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THERMOLYSIS OF 4-ALKYLIDENE-1-PYRAZOLINES

University — Université
UNIVERSITY OF ALBERTA

Degree for which thesis was presented — Grade pour lequel cette thèse fut présentée
Ph. D.

Year this degree conferred — Année d'obtention de ce grade
1980

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THE UNIVERSITY OF ALBERTA

THERMOLYSIS OF 4-ALKYLIDENE-1-PYRAZOLINES

by

MOON HO CHANG

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, 1980

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 THERMOLYSIS OF 4-ALKYLIDENE-1-PYRAZOLINES submitted by MOON HO CHANG in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

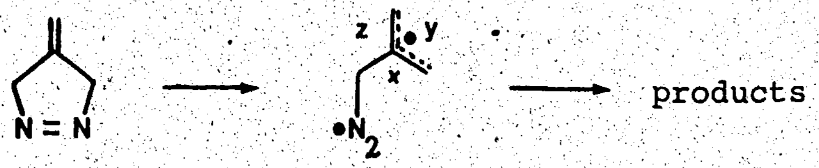
The gas phase thermolysis of seven different 4-alkylidene-1-pyrazolines was found to proceed at a convenient rate between 160 and 185° with 70-92% conversion into alkylidenecyclopropanes. The reaction was always accompanied by tautomerism of the pyrazolines. Reproducible first-order kinetics were observed after repeated thermolysis of the pyrazolines in a stainless steel reaction vessel. The activation parameters were then determined.

The deuterated derivatives of 4-methylene-1-pyrazoline (I), I-6,6-d_2 and I-3,3,5,5-d_4, have been synthesized and characterized. The ^{1}Hmr, ^{2}Hmr, infrared and mass spectra all indicated better than 95% D incorporation in the appropriate positions.

The secondary deuterium kinetic isotope effect has been studied in the thermolysis of I and its deuterated derivatives at 170.0°. The observed values of $\delta\Delta G^{\ddagger}$ per deuterium *via* a concerted two carbon-nitrogen bond cleavage process (62-71 cal mol^{-1}) and *via* a stepwise one C-N bond cleavage pathway (142 cal mol^{-1}; k_H/k_D = 1.38) are not within the frequently observed value of 90-120 cal mol^{-1}. However, the calculated values from ir frequencies (112 cal mol^{-1}; k_H/k_D = 1.29) are best interpreted in terms of the one-bond cleavage mechanism

in the rate determining process.

The product distributions in the thermolysis of I, I-6,6-d_2, I-3,3-d_2, I-3,3,5,5-d_4 and I-3,3,6,6-d_4 were determined by ^{1}Hmr and ^{2}Hmr spectroscopy. The product data was then analyzed in terms of both trimethylenemethane (TMM) and diazenyl radical intermediates. Investigation of all the possible thermolysis mechanisms demonstrates that by choosing the product distribution for 4-methylene-1-pyrazoline-3-^{13}C (II) as a model for I, all of the product data including the kinetic data can only be rationalized on the basis of a diazenyl intermediate, III, wherein the ring closure modes x, y and z are involved in the product forming process and vary in their role depending upon the position of deuterium substitution. The best fit of the data was found when x-closure was as fast as z-closure. The y-closure is an electrocyclic process.



II III

The deuterated derivatives of 4-ethylidene-1-pyrazoline (IV), *E*-IV-3,3-d_2, *Z*-IV-3,3-d_2 and IV-3,3,5,5-d_4 (isotopic purities: 96% at D) were thermolyzed at 175.2° and the intermolecular secondary deuterium kinetic isotope effects were calculated as 1.19, 1.07 and 1.29 respectively

($\delta\Delta G^{\ddagger}$ per deuterium : 113 cal mol^{-1}). This clearly indicates that the C-N bond *syn* to the methyl group of the exocyclic double bond in IV is lagging in the bond-breaking process. Such results can be best interpreted in terms of competitive one-bond cleavages.

The products for IV, *E*-IV-3,3-d_2 and *Z*-IV-3,3-d_2 were determined by 400 MHz ^{1}Hmr and 54.4 MHz ^{2}Hmr spectroscopy. These products together with the previously reported products for some 4-alkylidene-1-pyrazolines, could be qualitatively accounted for in terms of the one-bond cleavage process by assuming that in the diazenyl species, back-side attack of the allylic termini (x- or z-closure) was much favored over front-side displacement, and also that the strong steric effects due to the alkyl group(s) were involved in the rate-determining as well as in the product-forming process.

ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude to Professor Robert J. Crawford, who conceived this research problem, for his invaluable guidance and counselling during the course of this work.

The author also wishes to thank Dr. H. Tokunaga whose knowledge and help towards the end of this work were greatly appreciated.

The author wishes to thank the staff of the spectroscopy laboratories for their valuable contributions.

The support of technical staff of the Department of Chemistry was greatly appreciated.

The author is indebted to Mrs. J. Jorgensen for her typing expertise.

The author would also like to thank for his parents, brothers, sister and wife for their patience and understanding during the course of this work.

Finally, the author wishes to thank the Department of Chemistry and the University of Alberta for their financial support.

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HISTORICAL

A. Thermolysis of Azo Compounds

Although acyclic and cyclic azo compounds have been studied over forty years, both in solution and in the gas phase, the mechanism of their thermolysis is still a matter of investigation (1). Some authors favor concerted two-bond cleavage (eq. 1) wherein both carbon-nitrogen bonds are completely broken in a single unit process in which the starting material and the diradical are separated by a single maximum in free energy in a schematic energy reaction coordinate, and others favor stepwise one-bond cleavage (eq. 2) which involves nonconcerted and

$$R - N = N - R' \rightarrow R\cdot \quad N_2 \quad \cdot R' \qquad \text{(eq. 1)}$$

$$R - N = N - R' \rightarrow R - N = N\cdot \; \cdot R' \rightarrow R\cdot \quad N_2 \quad \cdot R' \qquad \text{(eq. 2)}$$

stepwise breaking of a carbon-nitrogen bond to give a short-lived intermediate diazenyl radical.

Several methods, including stereochemical studies, isotopic studies, solvent viscosity effects, pressure effects, CIDNP studies, trapping of diazenyl and diyl radicals as well as a kinetic approach have been used to study the mechanisms (2-6).

In the thermolysis of unsymmetrical acyclic azoalkanes, R-N=N-R', when R is phenyl, the evidence is overwhelmingly in favor of stepwise one-bond scission (2,3), and evidence has also been provided for one-bond cleavage in highly unsymmetrical acyclic azo compounds (2,3,5). The thermolysis of symmetrical acyclic azo compounds in solution are believed to proceed *via* two-bond cleavage (1).

Most cyclic azo compounds are thought to undergo thermolysis *via* concerted two-bond cleavage. However, there has been some argument (8,9) about the thermolysis of 1-pyrazolines, since they are believed to generate independently the very important species trimethylene (7). Trimethylenemethane is also an important species that may be generated from 4-methylene-1-pyrazoline (10,11) or 7-methylene-2,3-diazanorbornene (12) *via* two-bond cleavage.

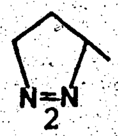
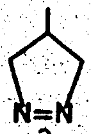
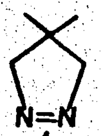
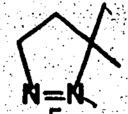
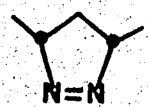
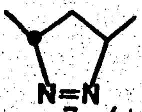
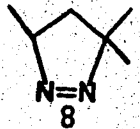
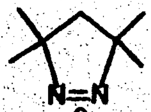
B. Thermolysis of 1-Pyrazolines

A trimethylene diradical species has been suggested as an intermediate in the isomerization of cyclopropane to propylene (13), and various 1-pyrazolines have been investigated as an alternative source of the same intermediate. Methylated 1-pyrazolines undergo thermolysis in the temperature range of 185-280°C, to produce cyclopropanes and olefins, and the kinetic parameters are shown in Table 1 (7).

Methyl substitution on carbon 3 or 5 of 1-pyrazoline produces a decrease of 1.2 ± 0.2 kcal per methyl group in the activation energy. Since the activation energies for the thermolysis of compounds 6 and 7 were about equal to

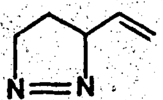
Table 1

Kinetic parameters for the thermolysis of 1-pyrazoline and methyl substituted 1-pyrazolines (7)

Compound	E_a (kcal)	log A	$\Delta S^{\ddagger}_{250}$ (e.u.)
 1	42.4 ± 0.3	15.93 ± 0.13	11.2 ± 0.6
 2	41.0 ± 0.3	15.70 ± 0.15	10.1 ± 0.7
 3	42.2 ± 0.2	15.85 ± 0.05	10.8 ± 0.3
 4	42.8 ± 0.2	14.10 ± 0.07	2.9 ± 0.3
 5	40.0 ± 0.2	15.85 ± 0.30	10.8 ± 0.2
 6 (*cis*)	40.3 ± 0.3	15.54 ± 0.11	9.4 ± 0.5
 7 (*trans*)	40.2 ± 0.3	15.67 ± 0.11	10.0 ± 0.5
 8	39.0 ± 0.4	15.42 ± 0.21	8.9 ± 0.9
 9	37.7 ± 0.4	14.49 ± 0.12	4.6 ± 0.8

that of 5, it was suggested that both carbon-nitrogen bonds were breaking simultaneously in the rate-determining step.

Crawford *et al.* (10b, 28) compared the kinetic data in the thermolysis of 3-vinyl-1-pyrazoline (10), *cis*- and *trans*-3,5-divinyl-1-pyrazoline (11 and 12) with those of 1-pyrazoline (1) and 5-ethyl-3-vinyl-1-pyrazoline (13) and concluded that both carbon-nitrogen bonds are broken in the rate determining step. The activation energies are



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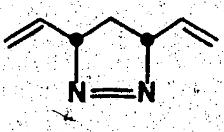

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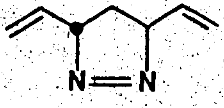

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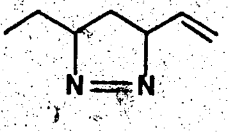
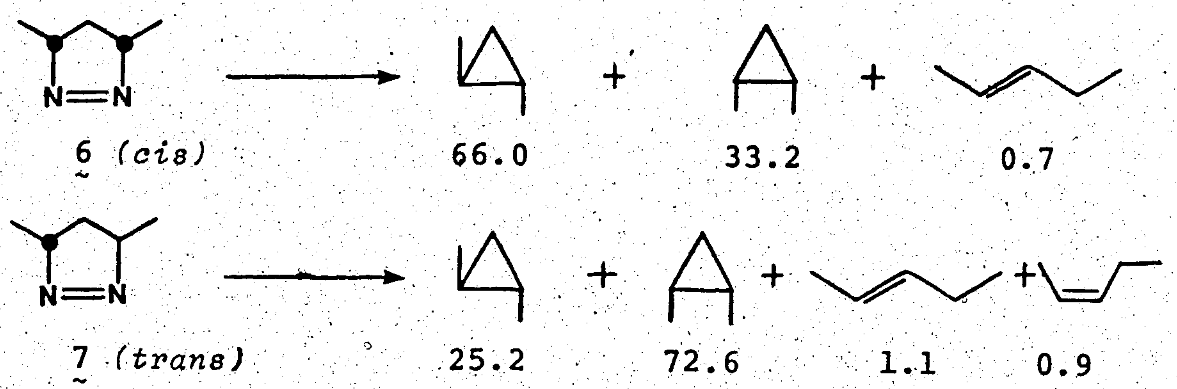


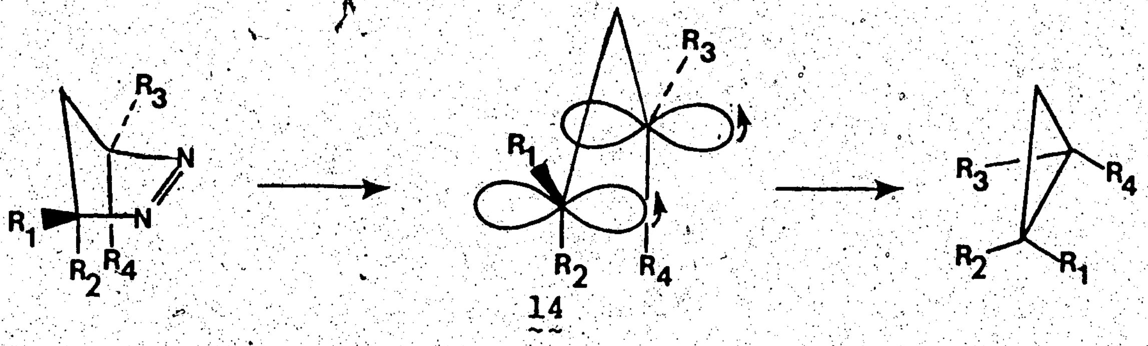
13

42.4, 32.2, 22.8, 25.7 and 30.7 kcal mol^{-1} for 1, 10, 11, 12 and 13, respectively, and a comparison of these values could indicate allylic resonance stabilization of the rate-determining transition state in addition to steric effects on the thermolysis rate by alkyl substitutions on the α-carbon.

In the case of the 1-pyrazoline substituted at carbons 3 and 5 by alkyl groups, the major product is a cyclopropane with an apparent single inversion of stereochemistry. Crawford and his co-workers (7b, 14) have investigated the thermolysis of 6 and 7, and they attributed



the single inversion process to the simultaneous breaking of both carbon-nitrogen bonds in which the extrusion of the



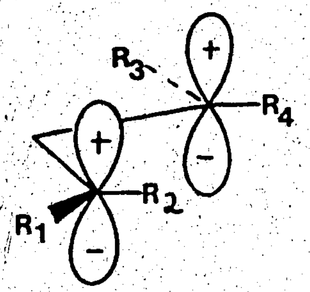
6, $R_1 = R_3 = CH_3$;

$R_2 = R_4 = H$

7, $R_1 = R_4 = CH_3$;

$R_2 = R_3 = H$

nitrogen caused a disrotation of the ring bonds, leading to a planar trimethylene diradical 14 which was then required to undergo conrotatory closure to cyclopropane. This conrotatory closure postulate received almost immediate theoretical support from some early extended Hückel molecular orbital (MO) calculations on 14 carried out by Hoffmann (15) in which he has suggested that 16 is more stable than 15. In this mechanism, the minor product would



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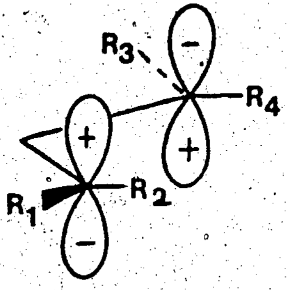
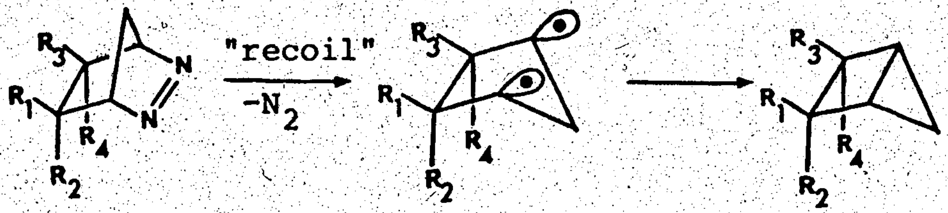


16

arise from the disrotatory closure of the diradical 14, and would lead either to double retention or double inversion of stereochemistry. Since the diradical 14 is planar, one expects to generate racemic products. However, the analysis of the optical purity of *trans*-1,2-dimethylcyclopropanes produced by the thermolysis of (*S*,*S*)-*trans*-3,5-dimethyl-1-pyrazoline (7) indicates an excess of double inversion as shown in Table 2 (7e). This observation can be rationalized by assuming that 6% of the product arises from a "pyramidal" diradical 19 which



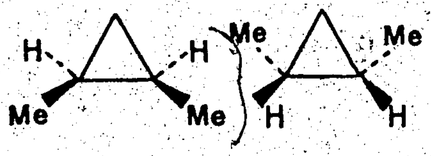
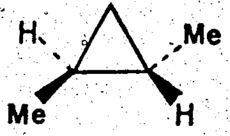
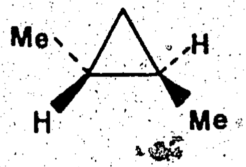
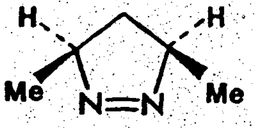
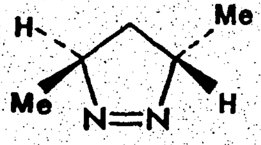
18

19

has already been suggested by Allred and Smith (4b) to explain the double inversion observed during the decomposition of bicyclic azo compounds 18 by postulating that the α-carbon atoms in 18 are forced to "recoil" into

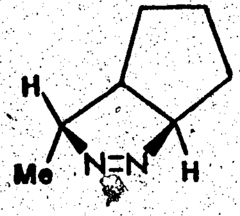
Table 2

Stereochemical analysis of the cyclopropane products in the thermolysis of 3,5-dimethyl-1-pyrazolines (**7**e)

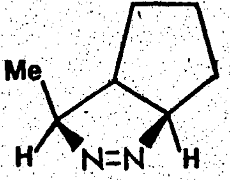
Starting material	Product, %		
	 **17***c*	 (*S*,*S*)-**17***t*	 (*R*,*R*)-**17***t*
 **6**	33	66	
 (*S*,*S*)-**7**	73	10	16

inverted configuration (**19**) by the departing nitrogen atoms.

In order to test Crawford's mechanism, Condit and Bergman (16) studied the decomposition of bicyclo azo compounds **20***t* and **20***c*. In these molecules, a three-carbon

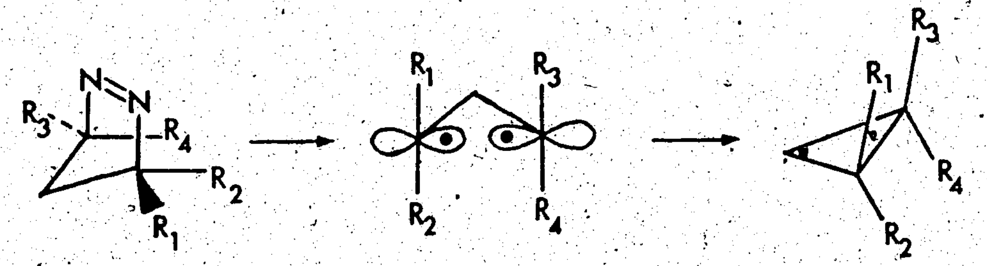


20*t*



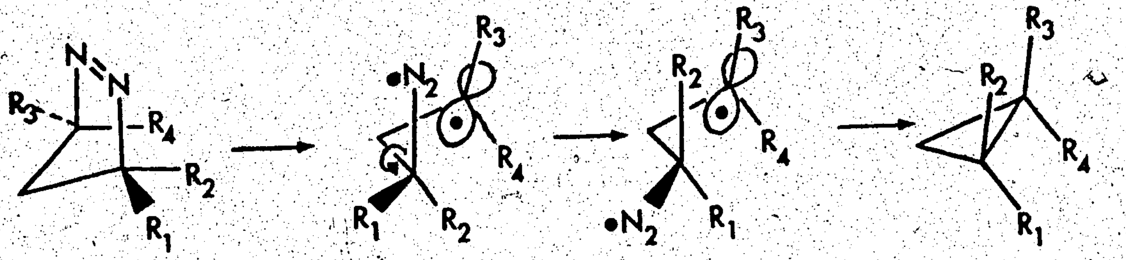
20*c*

bridge connects carbons 3 and 4, and should prevent the formation of a planar diradical. One might expect the simple extrusion of nitrogen, leading to the "face to face" diradical 21 by a disrotation of the ring bonds, to be the easiest path for the decomposition. Since the



21

diradical 21 can close again without activation energy (17), the major product should exhibit a double retention of configuration. However, a predominant single inversion of configuration was still observed. This result led Condit and Bergman to propose a new mechanism which is an extension of that suggested by Roth and Martin (4a). They suggested the slow step to be the breaking of only one carbon-nitrogen bond, leading to the diradical 22, followed



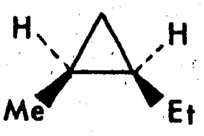
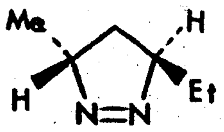
22

by the backside attack of the radical center at the remaining nitrogen-bound carbon 22 to produce a cyclopropane with an inverted stereochemistry as the major product. In the case of 1-pyrazolines, this mechanism can also explain a predominant single inversion of configuration (see Table 2). Later, other experimental data supported this two step mechanism (18).

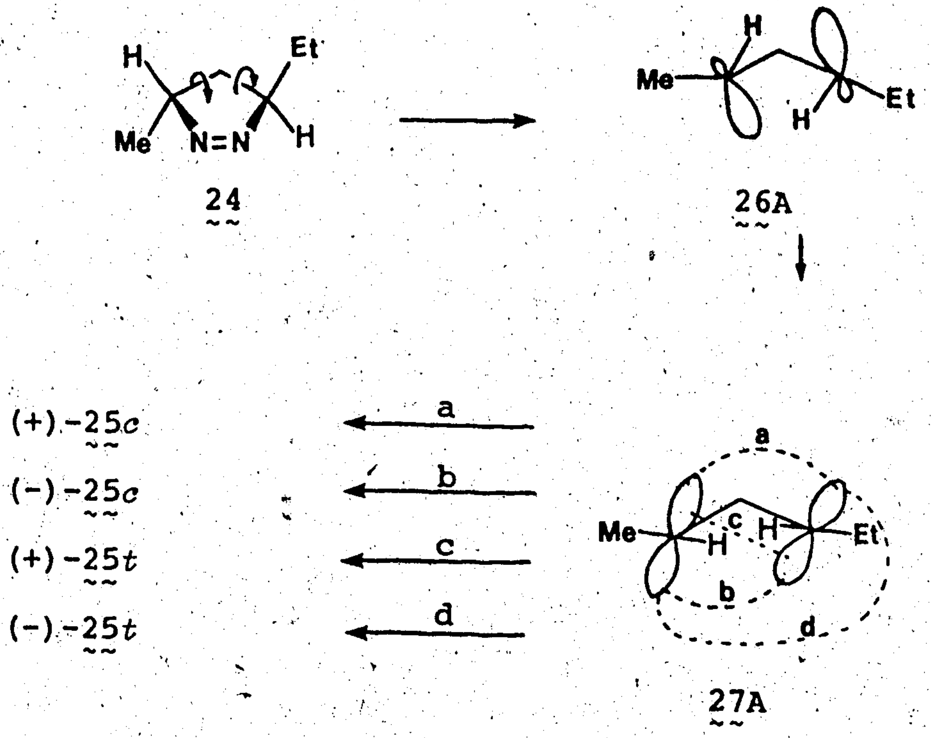
Recently, Clarke, Wendling and Bergman (8) analyzed the yield of each cyclopropane enantiomer formed from *cis*- and *trans*-3-ethyl-5-methyl-1-pyrazoline (**23** and **24**) and the results of this study are summarized in Table 3. The

Table 3

Yield of each cyclopropane enantiomer in the thermolysis of (+)-(3*R*,5*S*)- and (+)-(3*R*,5*R*)-3-ethyl-5-methyl-1-pyrazoline at 292°C (8).

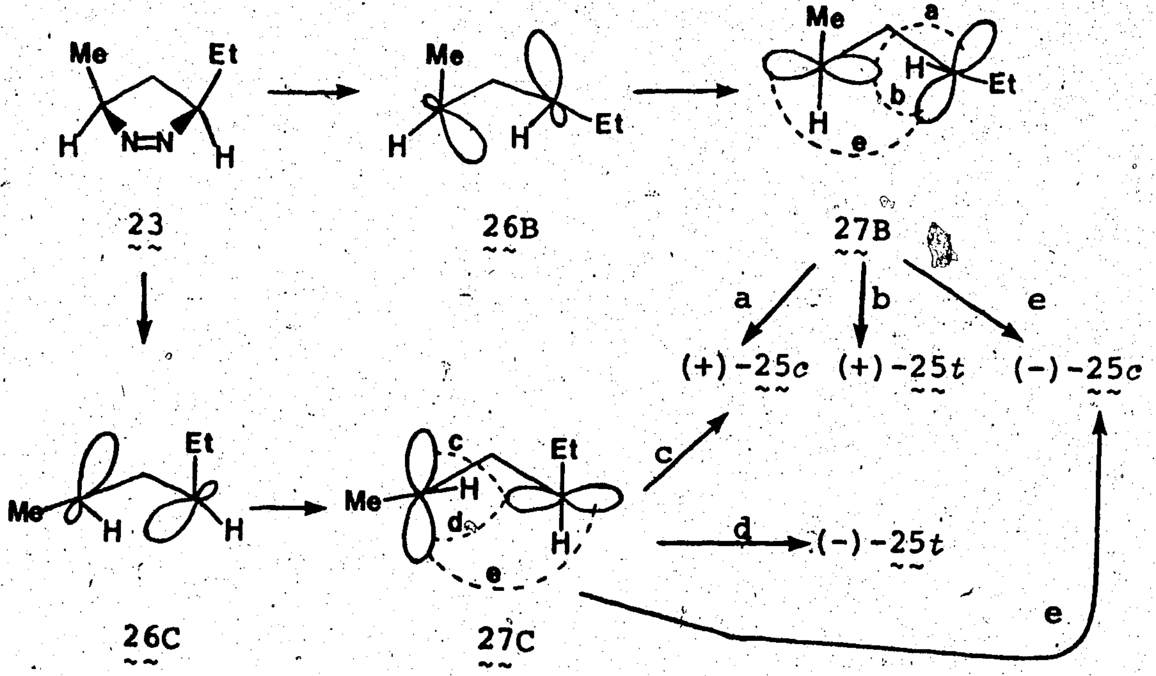
Starting material	Product, %			
	 (-)-**25***t*	 (+)-**25***t*	 (-)-**25***c*	 (+)-**25***c*
 **23**	28 methyl rotation	38 ethyl rotation	10 double inversion	22 double retention
 **24**	10 double retention	17 double inversion	35 ethyl rotation	36 methyl rotation

trans-pyrazoline leads to *trans*-cyclopropane with an excess of double inversion, and to nearly racemic *cis*-cyclopropane as a major product. On the other hand, the *cis*-pyrazoline leads to *cis*-cyclopropane with an excess of double retention, and to *trans*-cyclopropane as a major product with a predominant "ethyl rotation". These startling results led the authors to conclude that the product distribution cannot be understood on the basis of only one of the previously mentioned mechanisms. In agreement with a suggestion of Fukui (19), they proposed a new mechanism in which the azo compound travels along a reaction coordinate which "feels like" a $[\sigma^2s+\sigma^2a]$ pathway in the initial phases of thermolysis. A "nonlinear" extrusion of nitrogen causes a conrotation of the ring bonds. In the thermolysis of the *trans*-pyrazoline **24**, "clockwise" conrotation is preferable to "counterclockwise" rotation due to steric effects. This leads to transient **26A** having instantaneously pyramidal radical centers, followed by planarization to **27A** exclusively by motion of the hydrogen atoms attached to the radical carbons on the basis of mass effects. The least motion principle can then serve to account for the relative amounts of products. Pathways "a" and "b" lead to *cis*-product and are chemically of comparable energy, thus accounting for the formation of nearly racemic **25c**. Paths "c" and "d" lead to *trans*-product



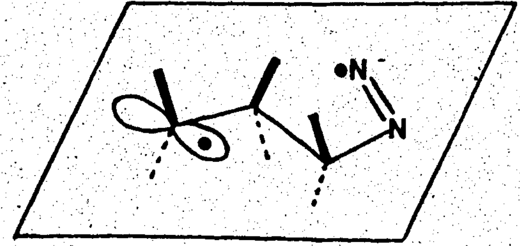
but "c" is clearly more favorable than "d", and thus 25*t* is formed with double inversion of configuration.

In the case of the *cis*-pyrazoline 23, the two possible nonlinear N_2 extrusions are energetically similar and should be competitive as shown in the following scheme.



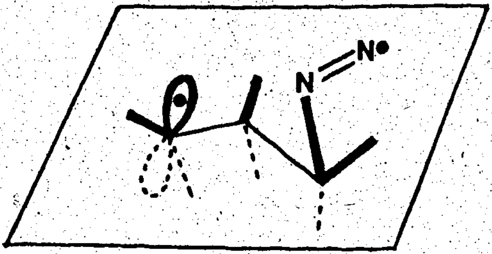
Each is also sterically more compressed than in the "clockwise" *trans* case, since in both instances one of the alkyl groups tends to be forced into a pseudo-axial position. This compression may let less rotation take place on the side of the molecule which experiences the axial interaction. This leads in one instance to a transient structure **26B**, and in the other instance to a structure **26C**. In **26B**, planarization again occurs by hydrogen motion to generate **27B**, and "closest approach" ring closure pathways "a" and "b" give doubly retained *cis*-product and a singly inverted, ethyl-rotated *trans*-product, respectively. Rehybridization in **26C** leads to **27C** which may close by path "c" to give once again a doubly retained *cis*-product, or by path "d" to produce a methyl-rotated *trans*-product. The doubly inverted *cis*-product (-)-**25***c* observed in smallest amount, can only be formed by path "e" through utilization of the most "remote" p-orbital lobe in **27B** and **27C**, which is less likely. The product distribution can be rationalized if one makes the reasonable assumption that the methyl compression rotational pathway leading to **26B** is somewhat favored over the ethyl compression pathway leading to **26C**.

Hiberty and Jean (9) recently carried out *ab initio* SCF calculations followed by a 3x3 configuration interaction (CI) using the Gaussian 70 series of programs, in which the geometries of the various conformations have been optimized with a minimal basis set (STO-3G), and the reaction paths recomputed with an extended basis set (4-31 G). Their calculations indicated that the most favorable pathway is the one involving a nitrogen-containing diradical 22 in a *trans* configuration, with an activation energy of 39.3 kcal/mol, followed by a pathway involving a nitrogen-containing diradical 28 in a gauche conformation with an activation energy of 42.0 kacl/mol. The concerted pathways involving a planar trimethylene diradical 14, and a "face to face" diradical 21 were found to give activation energies of 44.1 and 47.8 kcal/mol respectively, while the pathway involving 24 by "nonlinear" extrusion of nitrogen proved to be much more energetic.



22

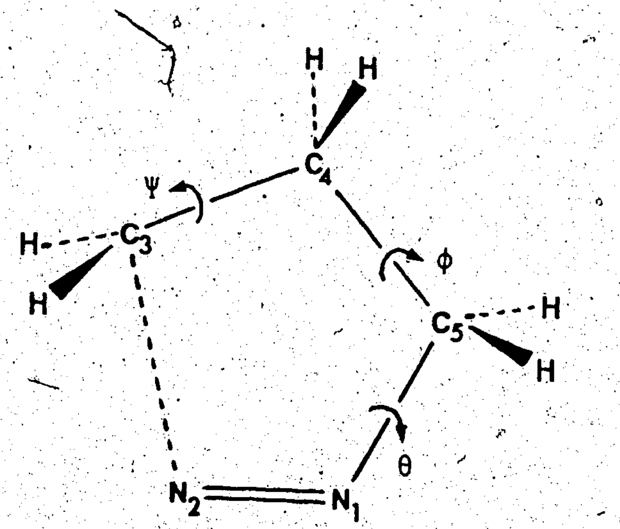
(ϕ = 180°, θ = 0°, Ψ = 0°)



28

(ϕ = 61.2°, θ = 220°, Ψ = 80.1°)

The conformation of the diradicals, 22 and 28 in the thermolysis of 1-pyrazoline was obtained from the two dimensional (θ,ϕ) potential surface, in which conformational energy of the nitrogen-containing diradical was plotted against the rotational angles θ and ϕ with the optimization at each point by the rotational angle Ψ. The rotational



angles are defined as shown: θ, rotational angle of N_1-N_2 around the C_5-N_1 bond; ϕ, dihedral angle between the $C_3C_4C_5$ and the $C_4C_5C_1$ planes; and Ψ, rotational angle of the methylene group C_3HH around the C_3-C_4 bond. The potential surface showed several minima in each curve. Among these, only two are absolute secondary minima on the potential surface: the first one is the *trans*-diradical 22 with the values ϕ = 180°, θ = 0°, and Ψ = 0°; the second one is the *cis*-diradical 28 with the values ϕ = 61.2°, θ = 220°, and Ψ = 80.1°.

On the basis of these results, the product distribution for the thermolysis of *cis*- and *trans*-3-ethyl-5-methyl-1-pyrazolines (23 and 24) were explained qualitatively in agreement with the experimental results in Table 3.

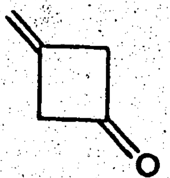
In order to explain the relative amounts of double inversion to double retention in the minor product, the most favorable pathway involving the diradical **22** was considered. The *trans*- or the *cis*-pyrazoline (**23** or **24**) should give **22** in which the two alkyl groups are *cis* or *trans* relative to the CCC plane. Owing to steric hindrance, the amount of the minor product with double inversion arising from this pathway should be more important for the *trans*- than the *cis*-pyrazoline, which is in agreement with the data in Table 3. The relative amounts of double retention in the minor product can be explained by considering the pathway involving the diradical **28**, in which the substituents are in sterically favorable pseudoequatorial positions starting from the *cis*-pyrazoline, whereas one of the substituents is in a pseudoaxial position in the case of the *trans*-pyrazoline. Thus, this reaction path can be expected to be more favorable for the *cis*- rather than the *trans*-pyrazoline. Consequently, the amount of double retention in the minor product should be larger in the case of the *cis*-pyrazoline, which is in agreement with the data in Table 3.

A possible explanation of the relative amounts of ethyl and methyl rotations in the major product may be based upon the interaction between the azo group and an alkyl substituent during the first step of both pathways using diradicals, **22** and **28**. For the *cis*-pyrazoline, the outward rotation is the easiest one, since it prevents any steric repulsion between the substituents. In this motion, the reaction in which the outgoing nitrogen atom N_2 attached to C_3 encounters the methyl substituent on C_5 should be easier than that in which the outgoing N_2 connected to C_5 encounters the ethyl group on C_3. Therefore, the ethyl rotation at C_3 is expected to be easier than the methyl rotation at C_5. In the case of the *trans*-pyrazoline, the ethyl (methyl) rotation at C_3 (C_5) can occur so that the nitrogen atom N_2 attached to C_3 (C_5) may avoid any interaction with the methyl (ethyl) group on C_5 (C_3). Therefore, both ethyl and methyl rotations are expected to be equally favorable, and these are in good agreement with the data in Table 3.

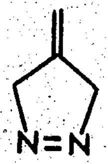
C. Thermolysis of 4-Alkylidene-1-pyrazolines

(i) Trimethylenemethane

Trimethylenemethane (TMM), a diradical of composition $C(CH_2)_3$, has proved to be of considerable theoretical and mechanistic interest. Over the past decade, Dowd and his collaborators (20) have demonstrated that planar TMM has a triplet ground state (33), and can be generated by the photolysis of either 3-methylenecyclobutanone (29) or 4-methylene-1-pyrazoline (30). Gajewski (21) observed that

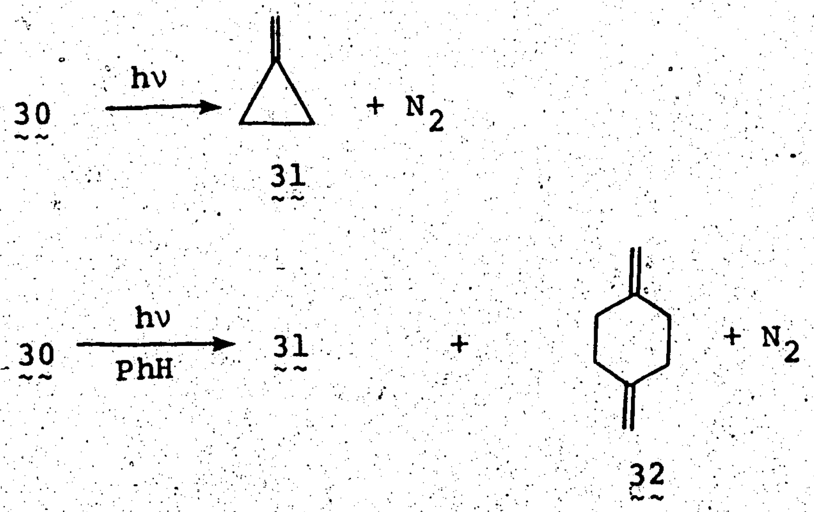


29



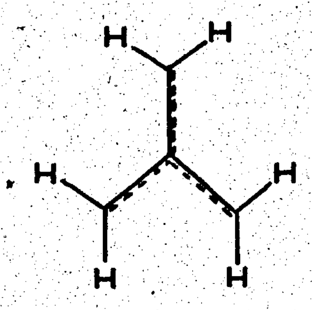
30

only methylenecyclopropane (31) was produced when 30 was photolyzed directly. However, 1,4-dimethylenecyclohexane (32) was also produced when 30 was photosensitized



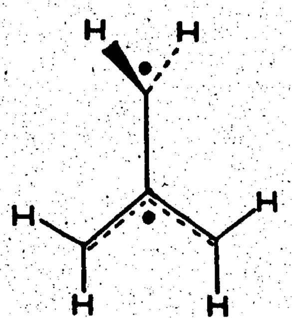
by benzene. The author proposes a singlet TMM intermediate for the direct photolysis, and singlet and triplet TMM's for the photosensitized photolysis, with possibly singlet 30 intersystem crossing to triplet 30.

Dewar and Wasson (22) have shown that both triplet and singlet states are possible for TMM, and that the



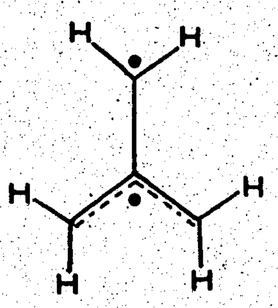
33

Planar Triplet TMM (D_{3h})



34

Orthogonal Singlet TMM (C_{2v})

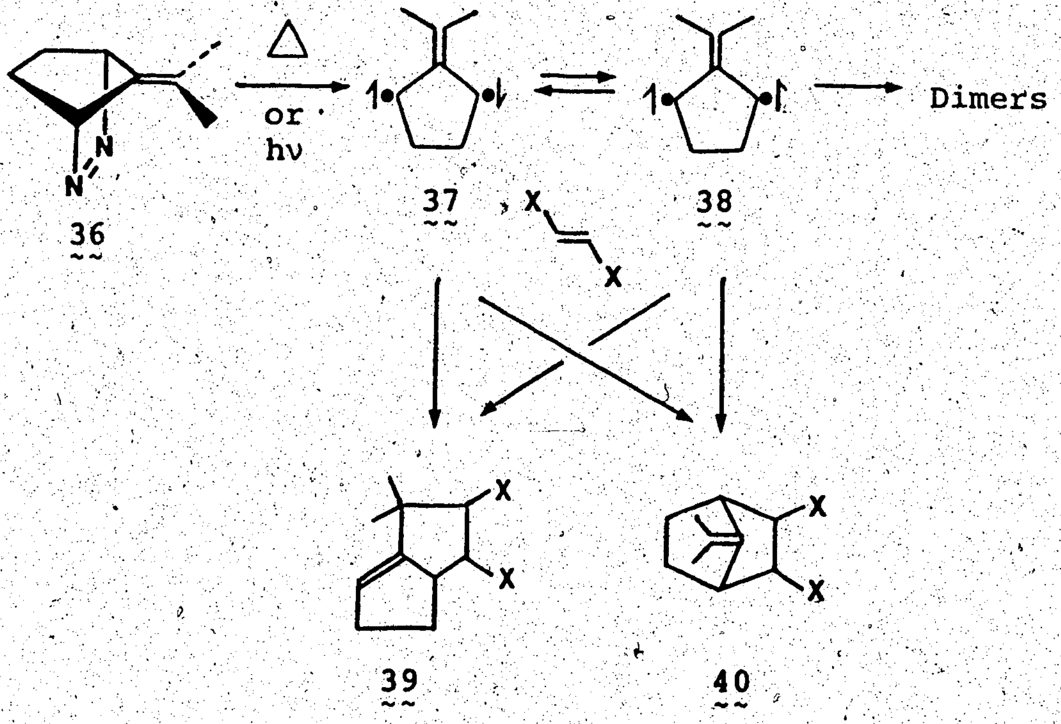


35

Planar Singlet TMM (C_{2v})

triplet TMM 33 with a planar geometry is the most stable structure. However, in a form where one terminal is orthogonal to the plane of the other two, the open-shell singlet 34, which has two unpaired electrons of opposite spin, is not much less stable than the planar triplet TMM 33. Theoretical studies have suggested that the orthogonal singlet TMM 34 is more stable than the planar singlet TMM 35 (23). It has been reported by Chesick (24) and Gajewski (25) that the orthogonal singlet TMM species are involved in the thermal rearrangement of various methylenecyclopropanes.

Structurally modified 4-methylene-1-pyrazolines, such as 7-isopropylidene-2,3-diazanorborneses (36), have been studied by Berson and collaborators (6b, 12) and have been demonstrated to produce both singlet and triplet 1,3-diyls (37 and 38), by photolysis and thermolysis, as evidenced by



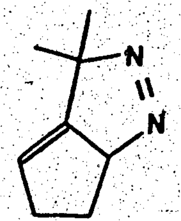
trapping experiments and by dimer formation. They observed that the dimers formed in the solution-phase thermolysis, seem to be products largely of a (triplet + triplet) reaction, and that the composition of cycloaddition products (39 and 40) of the 1,3-diyls with trapping olefin changes, as the initial concentration of the olefin changes as indicated in Table 4. The ratio for 39/40 was also found to be 30-75 when the azo compound 36 decomposes thermally

Table 4

Ratio for 39/40 with olefin in the thermolysis or photolysis of 7-isopropylidene-2,3-diazanorbornene (12c)

		39/40		
		Thermolysis	Photolysis	
Olefin	Conc, M		Direct	Xanthone-sensitized
Acrylonitrile	1.3	4.8	12	3.5
	1.7	7.8	12	3.5
	6.93	17	38	3.9
	13.9	26	34	3.6
Methyl acrylate	3.4	-	7.8	4.3
	5.1	-	14	4.2
	10.2	-	26	3.4

in the presence of high olefin concentrations or molecular oxygen (12d). This high ratio is characteristic of the singlet diyl 37 and provides a sensitive indicator of even a small amount of singlet contribution to the product mixture, since the triplet 39/40 ratio of 0.7-3 is much smaller. As indicated in Table 4, the xanthone photosensitized decomposition of 36 leads directly to the triplet ground state (12c). It has also been observed that the singlet products are formed not only with high regiospecificity for the fused structure 39 but also with high stereospecificity for *cis* addition when the triplet diyl 38 is scavenged by oxygen (12a, 12d). These results can be considered as evidence for the TMM type intermediates 37 and 38 in the decomposition of 36. However, a fused isomer 41 has been observed in the thermolysis of 36, but not in the photolysis of 36 (6a). They suggested that a concerted reaction may be allowed in the dia[illegible]excited state, where the orbital symmetry restrictio[illegible]ppropriate to the thermal reaction do not apply.

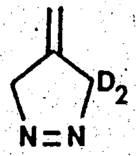

41

[illegible]though nitrogen free 1,3-diyls have been proposed by C[illegible]wford and collaborators (10) as possible intermediate[illegible] in the thermolysis of 4-methylene-1-pyrazoline (30), 4-isopropylidiene-1-pyrazoline (57), and 3,3-dimethyl-4-methylene-1-pyrazoline (56), they later found that the product distribution of the thermolysis of eleven other

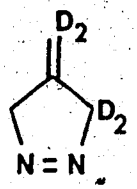
4-alkylidene-1-pyrazolines cannot be rationalized in terms of the planar or the orthogonal singlet type of intermediate (11). A detailed review of the thermolysis of these 4-alkylidene-1-pyrazolines is given in the following section.

