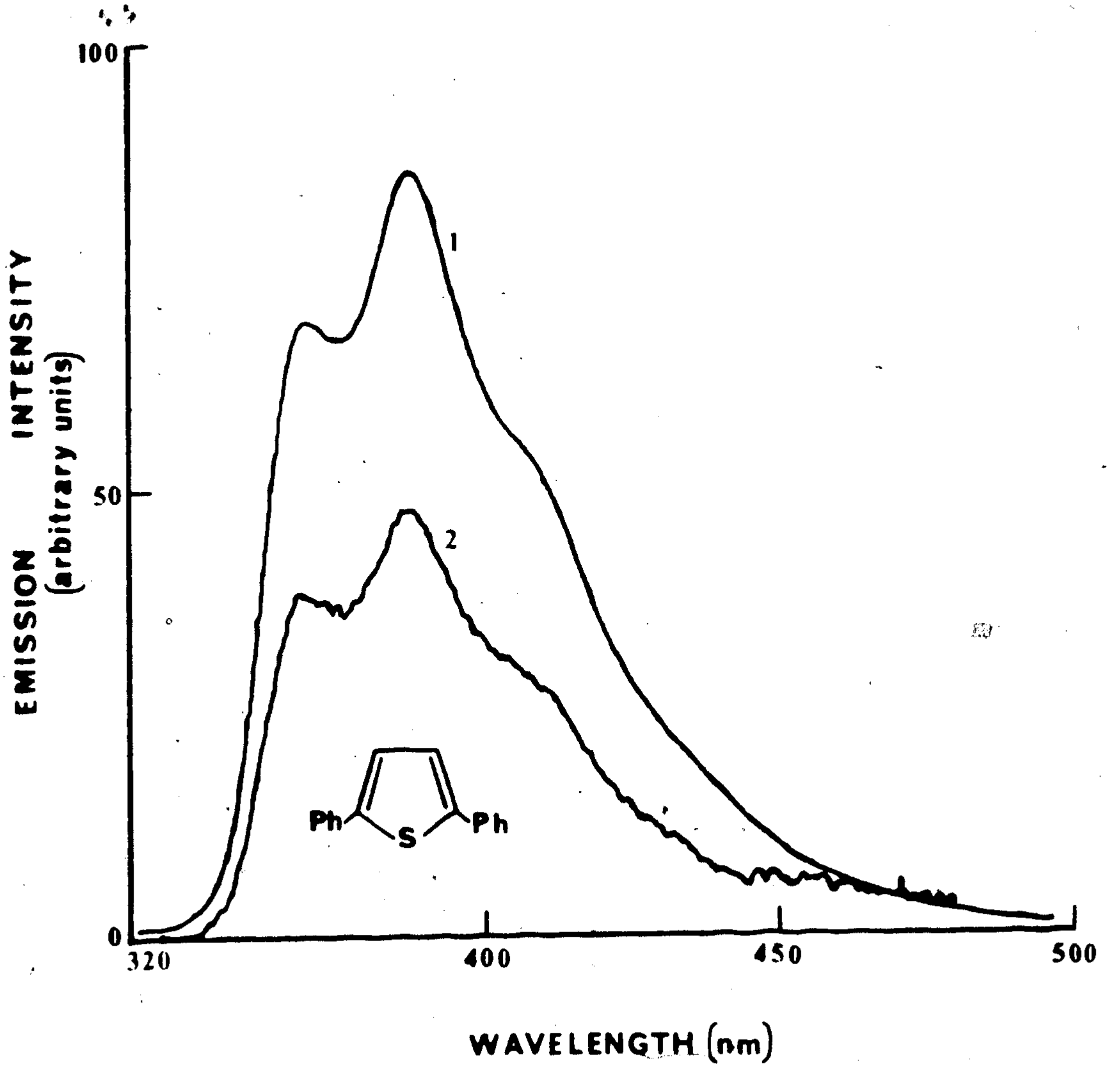


Figure 48. Emission spectrum of 2,5-diphenylthiophene (methanol, 1 × 10^{-5} M, 1) λ_{exc} 320 nm, 2) λ_{exc} 230 nm).

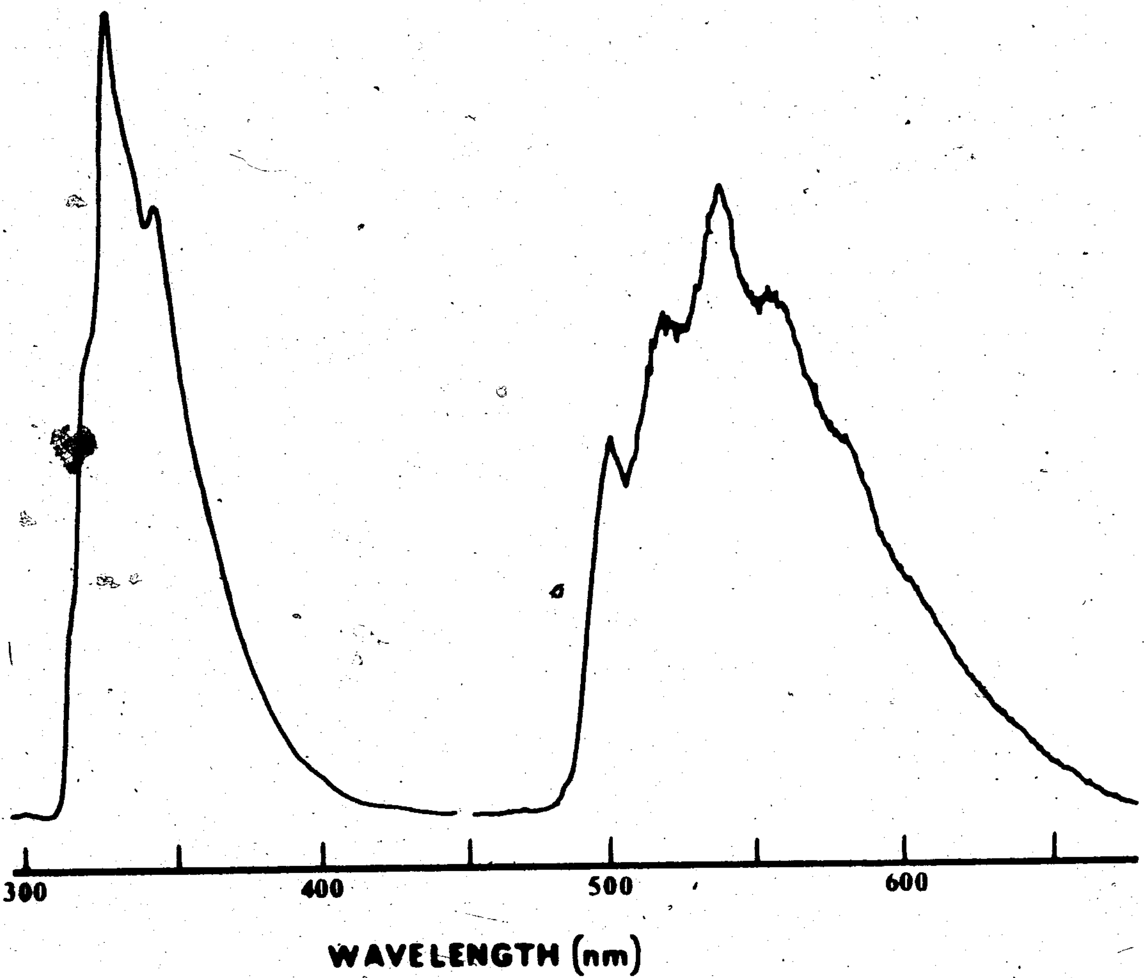


Figure 51. Total emission spectrum of 2-phenylthiophene (EPA, 77 K).

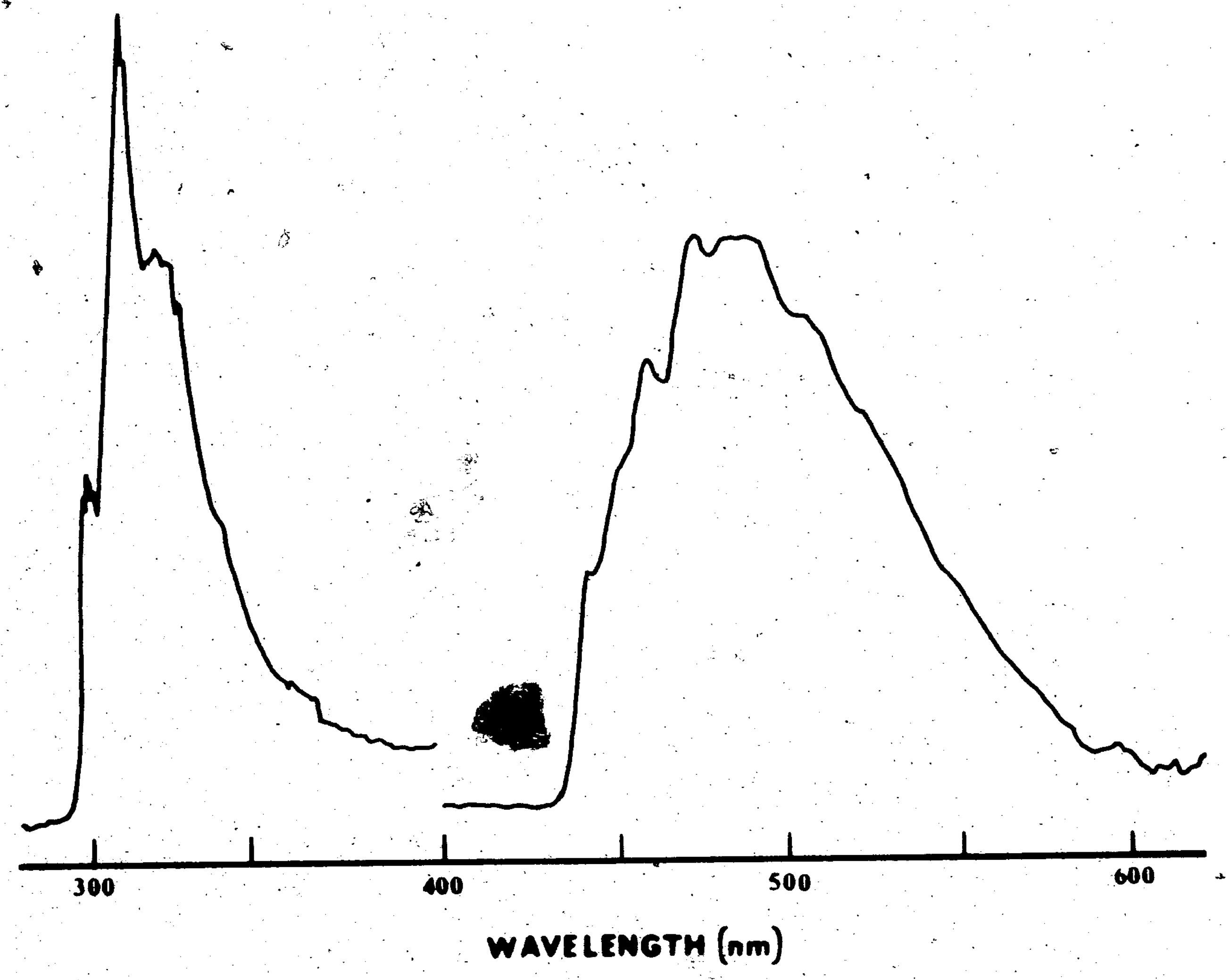


Figure 52. Total emission spectrum of 3-phenylthiophene (EPA, 77 K).

phenylthiophenes are summarized in Table 18, accompanied by data previously reported by Wynberg et al. [92].

The time resolved behaviour of the phenylthiophenes was also investigated. Inherent radiative lifetimes of the phenylthiophenes were calculated from their absorption spectra using the relation,

$$\tau_o \text{ (in ns)} = 3.5 \times 10^8/\bar{\nu}_m^2\, \Delta\bar{\nu}_{1/2}\, \varepsilon_m \qquad (39)$$

where:

$\bar{\nu}_m$ = mean frequency (cm^{-1}) for the absorption band.
$\Delta\bar{\nu}_{1/2}$ = the half-width of the absorption band (cm^{-1}).
ε_m = maximum extinction coefficient of the absorption band.

The τ_o values obtained ranged from 2.5-8 ns, as listed in Table 19. Although the values calculated in this manner contain a considerable margin of error, a useful upper limit to the fluorescence lifetime (i.e. assuming $\phi_F = 1$) of an emitting compound can sometimes be obtained.

The determination of the fluorescence lifetimes of some of the phenylthiophenes was attempted using our PRA 1000 nanosecond lifetime apparatus. The excitation pulse in this instrument is provided by a gas-filled flashlamp. The actual temporal profile, wavelength distribution, and intensity of the excitation pulse are dependent on a number of factors including the gas selected, its pressure within the lamp, the spacing of the lamp electrodes and other operational parameters [174]. For the current discussion it is sufficient to state that employing the optimum conditions for a narrow lamp pulse

TABLE 18

Steady-State Emission Characteristics of Phenylthiophenes

Compound	λ_{max}, (nm) Fluorescence		Phosphorescence	
	a	b	a[f]	b
2-phenylthiophene	334[c]	n.d.[e]	540±5	540
3-phenylthiophene	306[c]	n.d.[e]	485±5	490
2,3-diphenylthiophene	393[c]	390	580±5	560
2,4-diphenylthiophene	365[d]	362	545±5	545
2,5-diphenylthiophene	384[c]	390	none	none
3,4-diphenylthiophene	337[c]	342	480±5	480
tetraphenylthiophene	397[d]	n.d.[e]	600±10	n.d.[e]

[a] This work.

[b] Wynberg et al. [92]

[c] Methanol.

[d] Hexanes.

[e] Not described.

[f] EPA, 77 K.

TABLE 19

Calculated Inherent Radiative Lifetimes (τ_0) of Phenylthiophenes

Compound	Calculated τ_0 (ns)[a]
2-phenylthiophene	3.5
3-phenylthiophene	3.6
2,3-diphenylthiophene	4.3
2,5-diphenylthiophene	2.5
tetraphenylthiophene	8.0
2,4-diphenylthiophene	$S_0 \rightarrow S_1$ absorption not resolved
3,4-diphenylthiophene	

[a] τ_0 (in ns) = $3.5 \times 10^8/\bar{\nu}_m^2\ \Delta\bar{\nu}_{1/2}\ \varepsilon_m$.

our H_2 flashlamp profile had a full width at half-maximum (FWHM) in the range 1.5-2 ns. The fluorescence decay times of the phenylthiophenes proved to be very short in comparison to the duration of the lamp pulse. Although deconvolution techniques have been described for the extraction of meaningful kinetic data from experiments where the flash duration is comparable to the response of the sample, we considered that such an art was best left in the hands of those with considerable expertise in this area of photophysics. Demas has recently devoted an entire book to the subject of excited state lifetime measurements [175].

As a result, we approached Prof. W. Ware at the University of Western Ontario, who kindly consented to assist us by measuring the fluorescence lifetimes of our phenylthiophenes. Using their laser lifetime apparatus it is possible to evaluate fluorescence decay times in the picosecond domain and these are summarized in Table 20. The lifetimes of benzothiophene (BT) and dibenzothiophene (DBT) were also measured, using the recent mimic technique [176], and are included in Table 20 with the phenylthiophene series. Only 2,4-DPT revealed a clearly double exponential decay. Double exponential behaviour was also suspected for 3,4-DPT, and single exponential behavior was observed for all the other thiophenes listed in Table 20. The double exponential decay of the 2,4-DPT emission was probably caused by a very small quantity of impurity in the 2,4-DPT, also detected by capillary GC. The GC method indicated that all of the other compounds in Table 20 were pure. Lifetime investigations as a function of excitation and emission wavelength, as well as

TABLE 20

Fluorescence Lifetimes of Phenylthiophenes and Benzothiophenes

Compound	λ_{exc}, (nm)	λ_{emis}, (nm)	τ_1 (ps)
2-PT	283	343	49±5
3-PT	283	315	585±10
2,3-DPT	283	402	49±5
2,5-DPT	295	390	247±10
TPT	295	400	43±5
BT	283	320	383±20
DBT	283	340	783±20
2,4-DPT[a]	295	360	$A_1 = 0.939$ $\tau_1 = 169$
			$A_2 = 0.061$ $\tau_2 = 657$
3,4-DPT[a]	283	327	$A_1 = 0.980$ $\tau_1 = 128$
			$A_1 = 0.020$ $\tau_2 = 968$

[a] Probably double exponential decays, i.e. fitting function $D(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$.

temperature, supported the conclusion that the 2,4-DPT emission was composed of two spectral species having different lifetimes. Similar investigations are currently in progress for 3,4-DPT.

The phosphorescence lifetimes of the phenylthiophenes were all determined in an EPA glass at 77 K. We have performed these experiments with the Farrand spectrofluorimeter by redirecting the phosphorescence signals from the PMT to an external oscilloscope. Several photographic records were obtained for the phosphorescence decay of each compound. Where investigated, excitation at different wavelengths did not have much effect on the phosphorescence decays measured for the phenylthiophenes. The actual phosphorescence decay times are summarized in Table 21, and the experimental decay data extracted from photographic records of the 3-PT and TPT phosphorescence decays are plotted (as ln phosphorescence intensity vs time) in Figure 53, as examples of the results obtained.

Neither the fluorescence nor the phosphorescence decay studies provided any obvious insight into the photochemistry of the phenylthiophenes. It was thus concluded that at the level of this investigation the photophysics of these compounds was of little value in understanding their photorearrangement behaviour.

TABLE 21

Phosphorescence Data for Phenylthiophenes

Compound	λ_{exc} (nm)	$\lambda_{max\ phos}$ (nm)	Intensity relative to fluorescence	τ_p (ms)[a]
2-phenylthiophene	280,310	540±5	weak	28.8±0.5
3-phenylthiophene	230,260, 280	485±5	strong	298±7
2,3-diphenylthiophene	250,275	580±5	weak	11.0±0.3
2,4-diphenylthiophene	260	545±5	medium	n.d.[b]
2,5-diphenylthiophene		no phosphorescence detected		
3,4-diphenylthiophene	230,260, 270,280	480±5	strong	259±7
tetraphenylthiophene	270,315	600±10	weak	12.9±0.5

[a] All phosphorescence measurements were made in EPA at 77 K.

[b] Not determined.

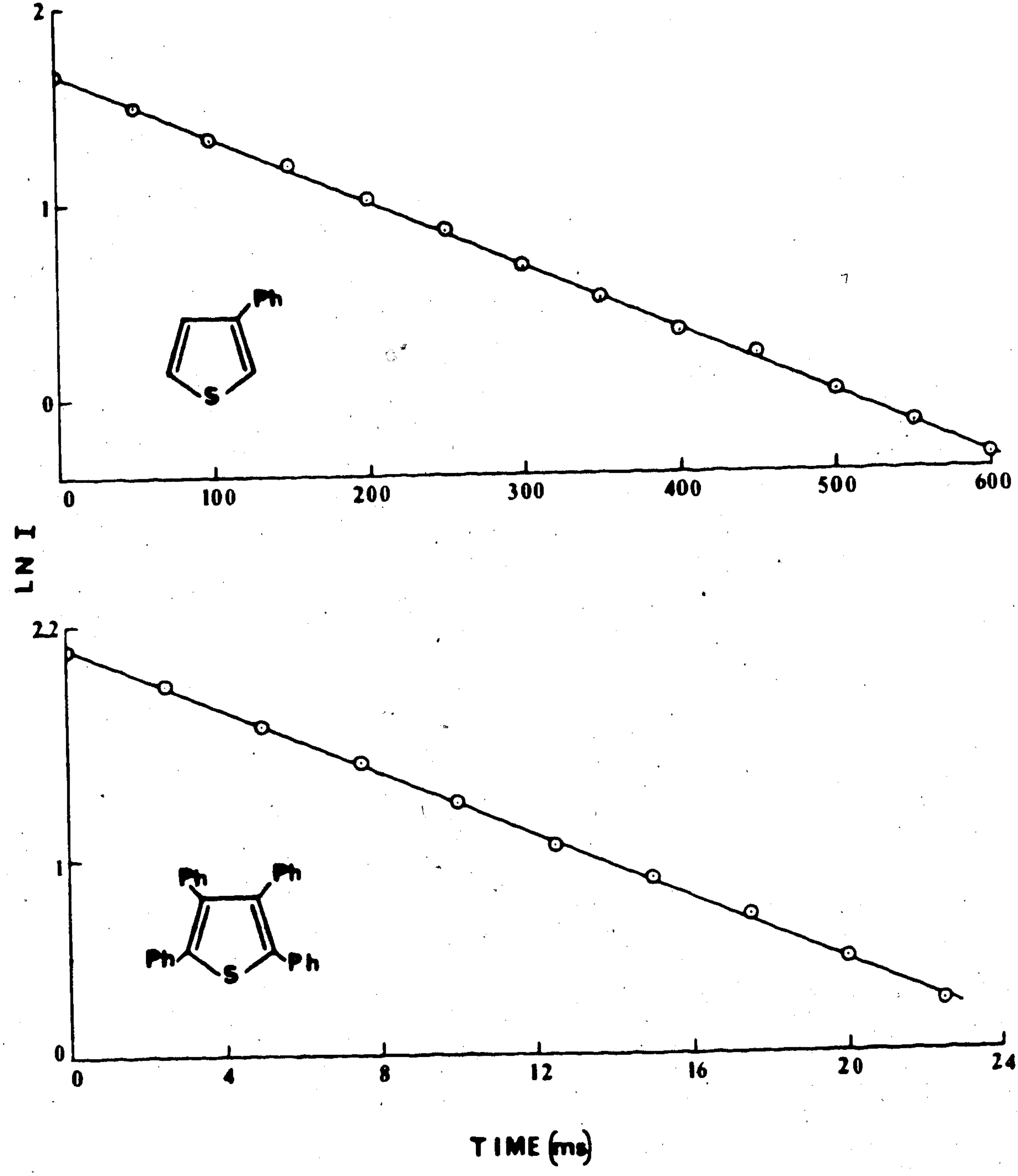


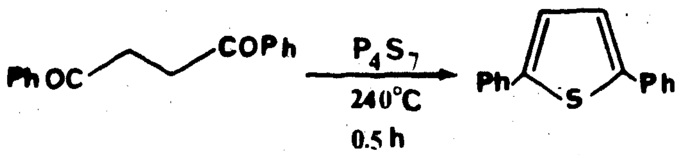
Figure 53. Phosphorescence decay results for 3-phenylthiophene and tetraphenylthiophene (EPA glass, 77 K).

EXPERIMENTAL

A. Reagents

1. Monophenylthiophenes and Diphenylthiophenes

The synthetic methods employed for the preparation of the mono- and diphenylthiophenes were each specific for one particular isomer. A typical phenylthiophene synthesis is illustrated below:



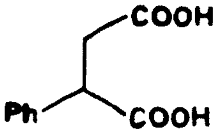
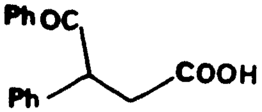
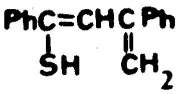
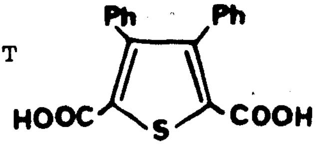
(40)

Dibenzoylethane, used as the precursor for this final step in the preparation of 2,5-DPT, was obtained in a two step process beginning with fumaryl chloride. Four of the six phenylthiophenes were synthesized in a similar manner. In the final step of each of these preparations, suitably phenyl substituted 1,4-dicarbonyl compounds were converted into phenylthiophenes by the action of P_4S_7 at elevated temperatures (250-300°C). This is the Paal-Knorr synthesis.