(ii) Thermolysis of 4-Methylene-1-pyrazoline (30) and Deuterated 4-Methylene-1-pyrazolines (42, 43, and 44)

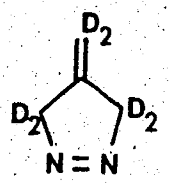
Crawford *et al.* (10a) studied the thermolysis of 4-methylene-1-pyrazoline (30) and obtained an activation energy of 32.6 ± 0.3 kcal mol^{-1}, which may be compared with those of 1-pyrazoline (1), 42.4 ± 0.3 kcal mol^{-1} (7d) and 3-vinyl-1-pyrazoline (10), 32.2 ± 0.3 kcal mol^{-1} (10b) previously mentioned. The last-mentioned represents the stabilization of the vinylmethylene intermediate by allylic resonance energy. The thermolysis of 30, which reacts at a rate 140 times greater than that of 1-pyrazoline (1) can be explained to be accelerated by a comparable stabilization. Further investigation of the mechanism has been carried out by studying the thermolysis of 4-methylene-1-pyrazoline-3,3-d$_2$ (42), 4-methylene-1-pyrazoline-3,3,6,6-d$_4$ (43), and 4-methylene-1-pyrazoline-3,3,5,5,6,6-d$_6$ (44). The secondary kinetic isotope effects for the thermolysis of these deuterated 4-methylene-1-pyrazolines are given in Table 5 (10a). Seltzer *et al.* (1b, 26, 27) have demonstrated that the substitution of a



42



43



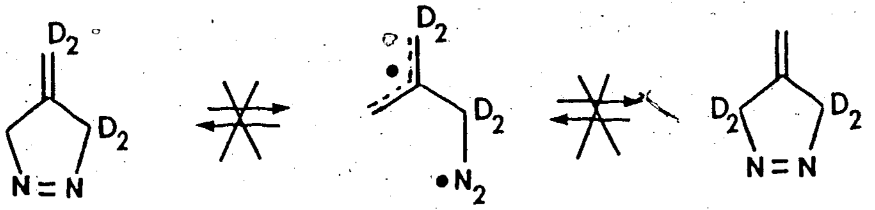
44

Table 5

Secondary deuterium kinetic isotope effects for the thermolysis of deuterated 4-methylene-1-pyrazolines (10a)

Compound	Temp. (°C)	k_H/k_D
42	167.8	1.26 ± 0.03
43	169.0	1.30 ± 0.03
44	172.9	1.60 ± 0.04

deuterium α to the azo nitrogen that is undergoing valence change in the rate determining transition state in such a manner as to decrease the number of H-C-X (*vs.* D-C-X) bending modes, leads to an increase in the free energy of activation $\delta\Delta G^{\ddagger}$ of 90-120 cal mol^{-1} per [illegible]uterium. Crawford and collaborators observed that the effect of the four α-deuteriums in **44** was 97 ± 3 cal mol^{-1} per deuterium. Since the $\delta\Delta G^{\ddagger}$ per α deuterium is 101 ± 6 cal mol^{-1} for **42**, and if **43** represents the effect of the two α-deuteriums plus two γ-deuteriums, then the two γ-deuteriums contribute an increase of 27 cal mol^{-1}. These results are in accord with a transition state wherein both carbon-nitrogen bonds have undergone considerable bond breaking (28). A control run of a sample of 43 carried out to 50% completion then re-isolated indicated that there was no observable increase

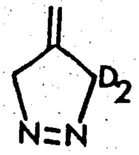
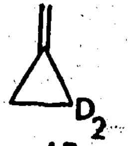
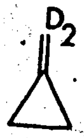
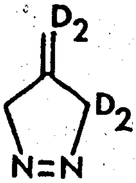
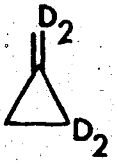
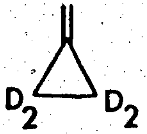


43 45 46

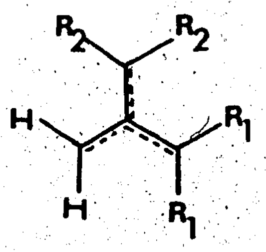
of protons at the vinylic position *via* formation of 4-methylene-1-pyrazoline-3,3,5,5-d_4 (46) as determined by ^{1}Hmr spectroscopy. They estimated that 2% rearrangement could have been detected and thus they were able to rule out the formation of any pre-transition state intermediate such as the diazenyl radical intermediate 45. The thermolysis of pyrazoline 42 gave the products: methylene-2,2-dideuteriocyclopropane (47) and dideuteriomethylene-cyclopropane (48). The pyrazoline 43 gave the products: dideuteriomethylene-2,2-dideuteriocyclopropane (49) and methylene-2,2,3,3-tetradeuteriocyclopropane (50) as in Table 6. If from 42 a diradical intermediate of composition equivalent to $(CH_2)_2CCD_2$ is produced, then there are two possible modes by which 47 can be produced. The rate constant for both of these modes is $2k'_H$ where k'_H represents the rate constant for the conversion of the protiomethylene group to the exo-methylene as in 47. There is also one mode by which 48 can be produced having rate constant k'_D,

Table 6

Product distribution in the thermolysis of deuterated 4-methylene-1-pyrazolines at 165°C (10a)

Starting material	Relative yields, %	
 42	 47 60 ± 1	 48 40 ± 1
 43	 49 73 ± 2	 50 27 ± 2

where k'_D is defined as the rate constant for the formation of the exo-methylene group by the deuteriomethylene as in 48. The ratio k'_H/k'_D in the product determining step then is 0.75 ± 0.03 for the products of 42 and by analogy, 0.74 ± 0.07 for the products of 43. The similarity of these results, besides the possibility of their being fortuitous, enabled Crawford *et al.* to suggest that there is an isotope effect in the product determining step and that the three methylene groups have either become equivalent as in the planar triplet TMM 51, or have become randomized in a set of intermediates equivalent to the orthogonal singlet TMM 52. Triplet planar TMM 33 is known to dimerize to produce 1,4-dimethylenecyclohexane (32) (20b, 21). Thus, the intermediate 51 can be ruled out since no dimer was



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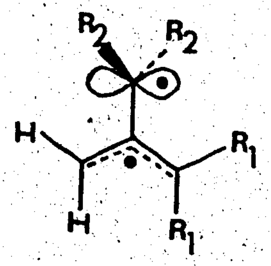


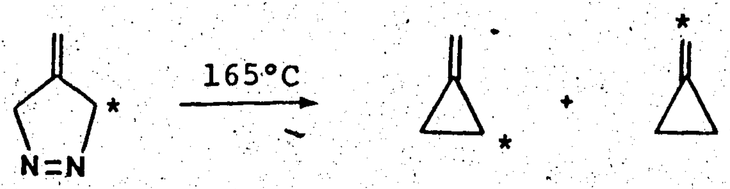
52

From 42 $R_1 = D;\ R_2 = H$

From 43 $R_1 = R_2 = D$

observed in any of the reactions, nor was there observed any addition product when it was attempted to trap the diradical with an olefin.

In a set of intermediates such as 52, the isotope effect was first thought to be a "ponderal effect" (29,30): the deuterium, being of greater mass, is slower to move out of the plane than is protium. Thus, can be rationalized a preference on the part of the protium for the ring methylene position of methylenecyclopropane. By using carbon-13, any ponderal entropy effect can be removed since the increase in mass is precisely on the axis of rotation. The following result was obtained upon studying the labelled pyrazoline **53** (10a). In this case, there



53 **54** **55**

64.0±0.5% 36.0±0.5%

cannot be a "ponderal effect", but still, the value found for the ratio **54** to **55** was 1.75, significantly different from the statistical value of 2.00.

An alternative explanation was that **42** and **43** can give rise to **47** and **49** in a concerted process and that in the gas phase, the methylenecyclopropanes produced are "hot" and undergo subsequent isomerizations; such a possibility is diminished by the observation that the same product ratios were obtained in solution as in the gas phase. This "hot species" was then ruled out since it had been observed that a sample of **47** prepared independently was unchanged after 3 hr at 180°, and upon heating at 250°, the ^{1}Hmr spectrum indicated an equilibrium mixture of 67.6 ± 1.1% of **47** and 32.4 ± 1.1% of **48** (10a).

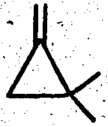
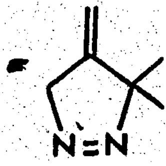
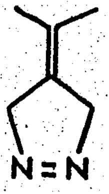
These results showed that the final position of the methylene group in methylenecyclopropane is dependent upon its original position in the pyrazoline, and cannot be accounted for by a mechanism producing intermediates like 52 alone.

(iii) Thermolysis of 3,3-Dimethyl-4-methylene-1-pyrazoline (56) and 4-Isopropylidene-1-pyrazoline (57)

Crawford and collaborators (10a) prepared two isomeric dimethyl substituted 4-methylene-1-pyrazolines (56 and 57) and studied their thermolysis. The product distribution is indicated in Table 7. From these results, a planar TMM intermediate, common to 56 and 57, could be ruled out since

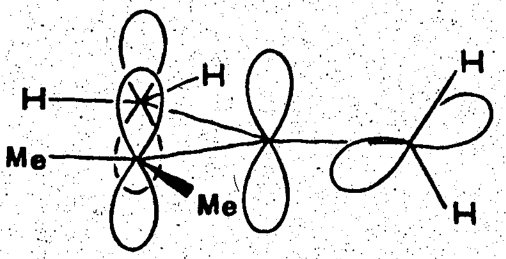
Table 7

Product distribution in the thermolysis of dimethyl substituted 4-methylene-1-pyrazolines at 165°C (10a)

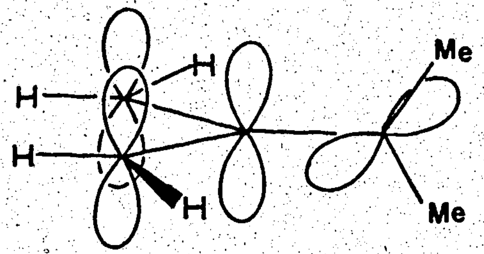
Starting material	Relative yields, %	
	 58	 59
 56	82 ± 1	18 ± 1
 57	63 ± 1	37 ± 1

the same ratio of 58:59 would have been expected from both 56 and 57.

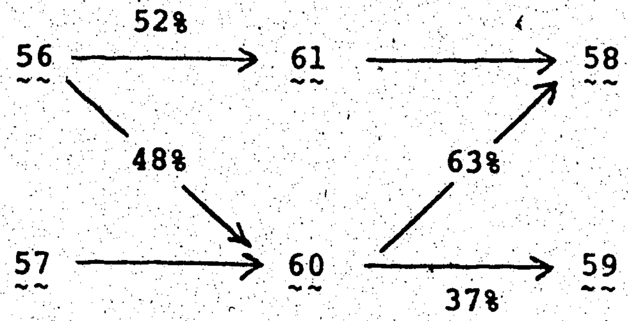
Instead, the orthogonal singlet intermediates 60 and 61 must be considered. They suggested, on the basis of the least motion principle (31), that the thermolysis of 57 produces only 60 whereas thermolysis of 56 gives rise to 61 as well as 60. The product proportions for both 56 and 57 could be then rationalized, assuming that the rotation of the isopropylidene group of 60 is favored by 63:37 over that of the methylene group.



60



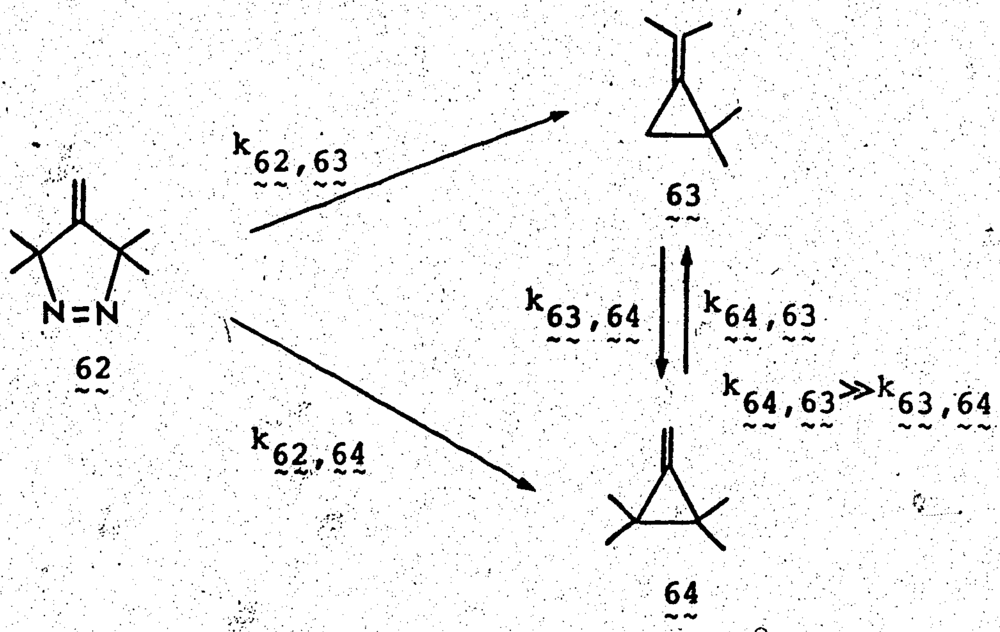
61



(iv) Thermolysis of 3,3,5,5-Tetramethyl-4-methylene-1-pyrazoline (62)

Tokunaga and Crawford (32) investigated the gas phase thermolysis of 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline (62) which presented the advantage that the tautomerism which affected the study of the previous 4-methylene-1-pyrazolines, was no longer possible. Thermolysis of 62 gave rise to the products 63 and 64, but 2,2,3,3-tetramethylmethylenecyclopropane (64) was not observed because of its rapid and nearly complete isomerization to 2,2-dimethylisopropylidenecyclopropane (63) under the reaction conditions.

A kinetic study was carried out in order to determine all the rate constants and the initial ratio of 63:64.

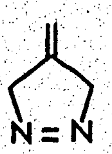
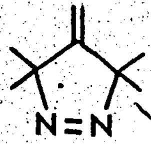
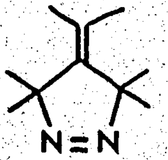
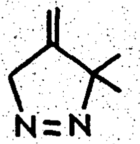
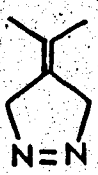


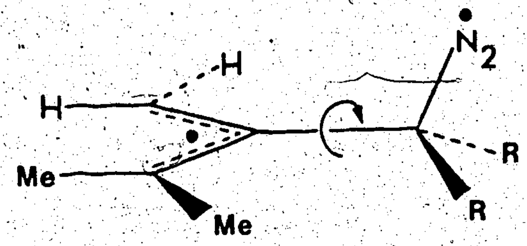
Comparison of the thermolysis rate of **62** with the thermolysis rates of some 4-alkylidene-1-pyrazolines, as listed in Table 8, proved to be interesting. It was found that the replacement of hydrogen by methyl slowed the rate from what is normally expected. Also the rate of **62** was found to be one third the rate of 3,3,5,5-tetramethyl-1-pyrazoline (**9**) as if there was no acceleration from the allylic nature of the corresponding radical. The authors proposed that the bulky methyl groups had prevented any manifestation of the allylic resonance and suggested that the cleavage of the carbon-nitrogen bond(s) in **62** was occurring in the plane of the ring. Furthermore, the results of Engel (33) showed that the thermolysis of 3,3,5,5-tetramethyl-4-isopropylidene-1-pyrazoline (**65**) was one thirty second of the rate of thermolysis of **62**. This was an indication that even methyl groups placed on the exo-methylene group influence, by their steric effect, the rate of the thermolysis of 4-alkylidene-1-pyrazolines.

Calculations gave 52:48 for the ratio of **64**:**63** from **62**, a result different from 63:37 for the ratio of **58**:**59** from **57**. This difference could be rationalized by considering the allylic diazenyl species **66** as a possible intermediate. Displacement of nitrogen by either of the allylic termini would then give rise to the products and this process may be controlled by the

Table 8

The relative rates, at 160.2°C, and activation parameters for the gas phase thermolysis of some 4-alkylidene-1-pyrazolines and for 3,3,5,5-tetramethyl-1-pyrazoline

Compound	E_a (kcal mol^{-1})	log A	$\Delta S^{\ddagger}_{200}$ (e.u.)	Relative rate	Reference No.
 30	32.6 ± 0.3	13.24	-1.1	62.8	10a
 62	40.7 ± 0.4	15.53	+9.8	1.0	32
 65	39.8 ± 0.6	13.6	+0.7	0.031	33
 56	-	-	-	21	10a
 57	-	-	-	24	10a
 9	37.7 ± 0.4	14.49	4.6	3.0	7d

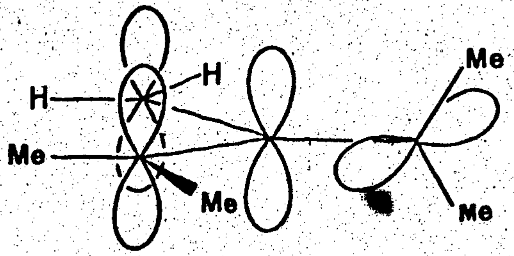


66

R = Me or H

rotational conformations of 66 which differ when going from R = H to R = Me.

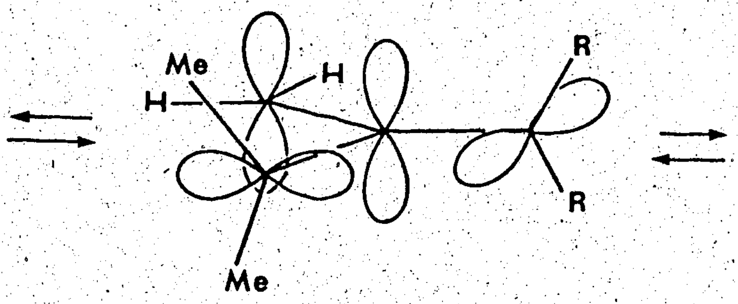
The authors also proposed the orthogonal singlet diradical 67 as a possible intermediate in the thermolysis



67

of 62. From this type of intermediate 67, similar in structure to 60, an explanation had to be found for the fact that the rotational propensity of the isopropylidene group with respect to the methylene group was greater (63:37) in 60 than it was in 67 (52:48). The authors also suggested that, when going from intermediates 60 and 67 to products 58 and 64 respectively, the reaction a, **58**

b, **64**



a, **60**

b, **67**

TS

a, R = H

b, R = Me

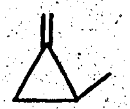
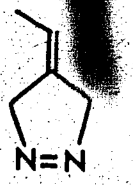
had to go through a transition state **TS**. The lower rotational propensity of the isopropylidene group in **67** relative to that in **60** would then be rationalized in terms of steric factors more important in $\mathbf{TS}_b$ than in $\mathbf{TS}_a$.

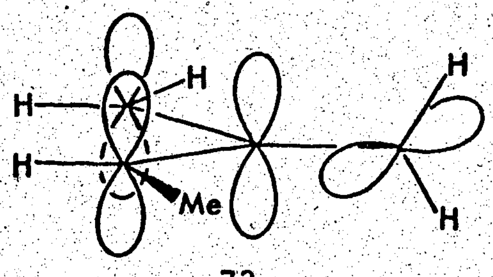
(v) Thermolysis of 3-Methyl-4-methylene-1-pyrazoline (**68**) 4-Ethylidene-1-pyrazoline (**69**), Dideuterated 4-Ethylidene-1-pyrazolines (**76** and **77**), 4-Neopentylidene-1-pyrazoline (**83**), and Dideuterated 4-Neopentylidene-1-pyrazoline (**84**)

Crawford and collaborators (11,34) then studied the thermolysis of the isomeric 3-methyl-4-methylene-1-pyrazoline (**68**) and 4-ethylidene-1-pyrazoline (**69**), two systems which have different steric and electronic effects than the previously studied 4-methylene-1-pyrazolines. The product distribution is given in Table 9. From the results, a planar singlet TMM intermediate was

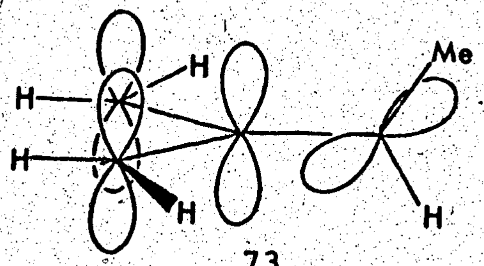
Table 9

Product distribution in the thermolysis of methyl substituted 4-methylene-1-pyrazolines at 175°C (11)

Starting material	Relative yields, %	
	 70	 71
	80 ± 1	20 ± 1
 69	90 ± 1	10 ± 1



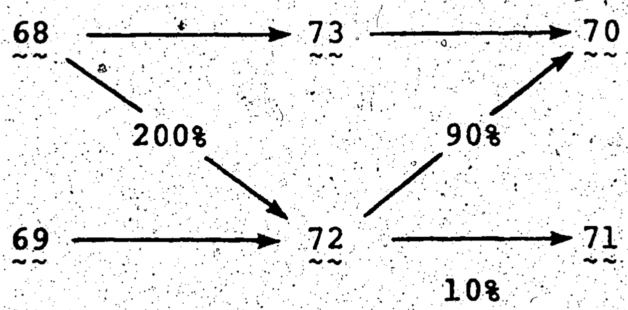
72



73

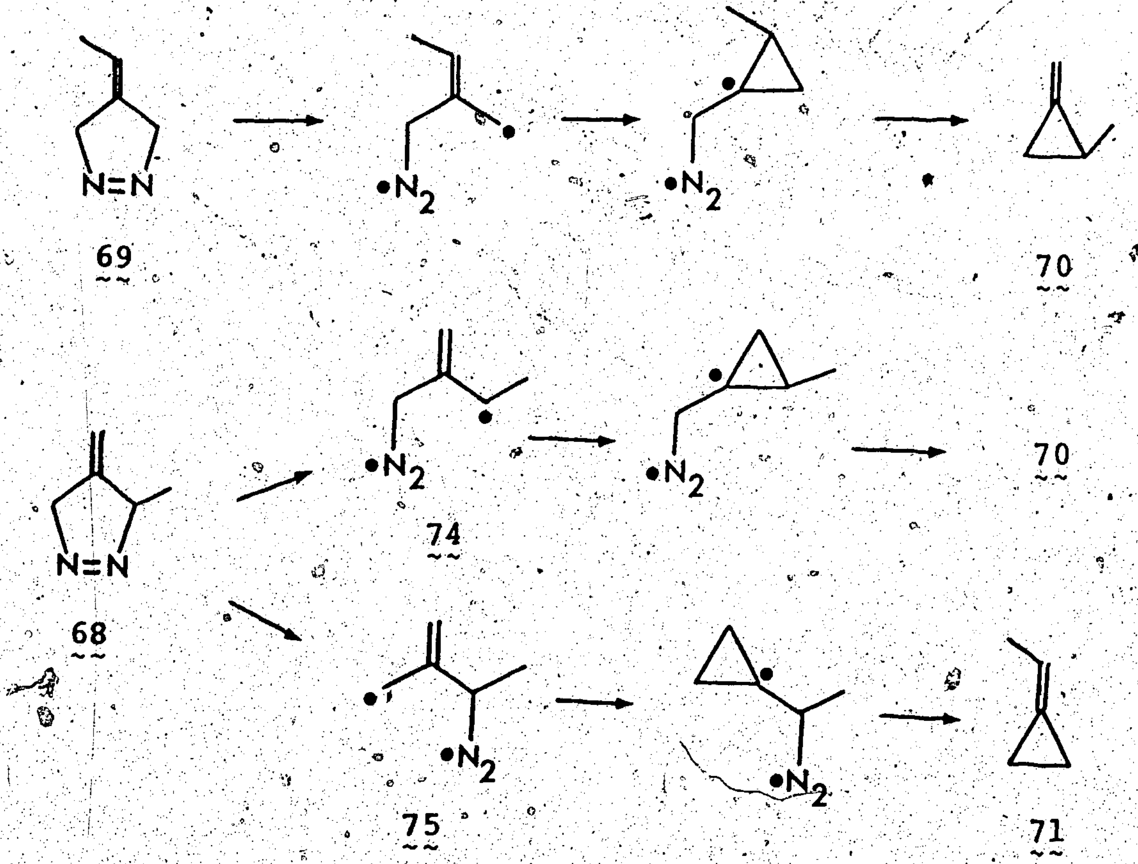
ruled out since it would have given the same ratio of **70**:**71** regardless of the reactant used.

The authors proposed that the intermediates **72** and **73** analogous to **60** and **61** could be usefully employed in rationalizing the proportions of **70** and **71**. The product proportions from **68** and **69** cannot be rationalized in a manner analogous to the scheme previously shown for



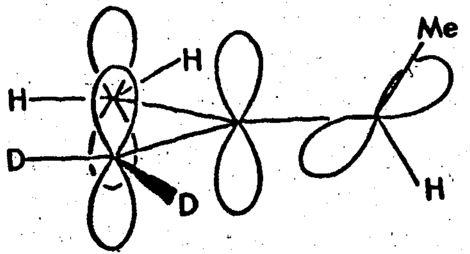
56 and **57**, since the % mole fractions of **68** going through **72** would need to be 200% in order to account for the formation of 20% of **71** as in the scheme above.

Schrijver (34) used a mechanism originally proposed by Cameron (35) and involving the breakage of only one carbon-nitrogen bond in the initial step and the formation of a cyclopropyl radical-bound diradical. With this mechanism, the fact that the methylallyl radical of the diazenyl radical **74** is easier to form than the allyl radical of the diradical **75** could account for the excess of **70** with respect to **71** produced from **68**. But this mechanism does not rationalize the 10% of **71** produced from **69**.



The authors (11) suggested that 73 may be the intermediate first produced from 69 to give the high portion of 70 and that 72 is that which is first derived from 68. However, such a sequence would not account for the formation of 10% of 71 from 69 unless there is some interconversion of 72 and 73. It would also appear to violate the least motion principle but Roth and Wegner (36) have observed the racemization of 3-methyl-6-ethylidenebicyclo[3.1.0]hexane at rates competitive with *cis-trans* isomerization supposedly by the involvement of the rotation of the exocyclic ethylidene groups at the same time as the cleavage of the $C_1 \rightarrow C_5$ bond. This novel observation was considered to imply that the least motion principle cannot always be used in such processes, and to suggest that 73 may be on the reaction path if extended to the thermolysis of 69.

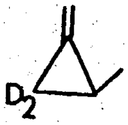
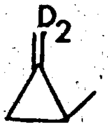
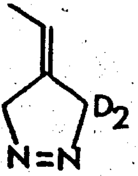
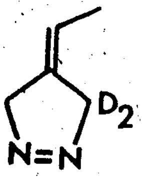
In order to test this possibility, the deuterium labelled pyrazolines, *E*-3,3-dideuterio-4-ethylidene-1-pyrazoline (76) and *Z*-3,3-dideuterio-4-ethylidene-1-pyrazoline (77), were thermolyzed. The relative proportions of 70 and 71 were unchanged on deuteration. The product distribution of the deuterated 2-methylmethylenecyclopropanes (78 and 79) separated by the preparative gc is given in Table 10. It was found that the degenerate rearrangement 78 ⇄ 79 does not proceed under the normal reaction condition as indicated by the last two entries in Table 10. They considered the possibility that 76 produces specifically 78 (77 produces 79) and that the excess vibrational energy produced in such unimolecular decomposition is not quenched sufficiently rapidly to prevent the formation of either 79 or dideuterated 71 from 76 (78 or dideuterated 71 from 77). Nevertheless, the results allowed them to conclude that the orthogonal singlet diradical 80 cannot



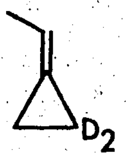
80

Table 10

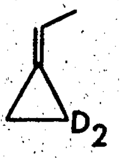
Deuterium distribution in the deuterated 2-methylmethylenecyclopropanes produced from the thermolysis of 76 and 77 at 160°C (11)

Reactant	Method of analysis	Time (h)	Distribution, %	
			 78	 79
 76	^{1}Hmr	1	74 ± 1	26 ± 1
	^{2}Hmr	1	76 ± 1	24 ± 1
 77	^{1}Hmr	1	22 ± 1	78 ± 1
	^{2}Hmr	1	19 ± 1	81 ± 1
78:79	^{1}Hmr	0	74 ± 1	26 ± 1
78:79	^{1}Hmr	1	73 ± 1	27 ± 1
78:79	^{1}Hmr	4	73 ± 1	27 ± 1

be the principal intermediate on the product determining pathway. It should be noted that their analysis, by ^{1}Hmr, of the small amount of dideuterated isomers of ethylidenecyclopropane 71 lead them to suggest that the principal isomer produced from 76 may be *E*-2,2-dideuterioethylidenecyclopropane (81) and that from 77 may be *Z*-2,2-ddeuterioethylidenecyclopropane (82).

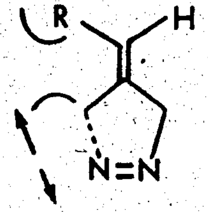


81



82

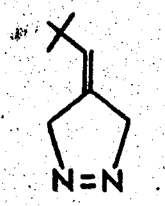
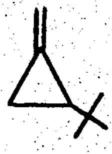
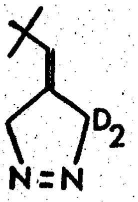
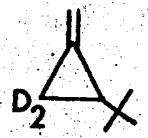
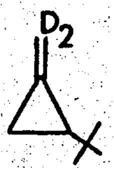
They were also concerned with the implied steric factor in the thermolysis of 76 and 77 and were led to speculate that the carbon-nitrogen bond *syn* to a methyl group of an exocyclic double bond may be lagging in the bond breaking process. The support for this came from the comparison of the thermolysis rates of 4-methylene-1-pyrazoline (30) and 4-isopropylidene-1-pyrazoline (57), the latter being a third the rate of the former and from the fact that thermolysis of 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline (62) is 32 times faster than that of 4-isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline (65), as indicated in Table 8. A normal mode of the reaction coordinate would be expected to consist of the C-N stretching and consequently the possibility of steric compression being an important factor led them to



investigate the thermolysis of the 4-neopentylidene-1-pyrazoline (83) and the *E*-3,3-dideuterio-4-neopentylidene-1-pyrazoline (84). The results of the thermolysis of 83 and 84 are given in Table 11. These data were

Table 11

Product distribution in the thermolysis of 4-neopentylidene-1-pyrazoline and *E*-4-neopentylidene-1-pyrazoline-3,3-d_2 at 189.4°C (11)

Starting material	Relative yields, %	
 83	 85 95.8	 86 4.2
 84	 87 70*	 88 30*

*Deuterium distribution in the deuterated 2-neopentylidene-1-pyrazoline was measured only.

considered to be an indication that the *syn-anti* relationship between the alkyl group and the methylene group of the ring is important and that there is a preference for the carbon *anti* to the alkyl group to become incorporated in the cyclopropane ring along with the exocyclic methylene of the product. It should also be noted that the thermolysis products of **84** are analogous to those of the *E*-3,3-dideuterio-4-ethylidene-1-pyrazoline (**76**), the ratio of **87**:**88** being 70:30 (the ratio of **78**:**79** was 74:26).

(vi) Thermolysis of *E*- and *Z*-Ethylidene-3-methyl-1-pyrazoline (**89** and **90**); *E*-4-Ethylidene-3-trideuteriomethyl-1-pyrazoline (**95**); *E*-4-Ethylidene-3,3-dimethyl-1-pyrazoline (**98**); and *cis*- and *trans*-4-Ethylidene-3,5-dimethyl-1-pyrazoline (**103** and **104**)

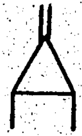
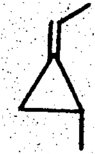
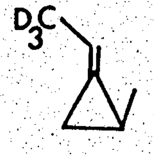
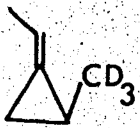
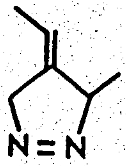
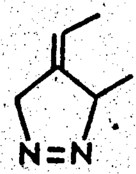
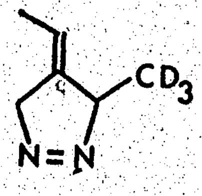
Crawford and collaborators (11) investigated the thermolysis of the pyrazolines **89**, **90**, **95**, **98**, **103**, and **104** in order to further test the criteria that the carbon-nitrogen bond *syn* to an alkyl group of an exocyclic double bond lags in the bond breaking process and that there is a preference for the methylene carbon of the pyrazoline ring *anti* to the alkyl group of the exocyclic double bond to be incorporated in the cyclopropane ring of the product.

The thermolysis of *E*- and *Z*-4-ethylidene-3-methyl-1-pyrazolines (89 and 90) gave the same four products 91, 92, 93 and 94 but in very different proportions. Some of these products were found to isomerize slowly under the thermolysis conditions and therefore the zero time values were obtained by the graphical extrapolation of the values at various thermolysis times. These zero time values are given in Table 12. The authors were able to identify the point of origin of the exo-ethylidene in the thermolysis of 89 by analysis of the deuterated *E*-2-methylethylidenecyclopropanes (96 and 97) from *E*-4-ethylidene-3-trideuteriomethyl-1-pyrazoline (95). The results in Table 12 indicate clearly that the C_3 carbon of 89 becomes a cyclopropane ring carbon in at least 84% of the products (23.1 + 54.4 + 20.0 x 0.35). The exocyclic carbon C_6 of 89 becomes a cyclopropyl carbon in 90% of the products (23.1 + 54.5 + 20.0 x 0.65) and the C_5 methylene of 89 is less than 23% of the products. The incorporation of the C_5 methylene of 90 into the cyclopropane ring of the products was found to be 67%.

As in Table 13, *E*-4-ethylidene-3,3-dimethyl-1-pyrazoline (98) was thermolyzed to give in excess of 70% of the thermodynamically least stable product 99 again with over 84% (71.5 + 12.5) of C_3 of the reactant 98 becoming a cyclopropane carbon in the products. The exocyclic ethylidene C_6 becomes incorporated into a

Table 12

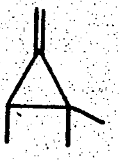
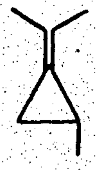
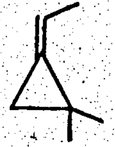
Percentage of isomeric products from the thermolysis of *E*- and *Z*-4-ethylidene-3-methyl-1-pyrazoline; and *E*-4-ethylidene-3-trideuteriomethyl-1-pyrazoline at 170.0°C (11)

Starting	yield, %					
	 91	 92	 93	 94	 96	 97
 89	23.1	54.5	20.0	2.4		
 90	19.5	13.5	31.5	35.5		
 95					65*	35*

*Deuterium distribution was measured only in the deuterated *E*-2-methylethylidenecyclopropane.

Table 13

Percentage* of isomeric products from the thermolysis of *E*-4-ethylidene-3,3-dimethyl-1-pyrazoline at 170°C (11)

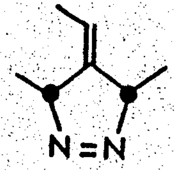
	Yield, %			
Starting material	 99	 100	 101	 102
 98	71.5	16.0	12.5	0.0

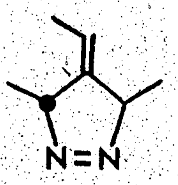
---

*By graphical extrapolation to zero time values.

cyclopropyl carbon in greater than 87% (71.5 + 16.0) of the products.

cis- and *trans*-4-Ethylidene-3,5-dimethyl-1-pyrazolines (103 and 104) were synthesized in almost equal amounts by


103

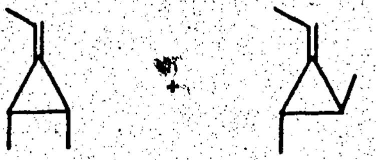

104

the addition of diazoethane to 2,3-pentadiene. One of the isomers was found to undergo thermolysis at a rate significantly faster than the other thus allowing the isolation of the less reactive one. The slower isomer had been assigned the *cis* configuration (103) on the basis of ^{1}Hmr and ^{13}Cmr spectra. The products of the thermolysis of 103 and 104 do not appear to give any important information at this stage.

Mixture of

94.6% 103 and $\xrightarrow[\text{30 min}]{\text{170°C}}$

5.4% 104

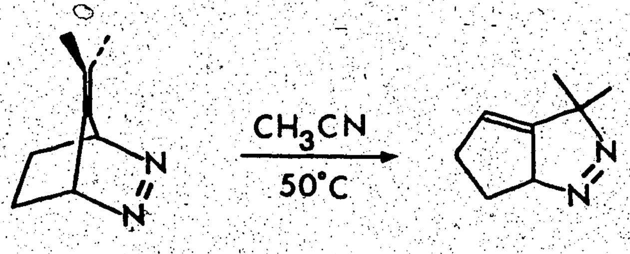


105 + 106

44.7% 55.3%

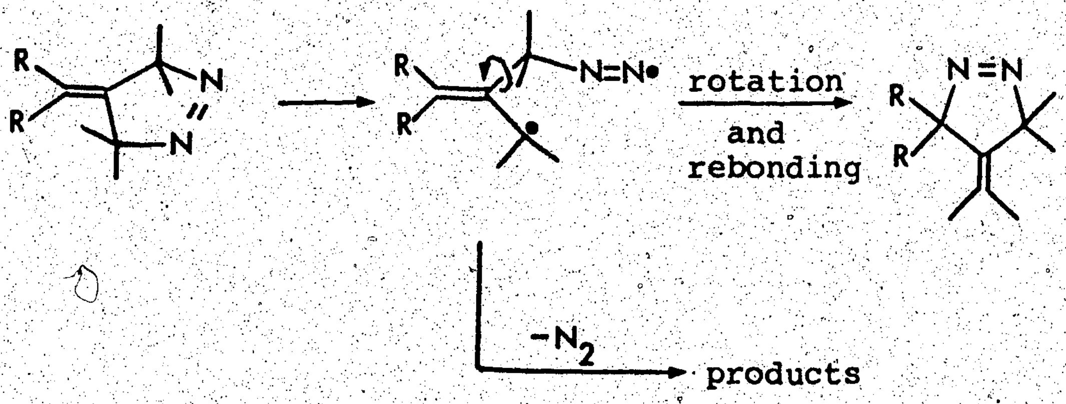
The authors were also concerned with two possibilities. Firstly, the pyrazolines 69, 76 and 77, the pyrazoline 98 or the pyrazolines 89, 90 and 95 might produce one product stereospecifically, followed by a degenerate thermal rearrangement to give other products due to chemical activation. Secondly, the pyrazolines 76 and 77 or the pyrazolines 89 and 90 might interconvert by thermal isomerization. However, some of the problems of such hot molecule chemistry can be discounted by the observations that the principal isomer produced from 76 is 81 (82 from 77), that there is so little of 94 present in the thermolysis of 89, that the control experiments with 89, 90 and 95 did not give any isomerized pyrazolines in the recovered samples, and that no 102 was found in the thermolysis of 98.

As mentioned previously, Berson and collaborators (6a) have observed an allylic rearrangement of the bicyclic pyrazoline 36 suggestive of a one-bond azo



36 41

cleavage mechanism. Crawford and collaborators (10a,11) have carried out the control experiments on the previously studied pyrazolines 30, 57, 68, 69, 83, 90, 95 and 98, and in no case have they been able to observe the analogous rearrangement since each sample was recovered essentially unchanged even though tautomerism of 57, 69, 83 and 98 prevented a definitive statement. The authors suggested the possibility that the cleavage of the second carbon-nitrogen bond is easier than rotation



and rebonding to the exocyclic alkylidene in the more planar monocyclic pyrazoline, but that the recombination to 41 can be facilitated in the bicyclic system 36 since the exocyclic isopropylidene group is much closer to the diazenyl nitrogen because of folding.

Although the authors attempted with limited success to use both the planar and orthogonal singlet TMM diradicals in the thermolysis of 4-alkylidene-1-pyrazolines, failure to develop a consistent pattern led them to suggest that nitrogen is implicated in the stereochemistry of the formation of the products.

OBJECTIVE

Assuming concerted two-bond cleavage for the thermolysis of the various 4-alkylidene-1-pyrazolines (10a,11,32), the product distributions cannot be rationalized in terms of a planar singlet trimethylenemethane (TMM) intermediate, nor, with a few exceptions, can they be reconciled in terms of an orthogonal singlet TMM intermediate. The product distributions which can be interpreted as arising from an orthogonal TMM intermediate are those from the thermolysis of 3,3-dimethyl-4-methylene-1-pyrazoline (56), 4-isopropylidene-1-pyrazoline (57) and 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline (62).

In the cases of 4-methylene-1-pyrazoline (30), 4-methylene-1-pyrazoline-3,3-d_2 (42) and 4-methylene-1-pyrazoline-3,3,6,6-d_4 (43), the kinetic data and the product distributions (see Table 5 and 6) can be rationalized in terms of a planar TMM intermediate (10a). Assuming two secondary deuterium kinetic isotope effects, one in the rate determining step (i.e., the step involving cleavage of the two C-N bonds) and the other in the product forming step, the values of the former isotope effect can be obtained from the kinetic data, and those of the latter isotope effect from the product distribution data.

On the basis of the magnitude of the isotope effects from the kinetic data and the observed $\delta\Delta G^{\ddagger}$ per α-deuterium of 101 ± 6 cal mol^{-1}, being within the frequently observed value of 90-120 cal mol^{-1} (26,27), both C-N bonds appear to break in the rate determining step (10a). However, a stepwise one-bond cleavage pathway cannot be ruled out unless the value of $\delta\Delta G^{\ddagger}$ per α-deuterium *via* this pathway becomes much larger than 120 cal mol^{-1}. 4-Methylene-1-pyrazoline-6,6-d_2 (107) and 4-methylene-1-pyrazoline-3,3,5,5-d_4 (46) should thus be prepared. The values of $\delta\Delta G^{\ddagger}$ per α-deuterium *via* both two-bond and one-bond cleavage pathways could then be estimated from the complete kinetic data of the thermolysis of 30, 42, 43, 46, 107 and 4-methylene-1-pyrazoline-3,3,5,5,6,6-d_6 (44) using the method described in the literature (7f) for nondeuterated and deuterated 1-pyrazolines.

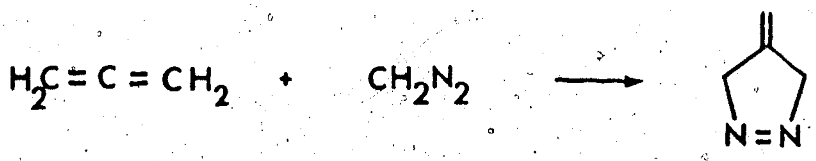
In the product forming step, the values of the isotope effect for the rotation of the deuteriomethylene group of the planar TMM to the ring methylene were obtained as 1.33 ± 0.06 for 42 and 1.35 ± 0.07 for 43 using the product distribution data in Table 6 (10a). These values are, surprisingly, comparable to the theoretical value, $k_H/k_D = 1.414$, derived from classical inertial argument that, for a given input of thermal energy, the ratio of the rotation of a CH_2 groups to the rotation of a CD_2 group will be in inverse proportion to the square root of their moments of inertia (25b). It would thus be of considerable interest to examine the product distributions in the thermolysis of 46 and 107 since the product ratios from 42 and 107 would be expected to be the same and so would those from 43 and 46.

A similar treatment to the above failed when applied to the product distributions from the thermolysis of *E*- and *Z*-4-ethylidene-1-pyrazoline-3,3-d_2 (76 and 77) (see Table 10) (11). The implied steric effect by a methyl group of an exocyclic double bond may have significantly altered the mechanism, e.g., the carbon-nitrogen bond *syn* to a methyl group may be lagging in the bond breaking process. An answer to this speculation would be provided by investigating kinetics for the thermolysis of 4-ethylidene-1-pyrazoline (69) and its dideuterio derivatives, 76 and 77.

RESULTS

A. Syntheses

D'yakonov (37) prepared 4-methylene-1-pyrazoline (**30**) for the first time by the addition of diazomethane to allene. It was obtained in low yield due to formation of tautomers (4-methylene-2-pyrazoline and 4-methylpyrazole) and unidentified high boiling compounds. A superior yield (65%) was obtained by using a large



30

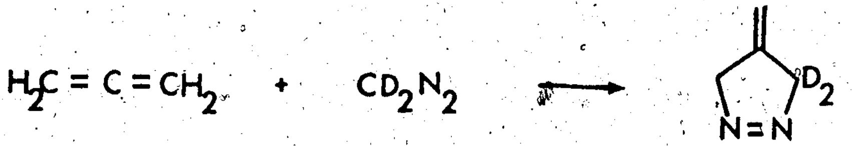
excess of allene in accord with Cameron's procedure (35).

The ^{1}Hmr spectrum of **30** (Figure 1) was taken in benzene-d_6, since it was found that most of 4-alkylidene-1-pyrazolines isomerize slowly at room temperature in chloroform but are stable in benzene for a day or so.

The Fourier transform infrared spectrum (FTIR) of gaseous **30** (Figure 28) has no absorption above 3100 cm^{-1} indicating the absence of any nitrogen-hydrogen bonds of tautomers. The bands at 1552 and 1685 cm^{-1} are consistent with the stretching modes of nitrogen-nitrogen and carbon-carbon double bonds.