Table 22 gives more details of the syntheses of phenylthiophenes. Specific procedural details can be found in the references cited. Each of the phenylthiophenes was purified by multiple recrystallization from an appropriate solvent or solvent mixture. Melting points were measured and compared with literature values. The purity of the recrystallized products was investigated by capillary GC (SE-52, ~0.25 mm × 20 m, appropriately temperature

TABLE 22

Synthesis of Phenylthiophenes

Compound	Precursor	Conditions[a]	Ref.	Yield[b]	M.p. Range (°C)[c]
2-PT		P_4S_7 250-260°C 0.5 h	177	10%	34.9 - 35.2
3-PT		P_4S_7 250-260°C 0.5 [illegible]	178	12%	91.0 - 91.4
2,3-DPT		P_4S_7 260-280°C 0.5 h	177	18%	83.4 - 84.1
2,4-DPT	 $\underset{\text{SH}}{\text{PhC}}{=}\text{CH}\underset{\overset{\|}{\text{CH}_2}}{\text{C}}\text{Ph}$	$Cu_2Cr_2O_4$ in xylenes, reflux, 3 h	179	40%	120.0 - 121.2
2,5-DPT		P_4S_7 240°C 0.5 h	177	unknown	152.9 - 153.4
3,4-DPT		350-360°C 4 h	180, 181	84%	114.5 - 115.0[d]

(Continued)

Footnotes for Table 22

[a] P_4S_7 (Eastman Kodak) can be purified by Soxhlet extraction with CS_2 [182].

[b] Actual experimental yield on the final step in each synthesis. Yield is based on the mass of product obtained from the first recrystallization step.

[c] Uncorrected.

[d] This dicarboxylic acid was prepared in a 3-step synthesis, beginning with thiodiacetic acid, $S(CH_2CO_2H)_2$.

programmed). All the phenylthiophenes were found to be pure, except 2,4-DPT which contained a small amount of a second component.

The phenylthiophenes were fully characterized by UV, IR, MS, and ^1H and ^{13}C NMR. The NMR data are presented in Tables 23 and 24. The ability of the high field NMR spectrometer to resolve a number of absorptions having very similar chemical shifts is dramatically revealed by these data. For instance, all the ^1H resonances in the spectra of all the phenylthiophenes were located in a reasonably narrow chemical shift range, δ ~7.0-7.7 ppm relative to TMS. With the aid of the Bruker WH-400 NMR spectrometer however, nearly all of these proton resonances could be assigned to specific phenyl or thienyl ring protons, and J_{H-H} coupling constants were measured, experimentally verifying the phenyl substitution patterns. Similar coupling data had previously been reported for some alkyl and halogen substituted thiophenes [183].

2. Tetraphenylthiophene

Commercial TPT (Alfa) was purified by repeated recrystallization from a 1/1 mixture of benzene and absolute ethanol. The purified product had a melting point range of 189.6-189.9°C.

3. Benzothiophene and Dibenzothiophene

Both benzothiophene (Aldrich) and dibenzothiophene (Eastman) were purified by multiple recrystallization prior to use.

4. Methylthiophenes

2- and 3-methylthiophene (Aldrich) were both used without further purification. The estimated purities of the commercial

TABLE 23

400 MHz ^{1}H NMR Data for the Phenylthiophenes

Compound	δ_H (ppm)[a]						
	Phenyl protons			Thienyl protons			
	o	m	p	H_2	H_3	H_4	H_5
Thiophene[b]	--	--	--	7.20	6.96	6.96	7.20
2-PT	7.62	7.38	7.27	--	7.31	7.08	7.27
3-PT	7.60	7.40	7.29	7.45	--	7.39	7.39
2,3-DPT[c]	--	--	--	--	--	7.18	7.35
2,4-DPT	7.66	7.43	7.34	--	7.42	--	7.63
2,5-DPT	7.66	7.42	7.31	--	7.32	7.32	--
3,4-DPT[c]	--	--	--	7.31	--	--	7.31

[a] Chemical shifts in $CDCl_3$ relative to TMS.

[b] Data taken from Ref. [183].

[c] Phenyl proton assignments not made because of complex overlapping proton resonances.

TABLE 24

100 MHz ^{13}C NMR Data for the Phenylthiophenes

Compound	δ_C (ppm)[a]							
	Phenyl carbons				Thienyl carbons			
	o	m	p	C_{Ph}	C_2	C_3	C_4	C_5
Thiophene[b]	--	--	--	--	124.9	126.7	126.7	124.9
2-PT	126.1	128.9	127.5	144.6	134.6	124.8	128.0[c]	123.1
3-PT	126.5	128.9	127.2	142.5	120.3[c]	136.0	126.4(?)	126.2(?)
2,3-DPT	128.5	129.4	127.4	138.8	134.5	136.7	130.5[c]	124.1[c]
2,4-DPT	126.4	129.0	127.7	145.1	134.5	119.7[c]	136.0	122.4[c]
2,5-DPT	125.7	128.9	127.5	143.3	134.4	124.0	124.0	134.4
3,4-DPT	126.4	129.0	127.7	145.1	124.0	136.6	136.6	124.0

[a] Chemical shifts in $CDCl_3$ relative to TMS.

[b] Data taken from Ref. [183].

[c] Assignments based on selective decoupling experiments.

products were 98% and 99+%, respectively.

5. Tetradeuterothiophene

Tetraiodothiophene was prepared (yield 36%, m.p. 196.7-198.9°C) from the action of I_2 on thiophene in the presence of mercuric oxide (HgO) and glacial acetic acid [184]. The C_4I_4S was converted into C_4D_4S [185] in a yield of 57%. If isotopically pure D_2O and purified anhydride are used this synthesis provides a thiophene which is completely deuterated.

$$C_4I_4S \xrightarrow[D_2O\text{ , }Zn \atop \Delta]{(CH_3CO_2)O} C_4D_4S \quad + \text{ products} \qquad (41)$$

The C_4D_4S was employed in LTMI experiments and was judged to be pure at the level indicated by IR spectroscopy.

6. Thiophene

Commercial thiophene (99+%) was purified by the procedure described in Perrin et al. [186], which involved a series of washing steps, followed by careful drying and finally a fractional distillation (b.p. ~84.3°C). In many photolysis experiments thiophene was used as commercially received. This practice did not affect relative adduct formation, nor were any new products obtained.

7. Cyclopentadiene

Dicyclopentadiene (Terochem, 95%) was dried with $CaCl_2$ and distilled. The distillation process depolymerizes the dimer producing the desired cyclopentadiene monomer (b.p. 41-42°C).

Cyclopentadiene was stored, uninhibited, in the freezer. After a few weeks, when GC or IR spectroscopy provided evidence for significant dimer reformation, more cyclopentadiene was freshly prepared.

8. 2,3-Dimethyl-1,3-butadiene

This symmetrical diene was utilized in solution phase trapping experiments, without further purification of the commercially available compound (Aldrich, 98%).

9. 1,3-Pentadiene (Piperylene)

Piperylene (Aldrich) was dried with $CaCl_2$ and distilled (b.p. 41.5-42.0°C) prior to use.

10. Furan

Commercial furan (Aldrich, inhibited with ~1 ppm BHT) was shaken with aqueous 5% KOH, dried with $CaSO_4$ and distilled under N_2 from Na, immediately prior to use [186]. The storage of purified, uninhibited furan results in the formation of photosensitive furan oxidation products, unless the furan is constantly maintained under an inert atmosphere. As a result of the large quantities of furan, about 75 mL per run, required for the cyclic photolysis reactor, it was sometimes used in these experiments as commercially received. This did not affect relative adduct formation nor were any new products, apart from BHT, detected after a photolysis.

B. Solution Phase Photolysis Experiments with Thiophenes

Solution phase photolysis experiments with thiophene and substituted thiophenes were carried out at room temperature, with irradiation times ranging from ~48-168 h. In the initial trapping experiments with substituted thiophenes all solutions were carefully deoxygenated, either under high vacuum with repeated freeze-pump-thaw cycles, or by bubbling N_2 for 0.5-1.0 h prior to irradiation. However, the presence of O_2 was found not to prevent, or even noticeably inhibit, adduct formation, and consequently many photolyses were later performed without the precaution of O_2 removal. The absence of any effect of O_2 on the photoinduced rearrangement of 2-PT to 3-PT had been reported by Wynberg et al. [92,95].

The selection of suitable photolysis wavelengths for each of the thiophenes irradiated depended on the UV absorption characteristics of both the thiophene and the trapping reagent. Table 25 summarizes the actual photolysis wavelengths employed. All solution phase photolyses of thiophenes were performed with roughly a ten-fold molar excess of the trapping agent present, and rapid stirring was maintained throughout the entire course of each photolysis in an attempt to maximize the homogeneity of the solutions. Small aliquots were often taken at various photolysis times and the product mixture analyzed by capillary GC. In this way the continuous growth of the 1:1 adducts was monitored.

Noticeable polymer formation occurred in the photolysis of every thiophene, except 2,5-DPT. The polymer was always yellow in colour,

TABLE 25

Photolysis Conditions for Thiophenes and Furan

Compound	Wavelength (nm)	Conditions
TPT	λ > 280	Medium pressure Hg arc lamp/2 mm Pyrex filter
2-PT 3-PT 2,3-DPT 2,5-DPT	254	Low pressure Hg arc lamp/2 mm Vycor 7910 filter
2-MT 3-MT C_4H_4S C_4H_4O	229	Cd resonance lamp/no filter
C_4H_4O	214	Zn resonance lamp/no filter

and accumulated on the inner surface of the photolysis cell. Periodic rotation of the cell in the irradiation beam provided for sample exposure through uncoated cell surfaces, however at long irradiation times much of the light intensity must have been attenuated. The polymer was insoluble in a large variety of organic solvents.

An interesting observation, relating to the extent of polymer formation, was that the irradiation of 3-PT in piperylene produced considerably more polymer than the irradiation of 2-PT under the same experimental conditions. Elemental analysis of a portion of the polymer recovered after a 3-PT photolysis showed that its empirical formula was approximately $C_3H_4S_2$. Owing to the insoluble nature of the polymer its molecular weight was not determined.

Separation of excess unreacted thiophene from the 1:1 adducts produced by photolysis was a difficult task in the phenylthiophene studies. For TPT simple recrystallization separated large amounts of the thiophene from the small quantity of adducts formed by irradiation and trapping. With the monophenylthiophenes, vacuum sublimation finally emerged as the separation technique of choice as it provided a residue fraction which was enriched in the adducts. Nevertheless, the work-up of the photolysis mixtures from the phenylthiophenes constituted a major problem in these investigations. For the case of the irradiation of thiophene in furan, separation of the adducts from the excess reagents can be readily accomplished on a rotary evaporator. Thiophene and furan were easily removed because of their volatility, while none of the adduct mixture was lost.

C. Solution Phase Photolysis Experiments with Furan

Photolyses were typically continued for about 60 h using either a Zn (214 nm) or Cd (229 nm) resonance lamp as the radiation source. Degassing of furan under high vacuum with repeated freeze-pump-thaw cycles, or deoxygenation by bubbling N_2 for 0.5 h was employed for small scale runs. However, the presence of O_2 did not prevent adduct formation. Photolyses were performed using both a "static" steady-state photolysis design and a modified system providing periodic cycling of the furan. Rapid stirring of the liquid furan was maintained during all photolyses.

In a high conversion conventional photolysis experiment complications due to secondary photolysis can arise and polymer formation on the inner cell walls severely attenuates the incident light intensity as the photolysis progresses. The heart of the cyclic photolysis apparatus was an all quartz reactor very similar in appearance to a Soxhlet apparatus, but modified to permit irradiation and stirring of the liquid furan, and fitted with a sidearm which siphons a portion of the solution (Figure 54). In this device, furan was distilled from a reservoir maintained at about 35°C and condensed thereby filling the photolysis zone. When this region was filled the lamp was started. As fresh furan continued to distill, the reactor was filled above the photolysis zone. After approximately 0.25 h the sidearm connected to the reactor siphoned roughly 50% of the furan solution back to the reservoir. At all times the liquid furan level filled the entire photolysis zone, thereby maximizing the "contact

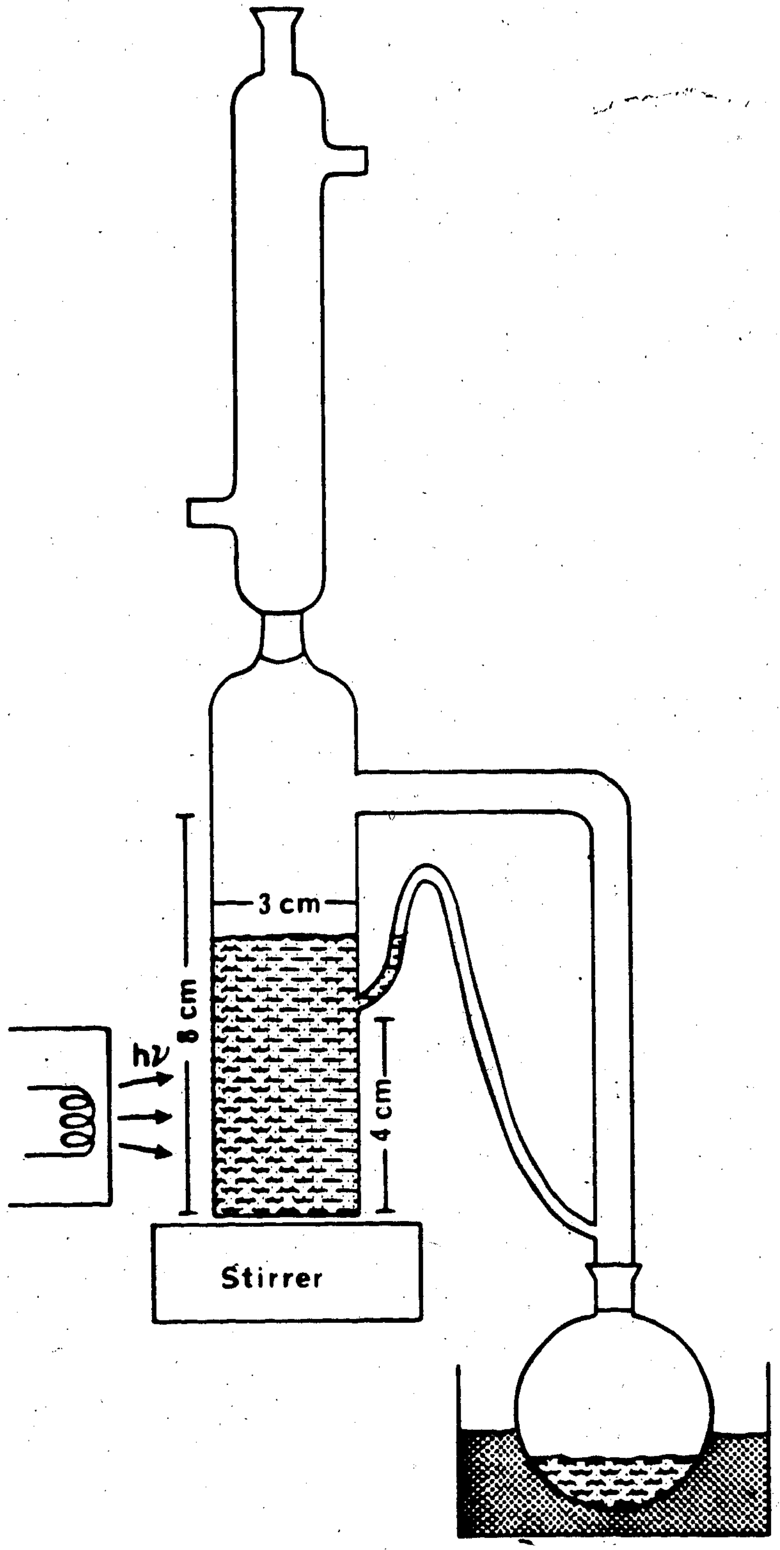


Figure 54. Cyclic photolysis reactor designed for the irradiation of neat liquid furan.

time" between the liquid and the incident light yet providing a means of removing some of the generated photolysis products from the irradiation region. From the reservoir unreacted furan redistilled back to the photolysis zone, while the adducts were retained. This design helped reduce the risk of secondary photolysis during long irradiations and considerably reduced attenuation of the incident light due to polymer formation, by washing the latter out of the reactor.

D. Low Temperature Irradiation of Thiophene with Post-Photolysis Trapping

The photolysis of thiophene was performed at -170°C in a glassy matrix (10% thiophene in diethyl ether v/v, degassed). The quartz sample cell was placed inside a quartz Dewar flask and the low temperature was maintained by a flow of very cold N_2 gas. The actual temperature of the sample fluctuated by roughly 5°C during the entire experiment. The photolysis was carried out using two Cd resonance lamps (229 nm) for increased irradiation efficiency. As the irradiation proceeded, the frozen sample turned yellow at the surface. Thus the sample cell was frequently rotated in order to ensure reasonable exposure of most of the thiophene to the incident radiation. In the glassy matrix only a thin surface layer of thiophene is actually photolyzed.

At the conclusion of irradiation (8 h), when the entire surface of the frozen sample was a fairly uniform yellow colour, previously degassed furan was slowly distilled under vacuum from a separate side arm and deposited on top of the glassy matrix. The mixture was allowed to warm up in a dry ice/acetone bath (-78°C) and rapid stirring was started. At this temperature the sample was a viscous liquid. The mixture was maintained at -78°C for several hours, and finally allowed to warm up overnight to 25°C before being analyzed as described earlier.

E. Instrumental Techniques

A number of analytical and spectroscopic techniques were employed during the course of this investigation. Since they are considered to be routine they will not be described in detail, however, the specific instruments used are listed in Table 26.

F. Low Temperature Matrix Isolation (LTMI)

The matrix isolation technique has now been in use for just over thirty years. Simultaneous proposals, suggesting the application of inert gas matrices at low temperatures to the examination of species which are unstable at room temperature, were put forth in 1954 by Porter [187] and Pimentel [188], and their coworkers. In a low temperature matrix the lifetime of a trapped molecule is considerably increased. The matrix cage severely restricts the possibility of bimolecular reactions, while the low temperatures employed, ca. 10 K, effectively prevent any reaction having an activation energy greater than a few kJ•mol^{-1}.

TABLE 26

Instrumentation

Technique	Instrument	Comments
Capillary GC	Hewlett Packard 5840A	Modified for capillary columns
Preparative GC	Varian Aerograph 90-P	
UV	Pye Unicam SP-1800	
MS	AEI MS12	Low resolution EI and CI
	AEI MS50	High resolution EI
GC/MS	AEI MS12/Varian Aerograph 1400	Packed column GC
	AEI MS9/Hewlett Packard 5730A	Capillary column GC
	VG 7070E/Varian Vista 6000	Capillary column GC
IR	Nicolet 7199 FTIR	Caste spectra
GC/FTIR	Nicolet 7199 FTIR/Varian 3700	Packed or capillary column GC
NMR	Bruker WH-200	200 MHz ^{1}H, 50 MHz ^{13}C
	Bruker WH-400	400 MHz ^{1}H, 100 MHz ^{13}C
Photophysical	Farrand MK-2 Spectrofluorimeter	Steady-state excitation and emission spectra, 77 and 300 K

LTMI is often combined with IR spectroscopy as a means of studying species isolated in the matrix. In our system IR spectra were recorded on either a Perkin Elmer 257 or a Nicolet 7199 FT infrared spectrophotometer. The matrix cage usually perturbs the vibrational levels of a solute and thus shifts the absorptions measured in such experiments, resulting in small frequency changes of the order of 10 cm^{-1}, as compared with gas phase data. Owing to both the low temperature of the MI experiments and the inhibition of molecular rotation caused by the matrix cage, vibrational transitions recorded for matrix isolated species are often quite sharp. This improvement in resolution is an advantage for LTMI. However, the matrix environment can also cause complications. For instance, the observation of splittings in vibrational bands is common, and these usually result from solute species located in physically different matrix sites. A careful determination of splittings due to multiple trapping sites usually involves studies of the concentration dependence, and the effect of temperature cycling on the structure of the vibrational bands.

Solute aggregation in the matrix can also complicate LTMI studies. For this reason the ratio of matrix material (M) to solute (S) is usually large, typically in the range 100-1000:1. The ratio selected depends on the individual system being examined, its tendency to form dimers or larger aggregates, and the intensity of the IR spectral features which must be observed. In our MI experiments M/S ratios were typically between 150/1 and 250/1. No evidence of aggregate formation was ever identified under these conditions.

A number of articles providing more detailed discussions of LTMI have been published [189-192] and a recent book describes the application of many spectroscopic tech[illegible] to matrix isolation [193].

An Air Products and Chemicals Inc. Model CS-202 Displex closed-cycle-helium refrigeration system was employed throughout the current investigation to maintain matrix temperatures at ~10 K. The vacuum shroud which encloses the cold sample window was equipped with two CsI windows (IR) and two spectrosil windows (UV). The optical cell was connected to a standard high vacuum apparatus which was used for all the preliminary and post-photolysis gas handling required during the MI experiments. The substrate was first thoroughly mixed with high purity inert gas, usually Ar, but some experiments were carried out with Xe or N_2. The homogeneous gas mixtures were then admitted to the cell through a deposit needle and condensed on the cold sample window. The deposition flow rate was regulated as desired. When sample generation was completed, <u>in-situ</u> photolytic generation of the reactive species of interest was initiated. In multiple layer experiments sample deposition and photolysis intervals were automatically controlled by means of a programmable Gralab 900 timer (Cole Parmer) which operated both a shutter assembly located between the photolysis source and the low temperature cell, and a solenoid valve situated in the sample deposition train.

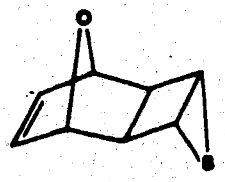
A number of different light sources and filters were used during the LTMI studies in order to isolate the desired photolysis wavelengths. The conditions already listed in Table 25 were frequently employed in the matrix experiments.

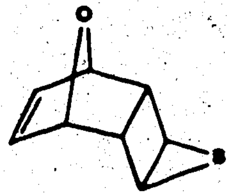
SUMMARY AND FUTURE INVESTIGATIONS

Having presented the results of the current investigation, a brief summation of the most significant discoveries should be made. As stated much earlier, the main thrust of this research effort was an attempt to uncover direct experimental evidence for the existence of the cyclopropenyl and Dewar type structures, which had been frequently implicated as potential intermediates in the photoisomerization reactions of furans and thiophenes, but much less often detected. This goal has been accomplished.

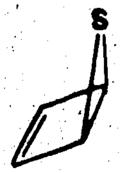
In the gas phase irradiation (214, 229 nm) and Hg sensitization of thiophene Wiebe and Heicklen [102] identified a number of products: C_2H_2, CH_2CCH_2, CH_2CHCCH, CH_3CCH and CS_2.

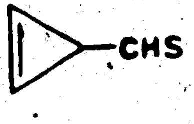
Irradiating thiophene (229 nm) in furan solutions we have generated two new products arising from Diels-Alder addition between Dewar thiophene and furan. These compounds were fully characterized on the basis of high resolution MS, FTIR, UV and ^{1}H and ^{13}C NMR, and assigned the following structures. Their stereochemistry was determined by selective proton decoupling experiments in the 400 MHz ^{1}H NMR.