Pure **30** could be stored at -40°C under argon atmosphere for a month without any noticeable formation of tautomers.

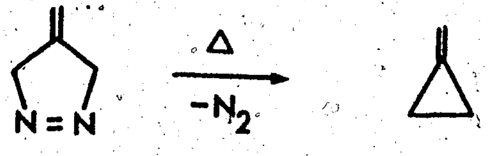
Preparation of 4-methylene-1-pyrazoline-3,3-d_2 (42) was accomplished by the addition of diazomethane-d_2 to allene as described by Cameron (35). The FTIR spectrum



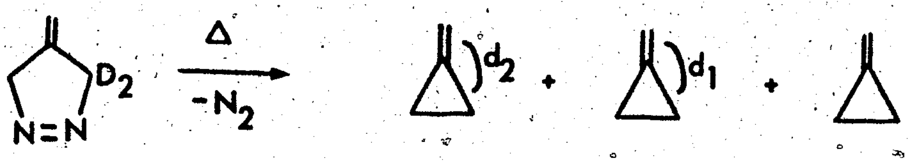
42

of gaseous 42 (Figure 30) shows the bands at 1051, 2142 and 2218 cm^{-1} which are not present in the spectrum of 30 (Figure 28). These bands are consistent with the bending and stretching modes of an α-carbon-deuterium bond.

The deuterium content was estimated to be 97 ± 1% by 100 MHz ^{1}Hmr spectroscopy (Figure 2). We were able to determine the more reliable isotopic purity of 42 by the comparison of the mass spectra, at low ionization potential, of methylenecyclopropane (31) and the mixture of non- and deuterated methylenecyclopropanes produced



30 31

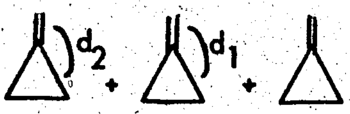


42

from the thermolysis of 30 and 42. The mass spectrum of 31 has a very small M-1 peak, only 1.18% of the molecular ion peak (M), and an M+1 peak, 4.39% of the M peak, comparable to the carbon-13 natural abundance (1.08% x 4 = 4.32%) as indicated in Table 14. However, it should be noted that the isotopic purity of 42 could not be determined directly from the mass spectra of 30 and 42 due to the very large M-1 peak indicating extreme ease of fragmentation even at low ionization potential.

Table 14

Fragmentation data from low ionization potential mass spectra of the methylenecyclopropane and the mixture of nondeuterated and deuterated methylenecyclopropanes

	Intensity, %	
m/e	 31	 31
53	1.18 (M-1)	
54	100 (M)	0.72
55	4.39 (M+1)	6.17
56	0.13 (M+2)	100
57		4.36
58		0.10

The fragmentation data on 31 in Table 14 was used as a standard in the calculation of the isotopic purity of 42 instead of the carbon-13 natural abundance. Assuming the same fragmentation pattern in the mixture of non-, mono- and dideurated methylenecyclopropanes as in 31, and defining their relative mole ratio as R_{d_0}, R_{d_1}, and R_{d_2}, the data in Table 14 would give

$$0.72 = R_{d_0} + 0.0118\, R_{d_1} \qquad \text{(eq. 3)}$$

$$6.17 = 0.0439\, R_{d_0} + R_{d_1} + 0.0118\, R_{d_2} \qquad \text{(eq. 4)}$$

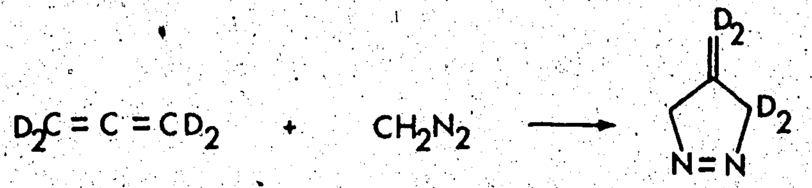
and

$$100 = 0.0013\, R_{d_0} + 0.0439\, R_{d_1} + R_{d_2} \qquad \text{(eq. 5)}$$

The simultaneous solution of these three linear equations gives $R_{d_0} = 0.66$, $R_{d_1} = 4.96$, and $R_{d_2} = 99.83$ which were then converted into percentage ratios to give $D_0 = 0.63\%$, $D_1 = 4.70\%$, and $D_2 = 94.67\%$ with an isotopic purity of 97.02% for 42.

The same calculations on the data from three independent samples were carried out to give the average values: $D_0 = 0.6 \pm 0.1\%$, $D_1 = 4.8 \pm 0.1\%$, and $D_2 = 94.6 \pm 0.1\%$ with an isotopic purity of 97.0 ± 0.1% for 42.

4-Methylene-1-pyrazoline-3,3,6,6-d_4 (43) was prepared by the addition of diazomethane to allene-d_4 according to Cameron's procedure (35). Similarly, the addition of diazomethane-d_2 to allene-d_4 gave 4-methylene-1-pyrazoline-3,3,5,5,6,6-d_6 (44). The FTIR spectrum of gaseous 43



43

44

(Figure 31) shows bands at 709, 2230 and 2331 cm^{-1} which are not present in the spectrum of 42 (Figure 30). These bands are consistent with the bending and stretching modes of a γ-carbon-deuterium bond. The FTIR spectrum of gaseous 44 (Figure 33) shows the absence of the bands at 1420, 2858 and 2940 cm^{-1} present in the spectrum of 43 (Figure 31) and indicating the bending and stretching modes of an α-carbon-hydrogen bond.

The deuterium content on 43 was estimated to be 97 ± 1% by 100 MHz ^{1}Hmr spectroscopy (Figure 3). The mass spectra at low ionization potential were analyzed in a way analogous to that previously described to give isotopic purities of 97.1 ± 0.1% (D_0 = 0.3, D_1 = 0.2, D_2 = 1.6, D_3 = 6.7, D_4 = 91.2) for 43, and 96.8 ± 0.1% (D_0 = 0.0, D_1 = 0.0, D_2 = 0.3, D_3 = 0.1, D_4 = 1.5, D_5 = 14.4, and D_6 = 83.7) for 44.

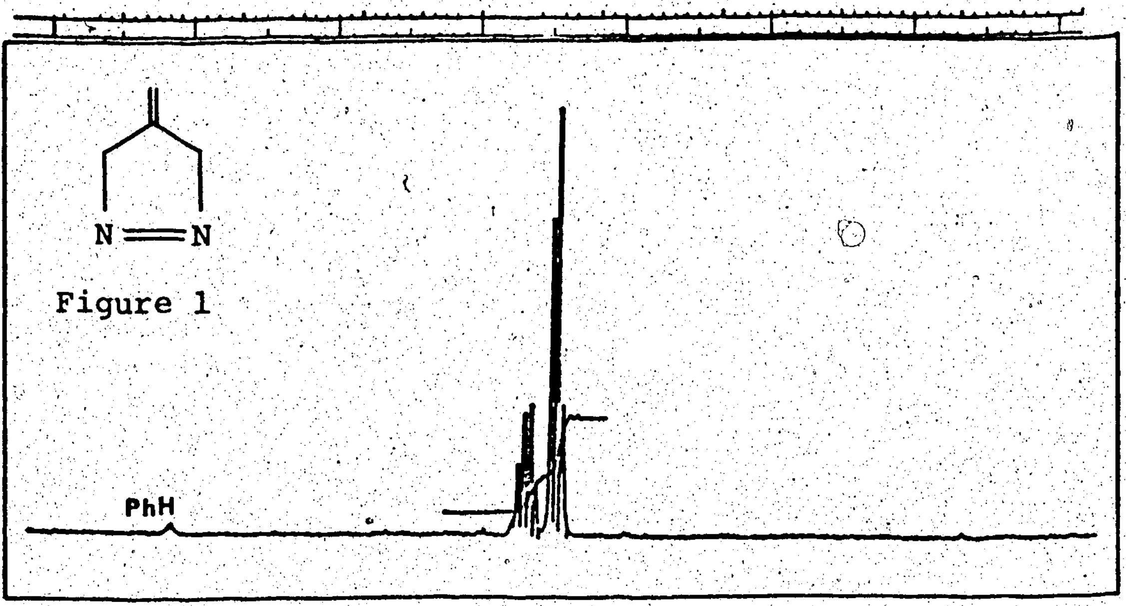


Figure 1

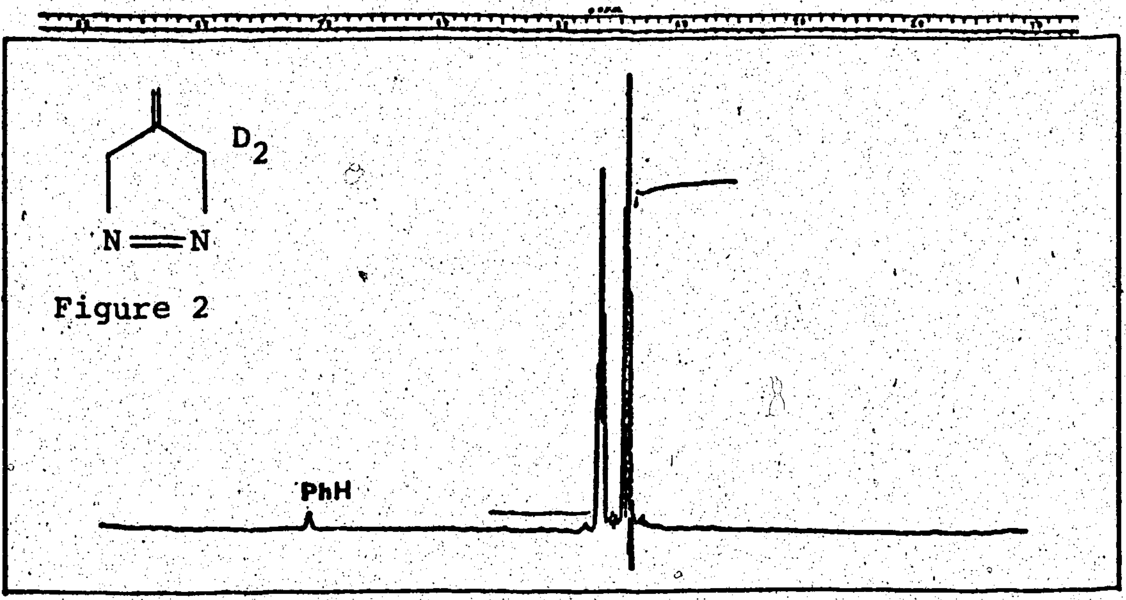


Figure 2

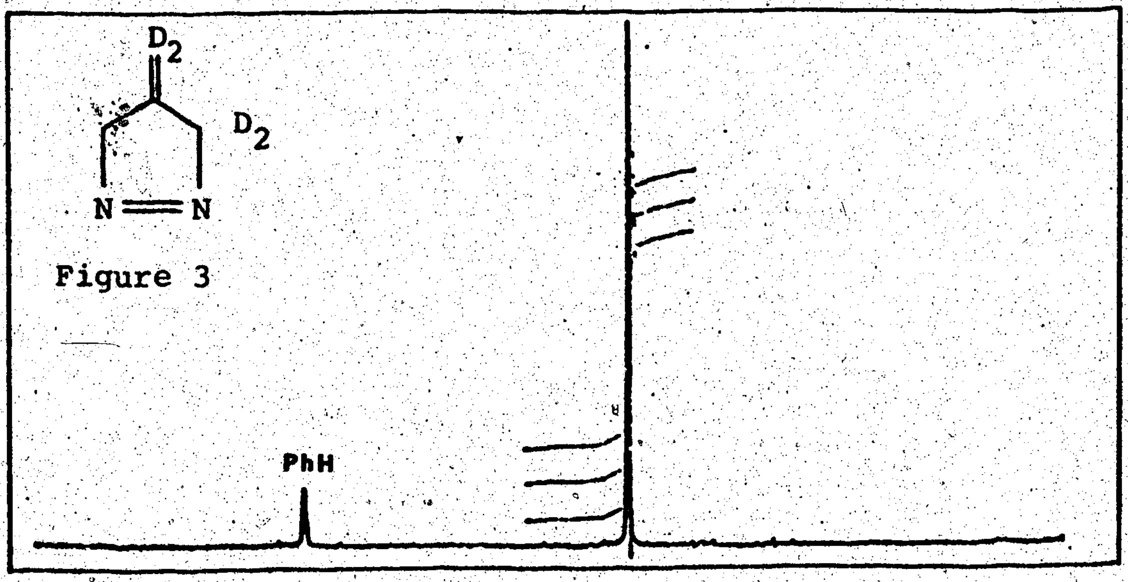
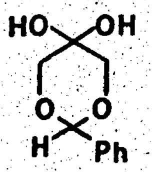


Figure 3

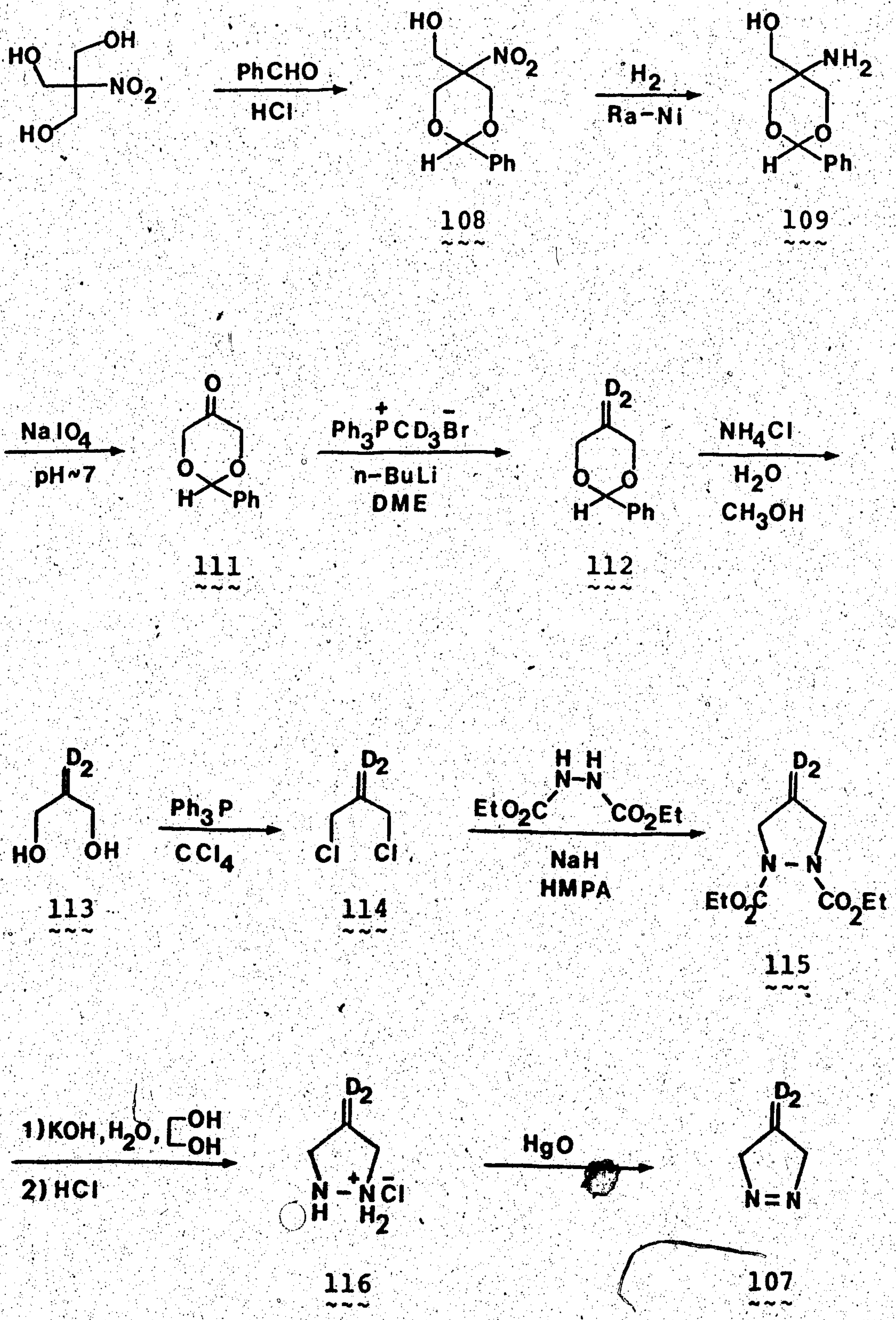
We successfully synthesized, for the first time, 4-methylene-1-pyrazoline-6,6-d_2 (**107**) and 4-methylene-1-pyrazoline-3,3,5,5-d_4 (**46**).

Compound **107** was prepared as outlined in Scheme 1. 5-Nitro-5-(hydroxymethyl)-2-phenyl-1,3-dioxan (**108**) (Figure 4) was obtained by the acid catalyzed condensation of tris-(hydroxymethyl)nitromethane with benzaldehyde by the procedure of Scattergood and Maclean (38). Hydrogenation of **108** with Raney-nickel, as described by Malei and Raphael (39), furnished 5-amino-5-(hydroxymethyl)-2-phenyl-1,3-dioxan (**109**) (Figure 5). The oxidation of **109** with sodium metaperiodate was followed by the sublimation of the resulting 5,5-dihydroxy-2-phenyl-1,3-dioxan (**110**) to produce 5-oxo-2-phenyl-1,3-dioxan (**111**) in very low yield (39). The yield of **111**



110

can be increased to 85% by vigorous stirring of a solution containing **109**, sodium metaperiodate and dichloromethane buffered at pH 6. Without buffering the pH increases and the yields are reduced. Dichloromethane serves to extract the ketone **111** leaving the gem diol **110** in the aqueous phase. The ketone **111** can be stored at -40° in an inert atmosphere for months. At room


PhCHO
HCl
108
H2
Ra-Ni
109
NaIO4
pH~7
111
Ph3P+CD3Br−
n-BuLi
DME
112
NH4Cl
H2O
CH3OH
113
Ph3P
CCl4
114
EtO2C(H)N-N(H)CO2Et
NaH
HMPA
115
1) KOH, H2O, ethylene glycol
2) HCl
116
HgO
107

Scheme 1

temperature it slowly deteriorates to a yellow oil having the odour of benzaldehyde. Recrystallization from pentane immediately before use is recommended.

Treatment of 111 with methylene-d_2-triphenylphosphorane produced from the reaction of methyl-d_3-triphenylphosphonium bromide with n-butyllithium according to an adaptation of the procedure of Malloy, Hedges, and Fisher (40) furnished 5-methylene-2-phenyl-1,3-dioxan-7,7-d_2 (112) in 80% yield. It should be noted that the deuterium content of 112 varies from 65 to 95% depending on the dryness of solvent (1,2-dimethoxyethane) and the ratio of reactants. A procedure in which the DME was distilled over lithium aluminum hydride three times under an argon atmosphere immediately before use, and methyl-d_3-triphenylphosphonium bromide, n-butyllithium and 111 were reacted in the approximate mole ratio of 1.24, 1.12 and 1.00 gave optimum yields.

The deuterium content of 112 was estimated to be 95 ± 1% by 100 MHz ^{1}Hmr spectroscopy (Figure 8). The mass spectrum at low ionization potential was analyzed to give an isotopic purity of 95 ± 1% (D_0 = 0.9, D_1 = 7.9, and D_2 = 91.2) based on the M-77 peak, since there was a very large M-1 peak. The integration of the 13.6 MHz ^{2}Hmr spectrum (CCl_4) corresponds to more than 99.8% of the total deuterium at the exo-methylene position, Figure 9.

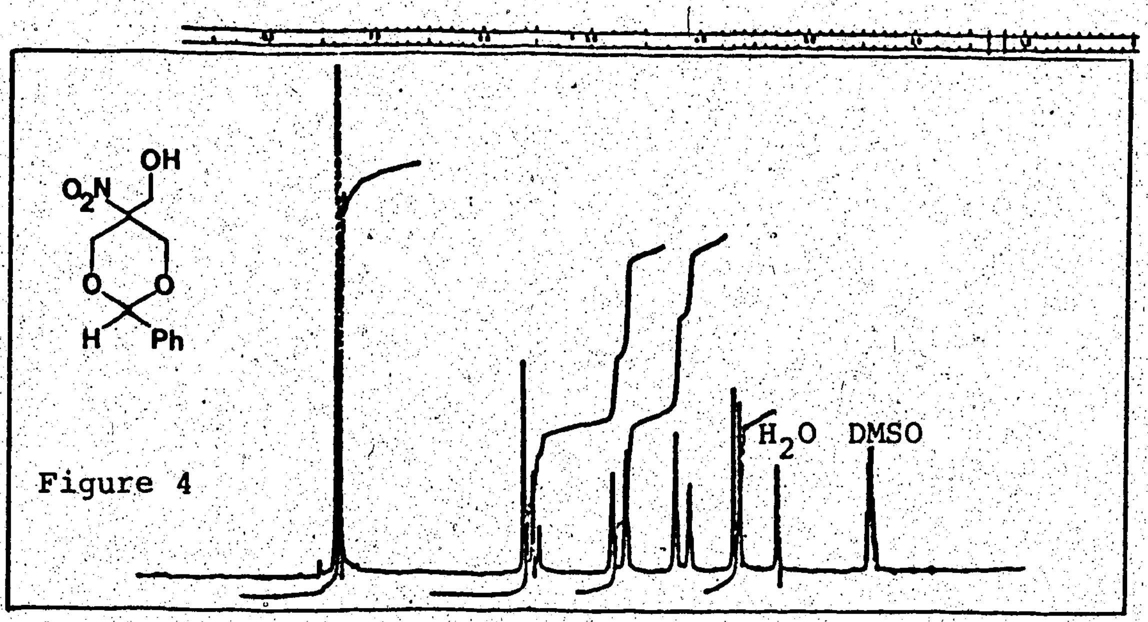


Figure 4

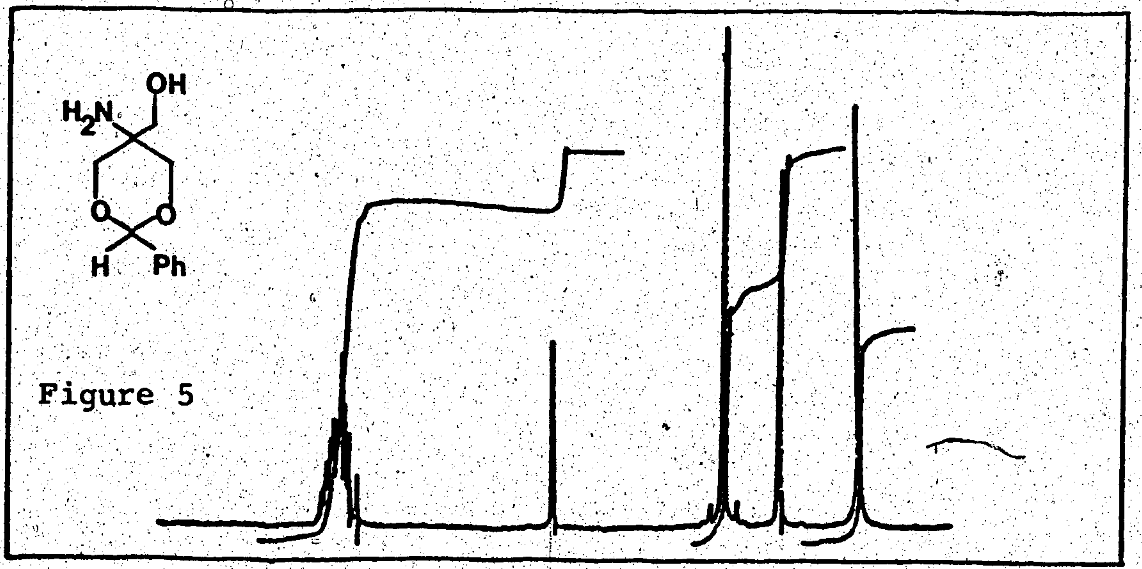


Figure 5

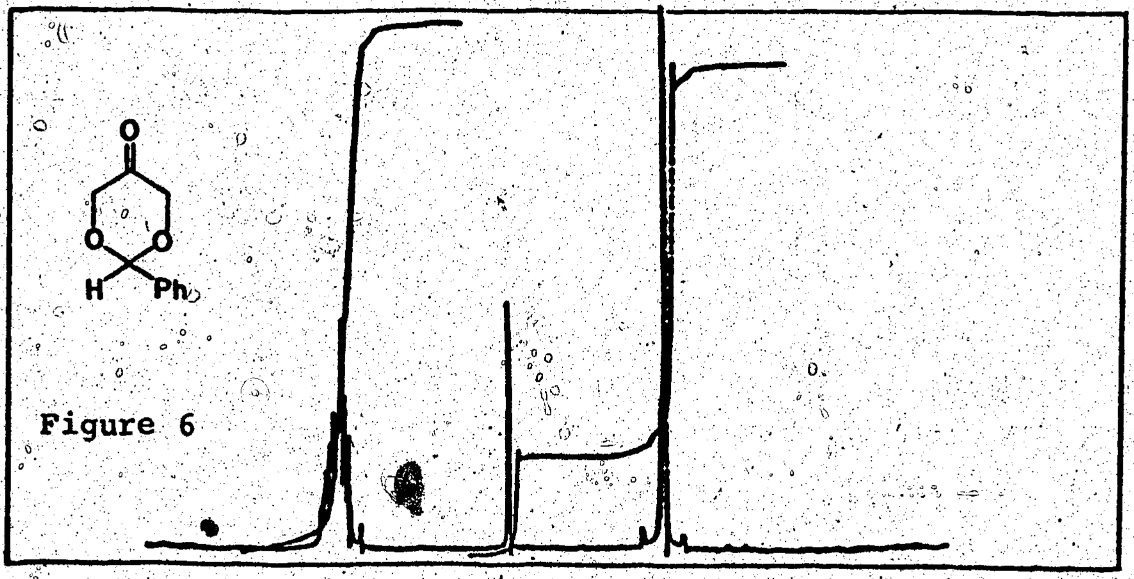


Figure 6

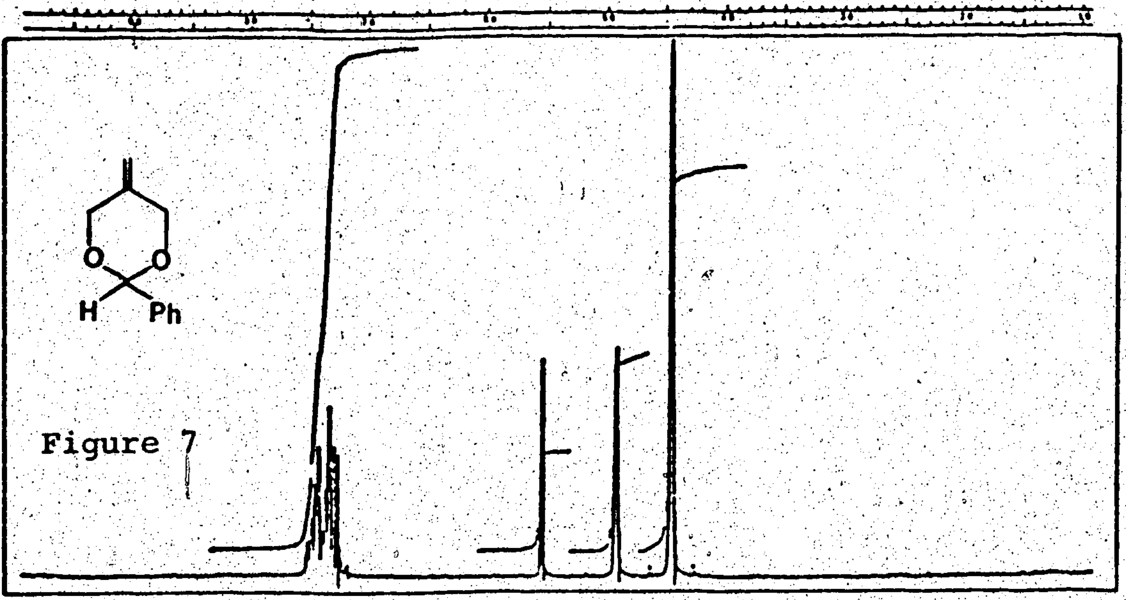


Figure 7

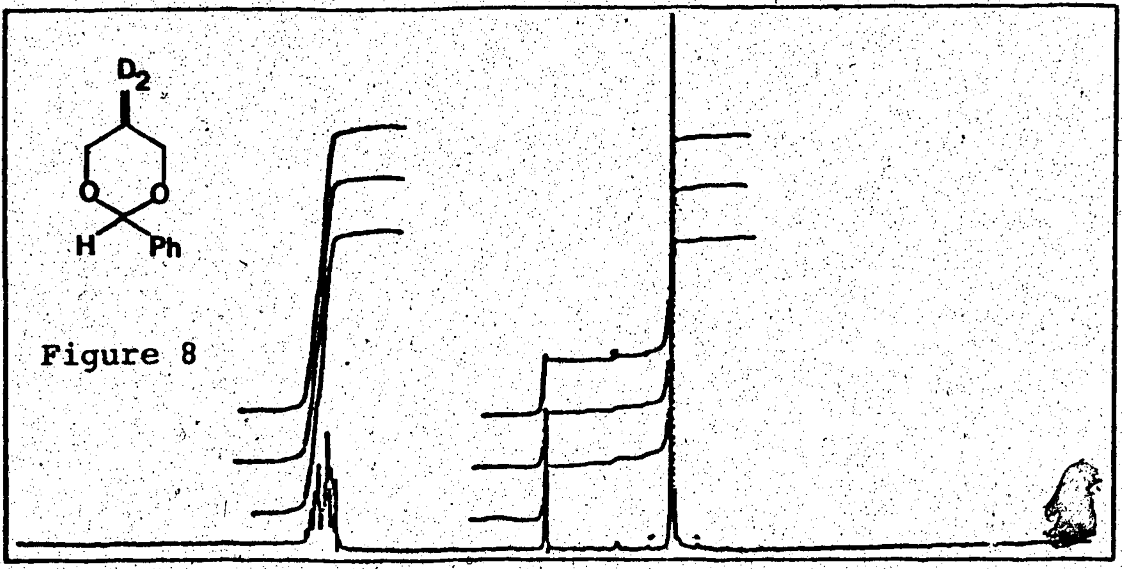


Figure 8

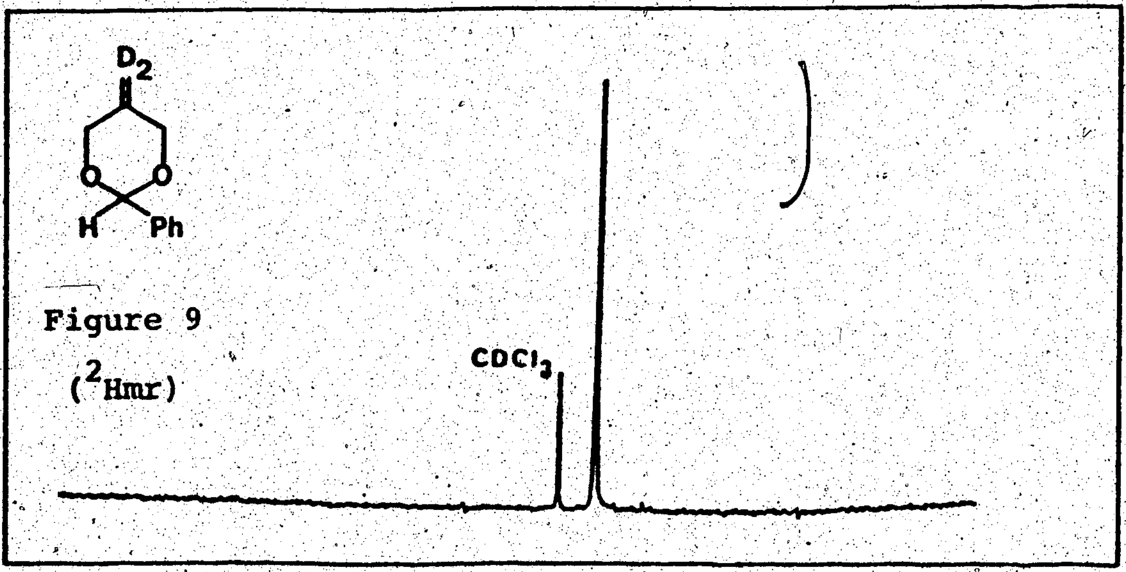


Figure 9

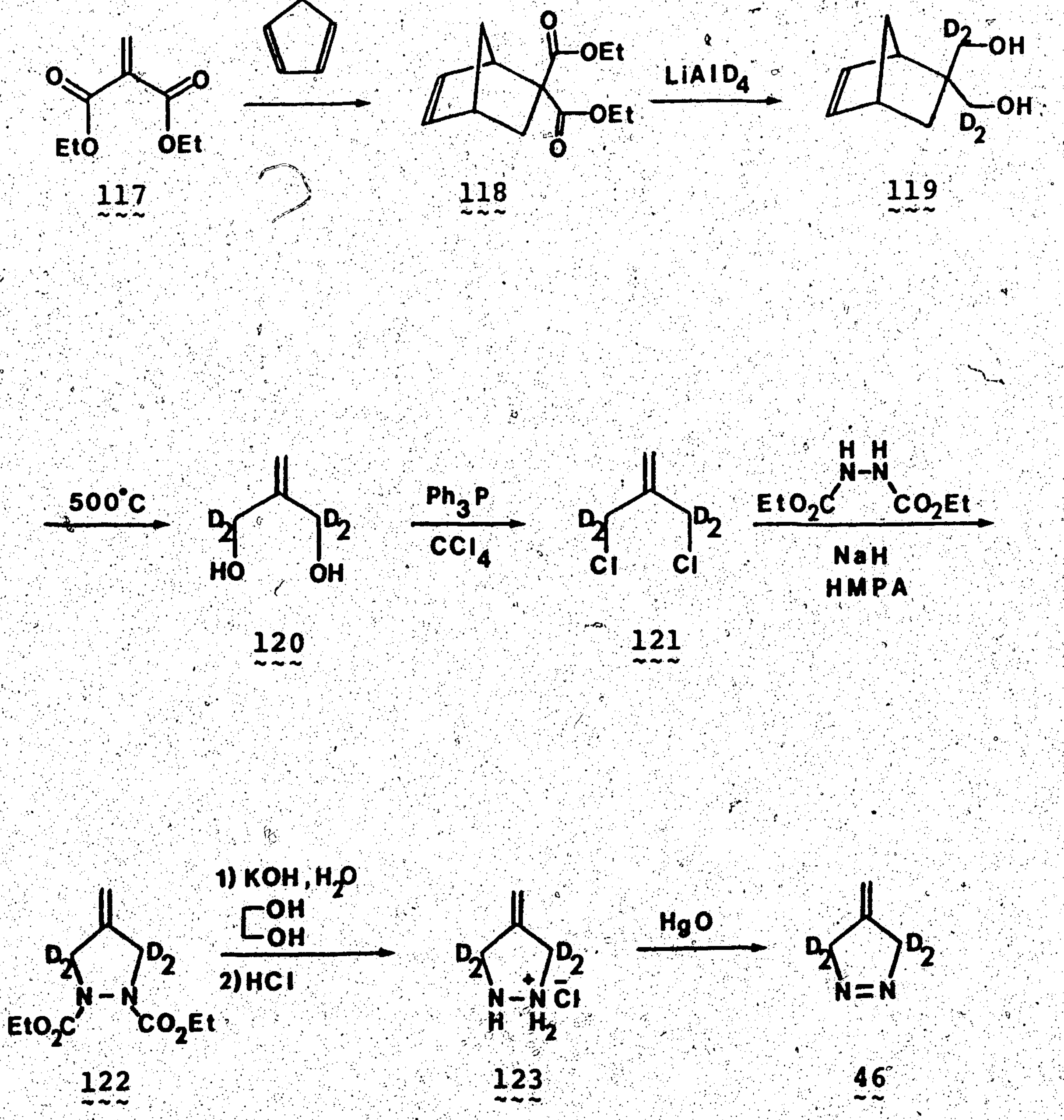
(^{2}Hmr)

Hydrolysis of 112 by ammonium chloride in water and methanol gave 2-(methylene-d_2)-1,3-propanediol (113) in 85% yield. The deuterium content was estimated to be 95 ± 1% by 100 MHz ^{1}Hmr spectroscopy (Figure 14). The extreme ease of the fragmentation as indicated by the low ionization potential mass spectrum prevented the determination of the isotopic distribution of 113.

Since the subsequent steps for the preparation of the pyrazoline 107 from the diol 113, shown in Scheme 1, were applied in the same manner to obtain 4-methylene-1-pyrazoline-3,3,5,5-d_4 (46) from 2-methylene-1,3-propanediol-1,1,3,3-d_4 (120), it is convenient at this point to consider the synthesis of 120. Scheme 2 shows the full synthetic route to 46.

Diethyl methylenemalonate (117) was prepared by the condensation of diethyl malonate with paraformaldehyde by the procedure of Bachman and Tanner (41). Diels-Alder addition of 117 to freshly prepared cyclopentadiene was carried out to furnish 5,5-dicarbethoxy-2-norbornene (118), bp 107-108.5°C/2.5 Torr. The structure of 118 was confirmed by microanalysis, ^{1}Hmr (Figure 10), infrared and exact mass measurement.

Lithium aluminum deuteride reduction of the ester 118 furnished 5,5-bis-(hydroxymethyl-d_2)-2-norbornene (119) in 82% yield. The deuterium content of 119 could not be determined by ^{1}Hmr spectroscopy since a water peak


EtO
OEt
117
OEt
OEt
118
LiAlD$_4$
D$_2$
OH
OH
D$_2$
119
500°C
D$_2$
D$_2$
HO
OH
120
Ph$_3$P
CCl$_4$
D$_2$
D$_2$
Cl
Cl
121
H H
N–N
EtO$_2$C
CO$_2$Et
NaH
HMPA
D$_2$
D$_2$
N – N
EtO$_2$C
CO$_2$Et
122
1) KOH, H$_2$O
OH
OH
2) HCl
D$_2$
D$_2$
N – N Cl
H H$_2$
123
HgO
D$_2$
D$_2$
N=N
46

Scheme 2

interferes with the methylene peaks of 5-hydroxymethyl groups as in Figure 12 even though this spectrum indicates high isotopic purity. The mass spectrum at low ionization potential shows the extreme ease of fragmentation making it impossible to estimate the isotopic purity.

Diol **119** was pyrolyzed at approximately 500°C using an adaptation of the procedure of Corey and Suggs (42) producing 2-methylene-1,3-propanediol-1,1,3,3-d_4 (**120**). The deuterium content of **120** was estimated to be 96 ± 1% by 100 MHz ^{1}Hmr spectroscopy (Figure 15).

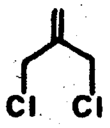
3-Chloro-2-(chloromethyl)propene-1,1-d_2 (**114**) was prepared in 52% yield by substitution reaction of the diol **113** with triphenylphosphine and carbon tetrachloride in tetrahydrofuran using an adaptation of the procedure of Hooz and Gilani (43). The 13.6 MHz ^{2}Hmr spectrum (CCl_4) of **114** indicates more than 99.8% of the total deuterium to be at the exo-methylene position. The deuterium content of **114** was estimated to be 95 ± 1% by 100 MHz ^{1}Hmr spectroscopy (Figure 17). The mass spectrum at low ionization potential was analyzed and gave an isotopic purity of 94 ± 1% ($D_0 = 1.8$, $D_1 = 9.0$ and $D_2 = 89.2$) based on the molecular ion peak.

Bromination of **113** has been attempted; however, significant scrambling between the deuterium at the exo-methylene and at the ring methylene position was observed in the ^{1}Hmr spectrum of the resulting dideuterated

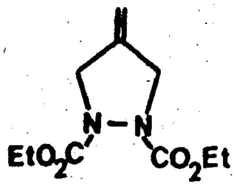
3-bromo-2-(bromomethyl)propene.

3-Chloro-2-(chloromethyl-d_2)-propene-3,3-d_2 (121) was synthesized from the diol 120 in a manner similar to the synthesis of the dichloride 114 from the diol 110. The deuterium content of 121 was estimated to be 96 ± 1% by 100 MHz ^{1}Hmr spectroscopy (Figure 18). The low ionization potential mass spectrum indicated an isotopic purity of 96 ± 1% (D_0 = 0.0, D_1 = 0.0, D_2 = 6.5, D_3 = 1.6 and D_4 = 91.9).

1,2-Dicarbethoxy-4-methylenepyrazolidine (125) was prepared in 70% yield *via* cyclization of 3-chloro-2-(chloromethyl)propene (124) with *sym*-dicarbethoxyhydrazine in the presence of sodium hydride in hexamethylphosphoramide using an adaptation of the procedure of Rubottom and Chabala (44). The structure of 125 was confirmed by microanalysis, ^{1}Hmr (Figure 19), infrared and exact mass measurement.



124

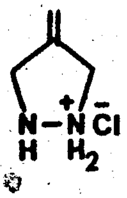


125

1,2-Dicarbethoxy-4-methylenepyrazolidine-6,6-d_2 (115) and 1,2-dicarbethoxy-4-methylenepyrazolidine-3,3,5,5-d_4 (122) were prepared from the corresponding dichlorides 114 and 121 by a procedure similar to the preparation of the ester 125. The 13.6 MHz ^{2}Hmr spectra indicate the absence of deuterium scrambling by only showing either the peak of exo-methylene deuterium for the ester 115 or that of ring methylene deuterium for 122. The deuterium contents of 115 and 122 were estimated to be 94 ± 1% and 95 ± 1% respectively by 100 MHz ^{1}Hmr spectroscopy (Figures 20 and 21). The mass spectra at low ionization potential were analyzed to give isotopic purities of 94.8 ± 0.1% ($D_0 = 0.7$, $D_1 = 9.1$, and $D_2 = 90.2$) for 115 and 95 ± 1% ($D_0 = 0.0$, $D_1 = 0.0$, $D_2 = 10.1$, $D_3 = 1.8$ and $D_4 = 88.1$) for 122 based on the molecular ion peaks.

Hydrolysis of the ester 125 with potassium hydroxide and subsequent treatment of the resulting 4-methylenepyrazolidine (126) with hydrochloric acid by an adaptation of the procedure of Crawford and Tokunaga (10a)

126



127

furnished 4-methylenepyrazolidine hydrochloride (127), mp 112-114°C in 88% yield. The microanalytical and spectroscopic data are consistent with the structure 127. The ^{1}Hmr spectrum is presented in Figure 22.

4-Methylenepyrazolidine-6,6-d_2 hydrochloride (116) and 4-methylenepyrazolidine-3,3,5,5-d_4 hydrochloride (123) were synthesized from the corresponding esters 115 and

122 in a manner analogous to the hydrochloride 127. The deuterium contents were estimated to be 94 ± 1% for 116 and 95 ± 1% for 123 by ^{1}Hmr spectroscopy (Figures 23 and 24).

Finally, oxidation of the hydrochlorides 116 and 123 with red mercuric oxide gave 4-methylene-1-pyrazoline-6,6-d_2 (107) and 4-methylene-1-pyrazoline-3,3,5,5-d_4 (46) respectively (10a). The 13.6 MHz ^{2}Hmr spectra indicate more than 99.8% of total deuterium at the exo-methylene position for 107 (Figure 25) and at the ring methylene position for 46. The deuterium contents were estimated to be 95 ± 1% for both 107 and 46 by 100 MHz ^{1}Hmr spectroscopy (Figures 26 and 27). The mass spectra at low ionization potential were analyzed and gave isotopic purities of 95.0 ± 0.1% (D_0 = 0.4, D_1 = 9.2 and D_2 = 90.4) for 107 and 95.4 ± 0.1% (D_0 = 0.6, D_1 = 0.0, D_2 = 7.0, D_3 = 2.0 and D_4 = 90.4) for 46.

The FTIR spectrum of gaseous 107 (Figure 29) shows bands at 712, 2224 and 2330 cm^{-1} which are not present in the spectrum of 4-methylene-1-pyrazoline (30), Figure 28. These bands are consistent with the bending and stretching modes of a γ-carbon-deuterium bond. The FTIR spectrum of gaseous 46 (Figure 32) indicates the absence of bands at 1422, 2860 and 2942 cm^{-1} present in the spectrum of 4-methylene-1-pyrazoline-3,3-d_2 (42) (see Figure 30) and representing the bending and

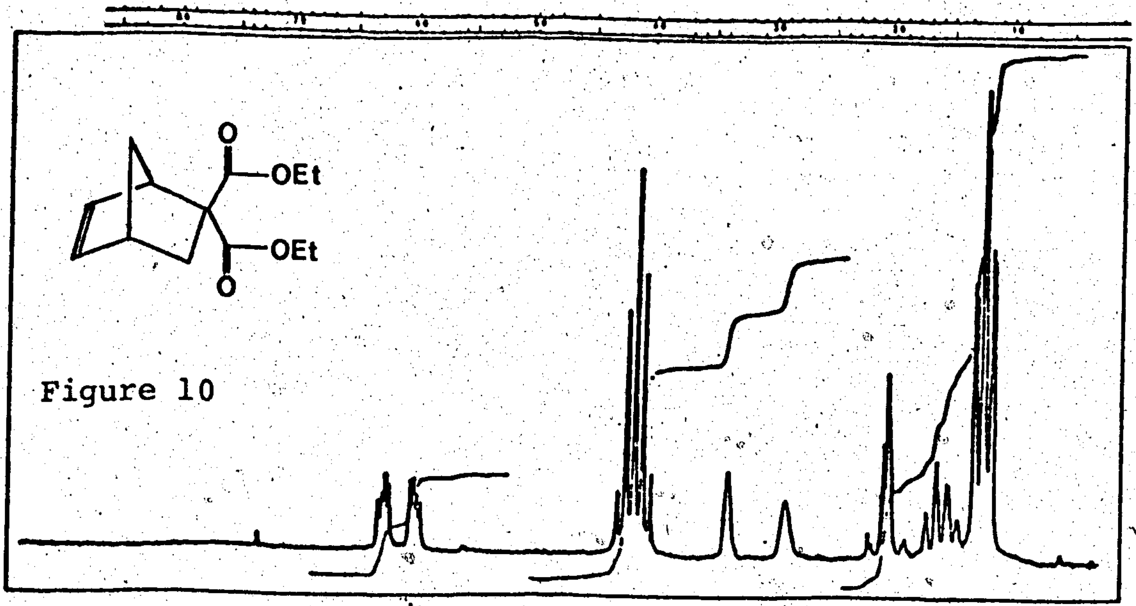


Figure 10

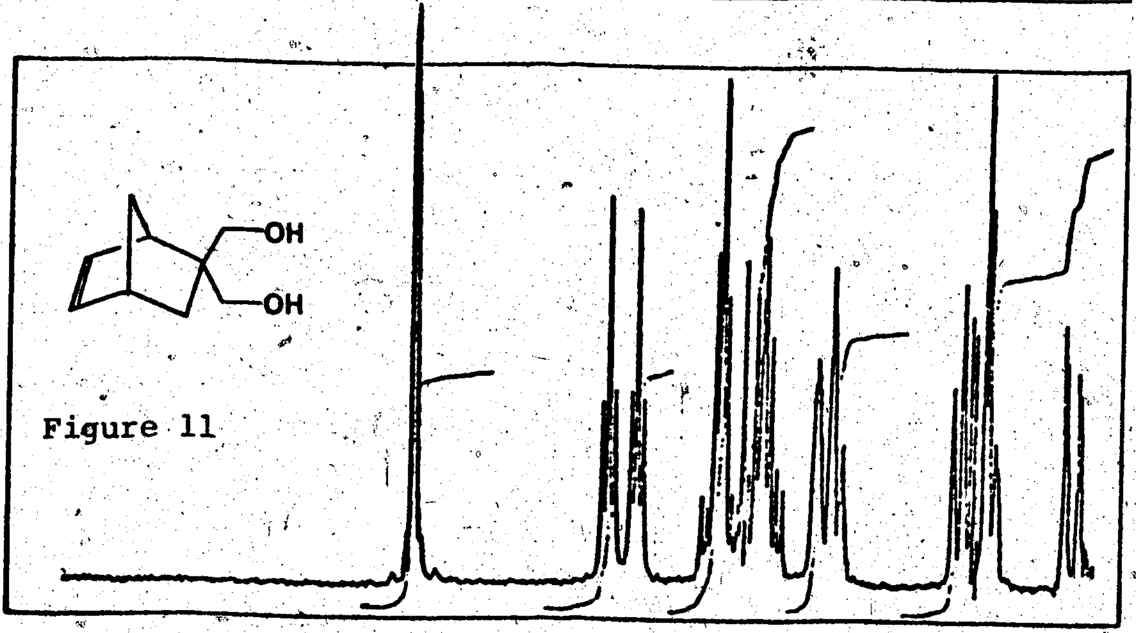


Figure 11

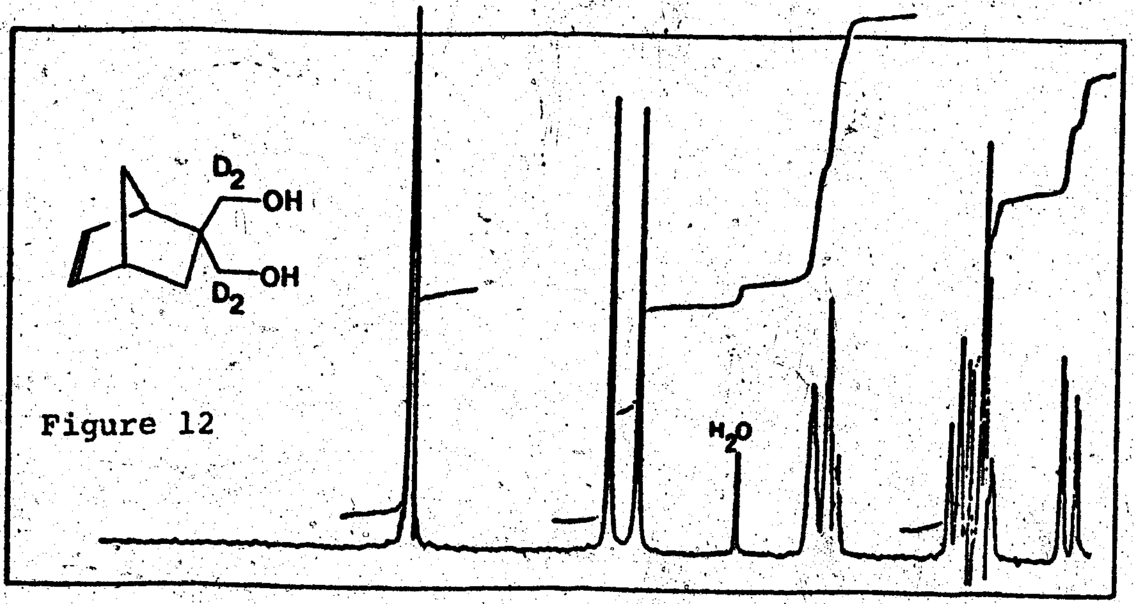


Figure 12

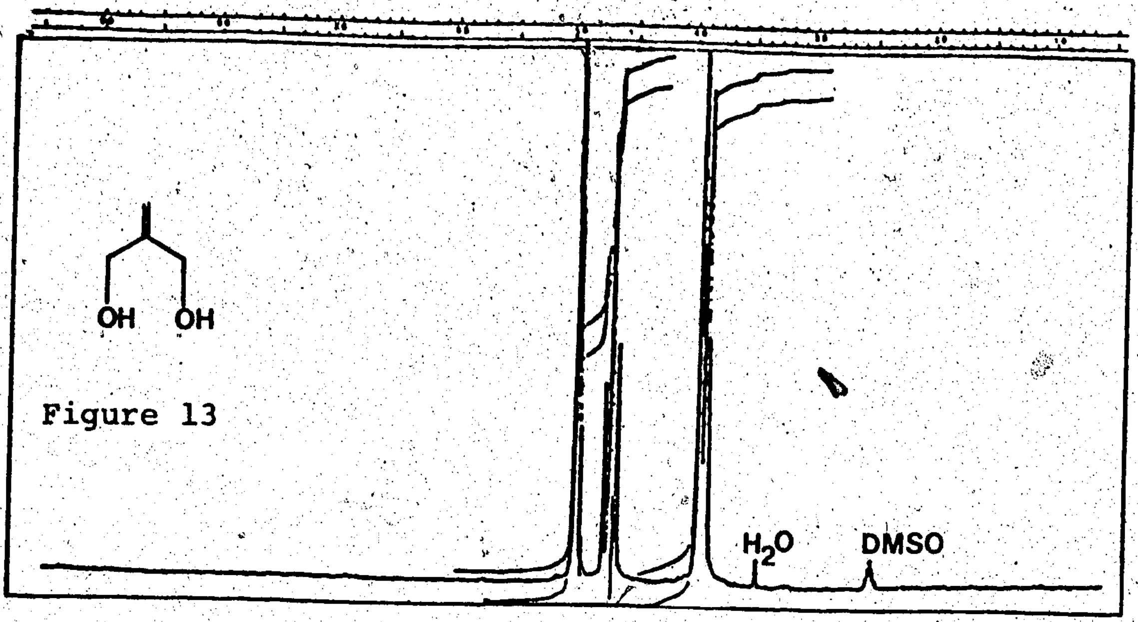


Figure 13

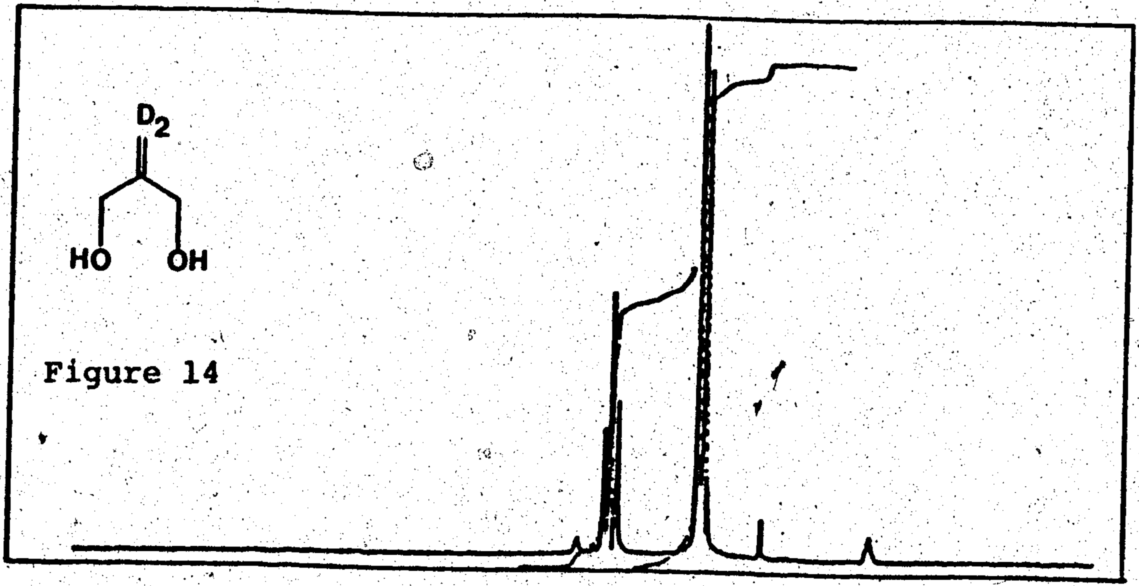


Figure 14

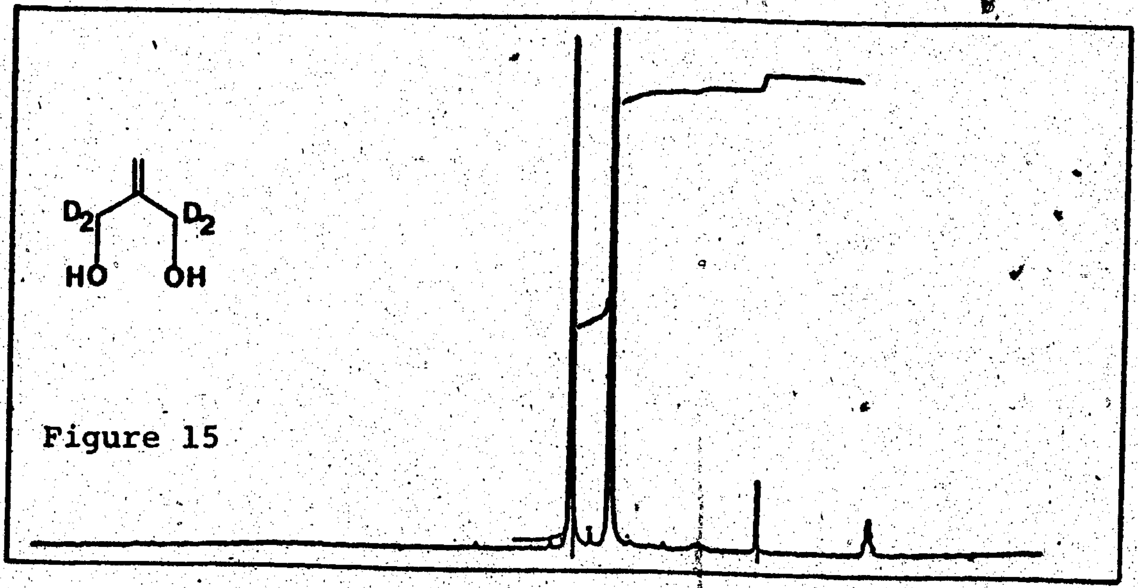


Figure 15

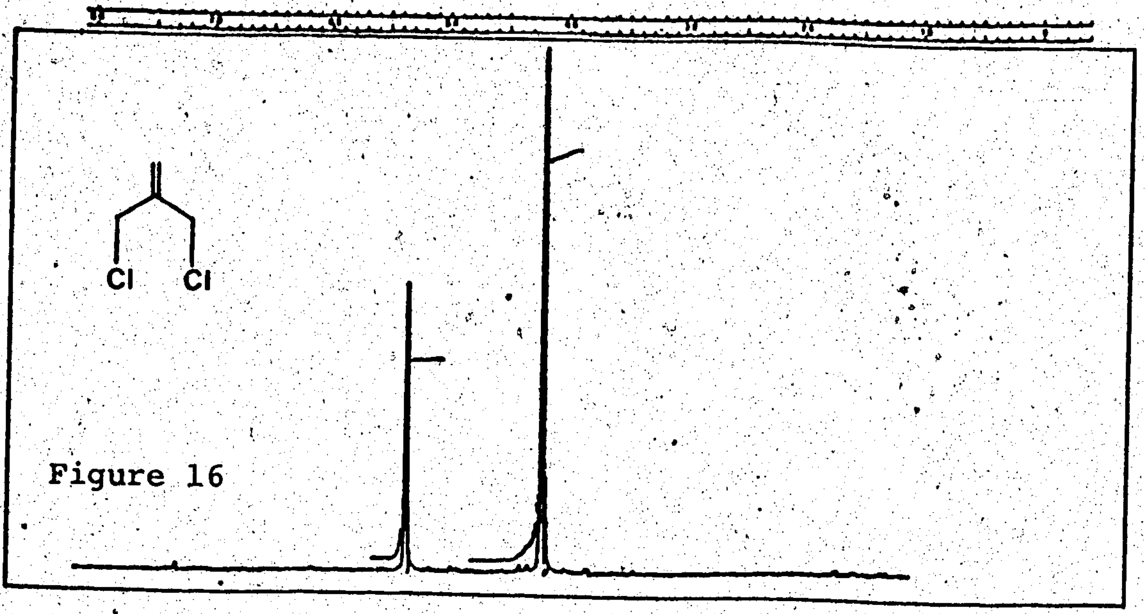


Figure 16

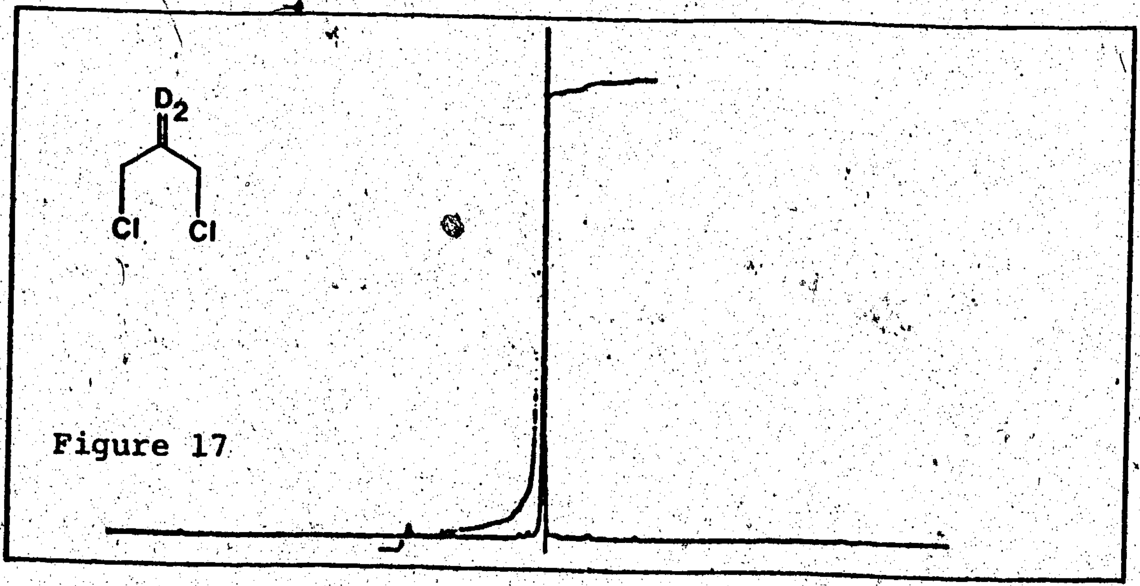


Figure 17

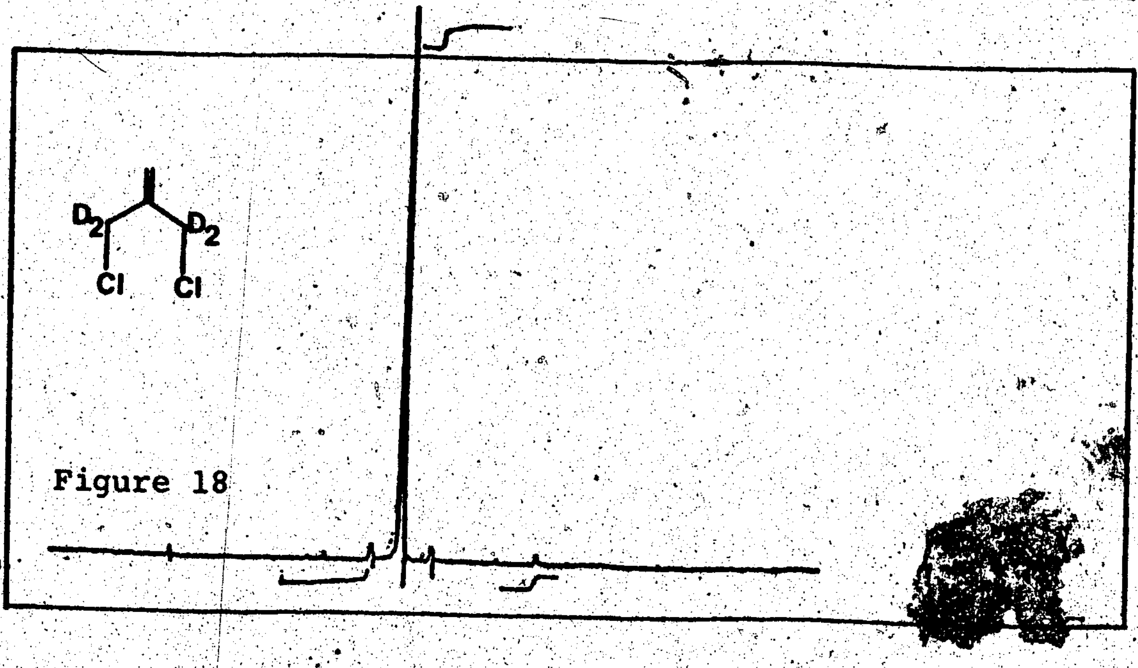


Figure 18

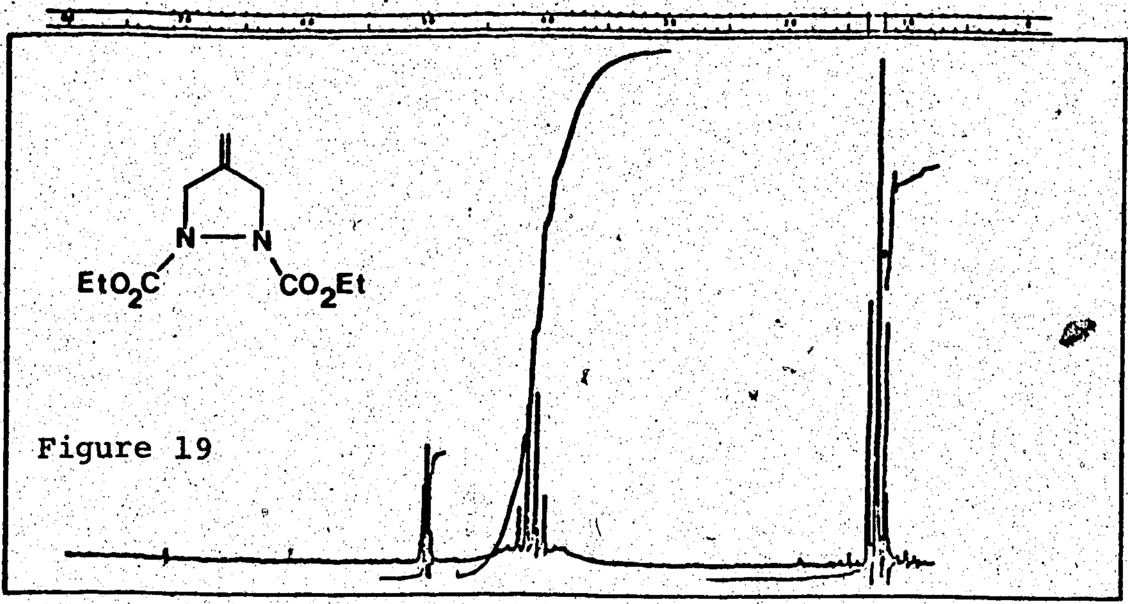


Figure 19

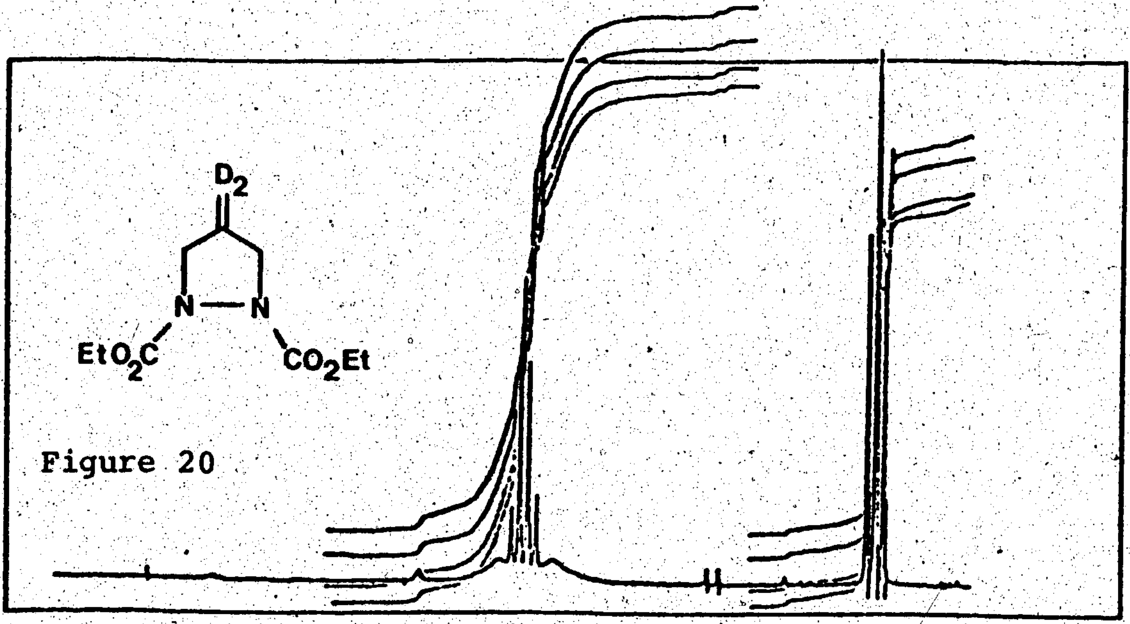


Figure 20

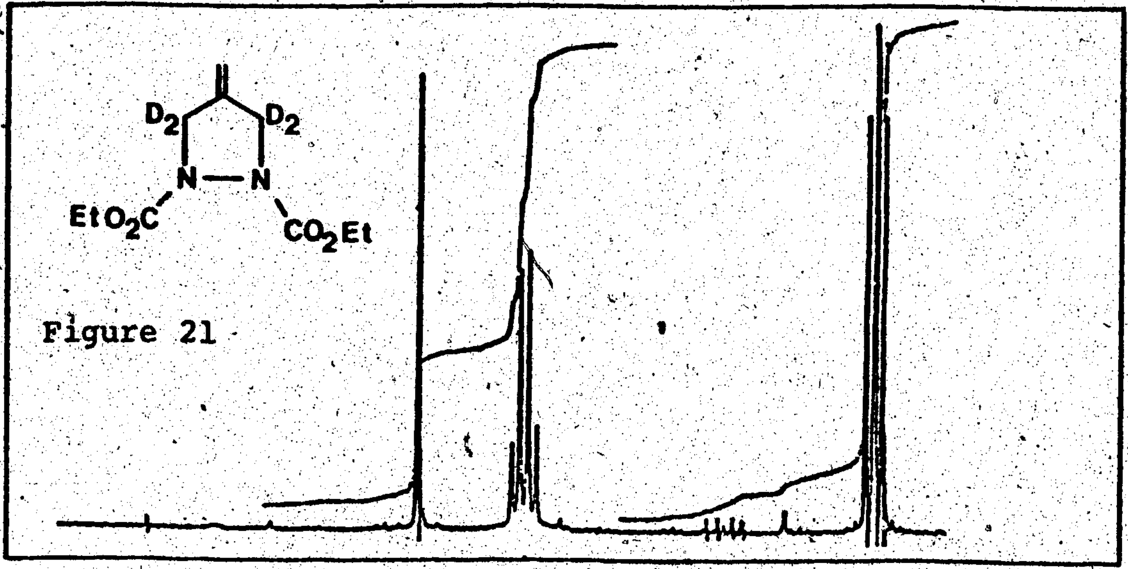


Figure 21

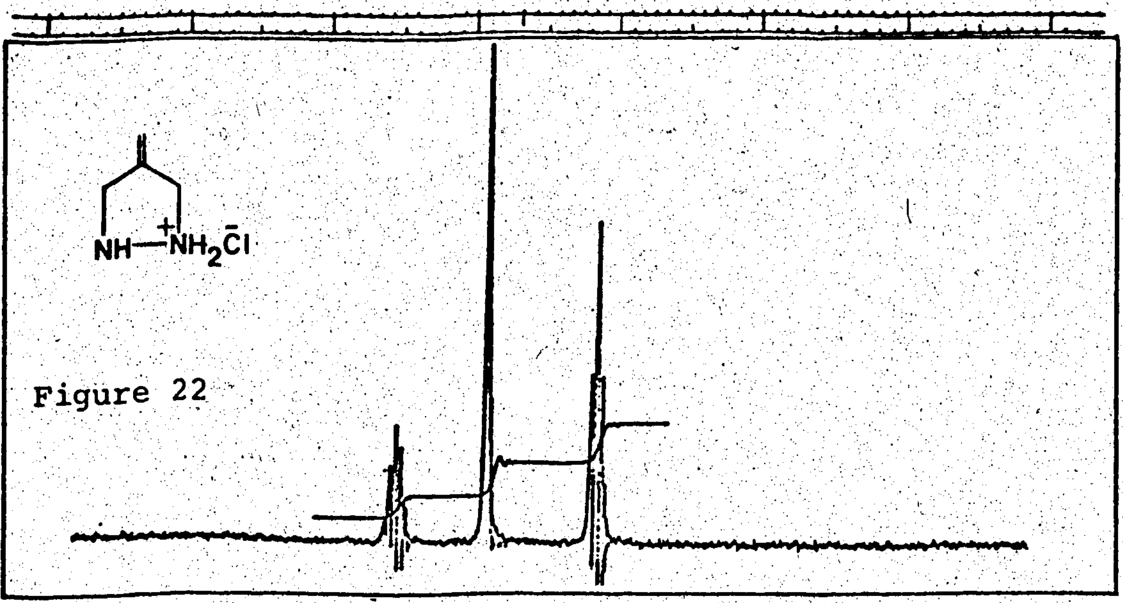


Figure 22

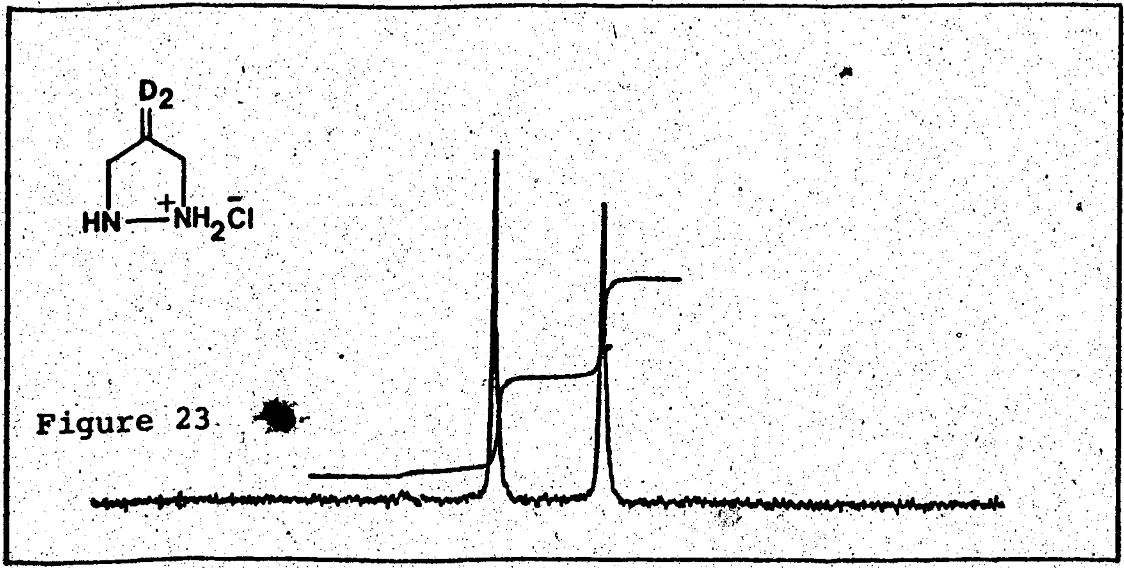


Figure 23

Figure 24

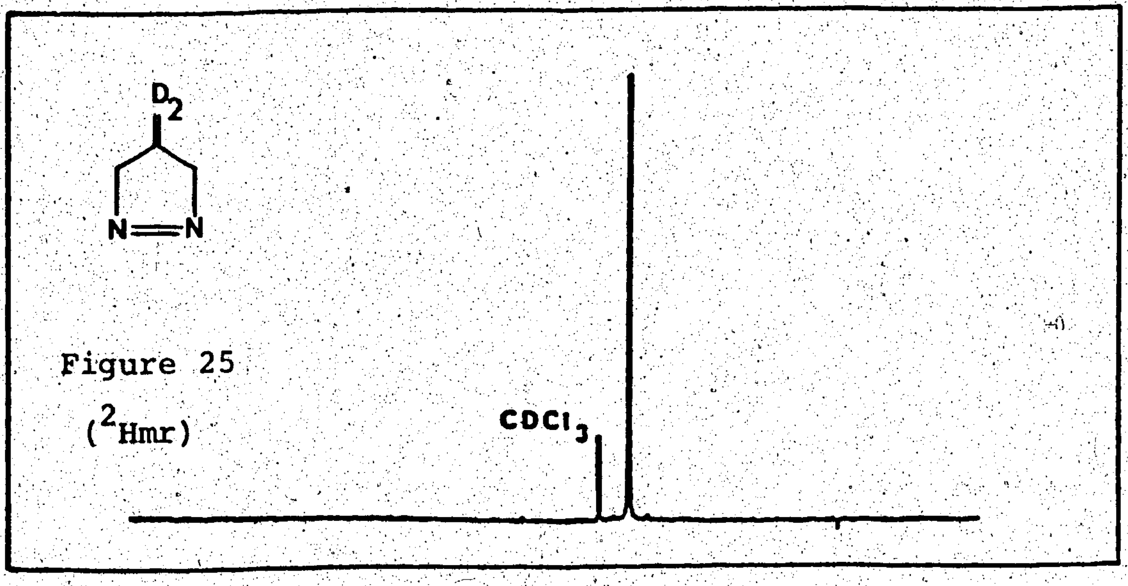


Figure 25
(^{2}Hmr)