Photolysis of thiophene (229 nm) in an Ar matrix at 10 K produced a number of new IR absorptions. Some of these were assigned to Dewar thiophene and cyclopropenyl thioaldehyde on the basis of comparison with the matrix IR spectra of suitable model compounds.



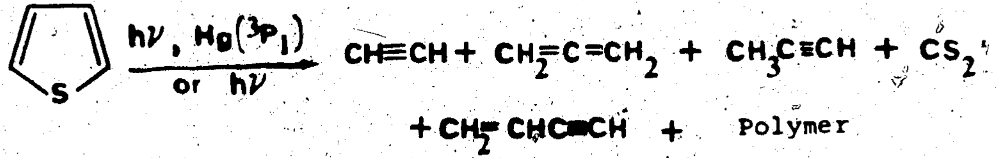


Although a small number of substituted Dewar thiophenes have been described previously, the parent species was not known. No cyclopropenyl thioaldehydes had ever been identified.

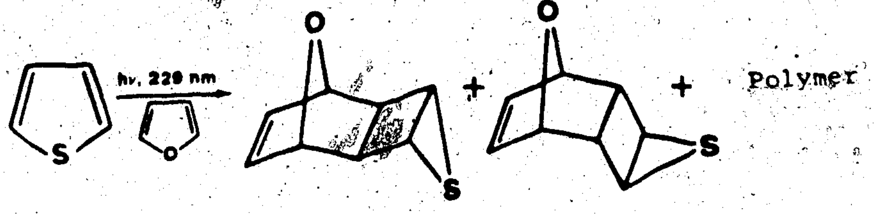
Other primary products which we identified in the matrix photolysis of thiophene were CH_2CHCCH and $CH_2CCHCHS$; while CH_2CCS, CH_3CCH and CS_2 were formed in secondary processes. It was also observed that secondary photolysis (254 nm) of Dewar thiophene and/or cyclopropenyl thioaldehyde regenerates thiophene and that for the cases of methylthiophene substrates, the selective photoregeneration of a particular isomer is probably a consequence of substituent control.

The photochemistry of thiophene is summarized in the following scheme, where previous contributions as well as our results are shown.

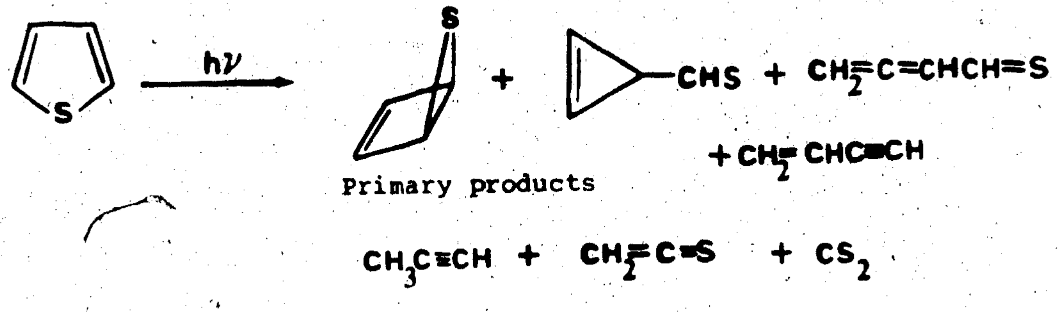
Gas phase - Ref. [102]

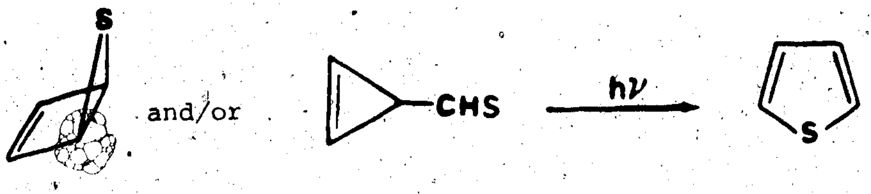


Solution phase - current investigation



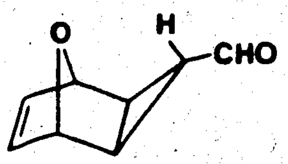
Low temperature matrix - current investigation





The gas phase photochemistry of furans has been extensively studied by Srinivasan and coworkers [33-37]. Decarbonylation of furan produces CO, CH_3CCH, CH_2CCH_2 and cyclopropene with the last C_3H_4 product being formed only during Hg($^3P_1$) sensitization experiments, and not on direct photolysis of furan.

We have irradiated (214 nm) neat liquid furan in a continuous cyclic photolysis reactor of our own design, and isolated four products. The products have been fully characterized by high



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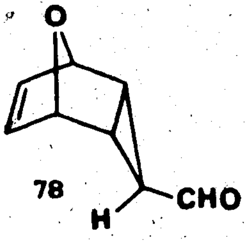
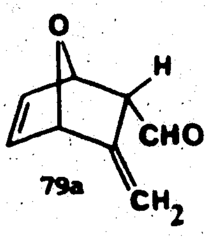
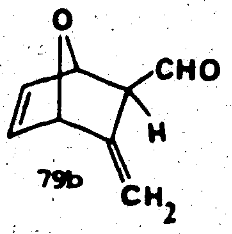


78

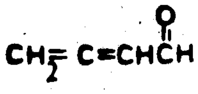


79a



79b

resolution MS, FTIR and ^1H and ^{13}C NMR. Selective decoupling experiments in the 400 MHz ^1H NMR permitted their stereochemistry to be assigned. Srinivasan previously reported the isolation of a single compound similar to 77 and 78 from the gas phase photosensitization of furan, however his product was not well characterized and he was unable to determine its stereochemistry. Our adducts **79a** and **79b** represent the first trapping of 2,3-butadienal.



$$\mathrm{CH_2{=}C{=}CH\overset{O}{\overset{\|}{C}}H}$$

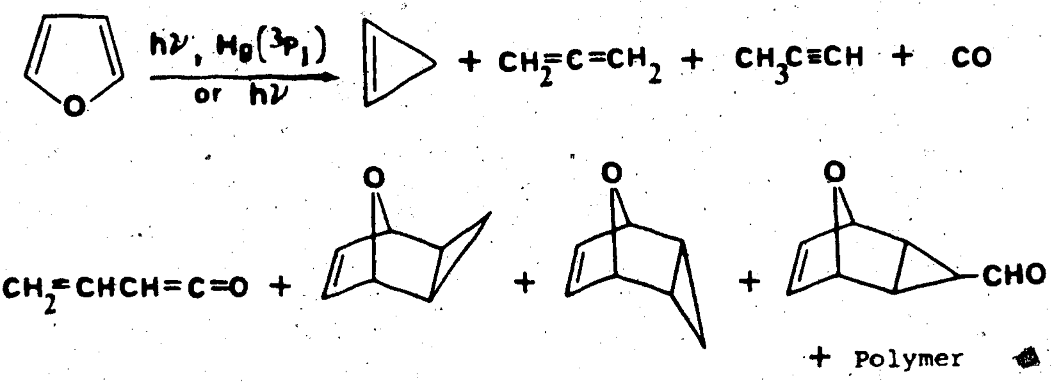
In the low temperature matrix (10 K) we have identified the same species that were trapped in our solution experiments. In addition, photolysis (214 nm) of matrix isolated furan has led to the first discovery of Dewar furan. No Dewar furans had ever been observed

before, in spite of efforts concentrated on their detection. In fact, as recently as December 1984 two communications appeared regarding Dewar furans. In the first, Warrener <u>et al.</u> [194] claimed the transient existence of tri- and tetramethyl Dewar furans in their photolysis systems, although only cyclopropenyl ketones were ever detected. These results were not obtained from the photolysis of furan, but rather by UV irradiation of carefully synthesized precursors which were designed to fragment on photolysis in a manner that would yield a Dewar furan. In their second communication, Warrener <u>et al.</u> [195] synthesized a DAa with a derivative of Dewar furan, the latter being so highly substituted however, that it was almost unrecognizable as a Dewar furan.

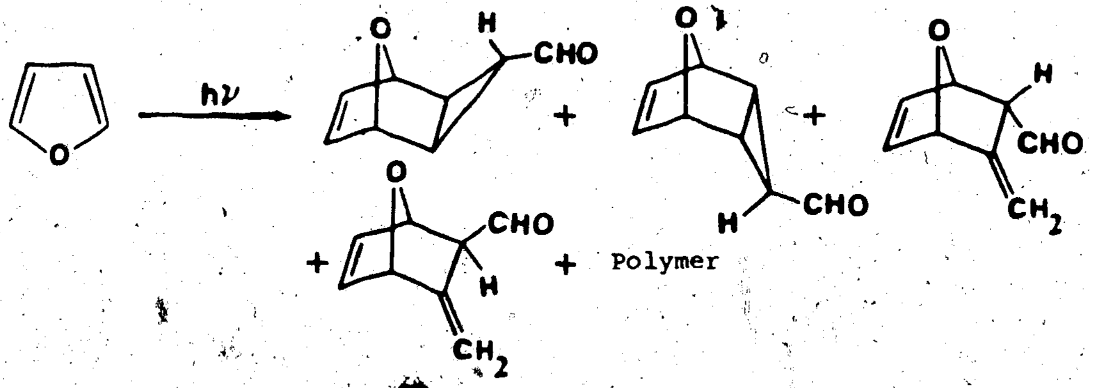
Vinylketene was also a primary photolysis product in the matrix. This species was previously described by Srinivasan [35]. In addition, CO, CH_2CCH_2 and CH_3CCH were found as secondary products. Direct irradiation (254 nm) of Dewar furan in the matrix resulted in its conversion to cyclopropenyl aldehyde, and not regeneration of furan. We believe that the greater stability of the cyclopropenyl aldehyde as compared with the thioaldehyde may provide a driving force which is responsible for the difference in behavior of Dewar furan and Dewar thiophene on their direct irradiation.

The photochemistry of furan is summarized below.

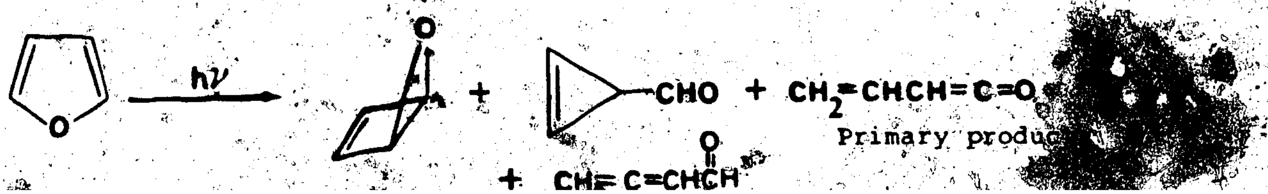
Gas phase - Ref. [33-37]



Solution phase - current investigation

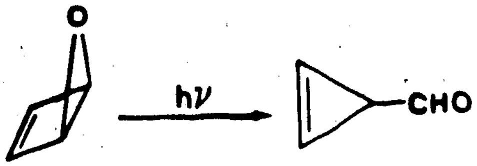


Low temperature matrix - current investigation



$CO + CH_2=C=CH_2 + CH_3C\equiv CH$

Secondary products



We have also investigated the matrix photolysis of cyclopentadiene, identifying its Dewar isomer, bicyclo[2.1.0]pent-2-ene, by ^1H NMR. This species was reported by van Tamelen et al. [171] following the solution phase photolysis of cyclopentadiene, however its generation in the matrix was an invaluable aid to the identification of Dewar furan and thiophene species in the matrix.

Preliminary studies of the matrix photolysis of pyrrole suggest that Dewar pyrrole may be produced. Further studies with pyrroles are in progress.

In summation, the present study has provided direct evidence for the generation of Dewar and cyclopropenyl species in the photolysis of furan and thiophene. As stated before, however, the fact that these species can be generated by photolysis does not guarantee their involvement in the photoisomerizations of substituted furans and thiophenes. In other words, the existence of these species should probably be regarded as a necessary, but not a sufficient, condition for their intermediacy in these reactions.