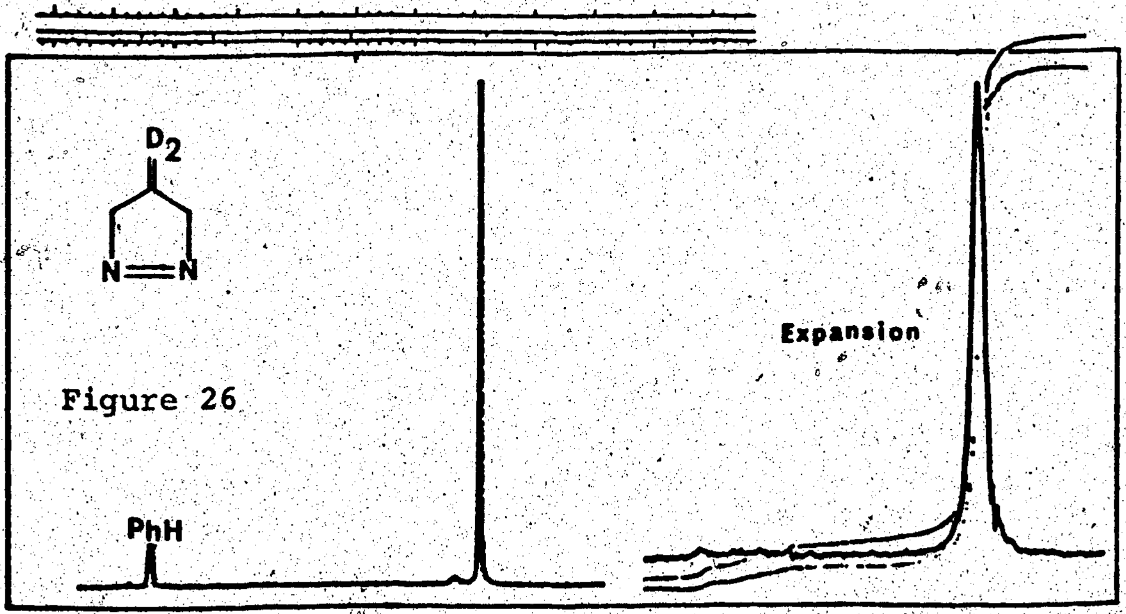


Figure 26

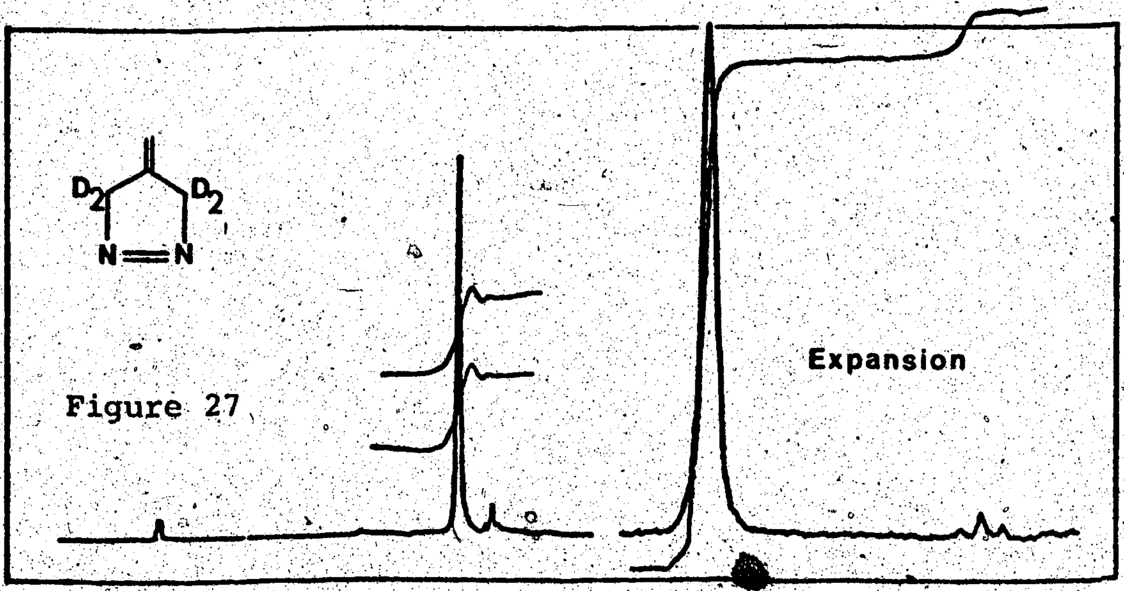


Figure 27

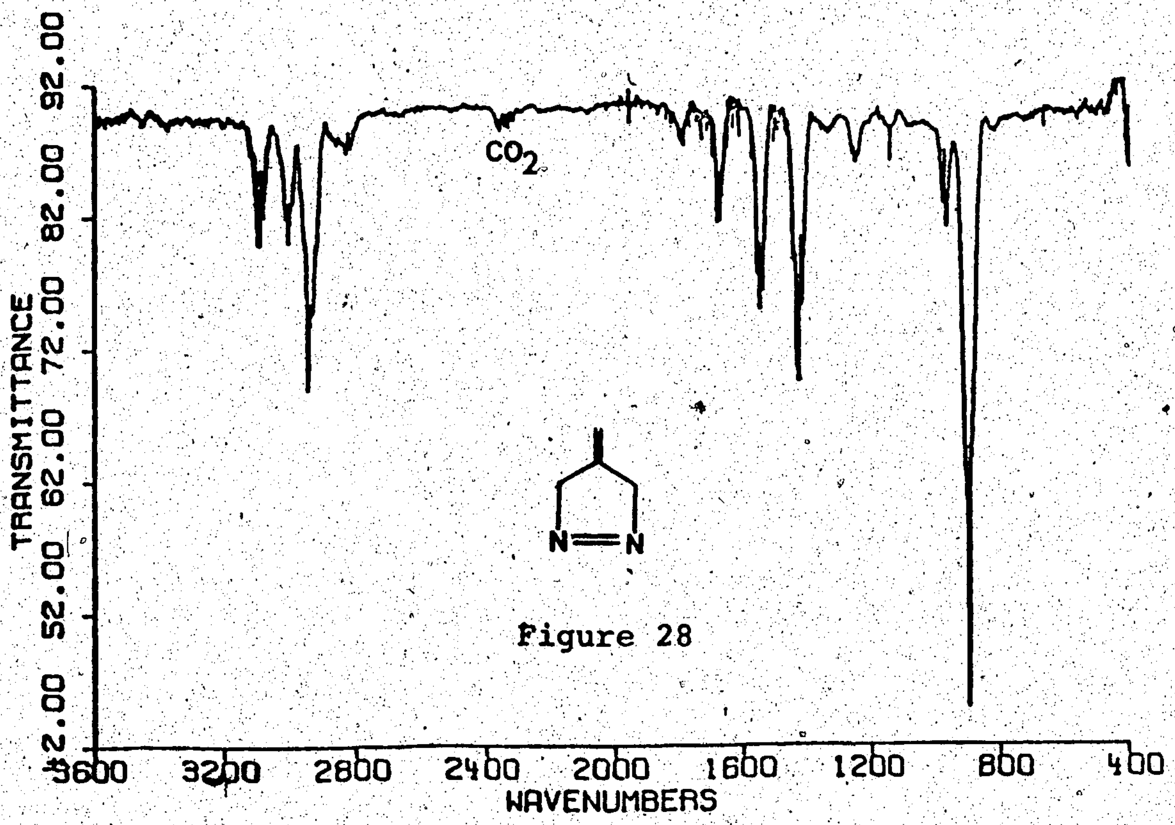


Figure 28

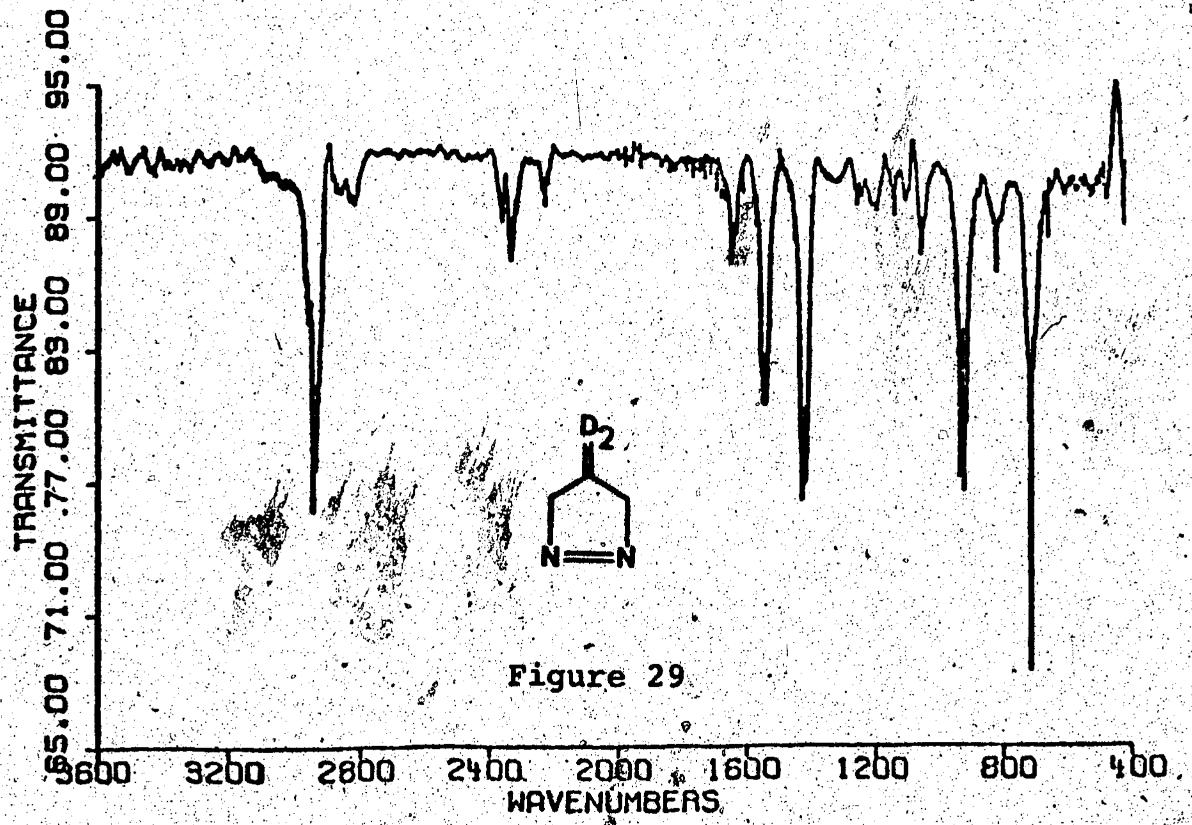


Figure 29

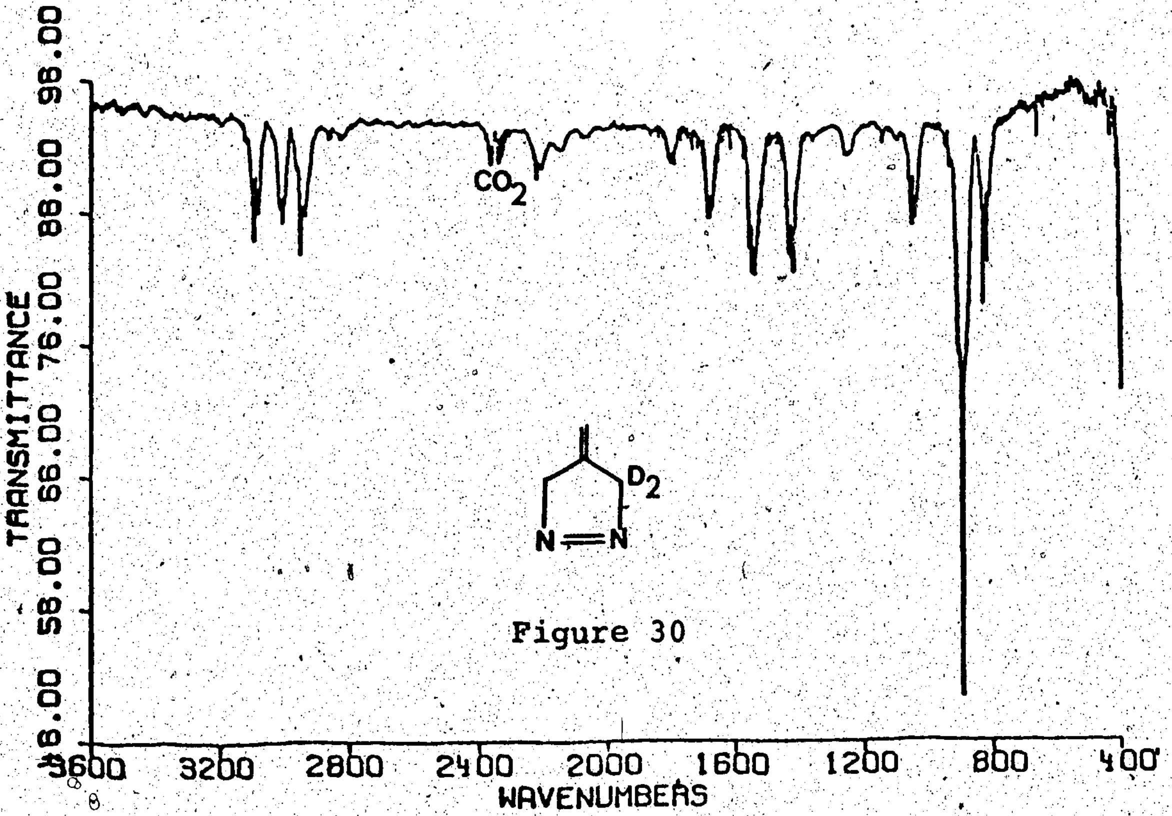


Figure 30

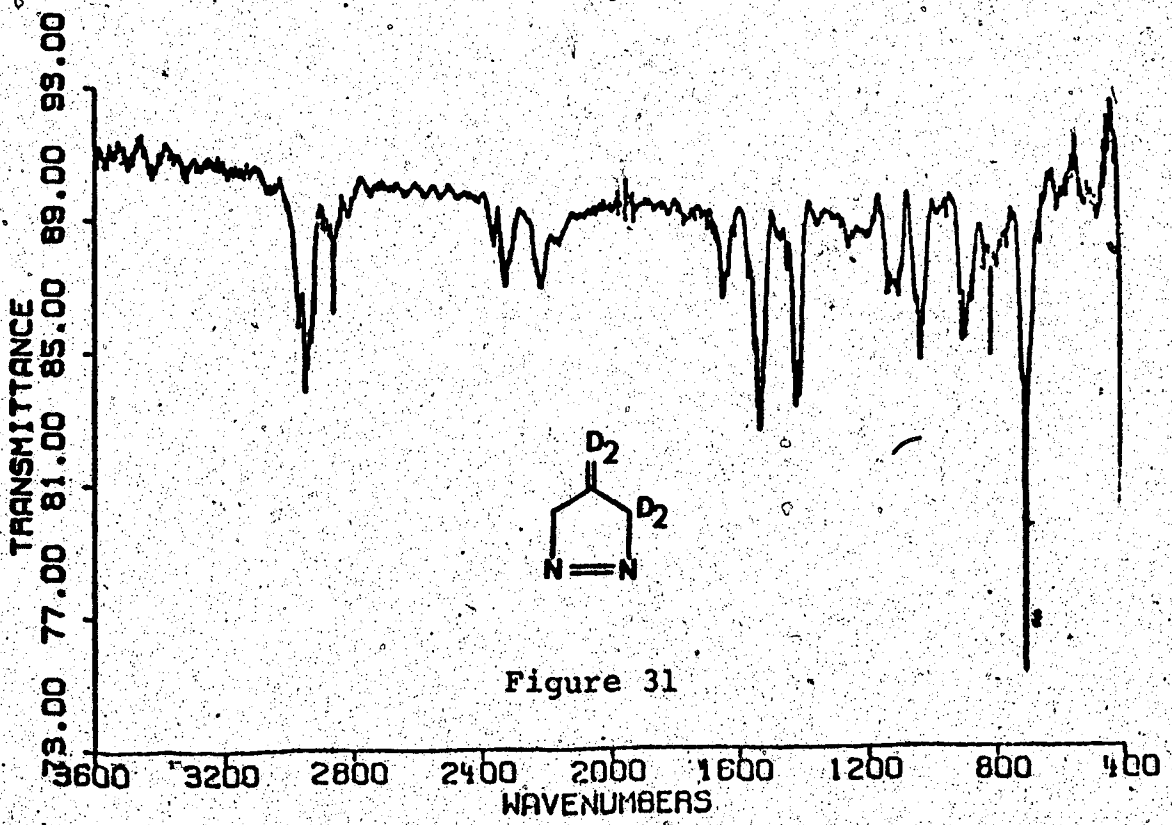


Figure 31

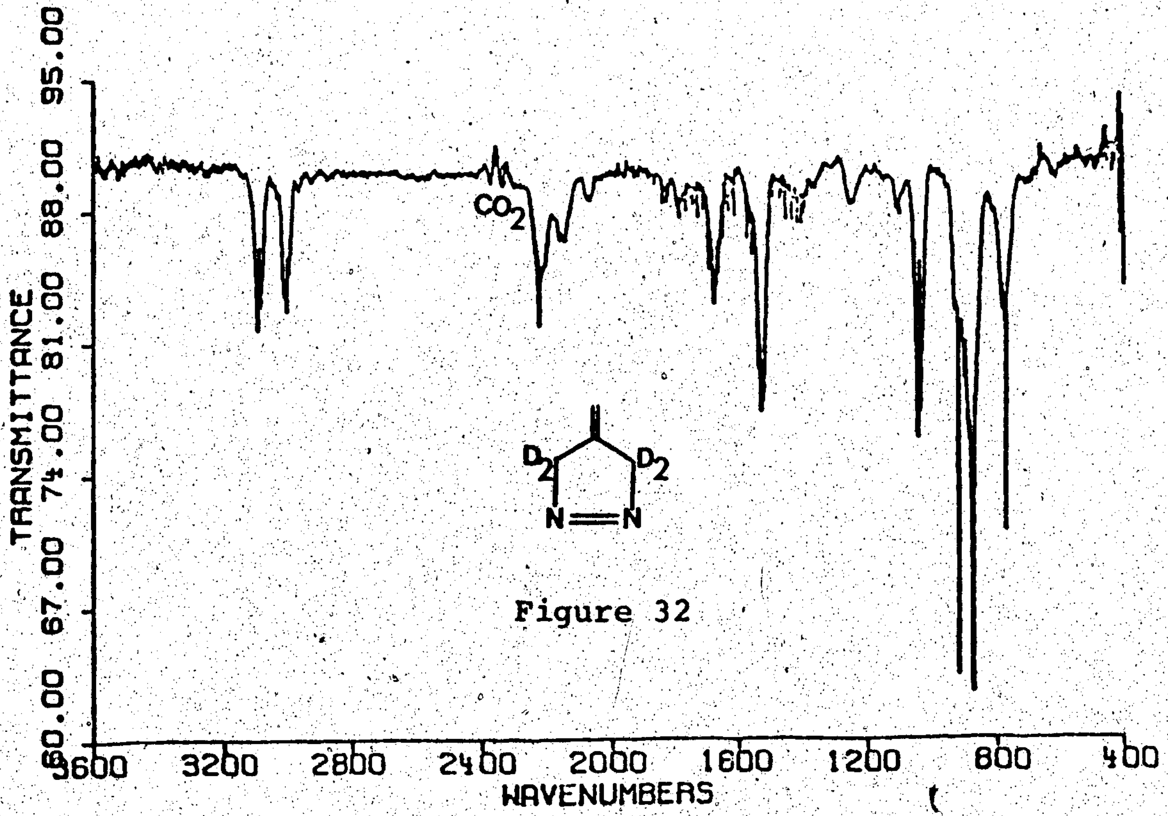


Figure 32

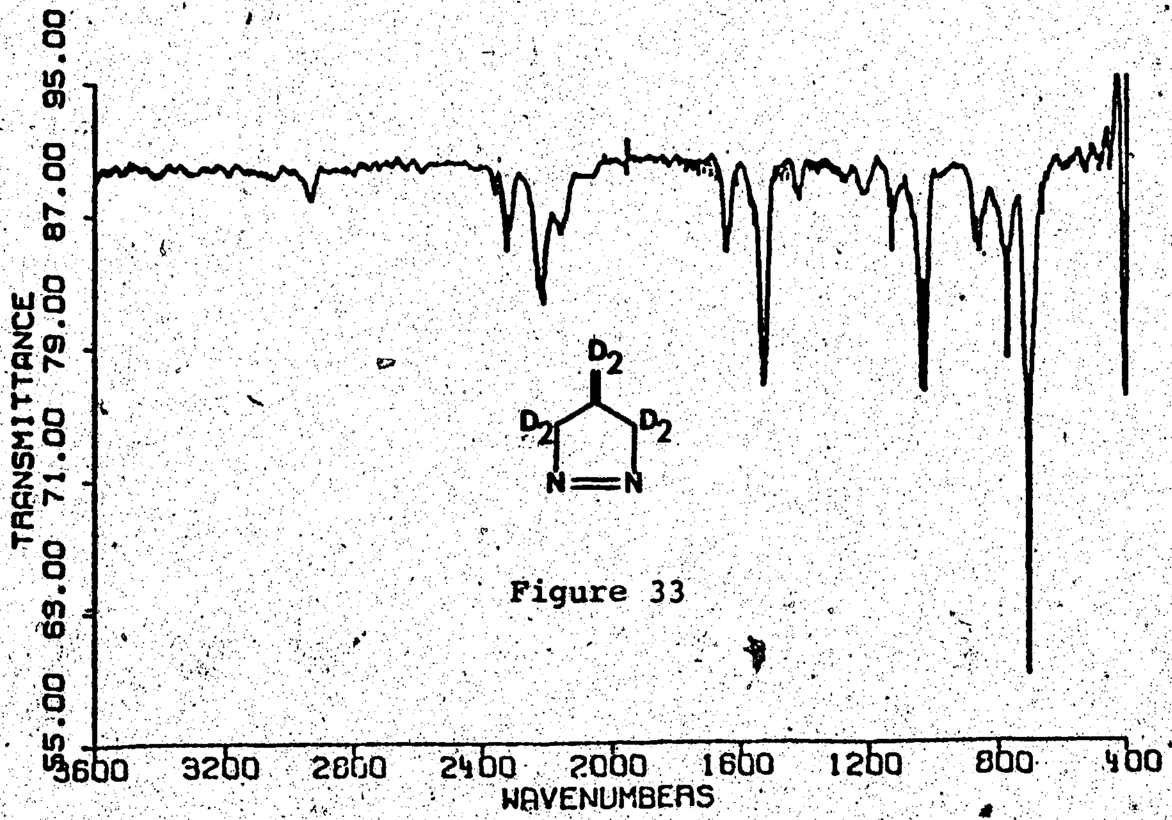


Figure 33

stretching modes of an α-carbon-hydrogen bond.

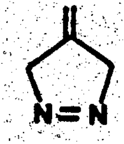
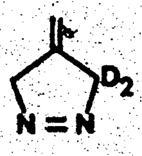
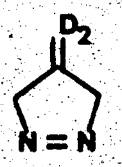
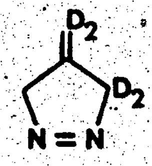
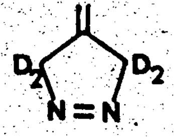
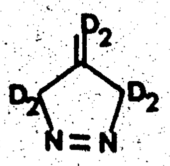
An assignment of the major frequencies from the FTIR spectra of the nondeuterated and deuterated 4-methylene-1-pyrazolines has been attempted with limited success as in Table 15 by comparison with those of 1-pyrazoline, methylenecyclopentane, methylenecyclopentane-2,2,5,5-d_4, methylenecyclopentane-2,2,5,5,6,6-d_6, ethylene, ethylene-1,1-d_2 and ethylene-d_4 (45,46,47). The bands representing the C-N stretching modes were tentatively assigned as in Table 15 by comparing the ir spectra of **107**, **43** and **44** (Figures 29, 31 and 33), since these bands are shielded by the large band representing the wagging mode of the γ-carbon-hydrogen bond (=CH_2) in the ir spectra of **30**, **42** and **46** (Figures 28, 30 and 32). The results in Table 15 can be regarded as important evidence supporting the structure of the nondeuterated and deuterated 4-methylene-1-pyrazolines.

The deuterium contents of the deuterated 4-methylene-1-pyrazolines obtained as described previously by the analysis of the mass spectra are summarized in Table 16.

Crawford *et al.* (48) were able to synthesize 4-ethylidene-1-pyrazoline (**69**) by the regiospecific addition of diazomethane to 1,2-butadiene. Similarly, *E*-4-ethylidene-1-pyrazoline-3,3-d_2 (**76**) and *Z*-4-ethylidene-1-pyrazoline-3,3-d_2 (**77**) were prepared by the addition of diazomethane-d_2 to 1,2-butadiene, and

Table 15

Assignment of major frequencies from the FTIR spectra of nondeuterated and deuterated 4-methylene-1-pyrazolines

Approximate description of modes[a]	Frequencies, cm^{-1}					
	 30	 42	 107	 43	 46	 44
$=CH_2$ asym. str.	3092	3094	2330	2331	3090	2325
$=CH_2$ sym. str.	3005	3005	2224	2230	3000	2227
α-CH_2 asym. str. (i.p.)	2947	2942	2949	2940	2217	2214
α-CH_2 asym. [illegible] (o.p.)	2940	2218	2938	2214	2154	2154
α-CH_2 sym. str. (i.p.)	2860	2860	2858	2858	2142	2138
α-CH_2 sym. str. (o.p.)	2849	2142	2846	2140	2068	2065
C=C str.	1685	1683	1652	1652	1682	1654
N=N str.	1552	1550	1543	1538	1532	1531

continued....

Table 15 (continued)

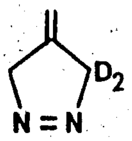
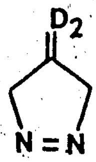
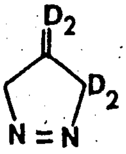
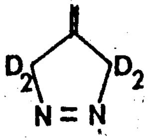
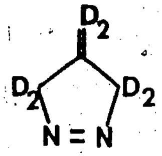
α-CH_2 deformation (i.p.)	1432	1422	1433	1420	1040	1037
α-CH_2 deformation (o.p.)	1418	1051	1417	1045	1027	1025
=CH_2 wagging	892	892	712	709	876	709
H_2C-N str. (o.p.)	*b*	*b*	912	900	*b*	872
H_2C-N str. (i.p.)	*b*	*b*	895	876	*b*	854

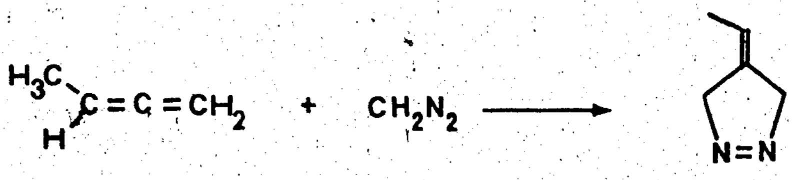
[a] Abbreviations used: sym. str. - symmetric stretch; asym. str. - antisymmetric stretch; (i.p.) - in-phase and (o.p.) - out-of-phase.

[b] Screened by large band of =CH_2 wagging mode.

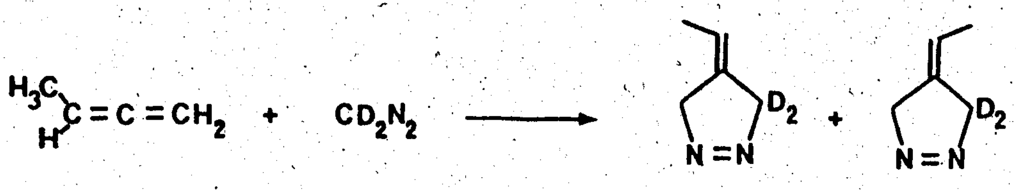
Table 16

Deuterium contents of the deuterated 4-methylene-1-pyrazolines from the low ionization potential mass spectra

Compounds	 42	 107	 43	 46	 44
Deuterium content, %	97.0 ±0.1	95.0 ±0.1	97.1 ±0.1	95.4 ±0.1	96.8 ±0.1



69



76 (major)

77 (minor)

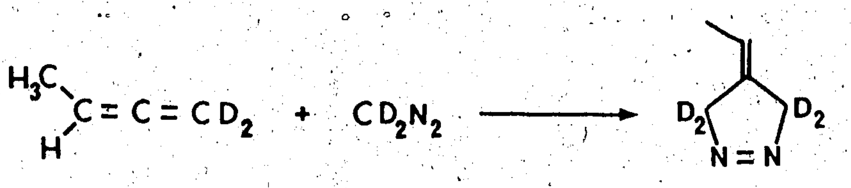
Synthetic route I

$$H_3C(H)C{=}C{=}CD_2 + CH_2N_2 \longrightarrow 76 + 77$$

(minor) (major)

Synthetic route II

diazomethane to 1,2-butadiene-1,1-d_2 respectively (synthetic routes I and II). We applied a similar procedure successfully to the synthesis of 4-ethylidene-1-pyrazoline-3,3,5,5-d_4 (128). Thus, diazomethane-d_2



128

was added to 1,2-butadiene-1,1-d_2.

Earlier ^{13}Cmr and 100 MHz ^{1}Hmr spectra of 76 and 77 led Crawford *et al.* (48) to assign the structures of these compounds, and to suggest that they were produced in high stereospecificity. A re-examination of these compounds using 400 MHz ^{1}Hmr and ^{2}Hmr demonstrates that some 77 is present from the synthesis of 76, and *vice versa* (see spectra in Figures 36, 38, 40 and 41). The 400 MHz ^{1}Hmr spectrum (Figures 34 and 35) of 69 shows a clear separation between the signals of the ring methylene protons *anti* and *syn* to the methyl protons of the 4-ethylidene group. Interestingly, it was observed that the 400 MHz ^{1}Hmr spectrum of 69 shows such separation only in benzene-d_6 medium, but not in chloroform-d. The ^{1}Hmr and ^{2}Hmr spectra of the product mixtures from synthetic routes I and II (Figures 36-41) and the ^{1}Hmr spectra of 128 (Figures 42 and 43) enabled us to assign all the signals and coupling constants of 69 as indicated

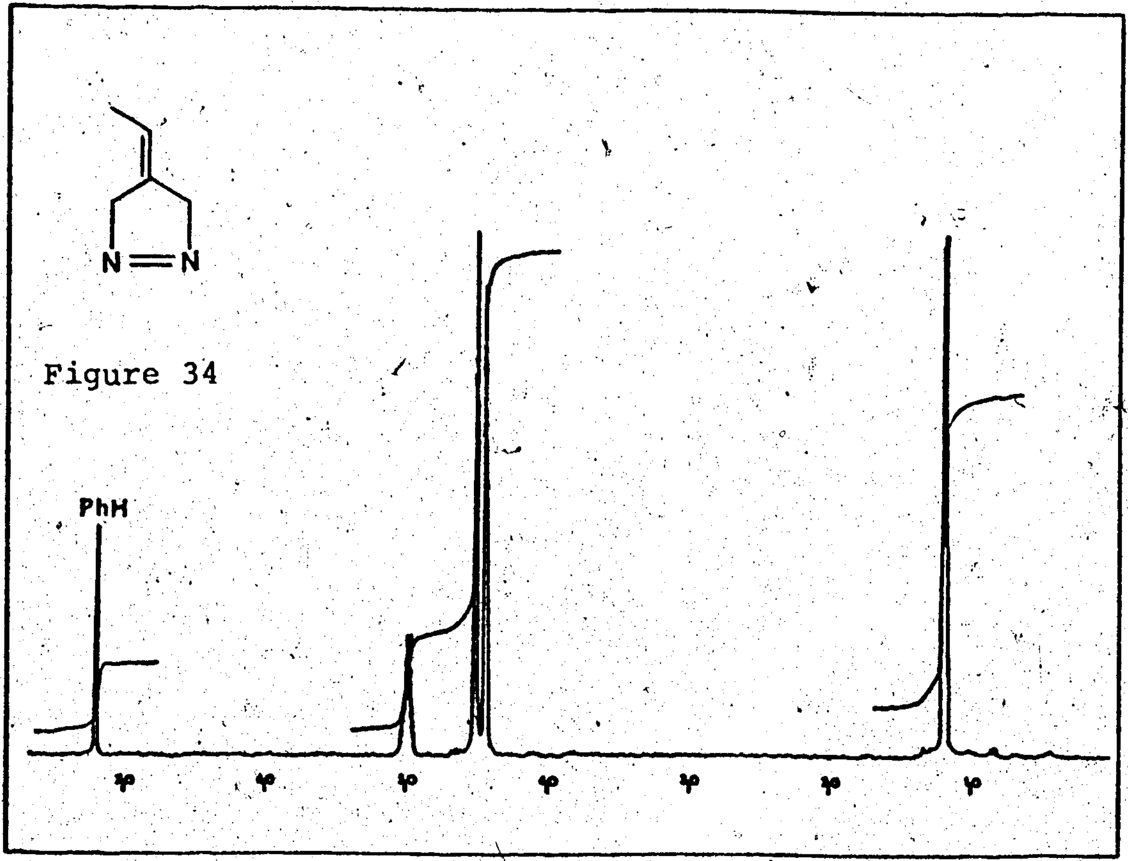


Figure 34

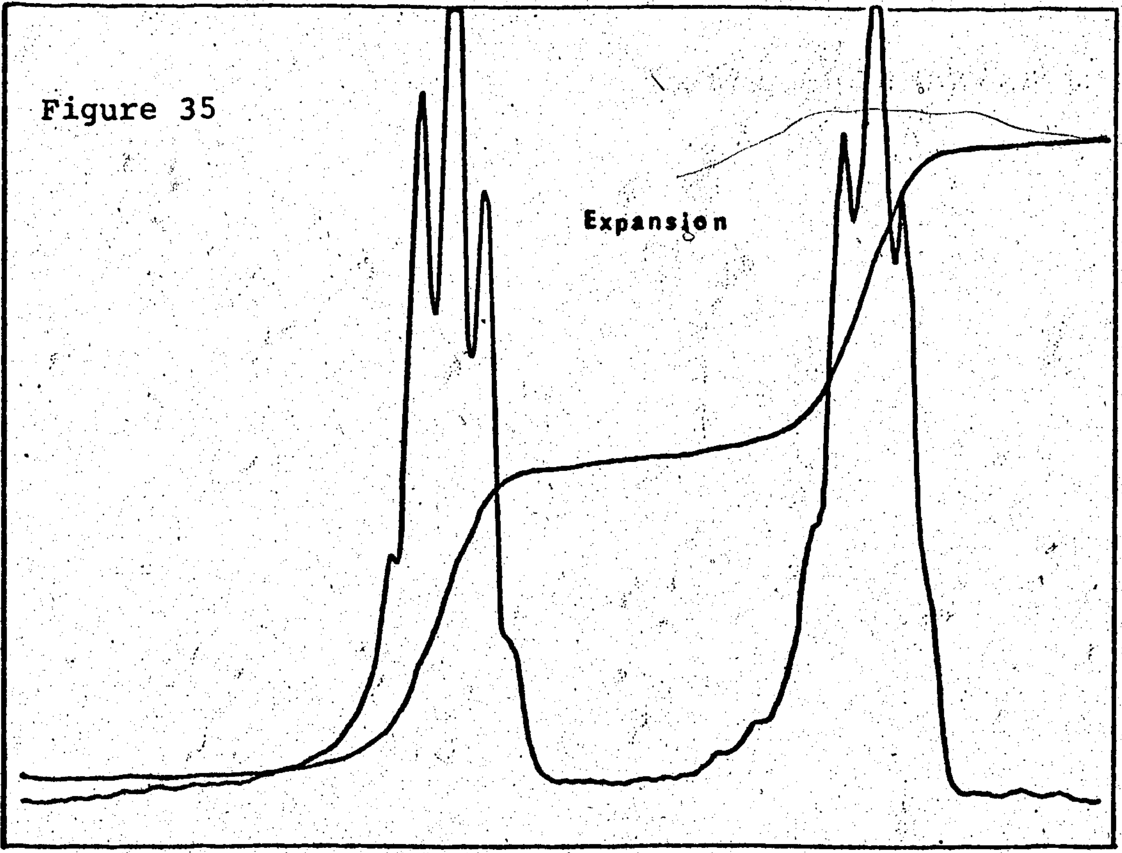


Figure 35

Mixture A

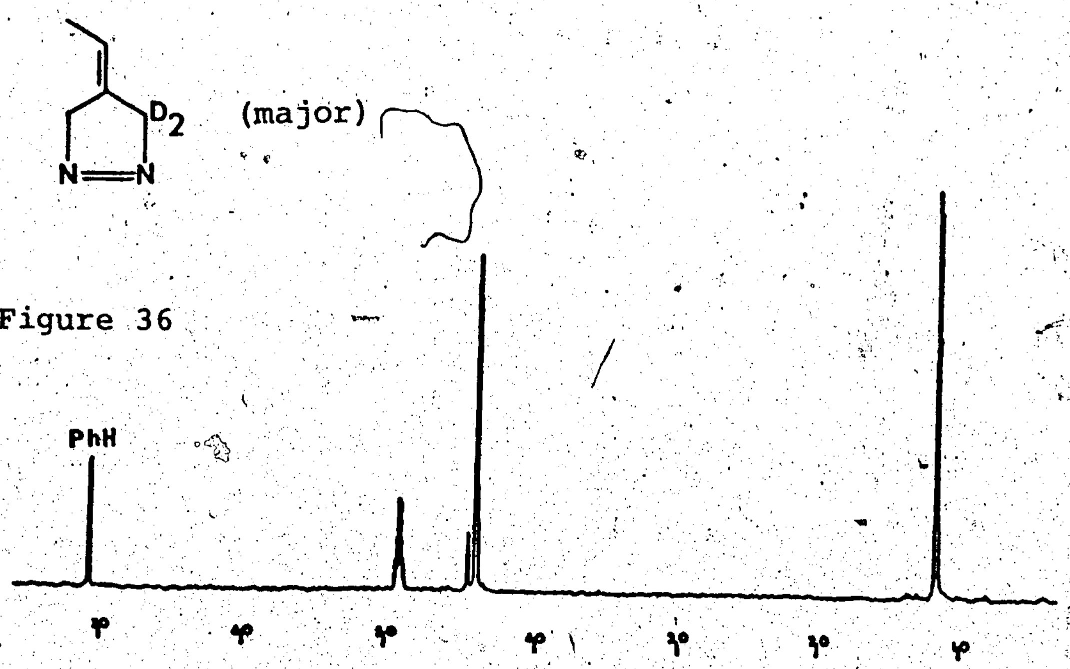
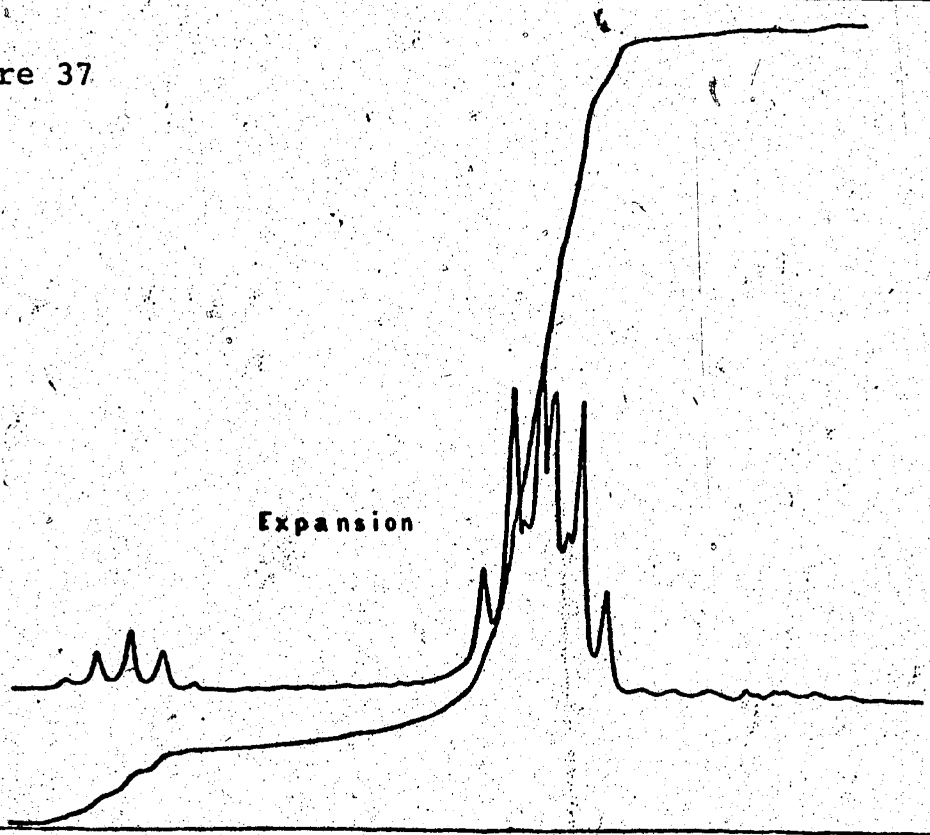


Figure 36

Figure 37



Mixture B

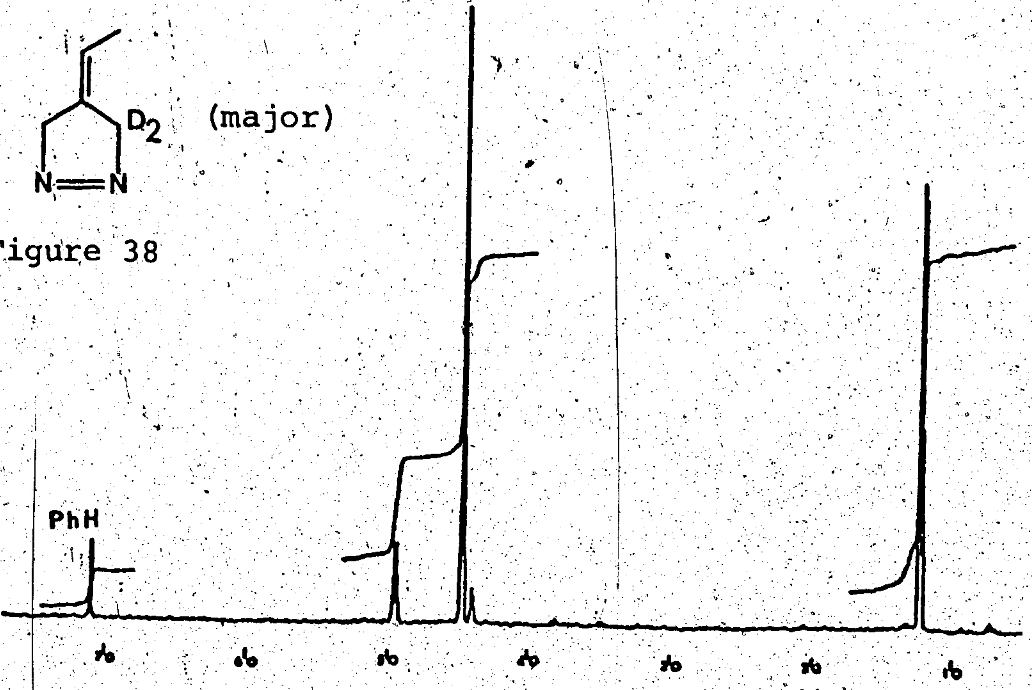
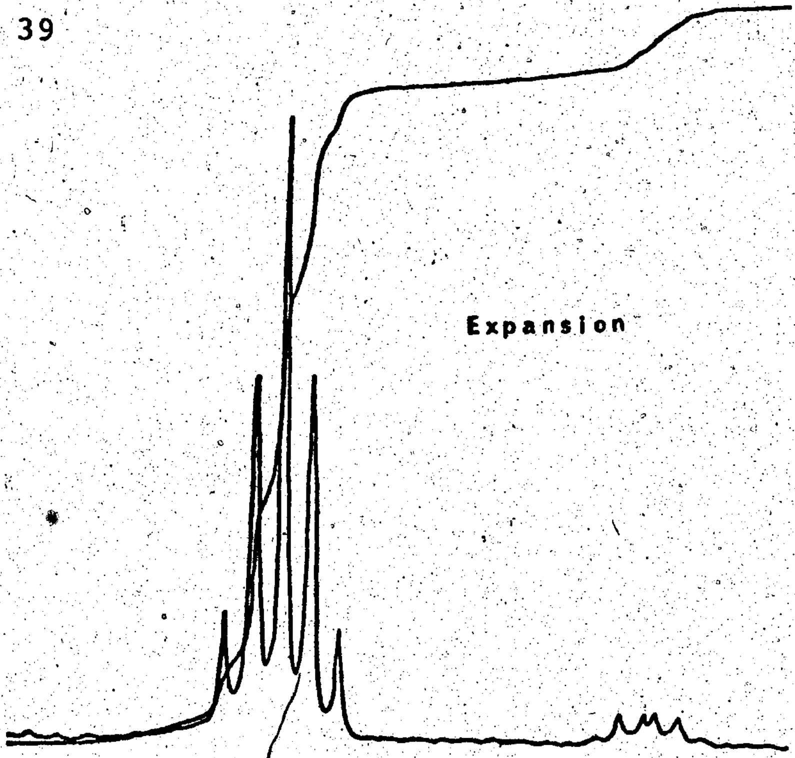
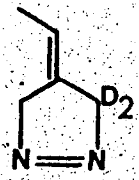


Figure 38

Figure 39

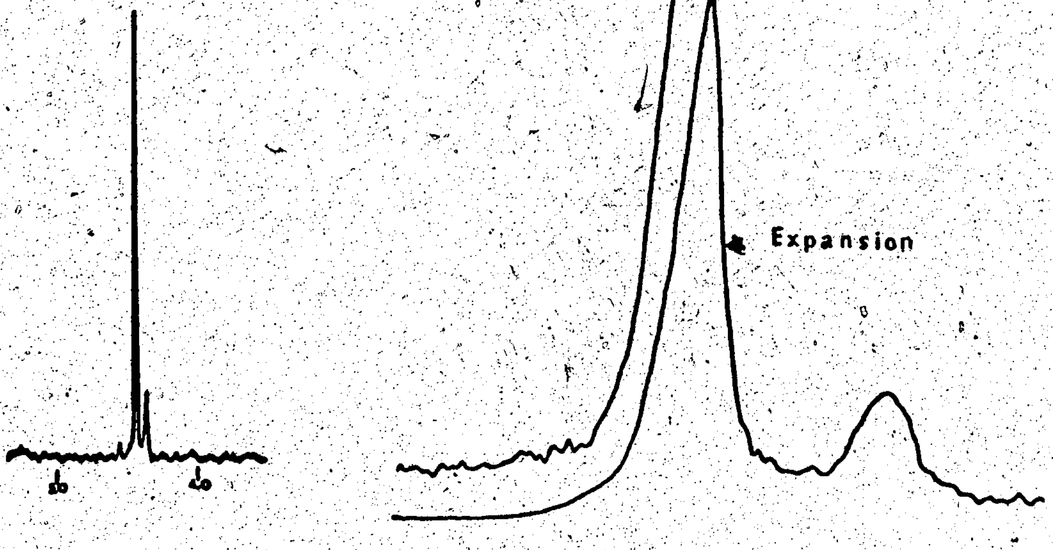


Mixture A

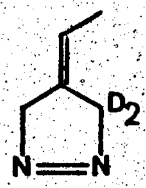


(major)

Figure 40 (^{2}Hmr)

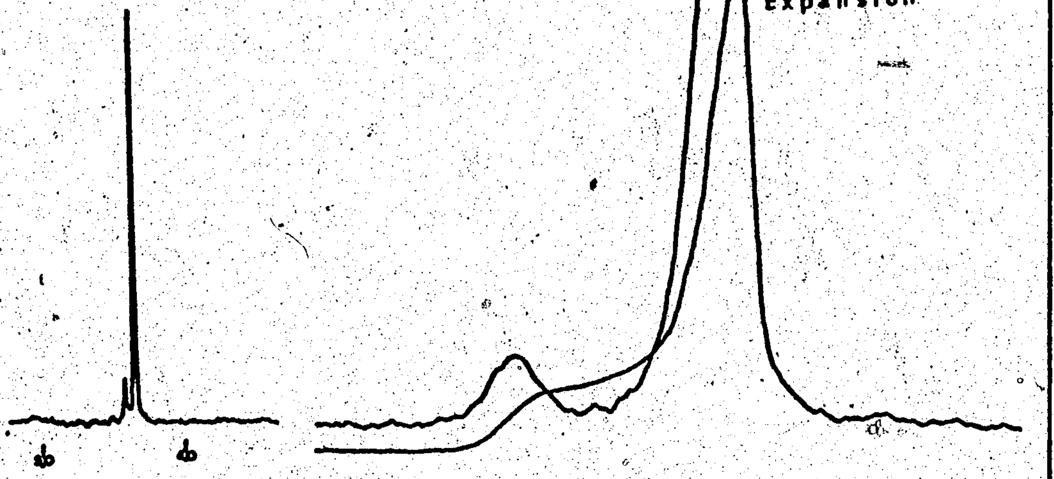


Mixture B



(major)

Figure 41 (^{2}Hmr)



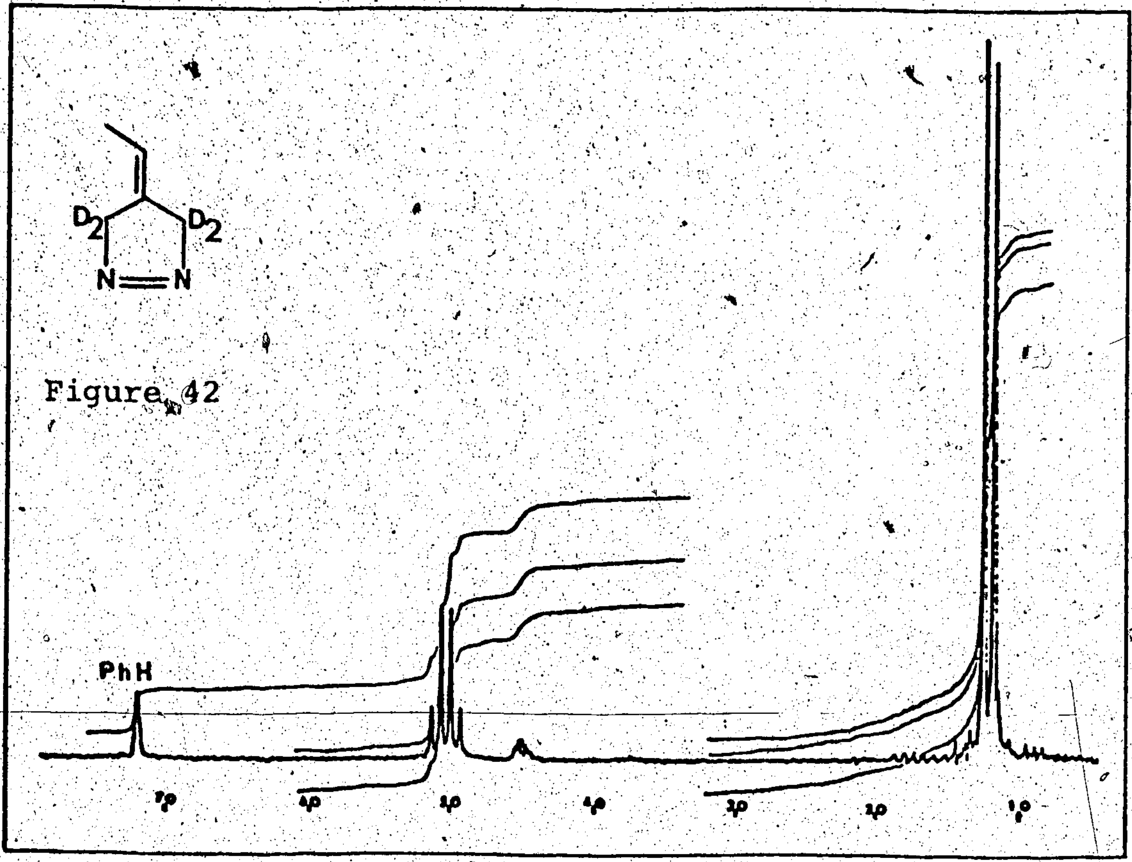


Figure 42

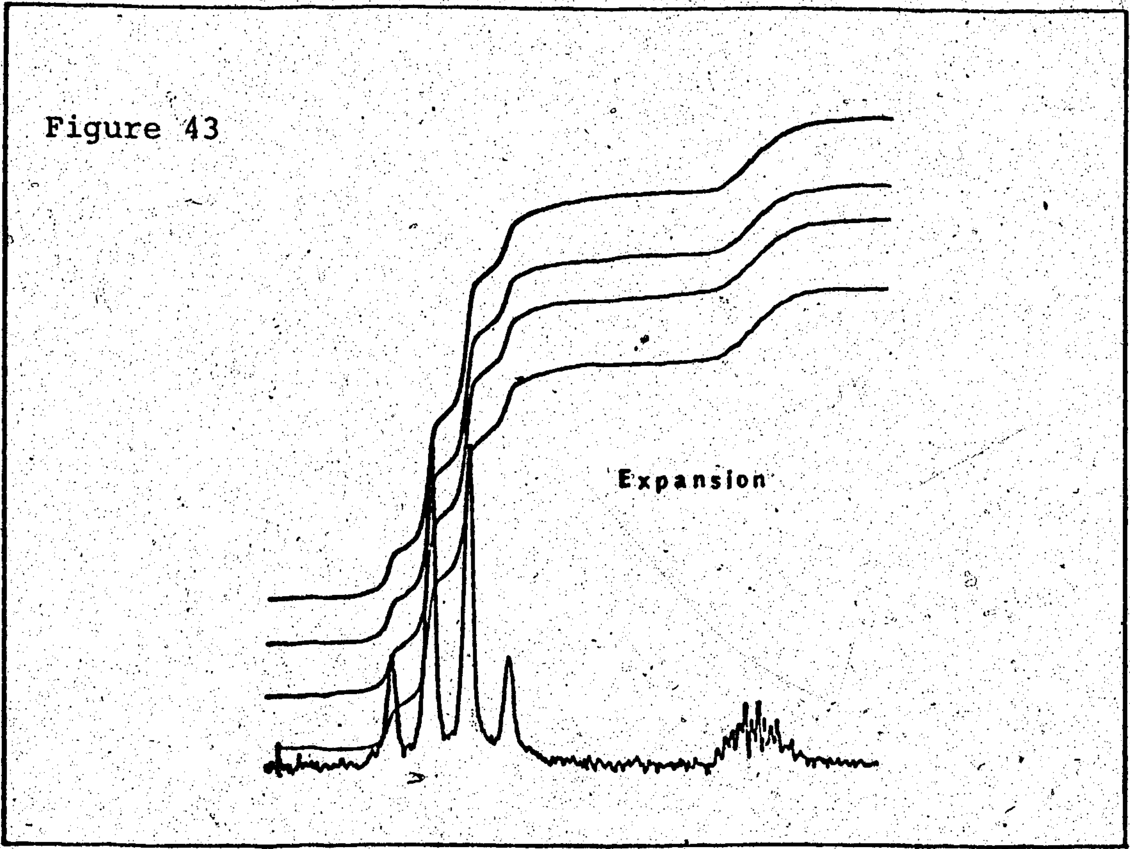
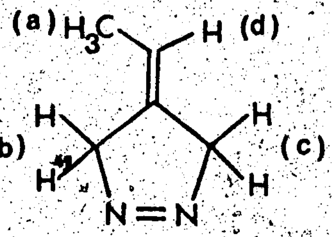


Figure 43

in Table 17. The magnetic resonance signals of protons H_b and H_c were observed at δ4.40 and δ4.48 respectively indicating a shielding of the proton H_b by the ansiotropic



69

H_b : ring methylene proton *syn* to proton H_a.

H_c : ring methylene proton *anti* to proton H_a.