We have examined the photophysics of a series of phenylthiophenes, studying their steady-state and time resolved emission characteristics. Although this information helps to further characterize these compounds we see no evidence that their photophysical behavior provides insight about the photoinduced isomerizations of phenyl substituted thiophenes.

It should be mentioned that as part of our matrix isolation (MI) studies on furan and thiophene we have developed a new multiple layer depositional technique which has greatly enhanced the amount of information obtainable from MI experiments with such substrates which cannot be investigated by the more conventional MI methods.

Numerous ideas for further experimentation in the field of heteroaromatic photochemistry have been generated during the course of this investigation. In the interest of brevity, only some of the most promising ones will be presented here.

1. Although strong evidence has been adduced for the formation of Dewar furan in the matrix photolysis of furan, we would like to have additional proof of its existence, preferably from trapping experiments similar to those carried out for thiophene. If Dewar furan is trapped during the solution phase photolysis of furan, its DAa must be formed in yields much lower than those of the principal adducts already identified in this system. By contrast, in the matrix, Dewar furan is a major primary photolysis product, in comparison to the cyclopropenyl aldehyde. These observations imply that Dewar furan is also generated in the room temperature solution phase photolysis of furan, but under these conditions its lifetime is too short for the trapping reaction to compete effectively with the other processes which consume this species.

Utilizing experimental conditions similar to those employed for the low temperature photolysis of thiophene with post-photolysis trapping, it might be possible to trap Dewar furan. The furan experiment would presumably be simpler in the sense that excess unreacted furan can function as the trapping agent for any Dewar furan produced.

2. In a similar vein, efforts should be made to trap the thioaldehyde from the solution phase photolysis of thiophene. The thioaldehyde has been assigned as a primary photoproduct formed in the matrix. It may have been undetected in solution since thioaldehydes tend to oligomerize readily. The cyclopropenyl thioaldehyde molecule has two reactive double bonds, one being contained in the cyclopropene ring and the second being the thiocarbonyl functional group itself. We have witnessed the ability of furan to successfully trap the cyclopropenyl aldehyde via a DA reaction with the cyclopropene double bond. In order to capture the cyclopropenyl thioaldehyde a dual trapping system might be tried. Mayer <u>et al.</u> [196] have reported that thioketones will react with alcohols to form acetals, eliminating H_2S in the process. Since ethanol is transparent at 229 nm it might be feasible to irradiate

$$>C{=}S \xrightarrow{2C_2H_5OH} >C(OC_2H_5)_2 + H_2S \qquad (42)$$

thiophene in mixtures of furan and ethanol and trap cyclopropenyl thioaldehyde in the form of a stable derivative.

3. Regarding the possible involvement of these Dewar and cyclopropenyl structures as intermediates in the photoisomerizations

labelled precursors might be worthwhile pursuing. For instance, the matrix photolysis of both 2- and 3-monodeuterothiophene should be examined. Secondary photolysis at 254 nm might reveal whether the irreversibility observed for the 2→3 rearrangement process in alkyl and aryl monosubstituted thiophenes is preserved in the deuterated compounds. If the implications of our matrix studies on 2- and 3-methylthiophene are correct the thiophene rearrangements can be substituent controlled and this is probably responsible for the observed irreversibility. Thus, since the replacement of H with D does not introduce any steric or electronic effects which could alter the course of the photoreaction, the rearrangement should be reversible for the monodeuterated thiophenes.

In addition, trapping of Dewar thiophenes from the solution phase irradiation of monodeuterated thiophenes might provide insight about the possible involvement of the Dewar isomer in the photorearrangements. Determination of the position of the D atom in the DAa should be possible by NMR.

REFERENCES

1. D. Phillips, J. Lemaire, C.S. Burton and W.A. Noyes, Jr., in "Advances in Photochemistry", W.A. Noyes, Jr., G.S. Hammond and J.N. Pitts, Jr. (eds.), Wiley-Interscience, New York, Vol. 5, 1968, pp. 329-363.
2. A.A. Lamola, G.S. Hammond and F.B. Mallory, Photochem. Photobiol., 4, 259 (1965).
3. R.M. Hochstrasser and R.B. Weisman, in "Radiationless Transitions", S.H. Lin (ed.), Academic Press, 1980, pp. 353-358.
4. J.M. Blair and D. Bryce-Smith, Proc. Chem. Soc., London, 287 (1957).
5. E.E. van Tamelen and S.P. Pappas, J. Am. Chem. Soc., 84, 3789 (1962).
6. E.E. van Tamelen and S.P. Pappas, ibid., 85, 3297 (1963).
7. H.G. Viehe, R. Merényi, J.F.M. Oth, J.R. Senders and P. Valange, Angew. Chem. Int. Ed., 3, 755 (1964).
8. J. Dewar, Proc. Roy. Soc. Edinburgh, 64, 1866/67.
9. A. Ladenburg, Ber. dtsch. chem. Ges., 2, 140 (1869); 5, 322 (1872).
10. E. Hückel, Z. Electrochem., 45, 752, 760 (1937).
11. D. Bryce-Smith, J. Chem. Soc, 1603 (1956).
12. H.F.J. Angus, J.M. Blair and D. Bryce-Smith, ibid., 2003 (1960).

13. K.E. Wilzbach, J.S. Ritscher and L. Kaplan, J. Am. Chem. Soc., 89, 1031 (1967).

14. L. Kaplan and K.E. Wilzbach, ibid., 90, 3291 (1968).

15. L. Kaplan, D.J. Rausch and K.E. Wilzbach, ibid., 94, 8638 (1972).

16. H.R. Ward and J.S. Wishnok, ibid., 90, 1086 (1968).

17. D. Bryce-Smith, A. Gilbert and D.A. Robinson, Angew. Chem. Int. Ed., 10, 745 (1971).

18. K.E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 86, 2307 (1964).

19. A.W. Burgstahler and P.L. Chien, ibid., 86, 2940 (1964).

20. L. Kaplan, K.E. Wilzbach, W.G. Brown and S.S. Yang, ibid., 87, 675 (1965).

21. K.E. Wilzbach and L. Kaplan, ibid., 87, 4004 (1965).

22. M.G. Barlow, R.N. Haszeldine and R. Hubbard, J. Chem. Soc. C, 1232 (1970).

23. D. Bryce-Smith and A. Gilbert, Tetrahedron, 32, 1309 (1976); 33, 2459 (1977).

24. D. Bryce-Smith and A. Gilbert, in "Rearrangements in Ground and Excited States", P. de Mayo (ed.), Academic Press, New York, Vol. 5, 1980, pp. 349-379.

25. G. Jones, II and S.W. Chiang, Tetrahedron, 37, 3397 (1981); G. Jones, II and W.G. Becker, J. Am. Chem. Soc., 103, 4630 (1981); J.E. Kent, P.J. Harman and M.F. O'Dwyer, J. Phys. Chem., 85, 2726 (1981); P.J. Harman, J.E. Kent, M.F. O'Dwyer and D.W.T. Griffith, ibid., 85, 2731 (1981).

26. C.A. Renner, T.J. Katz, J. Pouliquen, N.J. Turro and W.H.

Waddell, J. Am. Chem. Soc., 97, 2568 (1975).

27. B. Sztuba and E. Ratajczak, J.C.S. Perkin II, 823 (1982).
28. J.L.G. [illegible]uijker and C.A.G.O. Varma, Chem. Phys. Lett., 97, 513 (1983).
29. D.L. Miller and M.L. Gross, J. Am. Chem. Soc., 105, 4239 (1983).
30. A. Lablache-Combier, in "Photochemistry of Heterocyclic Compounds", O. Buchardt (ed.), Wiley-Interscience, New York, 1976, Ch. 3 and 4, pp. 123-206 and pp. 207-287.
31. A. Padwa, in "Rearrangements in Ground and Excited States", P. de Mayo (ed.), Vol. 3, Academic Press, New York, 1980, pp. 501-547.
32. Y. Kobayashi and I. Kumadaki, in "Advances in Heterocyclic Chemistry", A.R. Katritsky (ed.), Academic Press, New York, Vol. 31, 1982, pp. 169-206.
33. R. Srinivasan, J. Am. Chem. Soc., 89, 1758 (1967).
34. R. Srinivasan, Pure Appl. Chem., 16, 65 (1968).
35. R. Srinivasan, J. Am. Chem. Soc., 89, 4812 (1967).
36. H. Hiraoka and R. Srinivasan, J. Chem. Phys., 48, 2185 (1968).
37. H. Hiraoka and R. Srinivasan, J. Am. Chem. Soc., 90, 2720 (1968).
38. S. Boué and R. Srinivasan, ibid., 92, 1824 (1970).
39. H. Hiraoka, J. Phys. Chem., 74, 574 (1970).
40. K.B. Wiberg and W.J. Bartley, J. Am. Chem. Soc., 82, 6375 (1960).
41. E.E. van Tamelen and T.H. Whitesides, ibid., 90, 3894 (1968).

42. E.E. van Tamelen and T.H. Whitesides, <u>ibid.</u>, <u>93</u>, 6129 (1971).

43. A. Couture and A. Lablache-Combier, Chem. Commun., 891 (1971).

44. A. Couture, A. Delevallee, A. Lablache-Combier and C. Párkányl, Tetrahedron, <u>31</u>, 785 (1975).

45. H. Hiraoka, Chem. Commun., 1610 (1971).

46. H. Hiraoka, Tetrahedron, <u>29</u>, 2955 (1973).

47. R.D. Chambers and A.A. Lindley, J. Fluorine Chem., <u>12</u>, 337 (1978).

48. D. Wirth and D.M. Lemal, J. Am. Chem. Soc., <u>104</u>, 847 (1982).

49. K.E. Wilzbach and D.J. Rausch, <u>ibid.</u>, <u>92</u>, 2178 (1970).

50. M.G. Barlow, J.G. Dingwall and R.N. Haszeldine, J.C.S. Chem. Commun., 1580 (1970); J.C.S. Perkin I, 1542 (1973).

51. Z. Latajka, H. Ratajczak, W.J. Orville-Thomas and E. Ratajczak, J. Mol. Structure, <u>21</u>, 299 (1974).

52. M.J.S. Dewar, G.P. Ford, J.P. Ritchie and H.S. Rzepa, J. Chem. Res. Synop., 26 (1978).

53. S. Caplain and A. Lablache-Combier, Chem. Commun., 1247 (1970).

54. S. Caplain, J.-P. Catteau and A. Lablache-Combier, <u>ibid.</u>, 1475 (1970).

55. O.S. Pascual and L.Q. Tuazon, Philipp. Nucl. J., <u>1</u>, 51 (1966).

56. S. Caplain, A. Castellano, J.-P. Catteau and A. Lablache-Combier, Tetrahedron, <u>27</u>, 3541 (1971).

57. R.M. Kellogg, T.J. van Bergen and H. Wynberg, Tetrahedron Lett., 5211 (1969).

58. E. Ager, G.E. Chivers and H. Suschitzky, J.C.S. Chem. Commun., 505 (1972); J.C.S. Perkin I, 1125 (1973); J. Bratt and H.

Suschitzky, J.C.S. Chem. Commun., 949 (1972).

59. E. Mathias and J. Heicklen, Mol. Photochem., 4, 483 (1972).

60. O.L. Chapman, C.L. McIntosh and J. Pacansky, J. Am. Chem. Soc., 95, 614 (1973).

61. Y. Kobayashi, A. Ohsawa and Y. Iitaka, Tetrahedron Lett., 2643 (1973); Y. Kobayashi, A. Ohsawa, M. Baba, T. Sato and I. Kumadaki, Chem. Pharm. Bull., 24, 2219 (1976); Y. Kobayashi and A. Ohsawa, ibid., 24, 2225 (1976).

62. R.D. Chambers, R. Middleton and R.P. Corbally, J.C.S. Chem. Commun., 731 (1975); R.D. Chambers and R. Middleton, J.C.S. Perkin I, 1500 (1977).

63. R.D. Chambers and R. Middleton, J.C.S. Chem. Commun., 154 (1977).

64. K. Takagi and Y. Ogata, J.C.S. Perkin II, 1148 (1977).

65. Y. Ogata and K. Takagi, J. Org. Chem., 43, 944 (1978).

66. P.B.J. Driessen and H. Hogeveen, J. Organomet. Chem., 156, 265 (1978).

67. T.A. Molenaar-Langeveld, N.P.E. Vermeulen, N.M.M. Nibbering, R.P. Morgan, A.G. Brenton, J.H. Beynon, D.K.S. Sharma and K.R. Jennings, Org. Mass Spec., 14, 524 (1979).

68. E. Ratajczak, B. Sztuba and D. Price, J. Photochem., 13, 233 (1980).

69. D. Price and E. Ratajczak, J.C.S. Chem. Commun., 902 (1976).

70. I.A. Jacobson, Jr., H.H. Heady and G.V. Dinneen, J. Phys. Chem., 62, 1563 (1958); I.A. Jacobson, Jr. and H.B. Jensen, ibid., 66, 1245 (1962); 68, 3068 (1964).

71. L.A. Pine, Dissertation Abstr., 24, 522 (1963); J.M. Patterson and L.T. Burka, J. Am. Chem. Soc., 88, 3671 (1966).

72. J.M. Patterson and S. Soedigdo, J. Org. Chem., 33, 2057 (1968).

73. J.M. Patterson and S. Soedigdo, ibid., 32, 2969 (1967); J.M. Patterson, L.T. Burka and M.R. Boyd, ibid., 33, 4033 (1968).

74. J.M. Patterson and L.T. Burka, Tetrahedron Lett., 2215 (1969).

75. H. Hiraoka, Chem. Commun., 1306 (1970).

76. H. Hiraoka, ibid., 1610 (1971).

77. R. Hunt and S.T. Reid, ibid., 1576 (1970); R. Hunt and S.T. Reid, J.C.S. Perkin I, 2527 (1972).

78. O.L. Chapman, P.G. Cleveland and E.D. Hoganson, Chem. Commun., 101 (1966).

79. G.E.A. Coombes, J.M. Grady and S.T. Reid, Tetrahedron, 23, 1341 (1967).

80. E.C. Wu and J. Heicklen, J. Am. Chem. Soc., 93, 3432 (1971).

81. E.C. Wu and J. Heicklen, Can. J. Chem., 50, 1678 (1972).

82. A.B. Callear and H.K. Lee, Trans. Faraday Soc., 64, 308 (1968).

83. J.A. Barltrop, A.C. Day, P.D. Moxon and R.R. Ward, J.C.S. Chem. Commun, 786 (1975).

84. J.A. Barltrop, A.C. Day and R.R. Ward, ibid., 131 (1978).

85. J.A. Barltrop and A.C. Day, ibid., 177 (1975).

86. Y. Kobayashi, I. Kumadaki, A. Ohsawa and A. Ando, J. Am. Chem. Soc., 99, 7350 (1977); Y. Kobayashi, A. Ando and I. Kumadaki, J.C.S. Chem. Commun., 509 (1978); Y. Kobayashi, A. Ando, K. Kawada and I. Kumadaki, J. Org. Chem., 45, 2966 (1980); Y. Kobayashi, A. Ando, Y. Sugisawa and I. Kumadaki, Heterocycles,

19, 151 (1982).

87. Y. Kobayashi, A. Ando, K. Kawada and I. Kumadaki, J. Org. Chem., 45, 2968 (1980).

88. H. Wynberg and H. van Driel, J. Am. Chem. Soc., 87, 3998 (1965).

89. H. Wynberg and H. van Driel, J.C.S. Chem. Commun., 203 (1966).

90. H. Wynberg and A.P. Wolf, J. Am. Chem. Soc., 85, 3308 (1963).

91. H. Wynberg, R.M. Kellogg, H. van Driel and G.E. Beekhuis, ibid., 88, 5047 (1966).

92. H. Wynberg, H. van Driel, R.M. Kellogg and J. Buter, ibid., 89, 3487 (1967).

93. R.M. Kellogg and H. Wynberg, ibid., 89, 3495 (1967).

94. H. Wynberg, G.E. Beekhuis, H. van Driel and R.M. Kellogg, ibid., 89, 3498 (1967).

95. H. Wynberg, R.M. Kellogg, H. van Driel and G.E. Beekhuis, ibid., 89, 3501 (1967).

96. R.M. Kellogg, J.K. Dik, H. van Driel and H. Wynberg, J. Org. Chem., 35, 2737 (1970).

97. J.G. Calvert and J.N. Pitts, Jr., "Photochemistry", Wiley and Sons, Inc., New York, 1966, Chapter 7, pp. 686-814.

98. J.F. Rabek, "Experimental Methods in Photochemistry and Photophysics", Part 1, Wiley-Interscience, New York, 1982, Chapter 3, pp. 34-140.

99. R.M. Kellogg and H. Wynberg, Tetrahedron Lett., 5895 (1968).

100. A. Couture and A. Lablache-Combier, J.C.S. Chem. Commun., 524 (1969).

101. A. Couture and A. Lablache-Combier, Tetrahedron, 27, 1059 (1971).

102. H.A. Wiebe and J. Heicklen, Can. J. Chem., 47, 2965 (1969).

103. S. Braslavsky, H.A. Wiebe and J. Heicklen, Center for Air Environment Studies, Pennsylvania State University, Publication No. 164-170, 1970.

104. H.A. Wiebe, S. Braslavsky and J. Heicklen, Can. J. Chem., 50, 2721 (1972).

105. Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Sekine and H. Mochizuki, Chem. Pharm. Bull., 23, 2773 (1975).

106. Y. Kobayashi, I. Kumadaki, A. Ohsawa and Y. Sekine, Tetrahedron Lett., 1639 (1975).

107. Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Sekine and A. Ando, Heterocycles, 6, 1587 (1977).

108. Y. Kobayashi, I. Kumadaki, A. Ohsawa and Y. Sekine, Tetrahedron Lett., 2841 (1974).

109. N. Kikutani, Y. Iitaka, Y. Kobayashi, I. Kumadaki, A. Ohsawa and Y. Sekine, Acta Cryst., B31, 1478 (1975).

110. Y. Kobayashi, A. Ando, K. Kawada, A. Ohsawa and I. Kumadaki, J. Org. Chem., 45, 2962 (1980); Y. Kobayashi, A. Ando, K. Kawada and I. Kumadaki, ibid., 45, 2966 (1980).

111. Y. Kobayashi, K. Kawada, A. Ando and I. Kumadaki, Heterocycles, 20, 174 (1983); Tetrahedron Lett., 1917 (1984).

112. B. Verkoczy, A.G. Sherwood, I. Safarik and O.P. Strausz, Can. J. Chem., 61, 2268 (1983).

113. Y. Kobayashi and I. Kumadaki, Acc. Chem. Res., 14, 76 (1981).

114. D.M. Lemal and L.H. Dunlap, Jr., J. Am. Chem. Soc., 94, 6564 (1972).

115. A. Greenberg, J.F. Liebman and D. Van Vechten, Tetrahedron, 36, 1161 (1980).

116. D.C. Neckers, J.H. Dopper and H. Wynberg, J. Org. Chem., 35, 1582 (1970).

117. H. Wynberg, Acc. Chem. Res., 4, 65 (1971).

118. F. De Jong, H.J.M. Sinnige and M.J. Janssen, Org. Mass Spec., 3, 1539 (1970).

119. A.S. Siegel, Tetrahedron Lett., 4113 (1970).

120. R.G. Cooks, I. Howe, [illegible]m and D.H. Williams, J. Am. Chem. Soc., 90, 4064 (1968); [illegible] Cooks and S.L. Bernasek, ibid., 92, 2129 (1970).

121. T.A. Elwood, P.F. Rogerson and M.M. Bursey, J. Org. Chem., 34, 1138 (1969).

122. J.H. Bowie, R.G. Cooks, S.-O. Lawesson and C. Nolde, J. Chem. Soc. (B), 616 (1967); J.H. Bowie, B.K. Simons and S.-O. Lawesson, Rev. Pure Appl. Chem., 19, 61 (1969).

123. W.D. Weringa, H.J.M. Sinnige and M.J. Janssen, Org. Mass Spec., 5, 1399 (1971).

124. M.E. Rennekamp, W.O. Perry and R.G. Cooks, J. Am. Chem. Soc., 94, 4985 (1972).

125. J.A. Barltrop, A.C. Day and E. Irving, J.C.S. Chem. Commun., 881 (19[illegible]).

126. J.A. Barltrop, A.C. Day and E. Irving, ibid., 966 (1979).

127. G. Di Lonardo, G. Galloni, A. Trombetti and C. Zauli, J.C.S.

Faraday Trans. II, 68, 2009 (1972).

128. R. Abu-Eittah and R. Hilal, Bull. Chem Soc. Jpn., 49, 2158 (1976).

129. R. Hilal and R. Abu-Eittah, Tetrahedron, 34, 785 (1978).

130. B. Elpern and F.C. Nachod, J. Am. Chem. Soc., 72, 3379(1950).

131. V. Galasso and G. De Alti, Tetrahedron, 27, 4947 (1971).

132. G. Varasányi, L. Nyulászi, T. Veszprémi and T. Narisawa, J.C.S. Perkin II, 761 (1982).

133. M. Rico, J.M. Orza and J. Morcillo, Spectrochim. Acta, 21, 689 (1965).

134. E.F. Ullman and B. Singh, J. Am. Chem. Soc., 88, 1844 (1966).

135. E.F. Ullman and B. Singh, ibid., 89, 6910 (1967).

136. J.A. Ross, R.P. Seiders and D.M. Lemal, ibid., 98, 4325 (1976).

137. C.H. Bushweller, J.A. Ross and D.M. Lemal, ibid., 99, 629 (1977).

138. E. Vedejs, T.H. Eberlein and D.L. Varie, ibid., 104, 1445 (1982).

139. J.E. Baldwin and R.C.G. Lopez, J.C.S. Chem. Commun., 10[illegible] (1982).

140. E. Vedejs and D.A. Perry, J. Am. Chem. Soc., 105, 1683 (1983).

141. R.E. Davis, J. Org. Chem., 23, 1767 (1958).

142. V. Leon, R.A. Bolivar, M.L. Tasayco, R. Gonzalez and C. Rivas, Org. Magnetic Res., 21, 470 (1983).

143. S.R. Shrader, "Introductory Mass Spectrometry", Allyn and Bacon, Boston, 1971, pp. 70-77.

144. R.W. LaRochelle and B.M. Trost, J.C.S. Chem. Commun., 1353

(1970).

145. R.R. Fraser, Can. J. Chem., 40, 78 (1962).

146. K. Tori, M. Ueyama, T. Tsuji, H. Matsumura, H. Tanida, H. Iwamura, K. Kushida, T. Nishida and S. Satoh, Tetrahedron Lett., 327 (1970).

147. N.F. Chamberlain, "The Practice of NMR Spectroscopy", Plenum Press, New York, 1974, p. 300.

148. D. Dolphin and A. Wick, "A Tabulation of Infrared Spectral Data", Wiley-Interscience, New York, 1977.

149. H. Günther, "NMR Spectroscopy - An Introduction", Wiley and Sons, New York, 1980, p. 384.

150. C.J. Pouchert, "The Aldrich Library of Infrared Spectra", 1970, p. 34G.

151. F.W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden and Son, London, 1978, pp. 27-29, 37-38.

152. "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems", in Methods in Stereochemical Analysis, Vol. 1, A.P. Marchand (ed.), Verlag Chemie, Deerfield Beach, 1982, pp. 22-27.