Table 17

400 MHz ^{1}Hmr data for 4-ethylidene-1-pyrazoline

Proton	Chemical shift, δTMS (benzene-d_6)	Type of signal	Coupling constants
H_a	1.16	doulbet of slight multiplets	J_{ad} = 6.70 Hz
H_b	4.40	doublet of quartets	J_{ab} = 2.20 Hz
H_c	4.48	pentet	J_{bd} = 1.65 Hz
H_d	4.96	multiplet	J_{ac} = J_{cd} = 2.25 Hz

effects of the σ electrons of the C-C bond in the

4-ethylidene group of 69, and the coupling constants in Table 17 are comparable to the values of J_{ab}, J_{ac}, J_{bd} or J_{cd} = 0-3 Hz and J_{ad} = 4-10 Hz from the literature (49).

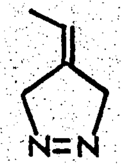
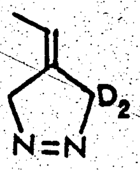
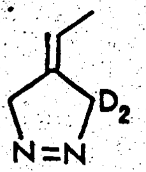
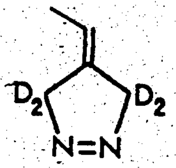
It was found from integration of the 400 MHz ^{1}Hmr (54.4 MHz ^{2}Hmr) spectra that the relative mole ratios of 76:77 are 92:8 (90:10) in mixture A derived from the synthetic route I, and 7:93 (9:91) in mixture B from the synthetic route II. The deuterium content for 128 is 96 ± 1% as indicated in Table 18.

A comparison of the low ionization potential mass spectra of the deuterated ethylidenecyclopropanes from the thermolysis of the mixtures led us to estimate the deuterium contents to be 96 ± 1% for mixture A, 97 ± 1% for mixture B and 96 ± 1% for 128 as in Table 18. The deuterated ethylidenecyclopropanes were separated from the deuterated 2-methylmethylenecyclopropanes by preparative gc. Since the mass spectrum of the latter shows a large M-1 peak, the analytical results from the former compound are used as an indication of isotopic purity of the latter. Combining the results from the 400 MHz ^{1}Hmr, 54.4 MHz ^{2}Hmr and mass spectra, we obtained the isotopic purities as shown in Table 18.

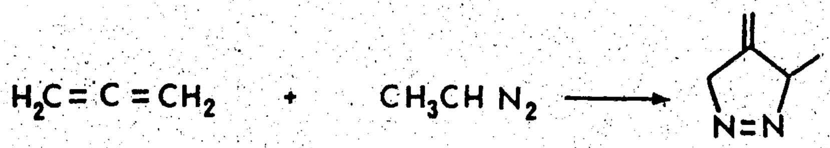
3-Methyl-4-methylene-1-pyrazoline (68) was prepared according to the procedure of Schrijver (34) by the addition of diazoethane to allene. 2-Diazopropane was added to allene to furnish 3,3-dimethyl-4-methylene-1-pyrazoline (56). The procedure of Crawford and Tokunaga

Table 18

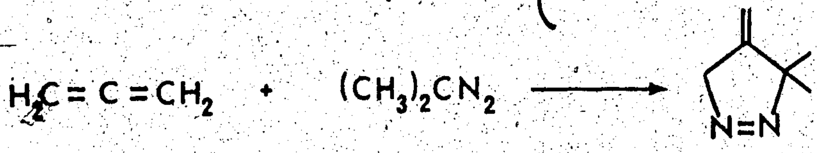
Percent compositions of mixture A, mixture B and 128

Mixtures	Method of Analysis	Composition, %			
		 69	 76	 77	 128
A	^{1}Hmr		92 ± 1	8 ± 1	
	^{2}Hmr		90 ± 1	10 ± 1	
	Mass & ^{1}Hmr	4 ± 1	88 ± 1	8 ± 1	
	Mass & ^{2}Hmr	4 ± 1	86 ± 1	10 ± 1	
B	^{1}Hmr		7 ± 1	93 ± 1	
	^{2}Hmr		9 ± 1	91 ± 1	
	Mass & ^{1}Hmr	3 ± 1	7 ± 1	90 ± 1	
	Mass & ^{2}Hmr	3 ± 1	9 ± 1	88 ± 1	
128	^{1}Hmr	4 ± 1			96* ± 1
	Mass	4 ± 1			96* ± 1

*Total deuterium content ($D_0 = 0.8$, $D_1 = 0.4$, $D_2 = 1.6$, $D_3 = 7.6$, $D_4 = 89.6$).



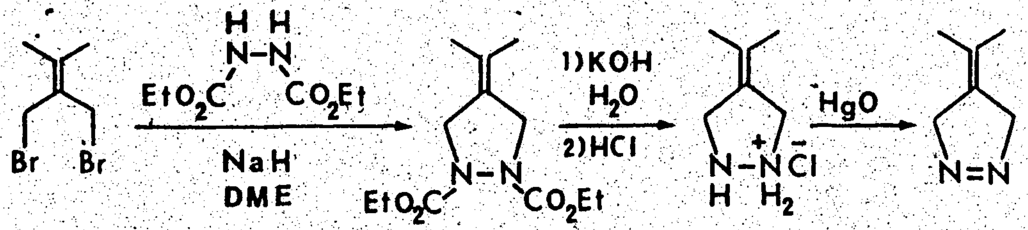
68



56

(10a) was modified in that the acetone hydrazone in the reaction mixture was removed by extraction with water followed by fractional distillation to give 56 containing 13% acetone azine as assessed from the ^{1}Hmr spectrum (Figure 45). This mixture was used without any further purification in the kinetic experiments since the acetone azine is known to be stable under the thermolysis conditions (10a).

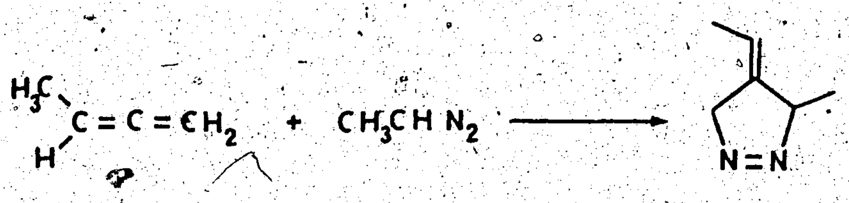
4-Isopropylidene-1-pyrazoline (57) was synthesized according to the procedure of Crawford and Tokunaga (10a)



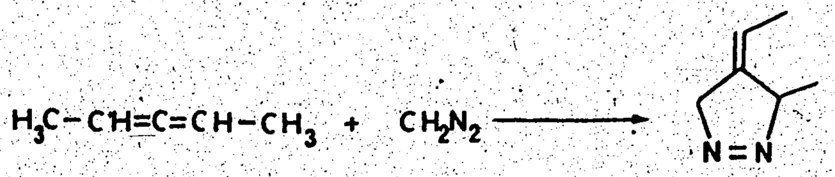
57

as shown.

E-3-Methyl-4-ethylidene-1-pyrazoline (89), and *Z*-3-methyl-4-ethyledene-1-pyrazoline (90) were prepared



89



90

as described earlier (48).

The ^{1}Hmr spectra of the pyrazolines 68, 56, 57, 89 and 90 were taken in benzene-d_6 medium. It was found that most of them isomerize slowly at room temperature in chloroform-d but that they are stable in benzene for a day or so (see Figures 44, 45, 46, 47 and 48).

It should be noted that all the 4-alkylidene-1-pyrazolines prepared in our laboratory could be stored at -40°C under argon for at least a month without any noticeable formation of tautomers.

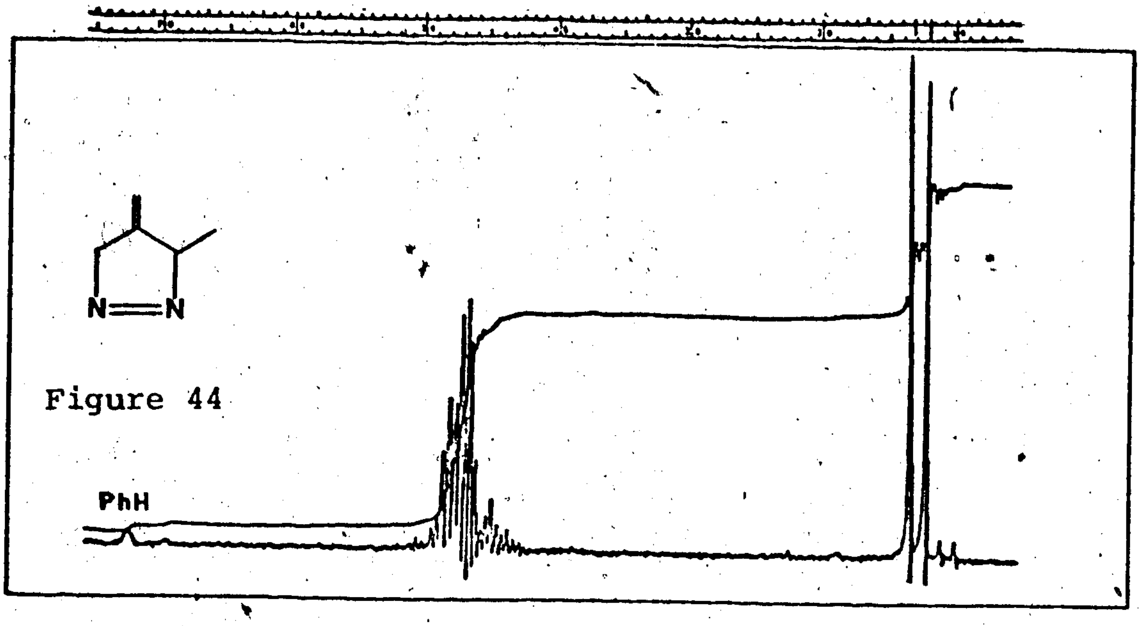


Figure 44

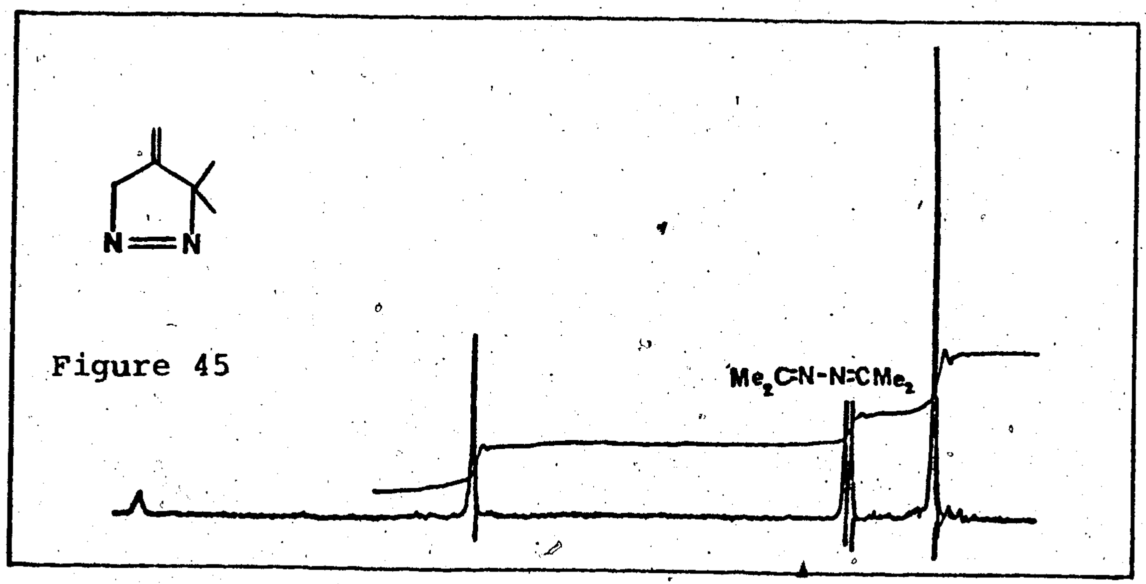


Figure 45

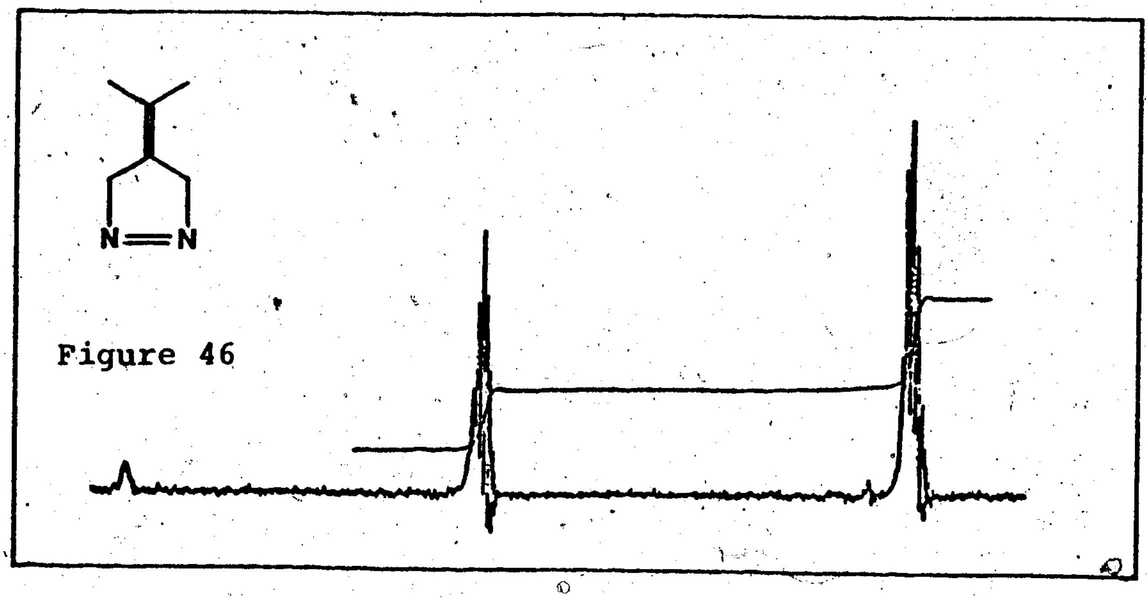


Figure 46

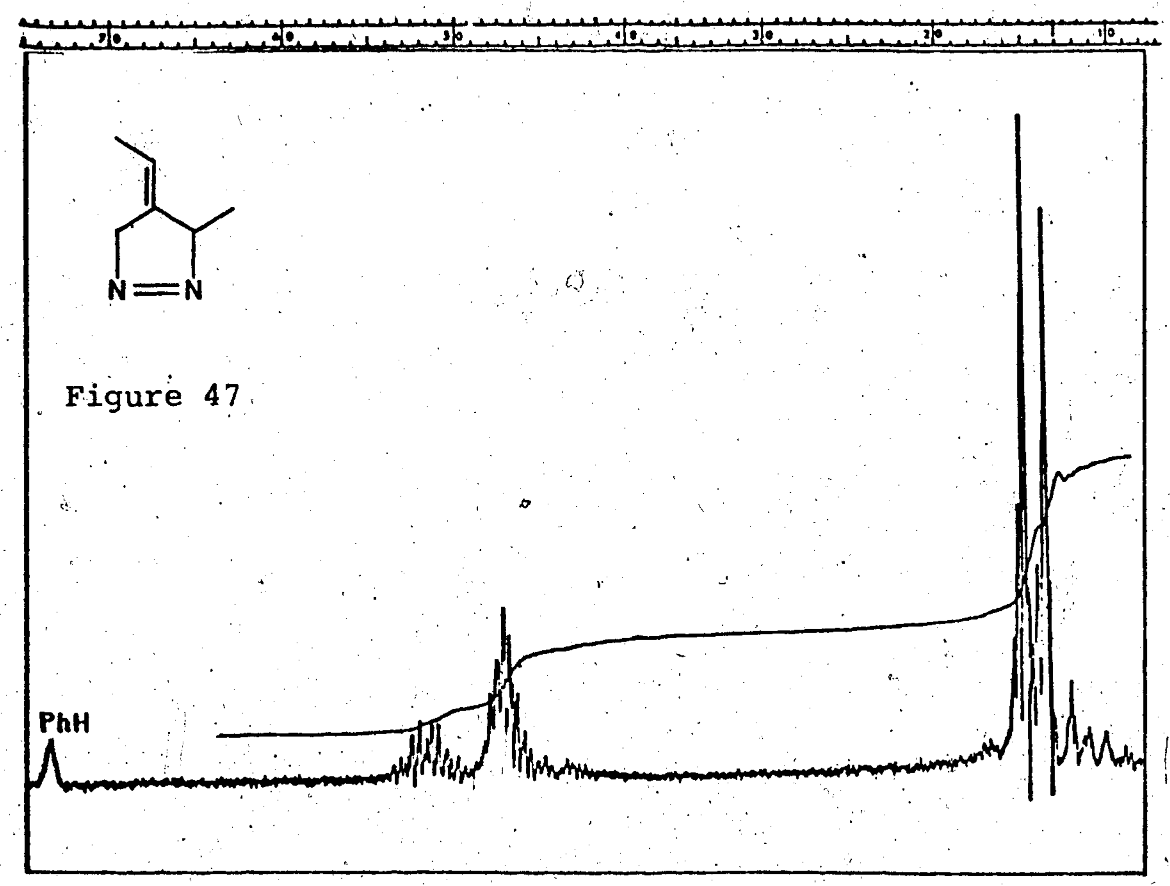


Figure 47

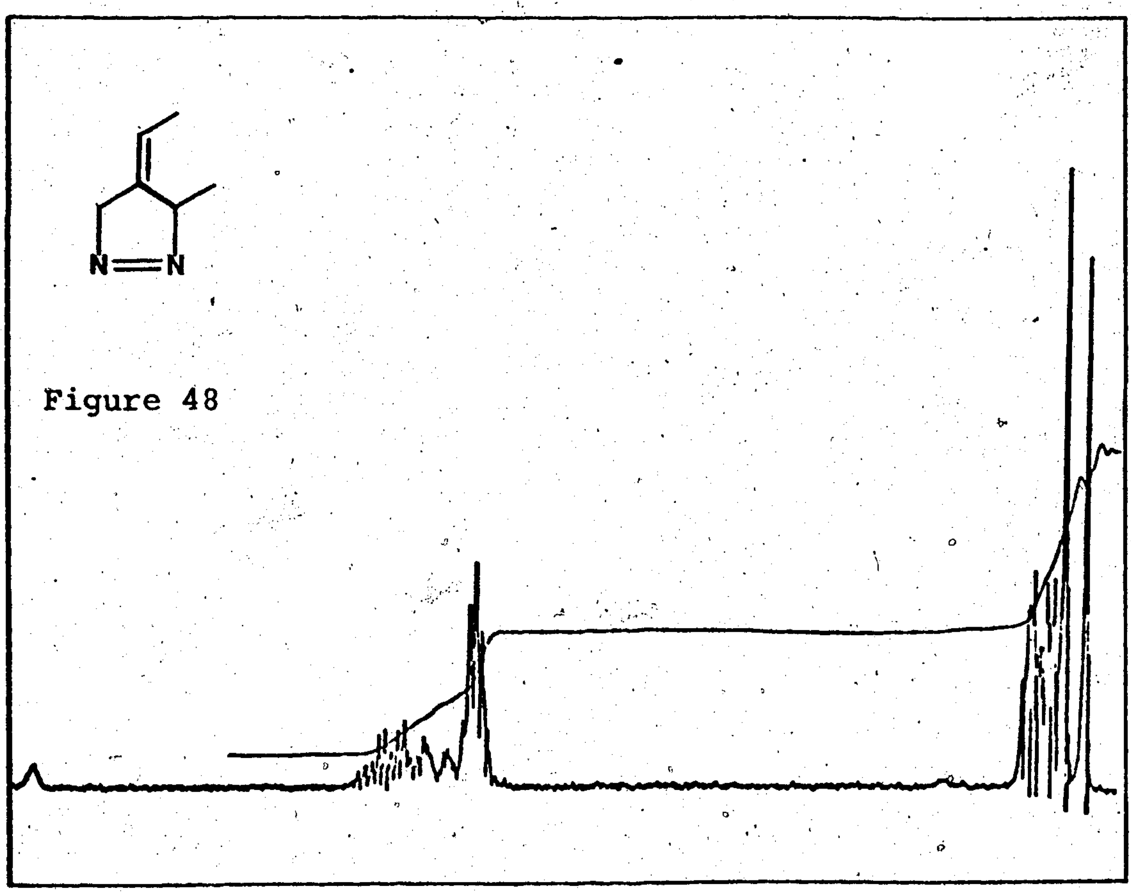


Figure 48

B. Kinetic Analyses

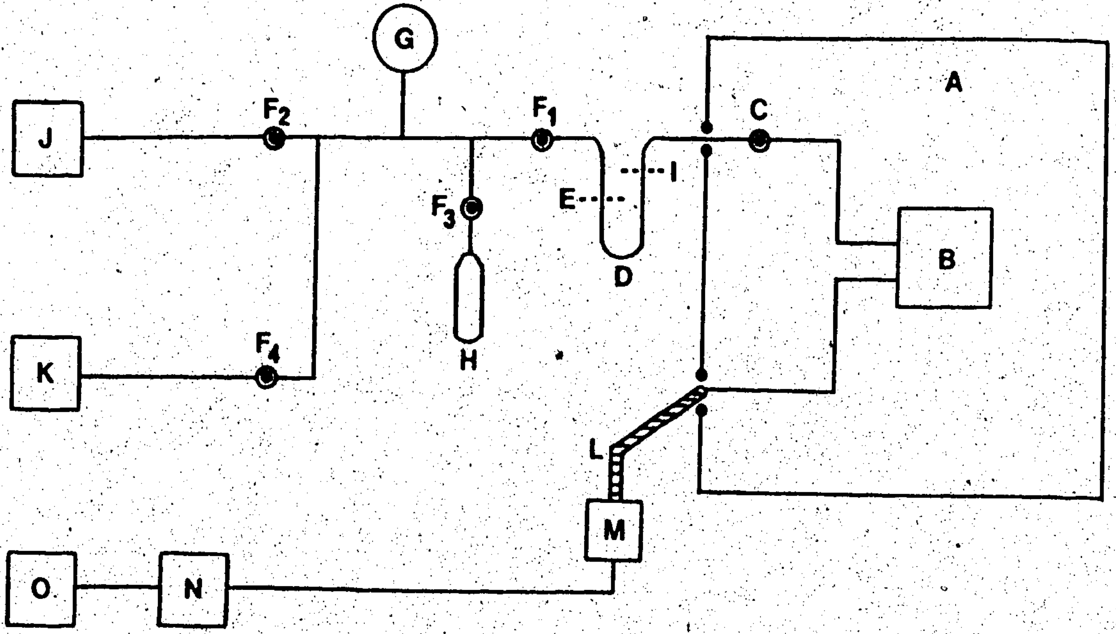
(i) Sample Injection and Pressure Measurements

The gas phase thermolysis reactions of the 4-alkylidene-1-pyrazolines were carried out in a 250 ml stainless steel reaction vessel contained in a well thermostatted air bath as described in detail in the Experimental section. The reactions were found to proceed at a convenient rate at temperatures between 160 and 185° with 70-92% conversion into alkylidenecyclopropanes depending on reactants and reaction temperatures. The reaction was always accompanied by isomerization of the pyrazolines to their tautomers, however the observed rate constants appear to be independent of the percent conversion of the reaction. A complete discussion of this point is given later. The temperature of the air bath was maintained constant throughout the reaction by a heater controlled by a proportional temperature controller. The long term stability of the bath temperature was better than ±0.1°.

The kinetic results were obtained by following the increase of pressure with time. The pressure inside the reactor would be expected to be doubled upon 100% completion of the reaction, by the formation of equimolar quantities of alkylidenecyclopropane and nitrogen. The pressure was measured as an emf by a transducer, National Semiconductor LX 1702A, which was hooked up to a voltmeter and a digital printer. The transducer emf was calibrated and was found to be directly proportional to the pressure used (0-200 Torr). A Pyrex tubing filled with high boiling GE Silicon Oil 710 was placed between the transducer and the reactor in order to avoid the condensation of reactants at the transducer, and to eliminate any dead-space effects (50) during the measurements. The long term stability of the transducer emf was found to be better than ± 0.002 volt throughout the thermolysis, and an emf of 1 volt was equivalent to approximately 75 Torr in our system.

Three reaction vessels were examined 1) Pyrex, 2) stainless steel 3) Teflon lined stainless steel. The best results, as judged by a minimum of tautomerism, were obtained using the stainless steel vessel.

Pure liquid samples (80 μl) of the pyrazolines were expanded into the evacuated reaction vessel from a heated (100°C) injection system (see Figure 49, U-tube D) over a period of 5 to 15 seconds to give a sample pressure of 30-60 Torr (0.4-0.8 volt). Prior to the injection of the sample, the U-shaped injection port (D) was sealed at E so that maximum injection into the reactor could be achieved. Otherwise, only a few Torr of the sample was introduced into the reaction vessel, since much of the remaining sample expanded in the wrong direction to the Hoke valve F_1. The highest sample pressure obtained was



A: air bath

B: reaction vessel

C: high temperature Hoke valve

D: injection port

E: point of sealing

F: Hoke valve

G: Pirani gauge

H: sample tube

I: cut

J: Pumps

K: argon tank

L: tubing with silicone oil

M: transducer

N: voltmeter

O: recorder

Figure 49. Schematic diagram of the apparatus used for the kinetic studies in the thermolysis of 4-alkylidene-1-pyrazolines.

75 Torr even upon heating 200 µl of the sample in the injection system at 150° for longer than a minute. Similar results were observed with n-octane, although n-hexane could be expanded into the reactor quantitatively. The injection time of 15 seconds was the upper limit, since most of the thermolysis reactions carried out had half-lives of 300 to 650 seconds. The thermolysis temperature could not be lowered below 160° since this led to an increase in the extent of tautomerism of the pyrazolines.

Reproducible first-order kinetics were observed only after repeated thermolyses of the pyrazolines in the stainless steel reaction vessel. The percent completion of the reaction increased dramatically from 37 to 92% after 10 thermolyses of 4-methylene-1-pyrazoline at 175°, and the rate constants calculated for the next five thermolysis reactions were found to be reproducible to 1%. The introduction of air into the reaction vessel caused the surface to be destroyed (51,52).

(ii) Kinetic Calculations and Analyses of Errors

The thermolysis of 4-methylene-1-pyrazoline has been shown to follow first-order kinetics (10a). For a process in which the pressure (P) doubles upon reaction, the rate constant (k) can be obtained from the integrated

30 31

form of the rate equation:

$$\ln(P_\infty - P_t) = -kt + \ln(P_\infty - P_0) \qquad \text{(eq. 6)}$$

where P_t is the actual pressure inside the reaction vessel at time t and P_0 is the initial pressure at time t_0 (53).

The transducer emf (E) is directly proportional to the pressure used (0-200 Torr). The equation 6 can be expressed as

$$\ln(E_\infty - E_t) = -kt + \text{const.} \qquad \text{(eq. 7)}$$

where E_∞ is the transducer emf at t_∞ (usually 8 x half-life) and E_t is that at time t. If the rates of thermolysis of 2-alkylidene-1-pyrazolines follow first-order kinetics then a plot of $\ln(E_\infty - E_t)$ *versus* time should be a straight line of slope -k. Figure 50 shows a typical plot of $\ln(E_\infty - E_t)$ *versus* time for a kinetic run in the thermolysis of 4-methylene-1-pyrazoline at 165.0°. The thermolysis of all the 4-alkylidene-1-pyrazolines studied by us followed first-order kinetics. In order to obtain precise first-order rate constants, the data points were chosen between 20 and 80% completion of the reaction.

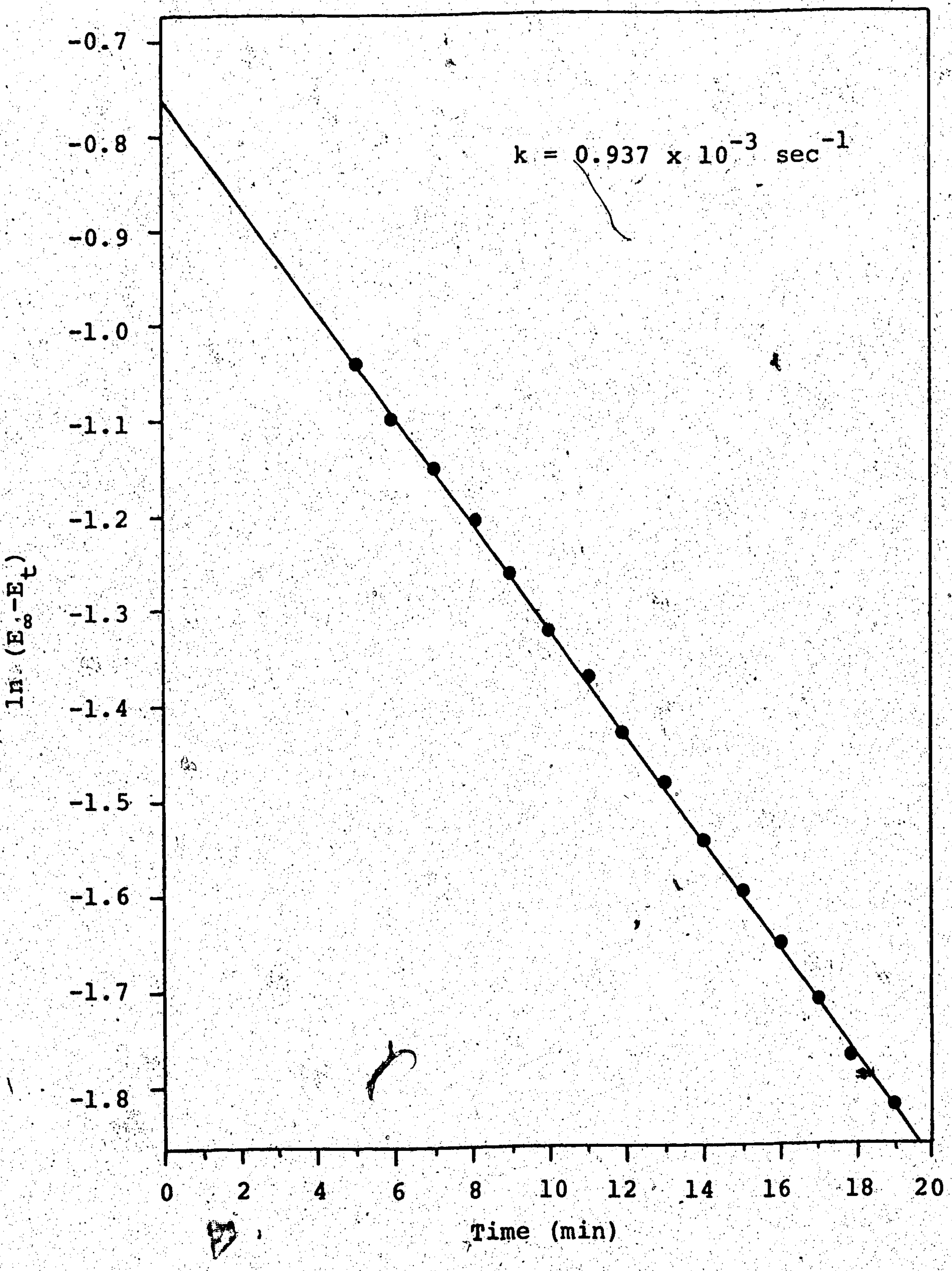


Figure 50. Plot of ln $(E_\infty - E_t)$ *versus* time in the thermolysis of 4-methylene-1-pyrazoline at 165.0°C.

The kinetic results together with the associated error limits were determined by an application of the method or least squares (54) in which the slope (m) and the y-intercept (b) for a linear equation y = mx + b are given by the equations

$$m = \frac{n\Sigma x_i y_i - \Sigma x_i \Sigma Y_i}{n\Sigma x_i^{\,2} - (\Sigma\, x_i)^2} \qquad \text{(eq. 8)}$$

and

$$b = \frac{\Sigma y_i \Sigma x_i^{\,2} - \Sigma x_i \Sigma x_i y_i}{n\Sigma x_i^{\,2} - (\Sigma\, x_i)^2} \qquad \text{(eq. 9)}$$

Assuming that the error resides solely in y_i and that the values of y_i all come from the same population and therefore have the same deviation, estimates of the standard deviations in the slope (σ_m) and the intercept (σ_b) are given by the equations

$$\sigma_m = \sqrt{\frac{n\sigma_y^{\,2}}{n\Sigma x_i^{\,2} - (\Sigma\, x_i)^2}} \qquad \text{(eq. 10)}$$

and

$$\sigma_b = \sqrt{\frac{\sigma_y^{\,2}\Sigma x_i^{\,2}}{n\Sigma x_i^{\,2} - (\Sigma\, x_i)^2}} \qquad \text{(eq. 11)}$$

where the standard deviation of y is defined as in the equation

$$\sigma_y = \sqrt{\frac{\Sigma(y_i - mx_i - b)^2}{n - 2}} \qquad \text{(eq. 12)}$$

The number of degrees of freedom in the case of the straight line fit is two less than the total number of data points. The method above is considered to be very reliable in our cases, since the time values are assumed to be correct and all the errors can be assumed to reside in the recorded values E_t.

The association of particular confidence limits with an estimated mean value implies a prediction of the reliability of this estimate as judged from both the spread of the data and the number of data in the sample from which the mean has been estimated. A commonly accepted practise is to quote the term "probable error (p.e.)" which is given for a least squares analysis as:

$$\text{p.e.} = 0.6745 \times \text{standard deviation} \qquad \text{(eq. 13)}$$

The probable error is the magnitude of deviation that has a 50% confidence limit which means that there is a 50% probability that the mean value is within the quoted error limit. The usefulness of the standard deviation as a predictor decreases considerably as the sample size decreases, but some compensation for errors involved in predicting from small samples is provided by the use of confidence limits (c.l.) which are found by multiplying the standard deviation of the mean by a factor "t" that is selected from a table of "t" values (55) on the basis of the desired confidence and the number of runs, i.e.

$$\text{c.l.} = \sigma \cdot t \qquad \text{(eq. 14)}$$

We used "t" values for a particular confidence level, a commonly chosen level being 90%.

The linear dependence of x_i on y_i can be indicated by a quantity known as the "correlation coefficient (ρ)" which is defined by the equation

$$\rho = \frac{\text{cov}(x_i, y_i)}{\sigma_{x_i} \sigma_{y_i}} \qquad \text{(eq. 15)}$$

where σ_{x_i} and σ_{y_i} are standard deviations, and $\text{cov}(x_i, y_i)$ is the covariance of x_i and y_i defined as $[\Sigma(x_i - \bar{x})(y_i - \bar{y})]/n$. It has been shown in the literature (55) that equation 15 can be expressed by the equation

$$\rho = m \frac{\sigma_{x_i}}{\sigma_{y_i}} \qquad \text{(eq. 16)}$$

which was used by us to calculate the ρ values.

A Texas Instruments programmable 59 calculator was used to perform the least squares analyses and to calculate the associated errors and the correlation coefficients.

The average rate constants (k) for three or five independent runs in the thermolysis of 4-alkylidene-1-pyrazolines at various temperatures are shown in Table 20. The individual rate constant (k_i) for each run together with its standard deviation (σ_{k_i}) and correlation coefficeint (ρ) is given in Appendix. The ρ values were found to be in the range between 0.99933 and 0.99984. This indicates a good linear dependence of $\ln(E_\infty - E_t)$ on time in the least squares analysis. The standard deviation of the average rate constant, σ_k, at each temperature was calculated from the individual rate constants (k_i). A typical example of kinetic calculations and error analyses is shown in Table 19 for the thermolysis of 4-methylene-1-pyrazoline. The error in each average rate constant (k) in Table 20 is based on the 90% confidence limit which was calculated from the corresponding σ_k.

(iii) Thermolysis and Tautomerism Control

From the thermolysis data in Appendix, we were able to estimate % completion of the reaction (i.e. conversion of the pyrazolines into alkylidenecyclopropanes) by the equation

$$\%\ \text{completion} = 100(E_\infty - E_0)/E_0 \qquad \text{(eq. 17)}$$

Table 19

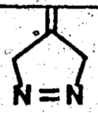
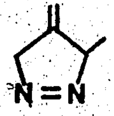
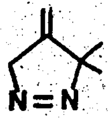
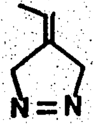
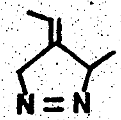
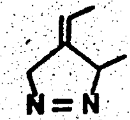
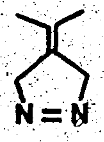
An example of kinetic calculations and error analyses for the thermolysis of 4-methylene-1-pyrazoline

Temp. (°C)	#Run	10^3k_i (sec^{-1})	10^3k (sec^{-1})	$\pm 10^3\sigma_k$	$\pm 10^3$p.e.	$\pm 10^3$(90% c.l.)
165.0	1	0.936				
	2	0.942	0.937	±0.004	±0.003	±0.006
	3	0.934				
170.0	1	1.450				
	2	1.458				
	3	1.450	1.450	±0.005	±0.004	±0.005
	4	1.443				
	5	1.451				
175.0	1	2.222				
	2	2.230	2.218	±0.014	±0.009	±0.019
	3	2.203				

Symbols used: k_i = individual rate constant, k = average rate constant, σ = standard deviation, p.e. = probable error, and c.l. = confidence limit.

Table 20

Kinetic results for the thermolysis of 4-alkylidene-1-pyrazolines

Compound	Temp. (°C)	10^3k (sec^{-1})
 30	165.0	0.937 ± 0.006[a]
	170.0	1.450 ± 0.005
	175.0	2.218 ± 0.019
 68	164.0	0.897 ± 0.025
	170.0	1.509 ± 0.025
	175.0	2.279 ± 0.014
 56	170.0	1.016 ± 0.015
	175.0	1.581 ± 0.020
	180.0	2.459 ± 0.032
 69	160.0	1.391 ± 0.019
	164.0	1.942 ± 0.010
	170.0	3.151 ± 0.051
 89	160.0	1.503 ± 0.022
	164.0	2.073 ± 0.039
	170.0	3.334 ± 0.080
 90	160.0	1.418 ± 0.033
	164.0	1.973 ± 0.034
	170.0	3.206 ± 0.069
 57	(170.0)	(0.802)[b]
	175.0	1.264 ± 0.031
	180.0	1.977 ± 0.027
	185.0	3.050 ± 0.035

[a] The errors are the 90% confidence limits.

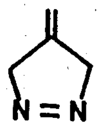
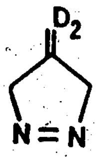
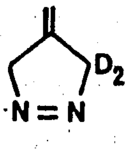
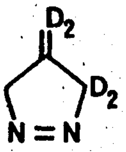
[b] Extrapolated value.

where E_∞ is the transducer emf at t_∞, and E_0 is that at t_0. The emf E_0 corresponding to the initial sample pressure was calculated from the value of the y-intercept, i.e. $\ln(E_\infty - E_0)$, in the least squares analyses. The results detailed in Table 21 clearly indicate that the thermolysis reactions of the 4-alkylidene-1-pyrazolines proceed at temperatures between 160 and 185° with 70-92% completion of the reactions depending on the pyrazoline used and the reaction temperature. The variation in % completion is presumably due to an accompanying tautomerization. Although a greater percentage of completion of the reaction was observed at higher temperatures, the thermolysis temperature cannot exceed that at which the half-life of the reaction becomes less than 300 seconds, since the error in the measurement of the kinetics would be expected to increase with lowered half-life. The degree of completion of the reactions appears to be better for 4-methylene-1-pyrazolines and 4-ethylidene-1-pyrazolines than for the other pyrazolines (see Table 21). It is also noted that the observed rate constants are independent of the percentage completion of the reaction at each temperature.

We observed that, at room temperature, upon catalysis by small amounts of triethylamine in benzene, 4-methylene-1-pyrazoline (**30**) tautomerizes to 4-methylene-2-pyrazoline (**129**) followed by subsequent very slow aromatization to

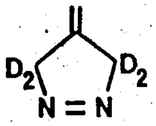
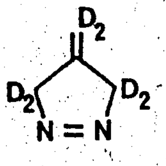
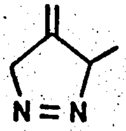
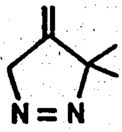
Table 21

Percentage Completion[a] of the reaction for the thermolysis of 4-alkylidene-1-pyrazolines

Compound	Temp. (°C)	#Run	Completion (%)	10^3k_i[b] (sec^{-1})
 30	165.0	1	77	0.936
		2	76	0.942
		3	78	0.934
	170.0	1	85	1.450
		2	84	1.458
		3	84	1.450
		4	85	1.443
		5	80	1.451
	175.0	1	92	2.222
		2	87	2.230
		3	89	2.203
 107	170.0	1	79	1.420
		2	88	1.417
		3	84	1.405
		4	82	1.411
		5	86	1.401
 42	170.0	1	86	1.267
		2	80	1.279
		3	85	1.264
		4	86	1.266
		5	82	1.274
 43	170.0	1	86	1.239
		2	87	1.235
		3	84	1.233
		4	80	1.220
		5	78	1.224

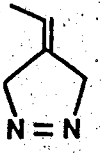
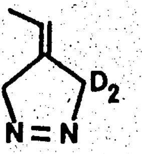
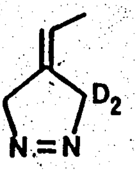
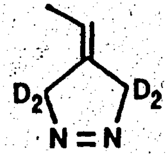
continued...

Table 21 (continued)

Compound	Temp. (°C)	#Run	Completion (%)	$10^3 k_i$ ^{b} (sec^{-1})
 46	170.0	1	88	1.076
		2	83	1.075
		3	86	1.075
		4	87	1.060
		5	82	1.069
 44	170.0	1	82	1.022
		2	83	1.042
		3	86	1.024
		4	87	1.033
		5	82	1.027
 68	164.0	1	75	0.894
		2	74	0.880
		3	73	0.917
	170.0	1	80	1.530
		2	75	1.501
		3	79	1.495
	175.0	1	83	2.289
		2	81	2.269
		3	85	2.278
 56	170.0	1	75	1.016
		2	71	1.005
		3	72	1.027
	175.0	1	75	1.590
		2	74	1.589
		3	77	1.564
	180.0	1	84	2.438
		2	81	2.454
		3	82	2.485

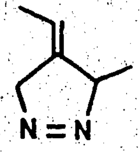
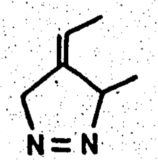
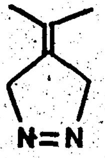
continued...

Table 21 (continued)

Compound	Temp. (°C)	#Run	Completion (%)	$10^3k_i{}^b$ (sec^{-1})
 69	160.0	1	75	1.405
		2	76	1.377
		3	76	1.391
	164.0	1	82	1.928
		2	85	1.950
		3	81	1.931
		4	84	1.948
		5	85	1.952
	170.0	1	85	3.111
		2	89	3.157
		3	84	3.186
 76	164.0	1	83	1.671
		2	86	1.661
		3	82	1.649
		4	81	1.639
		5	79	1.662
 77	164.0	1	79	1.820
		2	76	1.817
		3	80	1.806
		4	81	1.811
		5	86	1.797
 128	164.0	1	85	1.558
		2	80	1.536
		3	77	1.521
		4	80	1.527
		5	78	1.516

continued...

Table 21 (continued)

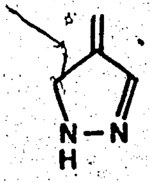
Compound	Temp. (°C)	#Run	Completion (%)	$10^3 k_i{}^b$ ($\sec^{-1}$)
 89	160.0	1	71	1.507
		2	73	1.485
		3	70	1.516
	164.0	1	75	2.076
		2	74	2.042
		3	76	2.100
	170.0	1	79	3.329
		2	84	3.278
		3	81	3.396
 90	160.0	1	73	1.412
		2	72	1.445
		3	74	1.397
	164.0	1	76	1.964
		2	76	2.001
		3	77	1.954
	170.0	1	86	3.203
		2	85	3.258
		3	85	3.156
 57	175.0	1	71	1.286
		2	70	1.241
		3	75	1.266
	180.0	1	79	2.000
		2	81	1.969
		3	82	1.963
	185.0	1	86	3.044
		2	85	3.078
		3	88	3.027

---

[a] Calculated from the data in Appendix using the equation % completion = $(E_\infty - E_0)/E_0 \times 100$ where E_0 is a transducer emf at t_0.

[b] Individual rate constants are in Appendix.