153. J.B. Stothers, C.T. Tan and K.C. Teo, Can. J. Chem., 51, 2893 (1973).

154. L.J. Bellamy, "The Infrared Spectra of Complex Molecules", Vol. 1, 3rd ed., Chapman and Hall, London, 1975.

155. S. Pinchas and I. Laulicht, "Infrared Spectra of Labelled Compounds", Academic Press, London, 1971.

156. R.W. Mitchell, E.A. Dorko and J.A. Merritt, J. Mol. Spectrosc.,

26, 197 (1968).

157. O.L. Chapman, Pure Appl. Chem., 40, 511 (1974).

158. E. Bjarnov, Z. Naturforsch., 34a, 1269 (1979).

159. M. Torres, A. Clement and O.P. Strausz, J. Org. Chem., 45, 2271 (1980).

160. L.H. Jones, M. Goldblatt, R.S. McDowell, D.E. Armstrong, J.F. Scott, J.G. Williamson and K.N. Rao, J. Mol. Spectrosc., 23, 9 (1967).

161. L.J. Bellamy, "Advances in Infrared Group Frequencies", Methuen, London, 1968.

162. J. Chouteau, G. Davidovics, M. Bertrand, J. Le Gras, J. Figarella and M. Santelli, B.S.C. France, 2562 (1964).

163. T. Tsuchiya, H. Arai and H. Igeta, J.C.S. Chem. Commun., 550 (1972); Tetrahedron, 29, 2747 (1973).

164. I.E. Dolgii, G.P. Okonnishnikova and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 28, 765 (1979).

165. [illegible] Popov, I.P. Yakovlev, E.D. Lubuzh and G.A. Kogan, J. Appl. Spectrosc., 8, 287 (1968).

166. G. Seybold and C. Heibl, Chem. Ber., 110, 1225 (1977).

167. M. Torres, I. Safarik, A. Clement, R.K. Gosavi and O.P. Strausz, Can. J. Chem., 62, 2777 (1984).

168. D.W.T. Griffith, J.E. Kent and M.F. O'Dwyer, Aust. J. Chem., 28, 1397 (1975).

169. P. de Mayo, Acc. Chem. Res., 9, 52 (1976).

170. R.P. Steer, Rev. Chem. Intermed., 4, 1 (1981).

171. J.I. Brauman, L.E. Ellis, E.E. van Tamelen, J. Am. Chem. Soc.,

88, 846 (1966).

172. E.E. van Tamelen, J.I. Brauman and L.E. Ellis, ibid., 93, 6145 (1971).

173. J.E. Baldwin and A.H. Andrist, ibid., 93, 3289 (1971).

174. C. Lewis, W.R. Ware, L.J. Doemeny and T.L. Nemzek, Rev. Sci. Instrum., 44, 107 (1973).

175. J.N. Demas, "Excited State Lifetime Measurements", Academic Press, New York, 1983.

176. D.R. James, D.R.M. Demmer, R.E. Verrall and R.P. Steer, Rev. Sci. Instrum., 54, 1121 (1983).

177. J.L. Melles and H.J. Backer, Recueil, 72, 314 (1953).

178. A. Chrzaszczewska, Chem. Abstr., 20, 1078 (1926).

179. E. Campaigne, J. Am. Chem. Soc., 66, 684 (1944).

180. O. Hinsberg, Ber., 43, 901 (1910).

181. H.J. Backer, C.C. Bolt and W. Stevens, Rec. Trav. Chim., 56, 1063 (1937).

182. A. Stock, Ber., 43, 414 (1910).

183. T.J. Batterham, "NMR Spectra of Simple Heterocycles", Wiley-Interscience, New York, 1973, pp. 429-446.

184. H.D. Hartough, "Thiophene and Its Derivatives", in The Chemistry of Heterocyclic Compounds, Vol. 3, A. Weissberger (ed.), Wiley-Interscience, 1952, p. 501.

185. B. Bak, D. Christensen, J. Rastrup-Andersen and E. Tannenbaum, J. Chem. Phys., 25, 892 (1956).

186. D.D. Perrin, W.L.F. Armarego and D.R. Perrin, "Purification of Laboratory Chemicals", 2nd ed., Pergamon Press, Oxford, 1980.

187. I. Norman and G. Porter, Nature, 174, 508 (1954).

188. E. Whittle, D.A. Dows and G.C. Pimentel, J. Chem. Phys., 22, 1943 (1954).

189. J.S. Ogden and J.J. Turner, Chem. Br., 7, 186 (1971).

190. L. Andrews, Ann. Rev. Phys. Chem., 22, 109 (1971).

191. G.C. Pimentel, Angew. Chem. Int. Ed., 14, 199 (1975).

192. I.R. Dunkin, Chem. Soc. Rev., 9, 1 (1980).

193. "Matrix Isolation Spectroscopy", A.J. Barnes, W.J. Orville-Thomas, A. Müller and R. Gaufres (eds.), D. Reidel, Dordrecht, Holland, 1981.

194. R.N. Warrener, I.G. Pitt and R.A. Russell, J.C.S. Chem. Commun., 1464 (1984).

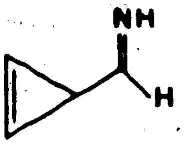
195. I.G. Pitt, R.A. Russell and R.N. Warrene[illegible], 1466 (1984).

196. R. Mayer, J. Morgenstern and J. Fabian, Angew. Chem. Int. Ed., 3, 277 (1964).

Appendix I - Matrix Photolysis of Pyrrole

We have made a preliminary investigation of the matrix photolysis (214 nm) of pyrrole. At least two new photoproducts were generated. One of these species can be destroyed by extended photolysis (~24 h), even at reasonably long wavelengths ($\lambda \gtrsim 305$ nm), and shows a number of IR absorptions. Among its prominent absorptions are peaks located near 795 and 825 cm^{-1}. When this species was destroyed by secondary photolysis (254 nm) the IR absorptions corresponding to the parent pyrrole simultaneously increased.

This behaviour is similar to that already described for the Dewar species found in the matrix studies of furan, thiophene and cyclopentadiene. Further investigations of the photolysis of matrix isolated pyrrole, including attempts to identify cyclopropenyl imine, 100, are currently in progress.



100

Appendix II - NMR Identification of Bicyclopentene

The Dewar isomer of cyclopentadiene, bicyclo[2.1.0]pent-2-ene **99**, has now been successfully identified by high field ^{1}H NMR following its generation by the UV photolysis of matrix isolated cyclopentadiene. The NMR spectrum of **99**, recorded at ~ -45°C, is given in Figure 55. The NMR data obtained for **99** are summarized in Table 27, along with the 100 MHz ^{1}H NMR data previously described by van Tamelen et al. [171]. These results confirm the assignment of bicyclopentene in our low temperature matrix, thereby lending further support to the matrix IR data for the Dewar isomers of furan and thiophene.

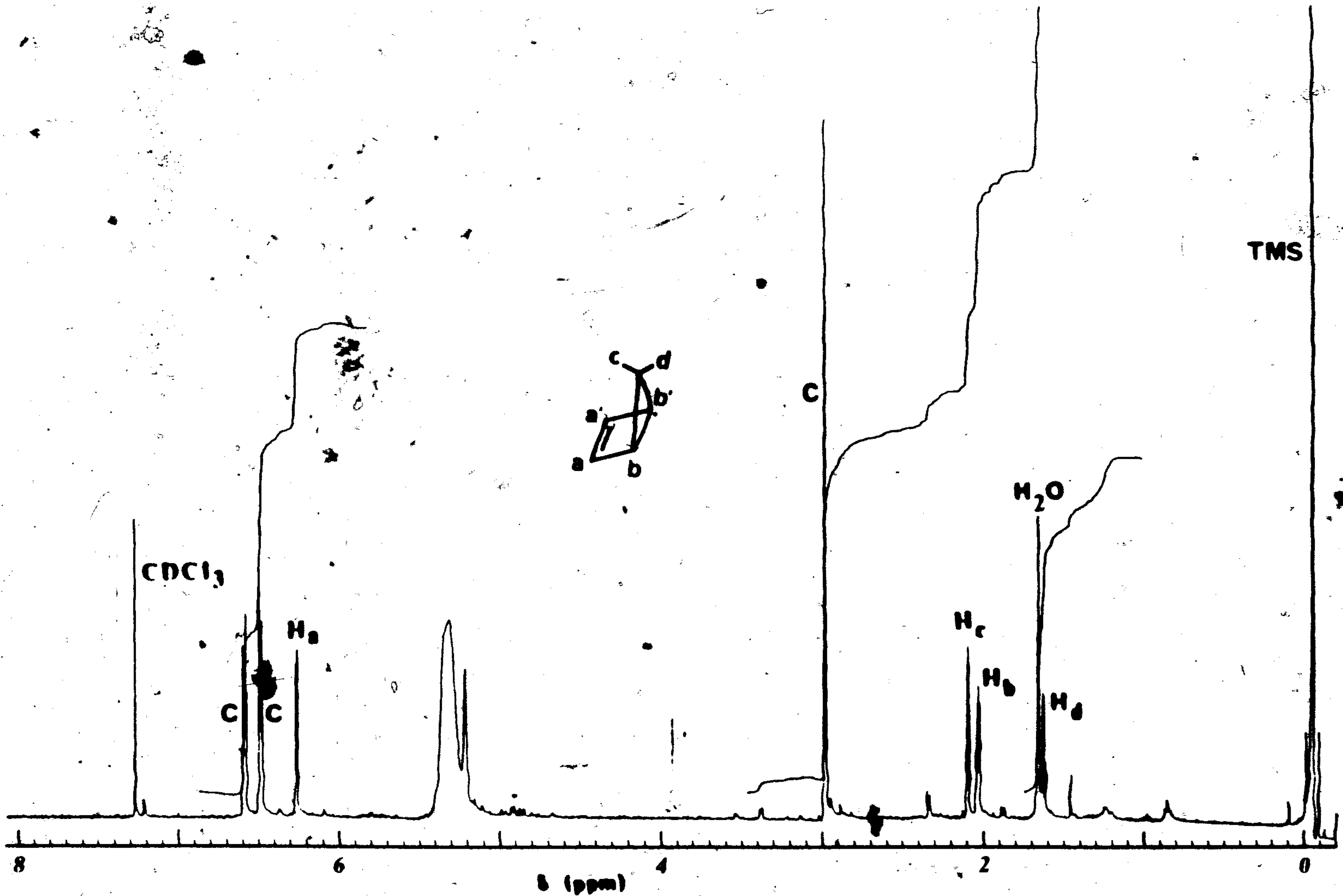


Figure 55. 400 MHz ^{1}H NMR spectrum of 99, recorded at 250 K (C-cyclopentadiene absorptions).

TABLE 27

400 MHz ^1H NMR Data for 99

	Chemical Shifts δ_H (ppm)	Integration	Assignment
This work[a]	6.26 d	2	a,a'[c]
	2.09 m	1	c[e]
	2.04 m	2	b,b'[c]
	1.64 m	1	d[e]
Van Tamelen *et al.*[b]	6.2 d	2	a,a'[c]
	2.0 m	n.d.[d]	n.d.[d]
	1.7 m	n.d.[d]	n.d.[d]

[a] 400 MHz ^1H NMR recorded in $CDCl_3$ at ~ -45°C.

[b] 100 MHz ^1H NMR recorded in CCl_4 at room temperature. Ref. [171].

[c] The prime notation is introduced to account for the magnetic nonequivalence within each set of chemically equivalent atoms.

[d] Not described.

[e] Assignments based upon the results of selective proton decoupling experiments.

TABLE

400 MHz ^{1}H NMR

	Chemical Shift δ_H (ppm)
This work[a]	6.26 d
	2.09 m
	2.04 m
	1.64 m
Van Tamelen *et al.*[b]	6.2 d
	2.0 m
	1.7 m

D