4-methylpyrazole (130). However, in the presence of even



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catalytic amounts of hydrochloric acid 30 rapidly deteriorates, possibly to its polymer, since the ^{1}Hmr peaks of the olefinic protons completely disappear immediately after the addition of the acid. Pseudo first-order kinetics have also been observed in the tautomerization of 30 to 129 in methanol at room temperature. Catalytic amounts of chloroacetic acid or triethylamine result in increasing intensity with time of the absorption band at 287 nm (λ_{max}) in the ultraviolet spectrum. This band is due to 129 (cf. λ_{max} = 322 nm for 30 in ethanol) (56). The two isomers were also detected by ^{1}Hmr in the product mixture collected after thermolysis, and ^{1}Hmr integrations have shown that the relative ratio of 129:130 changes from approximately 95:5 after 2 half lives to 10:90 after 10 half lives. This result indicates that 129 is the only isomer existing in the reaction mixture during the thermolysis. Polymerization to an unidentified high boiling compound did not occur to a detectable extent since the values of E_∞ (the transducer emf at t_∞) remained constant upon completion of the reaction.

(iv) Activation Parameters

The effect of temperature on the rate constant, k, is given by the Arrhenius equation (53):

$$k = A\, e^{-E_a/RT} \qquad \text{(eq. 18)}$$

where E_a is the activation energy and A is the frequency factor. This can be expressed in natural logarithmic form as:

$$\ln k = \ln A - (E_a/RT) \qquad \text{(eq. 19)}$$

Thus a plot of ln k *versus* 1/T should give a straight line of slope $-E_a/R$ and an intercept corresponding to ln A (or 2.303 log A). Using the data in Table 20, linear first-order plots were obtained. Figure 51 shows a typical plot of ln k *versus* 1/T for kinetic runs in the thermolysis of 4-methylene-1-pyrazoline. The activation energy and the frequency factor were determined by a least squares analysis in which the rate constants were not rounded off for computational purposes.

The entropy of activation is obtained in the following manner (53). According to the absolute reaction rate theory, the rate constant, k, of the reaction is given by the equation

$$k = \frac{\kappa k_B\, T}{h}\, e^{-\Delta H^{\ddagger}/RT}\, e^{\Delta S^{\ddagger}/R} \qquad \text{(eq. 20)}$$

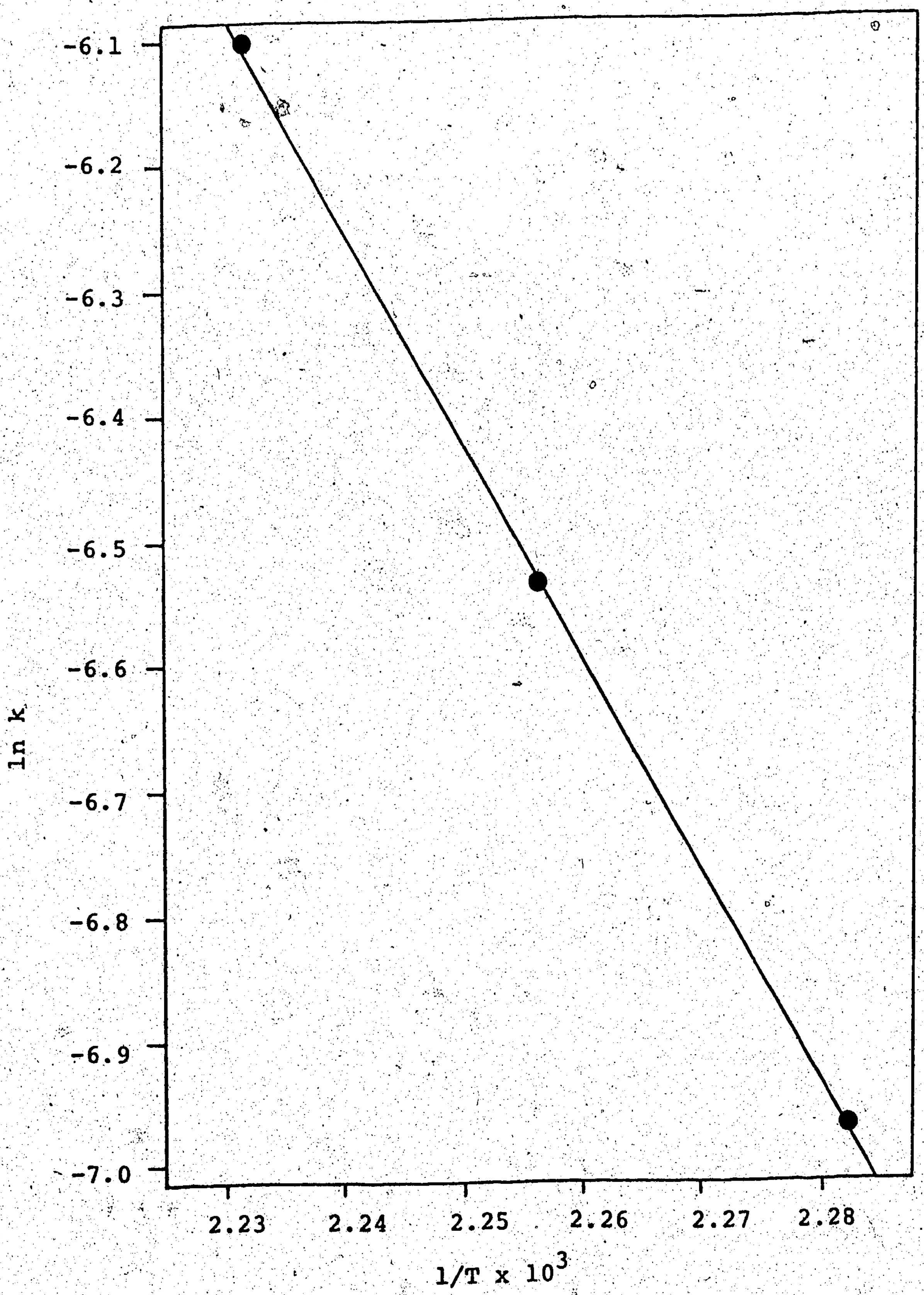


Figure 51. Plot of ln k *versus* 1/T in the thermolysis of 4-methylene-1-pyrazoline.

where κ is the transmission coefficient, k_B is Boltzmann's constant and h is Planck's constant. For a gaseous reaction, the following relationship holds

$$\Delta H^{\ddagger} = E_a - nRT \qquad \text{(eq. 21)}$$

where n is the molecularity (and order) of the reaction (53). It follows from equations 20 and 21 that

$$k = \frac{\kappa k_B\ T\ e}{h}\ e^{-E_a/RT}\ e^{\Delta S^{\ddagger}/R} \qquad \text{(eq. 22)}$$

for a unimolecular, first order, gaseous reaction. From equations 18 and 22

$$A = \frac{\kappa k_B\ T\ e}{h}\ e^{\Delta S^{\ddagger}/R} \qquad \text{(eq. 23)}$$

Rewriting equation 23, the entropy of activation is given by the equation:

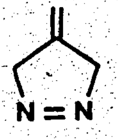
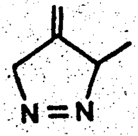
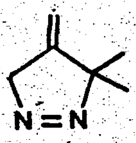
$$\Delta S^{\ddagger} = 4.576\ (\log A - \log T) - 49.198 \qquad \text{(eq. 24)}$$

The activation parameters for the various 4-alkylidene-1-pyrazolines are in Table 22. The errors and correlation coefficients were calculated from the least squares analyses. The ρ values were found to be in the range between 0.99930 and 0.99992 which indicates a satisfactory linear dependence of ln k on 1/T.

The errors in the activation parameters (see Table 22) are the maximum possible and were calculated in the

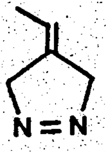
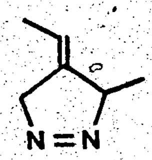
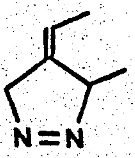
Table 22

Activation Parameters for the thermolysis of 4-alkylidene-1-pyrazolines

Compound	Temp. (°C)	10^3k (sec^{-1})	E_a ($kcal\ mol^{-1}$) (ρ)	log A	$\Delta S^{\ddagger}_{170}$ (e.u.) $\Delta S^{\ddagger}_{170}$ (e.u.)
	165.0	0.937 ± 0.006			1.6 ± 1.6
	170.0	1.450 ± 0.005	33.6 ± 0.7	13.75 ± 0.35	
30	175.0	2.218 ± 0.019	(0.99992)		1.3 ± 1.6
	164.0	0.897 ± 0.025			0.2 ± 4.6
	170.0	1.509 ± 0.025	33.0 ± 1.9	13.44 ± 0.99	
68	175.0	2.279 ± 0.014	(0.99951)		-0.1 ± 4.6
	170.0	1.016 ± 0.015			4.6 ± 2.7
	175.0	1.581 ± 0.020	35.3 ± 1.2	14.40 ± 0.60	
56	180.0	2.459 ± 0.032	(0.99972)		4.3 ± 2.7

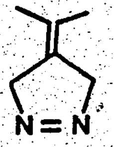
continued...

Table 22 (continued)

Compound	Temp. (°C)	10^3 k (sec^{-1})	E_a (kcal mol^{-1}) (ρ)	log A	$\Delta S^{\ddagger}_{170}$ (e.u.) $\Delta S^{\ddagger}_{170}$ (e.u.)
 69	160.0	1.391 ± 0.019			−2.4 ± 3.0
	164.0	1.942 ± 0.010	31.2 ± 1.3	12.87 ± 0.66	
	170.0	3.151 ± 0.051	(0.99968)		−2.8 ± 3.0
 89	160.0	1.503 ± 0.022			−4.1 ± 4.2
	164.0	2.073 ± 0.039	30.4 ± 1.7	12.51 ± 0.91	
	170.0	3.334 ± 0.080	(0.99935)		−4.4 ± 4.2
 90	160.0	1.418 ± 0.033			−2.5 ± 4.2
	164.0	1.973 ± 0.034	31.1 ± 1.7	12.85 ± 0.92	
	170.0	3.206 ± 0.069	(0.99930)		−2.8 ± 4.2

continued...

Table 22 (continued)

Compound	Temp. [illegible]	k [illegible]$^{-1}$)	E_a (kcal mol^{-1}) (ρ)	log A	$\Delta S^{\ddagger}_{170}$ (e.u.) $\Delta S^{\ddagger}_{170}$ (e.u.)
 57	175.0	1.264 ± 0.031			5.6 ± 4.5
	180.0	1.977 ± 0.027	35.9 ± 1.9	14.62 ± 0.97	
	185.0	3.050 ± 0.035	(0.99957)		5.3 ± 4.5

Symbols used: k = average rate constant, ρ = correlation coefficient and $\Delta S^{\ddagger}_{170}$ (or $\Delta S^{\ddagger}_{250}$)
= entropy activation at 170°C (or at 250°C).

The errors in E_a, log A and $\Delta S^{\ddagger}$ are the maximum possible.

following manner (57). From equation 22, the slope of the line obtained by plotting $\ln(k/T)$ against $1/T$ is equal to $-E_a/R$. Thus E_a can be calculated. Regardless of how the slope is evaluated, it is largely determined by the first and last data points. If three temperatures are used, the slope is determined solely by the first and third points, and the middle point controls only the value of the intercept. Thus, the value of E_a is given by

$$E_a = R \frac{T' T}{T'-T} \ln \frac{k' T}{k T'} \qquad \text{(eq. 25)}$$

where T and T' are the extreme temperatures and k and k' are the corresponding rate constants.

If α is the maximum fractional error in the rate constants, and ρ is the error in E_a, then

$$E_a + \delta = R \frac{T' T}{T' - T} \ln \frac{(1 + \alpha)\, k' T}{(1 - \alpha)\, k T'} \qquad \text{(eq. 26)}$$

or

$$\delta = R \frac{T' T}{T' - T} \ln \frac{1 + \alpha}{1 - \alpha} \qquad \text{(eq. 27)}$$

When $\alpha << 1$, as is usually the case, the logarithmic part may be expanded as a series and only the first term taken. Then δ may be expressed as

$$\delta = 2\,R\,\frac{T'\,T}{T' - T}\,\alpha \qquad \text{(eq. 28)}$$

If σ is the error in $\Delta S^{\ddagger}$, from equation 22 it follows that

$$\Delta S^{\ddagger} + \sigma = (E_a + \delta)/T + R\ \ln\ \frac{(1 + \alpha)\ k'h}{\kappa\ k_B\ T\ e} \qquad \text{(eq. 29)}$$

and

$$\sigma = \delta/T + R\ \ln\ (1 + \alpha) \qquad \text{(eq. 30)}$$

Again, when $\alpha << 1$, this reduces to

$$\sigma = \delta/T + \alpha R \qquad \text{(eq. 31)}$$

The errors in E_a, $\Delta S^{\ddagger}$ and log A were calculated by using equations 28, 31 and 24 respectively and are presented in Table 22. It should be noted that the activation parameters for 4-methylene-1-pyrazoline listed in Table 22 are comparable to the values (E_a = 32.6 kcal mol^{-1}, log A = 13.24, and $\Delta S^{\ddagger}_{250}$ = -1.1 e.u.) previously reported in the literature by Cameron and Crawford (10a); however, our results are believed to be more reliable because of improved methods of control and measurement of the reaction temperatures. Only short term stability of the reaction temperature was possible with the system (58) used by these authors.

Similarly, the secondary deuterium kinetic isotope effects observed by us for the thermolysis of deuterated 4-methylene-1-pyrazolines as detailed in the following section are believed to be more precise than those obtained earlier (see Table 5) (10a).

(v) Secondary Deuterium Kinetic Isotope Effects

The thermolysis reactions of the deuterated 4-methylene-1-pyrazolines and 4-ethylidene-1-pyrazolines were conducted in the static stainless-steel system at 170 and 164° respectively.

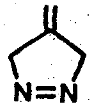
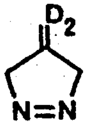
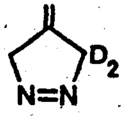
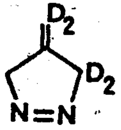
The average observed rate constants, k_{obs}, with their 90% confidence limits from five independent runs are shown in Tables 23 and 24. The individual rate constants, k_i, together with their standard deviations, σ_{k_i}, and correlation coefficients, ρ, are detailed in Appendix. The ρ values were calculated to be in the range between 0.99959 and 0.99985 indicating a good linear dependence of $\ln(E_\infty - E_t)$ on time.

These observed rate constants, k_{obs}, were corrected for the isotopic purities of the 4-alkylidene-1-pyrazolines which had been determined by mass or nmr spectral analyses (see Tables 16 and 18). In the case of the deuterated 4-methylene-1-pyrazolines, the corrections were made by using the equation

$$k_D \text{ (corrected)} = \frac{k_{obs} - k_H f_H}{f_D} \qquad \text{(eq. 32)}$$

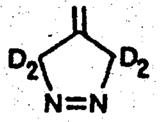
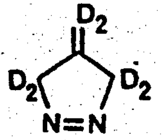
Table 23

Secondary deuterium kinetic isotope effects for the thermolysis of the deuterated 4-methylene-1-pyrazolines (170.0°C)

Compound	Deuterium isotopic purity[a] (%)	$10^3 k_{obs}$[b] (sec^{-1})	$10^3 k_D(corr)$[c] (sec^{-1})	k_H/k_D
 30		1.45 ± 0.01[d]		
 107	95.0 ± 0.1[d]	1.41 ± 0.01	1.41 ± 0.01[d]	1.03 ± 0.01[d]
 42	97.0 ± 0.1	1.27 ± 0.01	1.26 ± 0.01	1.15 ± 0.01
 43	97.1 ± 0.1	1.23 ± 0.01	1.22 ± 0.01	1.19 ± 0.01

continued...

Table 23 (continued)

Compound	Deuterium isotopic purity[a] (%)	$10^3 k_{obs}$[b] (sec^{-1})	$10^3 k_D(corr)$[c] (sec^{-1})	k_H/k_D
 46	95.4 ± 0.1	1.07 ± 0.01	1.05 ± 0.01	1.38 ± 0.02
 44	96.8 ± 0.1	1.03 ± 0.01	1.02 ± 0.01	1.42 ± 0.02

[a] Determined by mass spectral analysis as indicated in Table 16.

[b] At 170.0°C.

[c] Corrected for incomplete deuteration $k_D = (k_{obs} - k_H f_H)/f_D$ where f_D is the fraction deuterated.

[d] The errors quoted are the 90% confidence limits.

where f_D is the fraction deuterated, and f_H is the fraction nondeuterated. The corrected rate constants, k_D, and the values of k_H/k_D for the deuterated 4-methylene-1-pyrazolines are given in Table 23.

Equation 32 was also used to correct the observed rate constant for 4-ethylidene-1-pyrazoline-3,3,5,5-d_4 (**128**). However, the corrected rate constants for *E*- and *Z*-4-ethylidene-1-pyrazoline-3,3-d_2 (**76** and **77**) were obtained by using the equation

$$k_{obs} = k_H\, f_H + k_D^E\, f_D^E + k_D^Z\, f_D^Z \qquad \text{(eq. 33)}$$

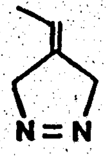
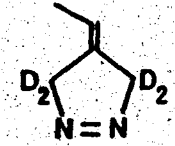
where k_D^E and k_D^Z are the corrected rate constants for **76** and **77** respectively, and f_D^E and f_D^Z are the deuterated fractions of **76** and **77** in mixture A or B. Mixture A resulted from the preparation of **76** and mixture B from the preparation of **77** since formation of the desired compound was accompanied by formation of small amounts of its isomer (see Table 18). The data from mass, ^{1}Hmr and ^{2}Hmr spectral analyses in Table 18 are cited in Table 24 for the sake of convenience. Inserting the ^{1}Hmr data and the values of the observed rate constants in Table 24 into equation 33, we obtain

$$\begin{aligned} 1.66 \times 10^{-3} = (1.94 \times 10^{-3})(0.04) + 0.88\, k_D^E \\ + 0.08\, k_D^Z \end{aligned} \qquad \text{(eq. 34)}$$

for mixture A, and

Table 24

Observed rate constants for the thermolysis of deuterated 4-ethylidene-1-pyrazolines at 164.0°C

	Deuterium isotopic purity[a]					
Compound	Analysis method	%				$10^3 k_{obs}$[b] (sec^{-1})
		d_4	**76**	**77**	d_0	
 **69**		-	-	-	100	1.94 ± 0.01
Mixture A	Mass & ^{1}Hmr	-	88	8	4	1.66 ± 0.01
	Mass & ^{2}Hmr	-	86	10	4	
Mixture B	Mass & ^{1}Hmr	-	7	90	3	1.81 ± 0.01
	Mass & ^{2}Hmr	-	9	88	3	
 **128**	Mass & ^{1}Hmr	96	-	-	4	1.53 ± 0.01

---

[a] Obtained by the analyses of 400 MHz ^{1}Hmr (or 54.4 MHz ^{2}Hmr) and mass spectra as previously indicated in Table 18.

[b] The errors quoted are the 90% confidence limits.

$$1.81 \times 10^{-3} = (1.94 \times 10^{-3})(0.03) + 0.07\, k_D^E + 0.90\, k_D^Z \quad \text{(eq. 35)}$$

for mixture B. Simultaneous solution of these two linear equations gives $k_D^E = 1.63 \times 10^{-3}$ sec^{-1} and $k_D^Z = 1.82 \times 10^{-3}$ sec^{-1}. Using the ^{2}Hmr data in Table 24, we obtained the same values. The corrected rate constants and the calculated values of k_H/k_D for the deuterated 4-ethylidene-1-pyrazolines are shown in Table 25. It should be noted that the correction of the observed rate constant for 128 was made by using equation 32 to give $k_D = 1.51 \times 10^{-3}$ sec^{-1} with the assumption that 128 consists of a 96:4 mixture of d_4:d_0. Considering the extreme case in which 128 is assumed to be a 92:4:4 mixture of d_4:76:77, we can then use equation 33. Such a change does not affect the value obtained since calculation gives $k_D = 1.51 \times 10^{-3}$ sec^{-1}. Therefore, this value can be considered as a corrected rate constant for 128.

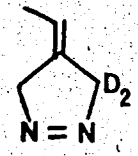
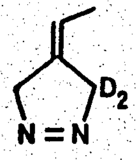
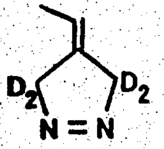
C. Product Analyses

(i) Thermolysis of Deuterated 4-Methylene-1-pyrazolines (107, 42, 43 and 46)

Samples of the deuterated 4-methylene-1-pyrazolines (ca. 60 Torr) were thermolyzed in the thermostatted static air-bath system at 175.0° for 20 min. It is known that interconversion between 49 and 50 or between 47 and 48 is negligible at this temperature (10a). As

Table 25

Secondary deuterium kinetic isotope effects for the thermolysis of deuterated 4-ethylidene-1-pyrazolines

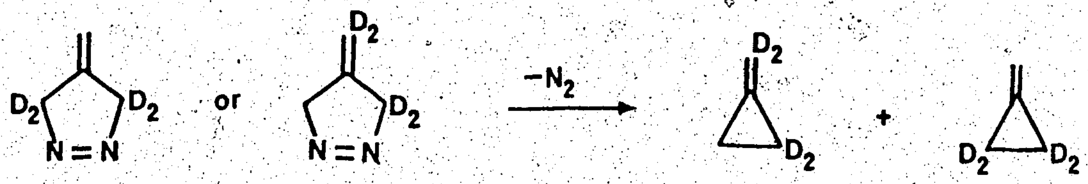
Compound	Data used[a]	$10^3 k_D$(corr)[b]	k_H/k_D
 76	Mass & ^{1}Hmr	1.63 ± 0.04[c]	1.19 ± 0.03[c]
	Mass & ^{2}Hmr	1.63 ± 0.04	
 77	Mass & ^{1}Hmr	1.82 ± 0.04	1.07 ± 0.02
	Mass & ^{2}Hmr	1.82 ± 0.04	
 128	Mass & ^{1}Hmr	1.51 ± 0.03	1.29 ± 0.03

---

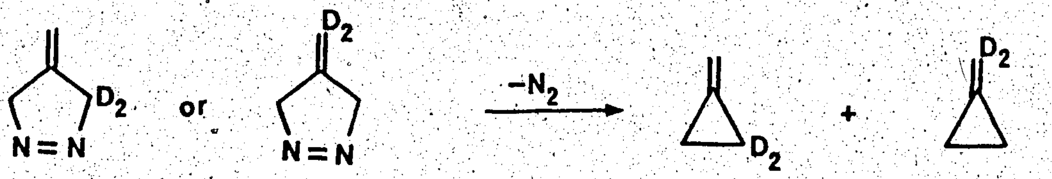
[a] From Table 24 (or 18).

[b] Corrected for incomplete deuteration by using the equation $k_{obs} = k_H f_H + k_D^E f_D^E + k_D^Z f_D^Z$ where k_D^E and k_D^Z are the corrected rate constant for 76 and 77 respectively, and f_D^E and f_D^Z are the deuterated fraction of 76 and 77 in mixture A, B or 128 as in Table 24.

[c] The errors quoted are the 90% confidence limits.



46 43 49 50



42 107 47 48

described in the experimental section, the products after thermolysis were trapped in a liquid nitrogen cooled tube. On warming these products in an ice-water bath only the deuterated methylenecyclopropanes were vaporized to be trapped again at liquid nitrogen temperature, so that the tautomers were left behind. Chloroform-d or carbon tetrachloride was then added to the deuterated methylenecyclopropanes, and the 100 MHz ^{1}Hmr or 13.8 MHz ^{2}Hmr spectra shown in Figures 52-58 were obtained.

The ratios of the deuterated methylenecyclopropanes obtained from 46 and 43 were determined by ^{1}Hmr integration (see Figures 55 and 54) in the following manner. Let R_H be the ratio of ^{1}H integration at δ5.33 to that at δ1.01. The ratio $f_{49}:f_{50}$ was then calculated by the equation

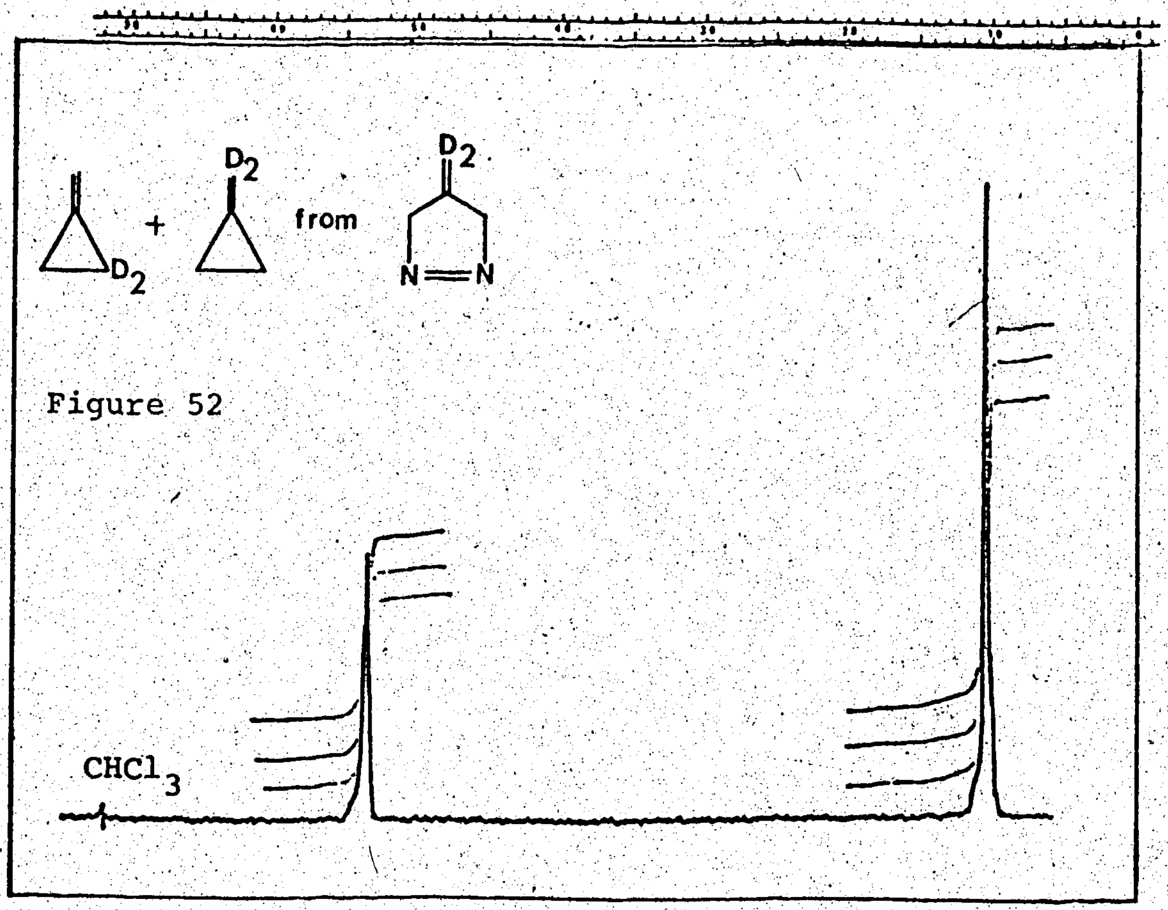


Figure 52

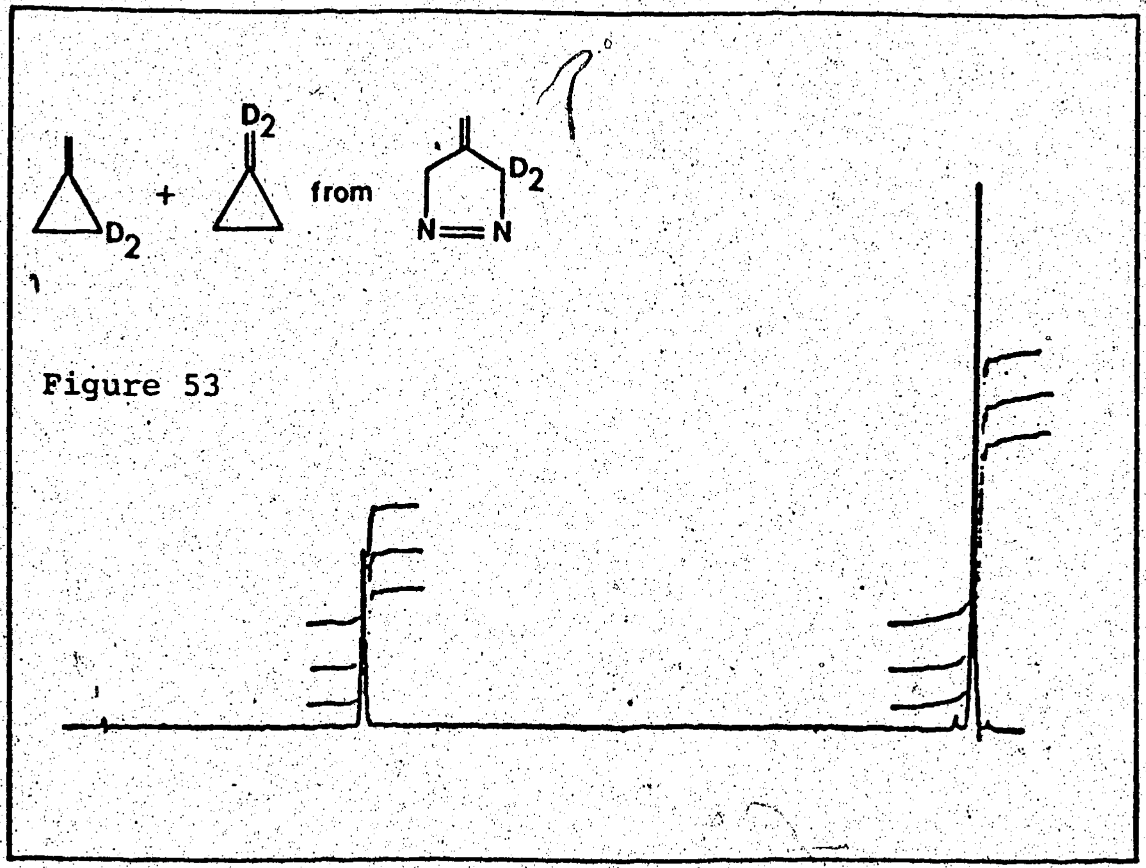


Figure 53

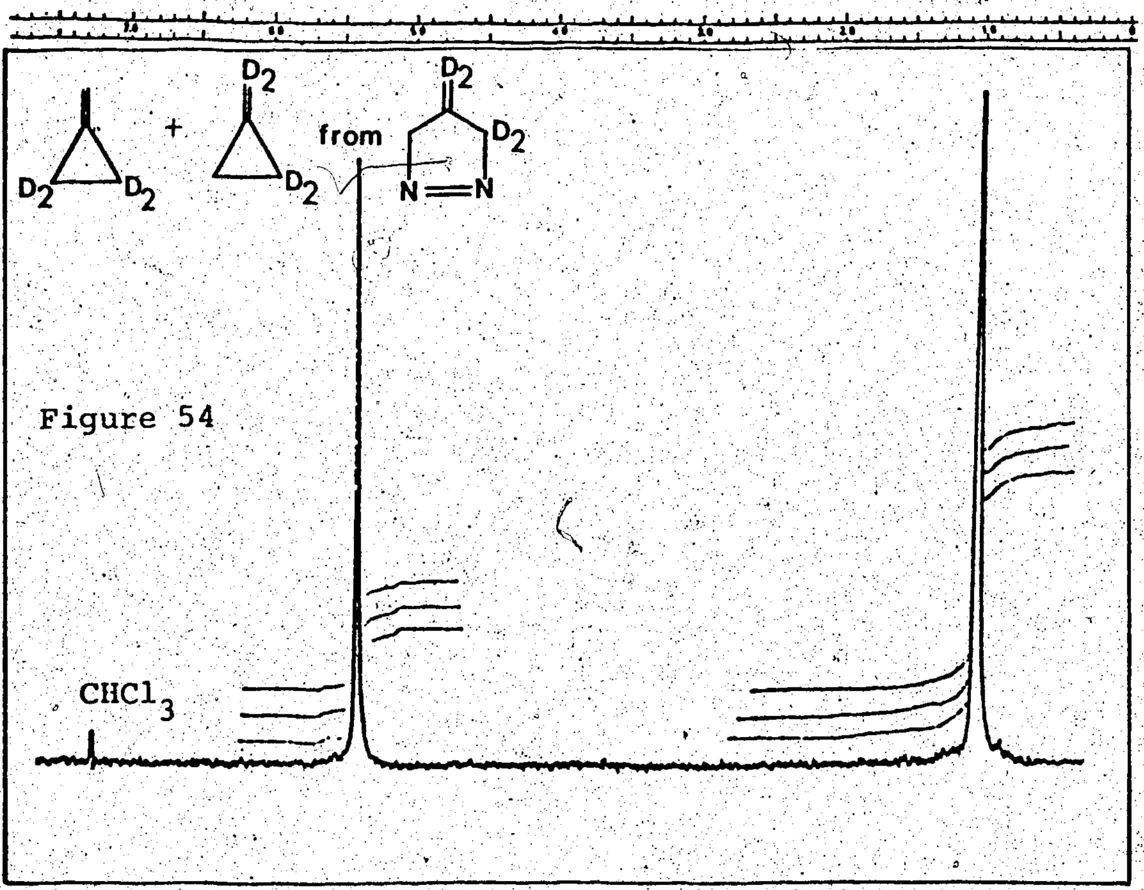


Figure 54

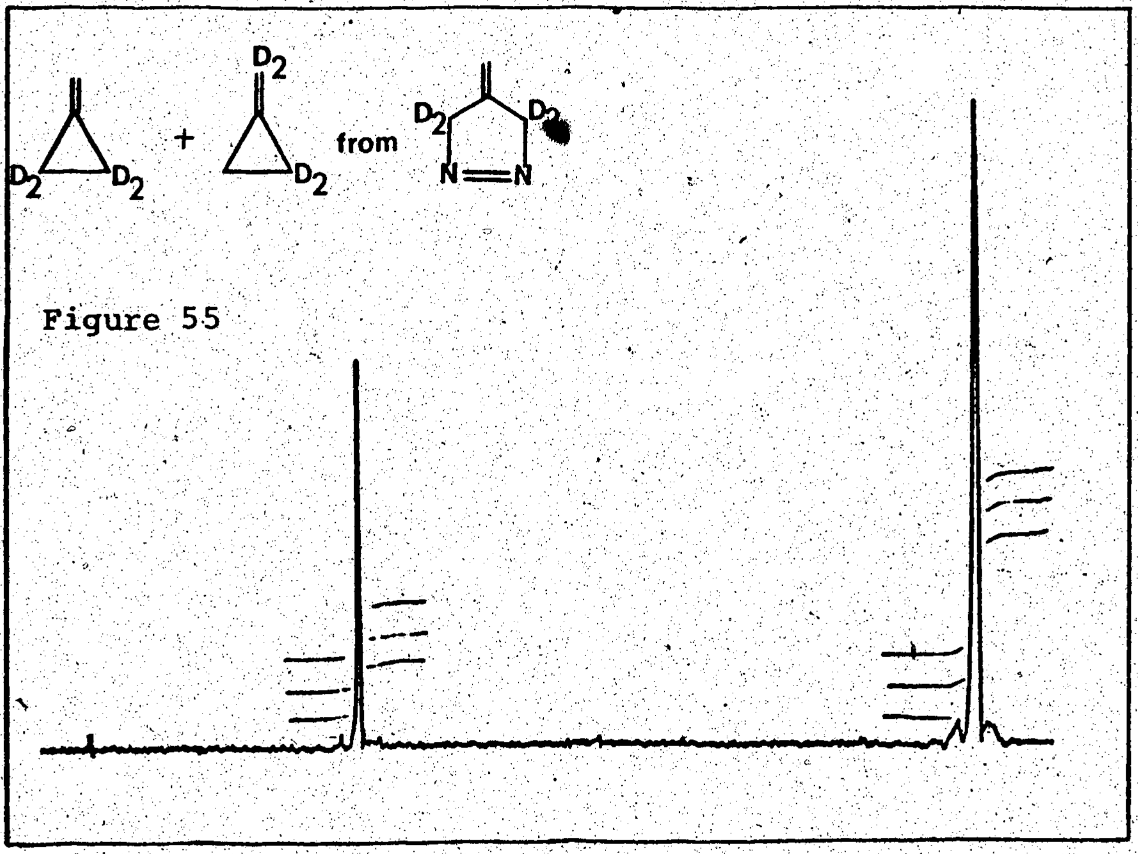


Figure 55

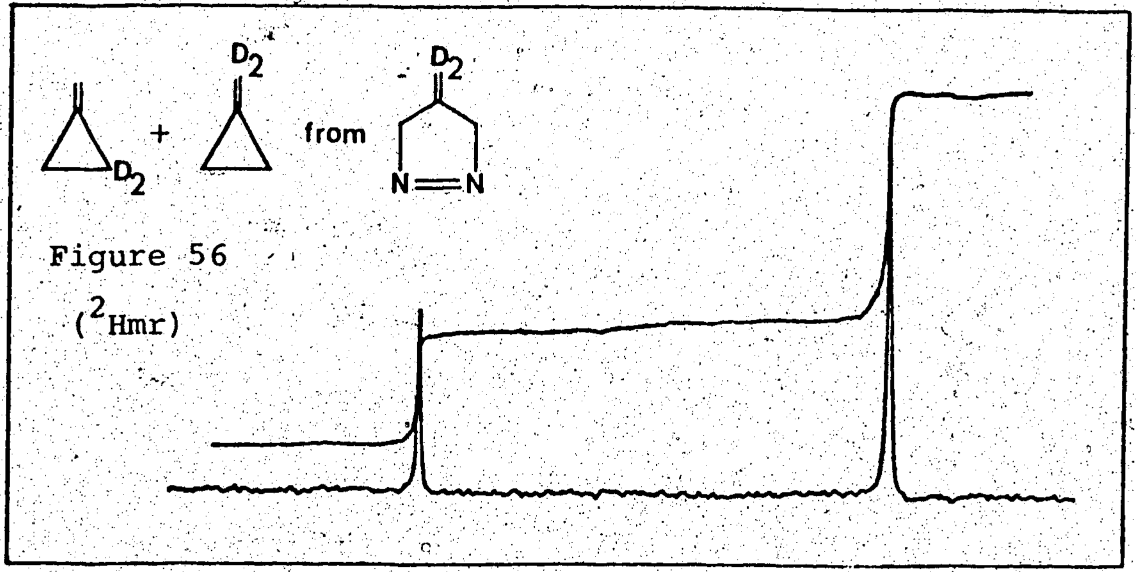


Figure 56
(^{2}Hmr)

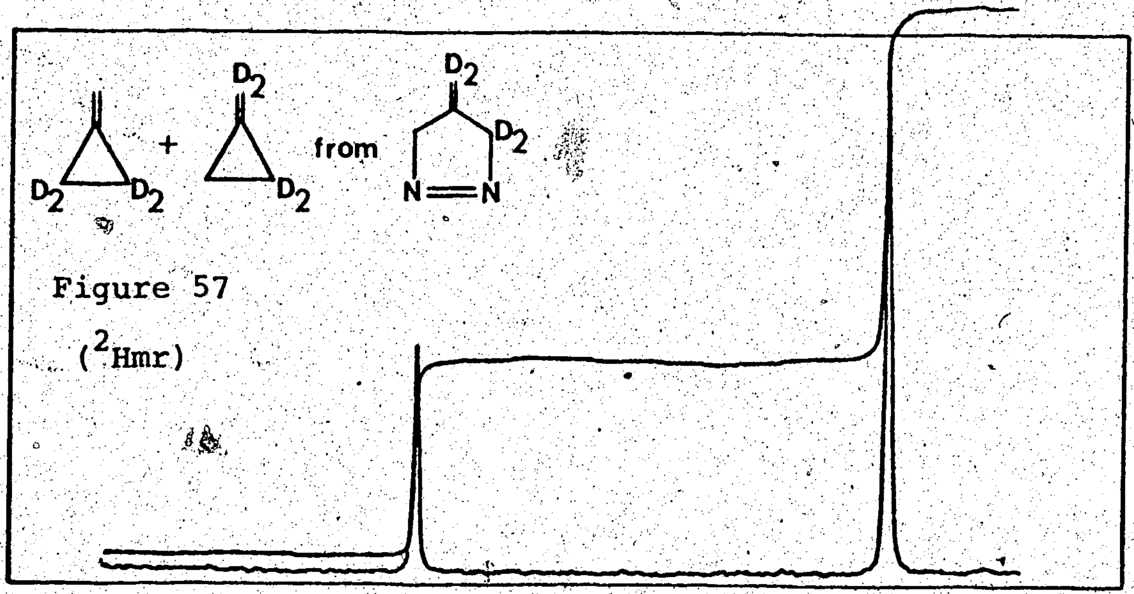


Figure 57
(^{2}Hmr)

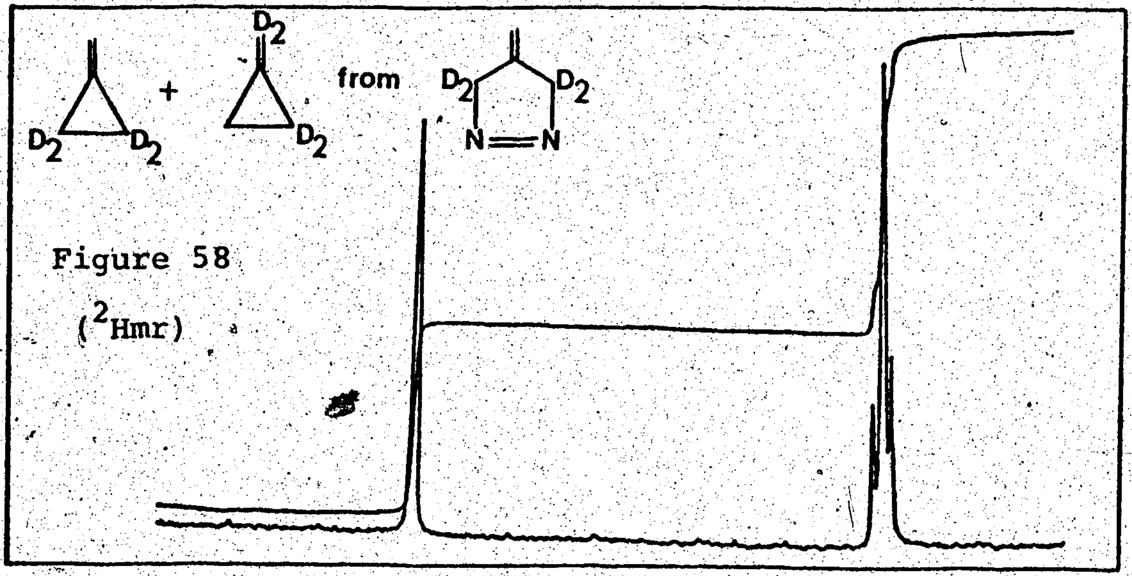


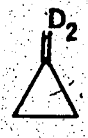
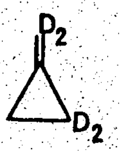
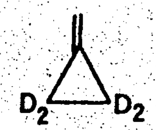
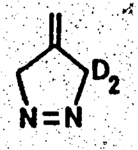
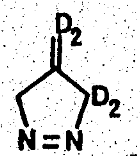
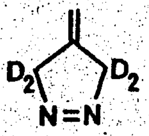
Figure 58
(^{2}Hmr)

$$R_H = \frac{2f_{50} + 2f_{31}}{2f_{49} + 4f_{31}} \qquad \text{(eq. 36)}$$

where f_{3}[illegible]nd f_{50} represent the mole fractions of **31** (4-me[illegible]-pyrazoline), **49** and **50** respectively. From mass [illegible]oscopy, $f_{31} = 0.046$ and $f_{49} + f_{50} =$ 0.9[illegible] for [illegible] see Table 16). Solving for f_{49} and f_{50}, we o[illegible]aine[illegible] the ratio $f_{49}:f_{50} = 77:23$ for **46** from ^{1}Hmr spect[illegible]sc[illegible]y ($R_H = 0.319$). The analogous value from ^{2}Hmr s[illegible]roscopy (see Figure 58) was $f_{49}:f_{50} = 76:24$. It sho[illegible] be noted that $f_{49}:f_{50}$ was calculated without need of [illegible]nsidering the isotopic purity when ^{2}Hmr data was used[illegible] The ratio $f_{49}:f_{50}$ for **43** and the ratios, $f_{47}:f_{48}$, [illegible]r **42** and **107** were calculated similarly. All of the results are given in Table 26. Each value of the percent distribution in Table 26 is the average from three inde[illegible]nt samples, and the error quoted is the 90% confidence limit. It should be noted that the percent distribution of the deuterated methylenecyclopropanes from **42** or **43** obtained by us is the same within experimental error as that obtained by Crawford and Cameron (see Table 6) (10a).

Table 26

Deuterium distribution in the methylenecyclopropanes from the thermolysis of deuterated 4-methylene-1-pyrazolines (175.0°C)

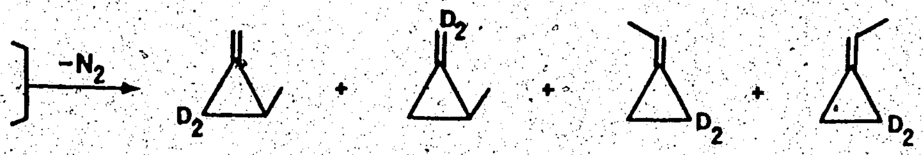
Reactant	Method of analysis	distribution* (%)			
		 47	 48	 49	 50
 107	^{1}Hmr	66 ± 1	34 ± 1		
	^{2}Hmr	66 ± 1	34 ± 1		
 42	^{1}Hmr	59 ± 1	41 ± 1		
	^{2}Hmr	60 ± 1	40 ± 1		
 43	^{1}Hmr			72 ± 1	28 ± 1
	^{2}Hmr			71 ± 1	29 ± 1
 46	^{1}Hmr			77 ± 1	23 ± 1
	^{2}Hmr			76 ± 1	24 ± 1

*The errors quoted are the 90% confidence limits from three samples.

(ii) Thermolysis of *E*- and *Z*-4-Ethylidene-1-pyrazoline-3,3-d_2 (76 and 77)

Pyrazolines 76 and 77 contained small quantities of their isomers 77 and 76. These mixtures were designated A and B respectively (see Table 18). Thermolysis of

mixture A
or
mixture B



78 79 81 82

mixtures A and B were carried out in a breakseal at a pressure of approximately one atmosphere for 15-60 min in a thermostatted oil bath at 175.2°. Under these conditions, it is known that the interconversion between 2-methylmethylenecyclopropane (70) and ethylidenecyclopropane (71) is negligible (24, 34, 11). After the thermolysis tubes were cooled in an ice-water bath, the products were vapor transferred into a receiver and benzene or chloroform was added. The products were then separated by preparative gc into the two species: deuterated 2-methylmethylenecyclopropanes (78 and 79) and deuterated ethylidenecyclopropanes (81 and 82). The 100 MHz ^{1}Hmr and 54.4 MHz ^{2}Hmr spectra of the products, 78 and 79, from mixture A and B are shown in Figures 59-63, and the 400 MHz ^{1}Hmr and 54.4 MHz ^{2}Hmr spectra of 81 and 82 from mixtures A and B are given in Figures 64-69.

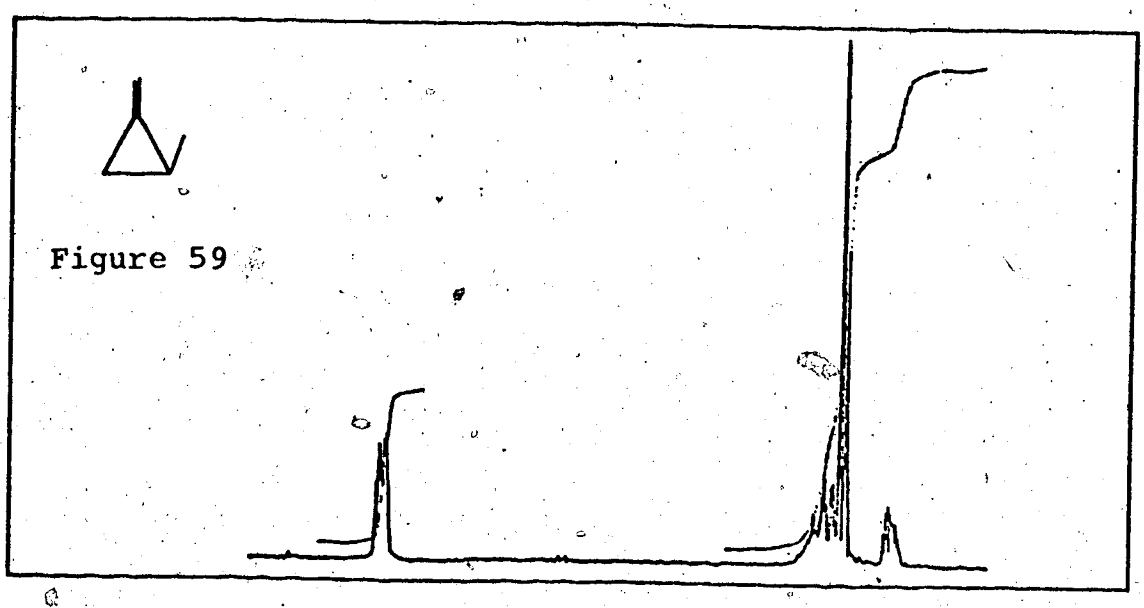
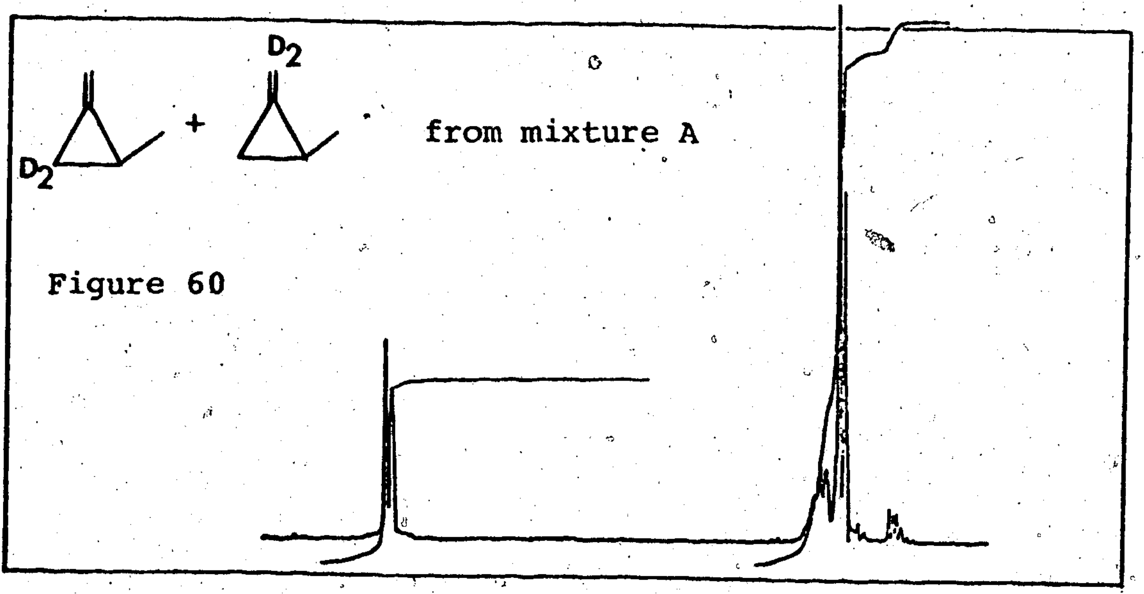
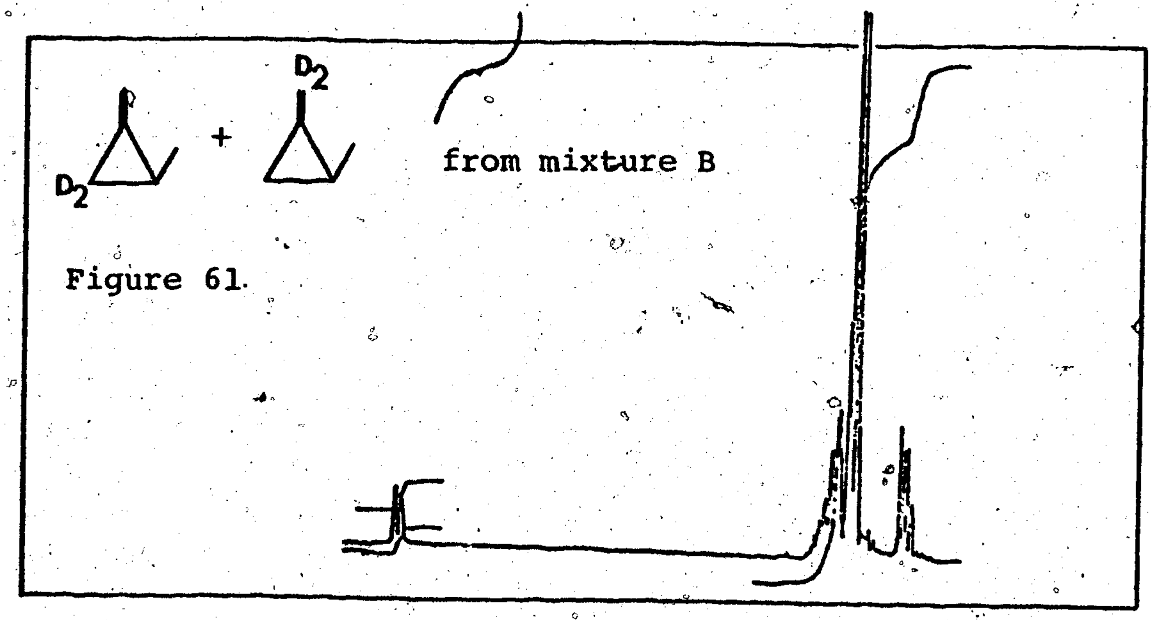


Figure 59



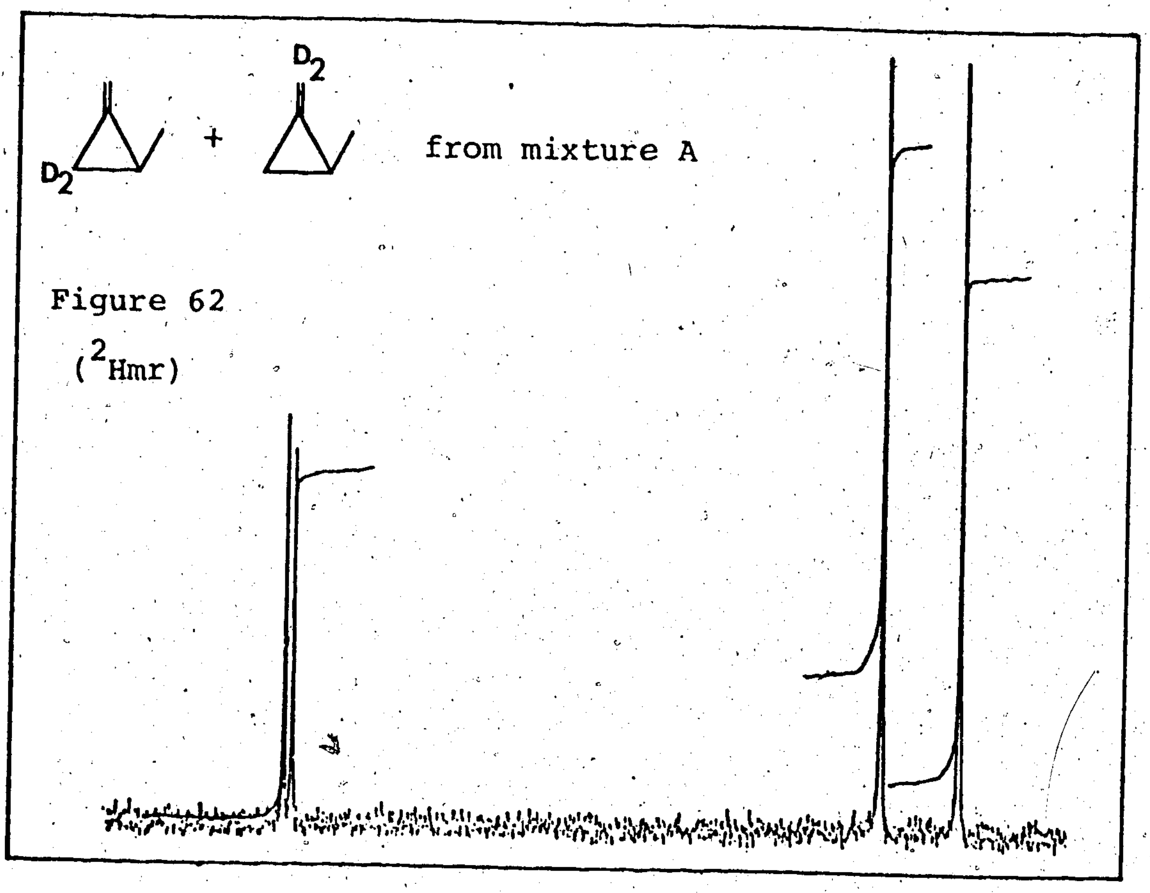
from mixture A

Figure 60



from mixture B

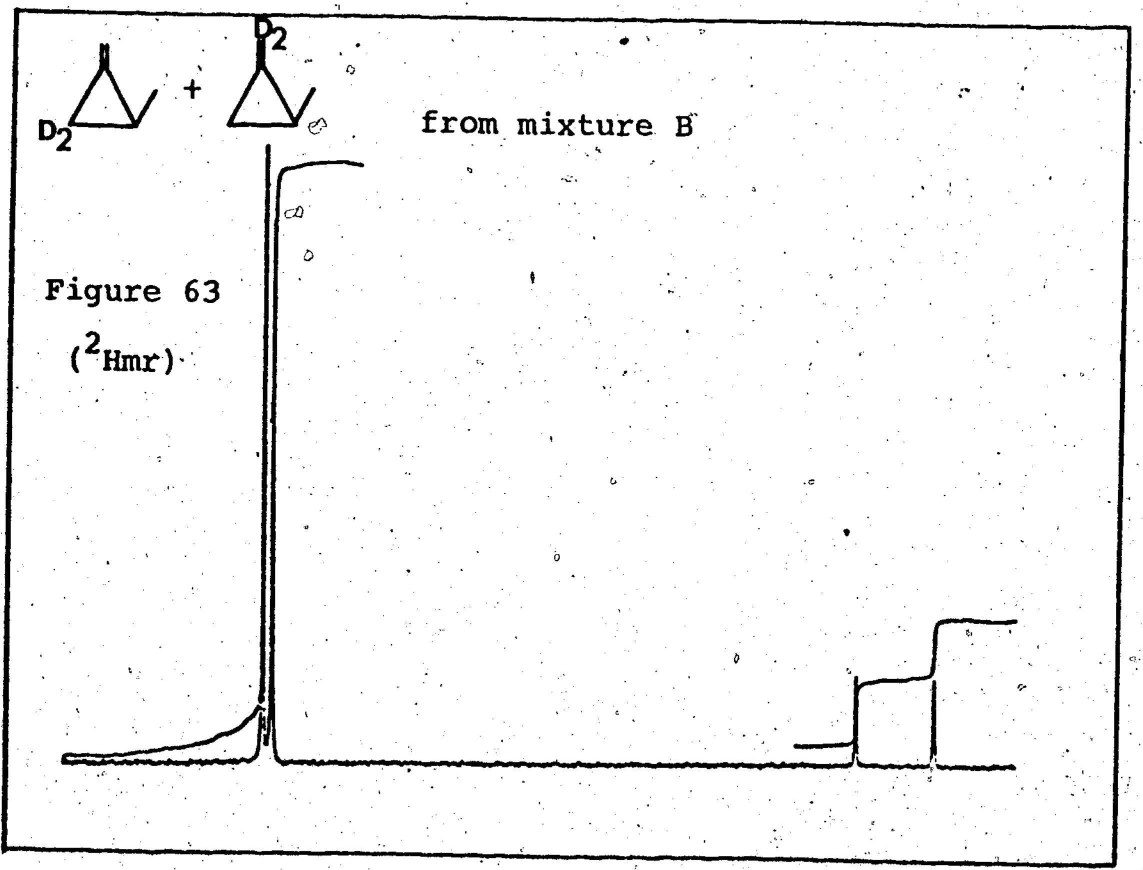
Figure 61



from mixture A

Figure 62

(^{2}Hmr)



from mixture B

Figure 63

(^{2}Hmr)

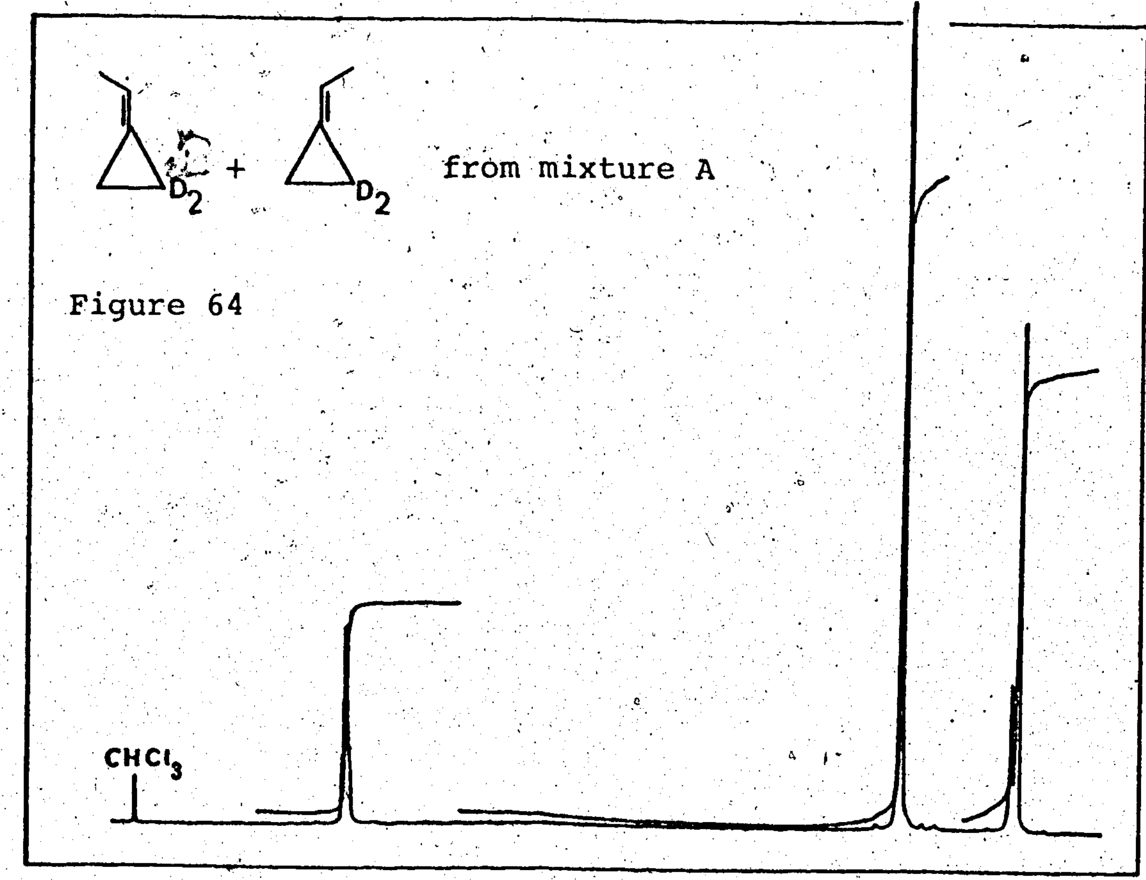


Figure 64

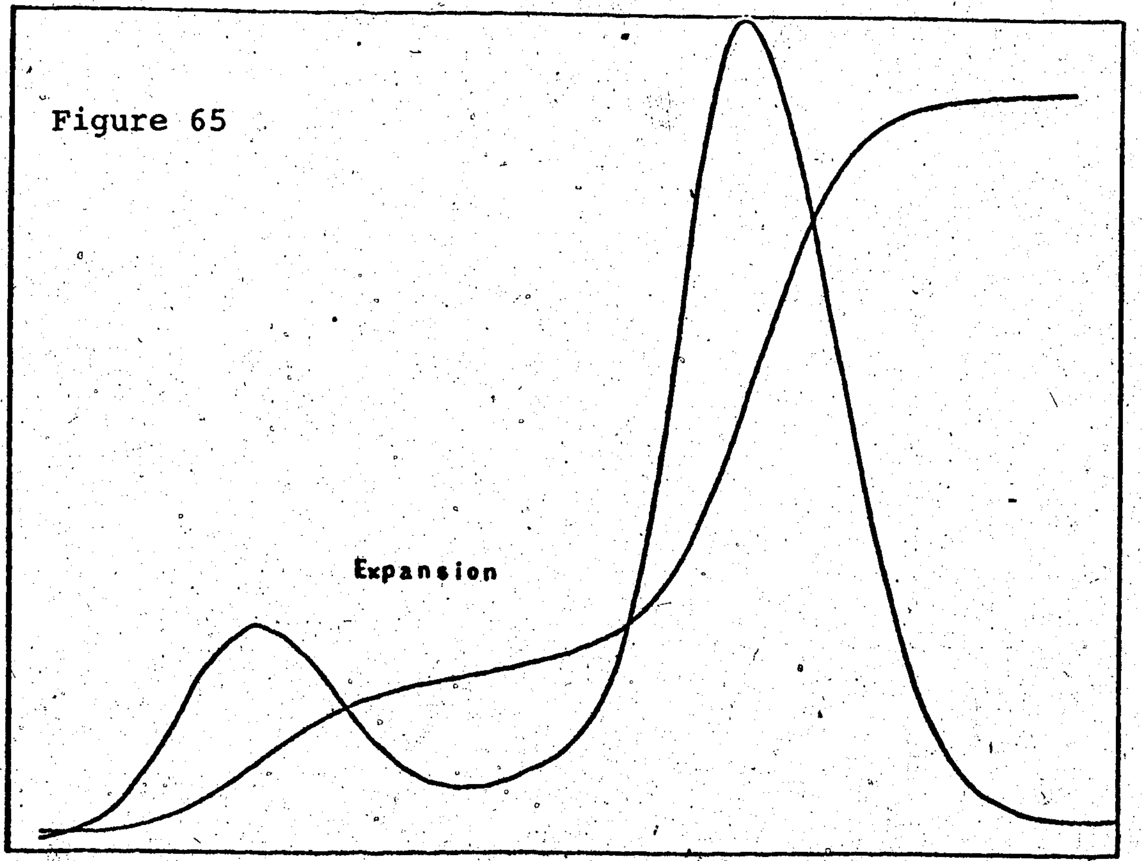


Figure 65

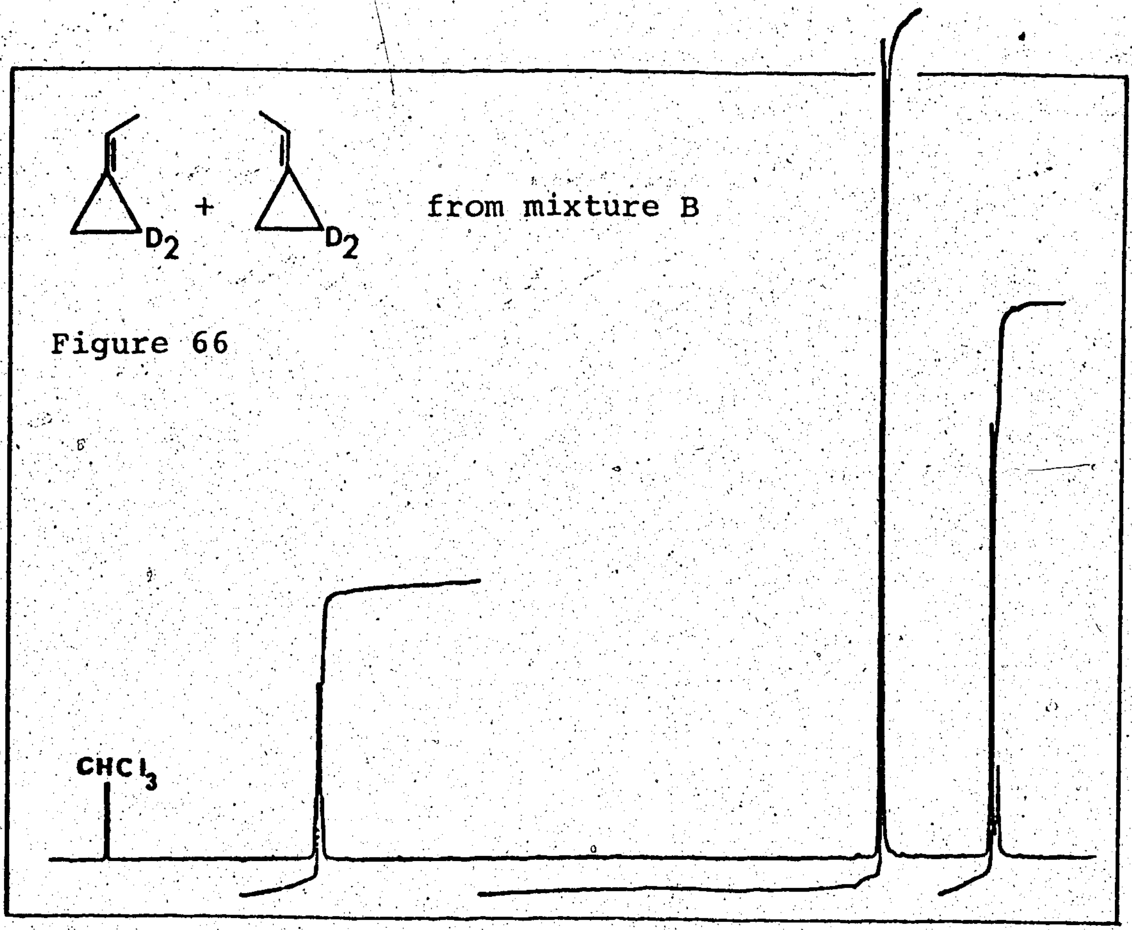


Figure 66

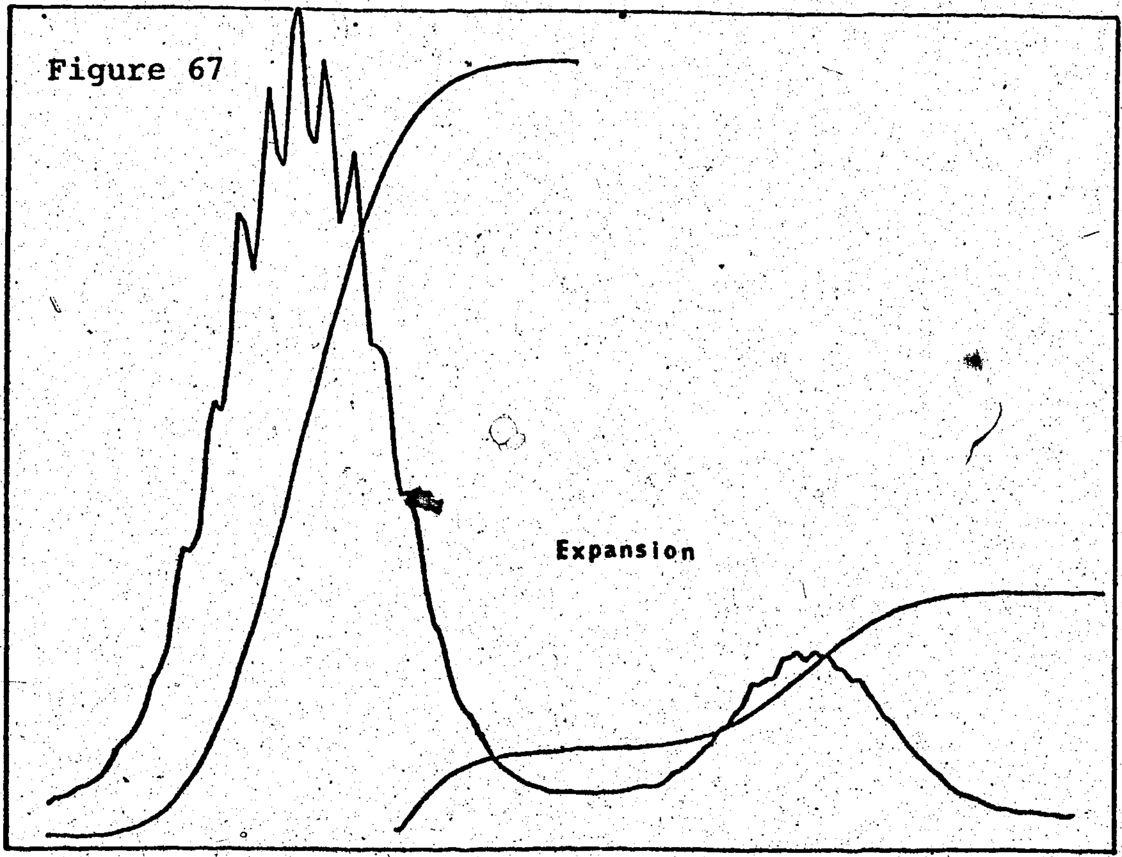


Figure 67

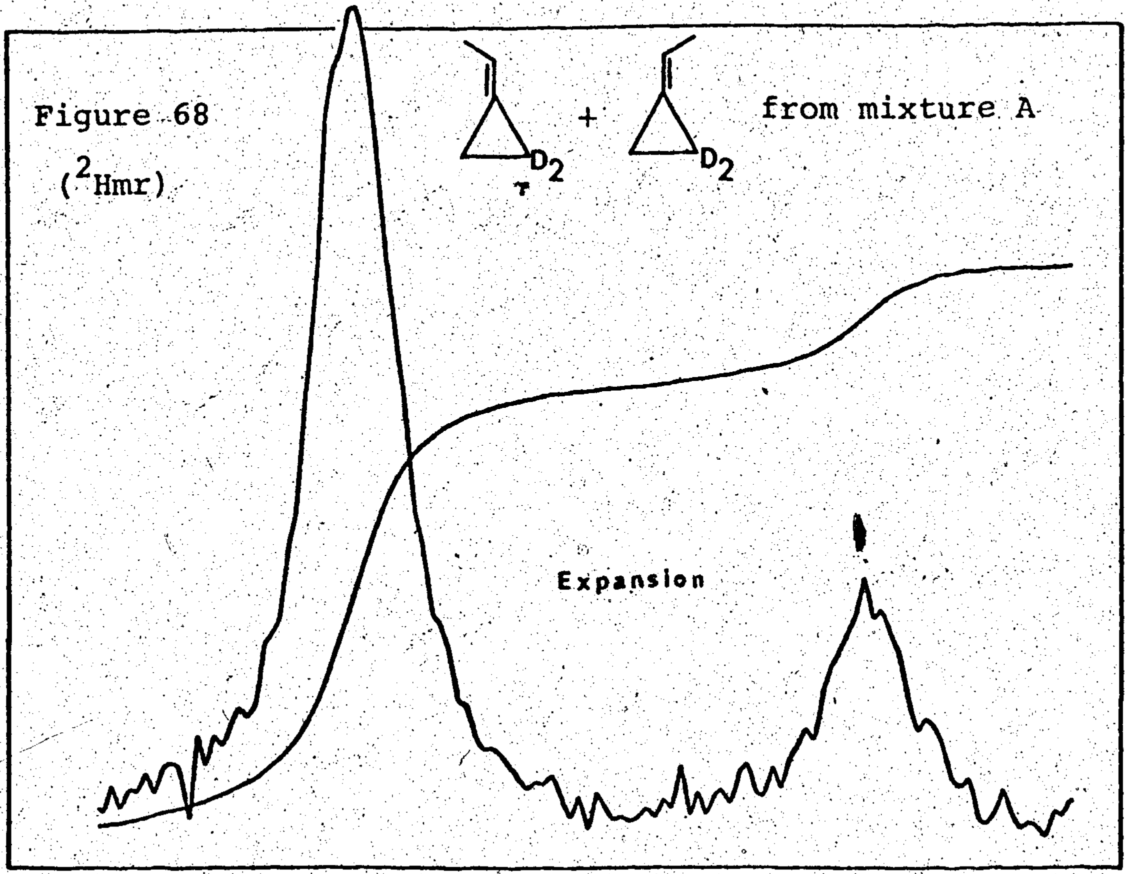


Figure 68 (^{2}Hmr)

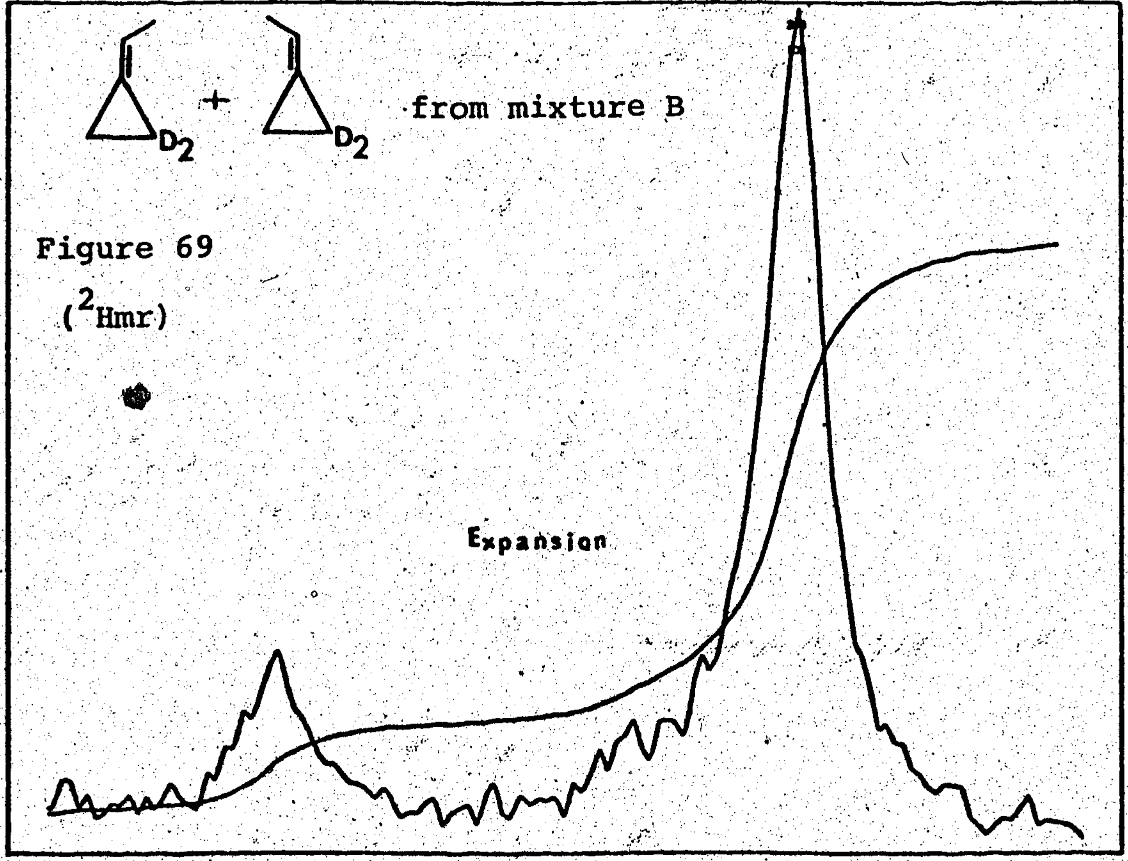
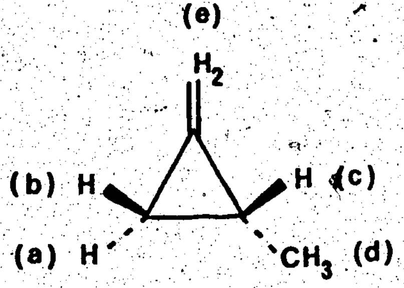
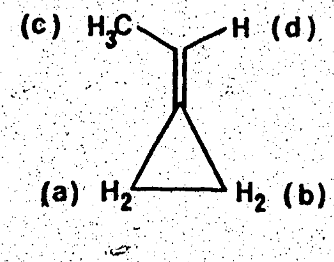


Figure 69 (^{2}Hmr)

The ratios of 78:79 and 81:82 were determined by integration of the spectra. In order to do this, we must first know the correct assignments of the protons in the ^{1}Hmr spectra of 70 and 71. The assignments for the ^{1}Hmr spectrum of 70 (Figure 59) have been reported previously by Crawford *et al.* (48) and are shown in Table 27. This Table also lists the assignments for the ^{1}Hmr spectrum of



70



71

Table 27

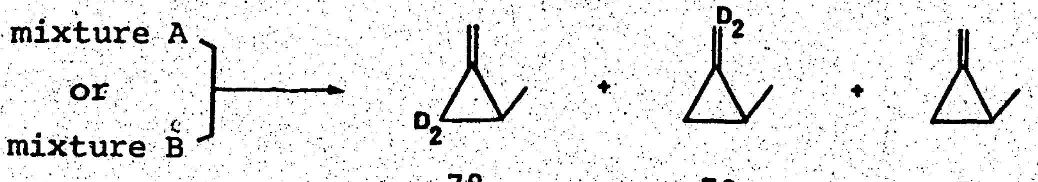
Chemical shifts in 400 MHz ^{1}Hmr for 2-methylmethylenecyclopropane (47) and ethylidenecyclopropane (δ from TMS, $CDCl_3$)

	Position of proton				
Compound	H_a	H_b	H_c	H_d	H_e
70	0.65m	1.3m	1.46m	1.11	5.36
71	0.97m	1.02m	1.80	5.77	-

Note: m = multiplet.

71 which are comparable to those previously obtained by Crawford *et al.* (48), except that the signals of the ring methylene protons H_a and H_b *syn* and *anti* to the methyl group at the exo-methylene position were, for the first time, separated by the 400 MHz ^{1}Hmr (in $CDCl_3$) as in Figures 64 and 66. The signals at $\delta 0.97$ and $\delta 1.02$ were assigned to the protons H_a and H_b respectively, since H_a is shielded by the adjacent C-C bond attached to the exo-methylene carbon, while H_b is not (49). The assignment of H_a and H_b is confirmed by the reported chemical shift data (48) indicating that the ring proton signals appear at $\delta 1.01$ for methylenecyclopropane (**31**) and $\delta 0.98$ for isopropylidenecyclopropane (**59**). The expanded ^{1}Hmr and ^{2}Hmr spectra of the signals, H_a and H_b for mixtures A and B are shown in Figures 65, 67, 68 and 69.

The ratios of **78**:**79** from mixtures A and B were determined by 100 MHz ^{1}Hmr spectroscopy (see Figures 60 and 61) in three different ways using three integration ratios; (i) R_A, the ratio of the proton H_a to the protons H_b, H_c and H_d, (ii) R_B, the ratio of the proton H_a to the proton H_e and (iii) R_C, the ratio of the protons H_b, H_c and H_d to the proton H_e (see Table 27).



78 **79** **70**

If $f_{\mathbf{70}}$, $f_{\mathbf{78}}$ and $f_{\mathbf{79}}$ represent the mole fractions of **70**, **78** and **79** respectively, we can write the following equations:

$$R_A = \frac{f_{\mathbf{79}} + f_{\mathbf{70}}}{4f_{\mathbf{78}} + 4f_{\mathbf{79}} + 5f_{\mathbf{70}}} \qquad \text{(eq. 37)}$$

$$R_B = \frac{f_{\mathbf{79}} + f_{\mathbf{70}}}{2f_{\mathbf{78}} + 2f_{\mathbf{70}}} \qquad \text{(eq. 38)}$$

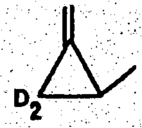
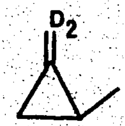
and

$$R_C = \frac{4f_{\mathbf{78}} + 4f_{\mathbf{79}} + 5f_{\mathbf{70}}}{2f_{\mathbf{78}} + 2f_{\mathbf{70}}} \qquad \text{(eq. 39)}$$

where $f_{\mathbf{70}} = 0.04$ and $f_{\mathbf{78}} + f_{\mathbf{79}} = 0.96$ for mixture A, and $f_{\mathbf{70}} = 0.03$ and $f_{\mathbf{78}} + f_{\mathbf{79}} = 0.97$ for mixture B from mass spectroscopy (see Table 18). These equations were solved for $f_{\mathbf{78}}$ and $f_{\mathbf{79}}$. For example, for the thermolysis of of mixture A at 175.2° for 30 min, we obtained values of $f_{\mathbf{78}}:f_{\mathbf{79}}$ of 74.2:25.8, 73.1:26.9 and 75.0:25.0 from ^{1}Hmr spectroscopic data ($R_A = 0.071$, $R_B = 0.191$ and $R_C = 2.685$). The average of these three values was taken as 74:26. Similarly, $f_{\mathbf{78}}:f_{\mathbf{79}}$ for mixture B was calculated. The complete results for different thermolysis times are given in Table 28. The ratios of **78**:**79** from mixtures A and B were also determined by integration of the 54.4 MHz

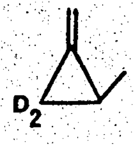
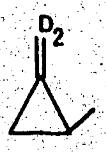
Table 28

Percentage ratios between the deuterated 2-methylmethylenecyclopropanes, 78 and 79, from the thermolysis of mixtures A and B at 175.2°C (0.7 atmosphere)

Reactant	Time (min)	Distribution (%)			
		 78		 79	
		^{1}Hmr^{a}	^{2}Hmr^{a}	^{1}Hmr	^{2}Hmr
Mixture A	15	75 ± 1^{b}	74 ± 1^{b}	25 ± 1^{b}	26 ± 1^{b}
	30	74 ± 1	73 ± 1	26 ± 1	27 ± 1
	60	74 ± 1	73 ± 1	26 ± 1	27 ± 1
78:79^{c} from mixture A	0	74 ± 1	73 ± 1	26 ± 1	27 ± 1
	60	73 ± 1	72 ± 1	27 ± 1	28 ± 1
	120	72 ± 1	71 ± 1	28 ± 1	29 ± 1
	300	70 ± 1	69 ± 1	30 ± 1	31 ± 1
Mixture B	15	18 ± 1	17 ± 1	82 ± 1	83 ± 1
	30	19 ± 1	18 ± 1	81 ± 1	82 ± 1
	60	19 ± 1	18 ± 1	81 ± 1	82 ± 1

continued...

Table 28 (continued)

		Distribution (%)			
		 78		 79	
Reactant	Time (min)	^{1}Hmr[a]	^{2}Hmr[a]	^{1}Hmr	^{2}Hmr
78:79	0	19 ± 1[b]	18 ± 1[b]	81 ± 1[b]	82 ± 1[b]
from	60	21 ± 1	20 ± 1	79 ± 1	80 ± 1
mixture B	120	22 ± 1	21 ± 1	78 ± 1	79 ± 1
	300	24 ± 1	22 ± 1	76 ± 1	78 ± 1

[a] Method of analysis.

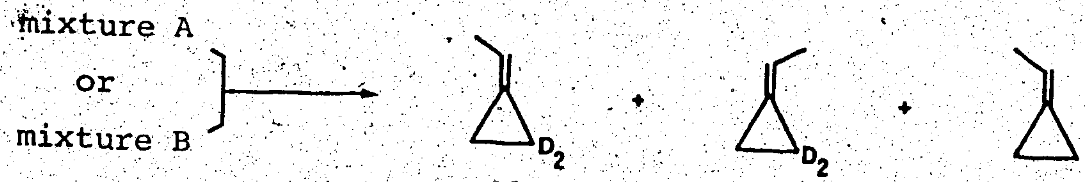
[b] Errors quoted are the 90% confidence limits from three samples after separation from ethylidenecyclopropane by preparative gc.

[c] Samples from the thermolysis of mixtures A and B used as a control for the interconversion of 78 to 79 (1.3 atmosphere).

^{2}Hmr spectra of the reaction products (see Figures 62 and 63). The ^{2}Hmr spectrum shows three distinct signals at δ0.65, δ1.3 and δ5.36 just as in Figures 62 and 63. The ratio of f_{78}/f_{79} was calculated directly from the integration ratio of the ring deuterium signals at δ0.65 and δ1.3 to the exo-methylene incorporation in 78 and 79. The results are given in Table 28. Each value of the % ratio in Table 28 is the average from three independent samples, and the error quoted is the 90% confidence limit.

Table 28 indicates that, within experimental error, the ratio of 78:79 appears to change very little with time during the hour-long thermolysis of mixtures A and B at 175.2°. A degenerate rearrangement $78 \rightleftarrows 79$ was previously found by Crawford *et al.* (11) to be unlikely to occur at 160.2°. In order to test the occurrence of this rearrangement under our conditions, control experiments were performed. A sample of the product mixture, 78 and 79, from the thermolysis of mixtures A and B at 175.2° for 30 min was degassed and heated at 175.2°. The sample was then analyzed by ^{1}Hmr and ^{2}Hmr spectroscopy. The results are given in Table 28 and indicate a very slow interconversion of 78 to 79.

The ratios between the deuterated ethylidenecyclopropanes, 81 and 82, from mixtures A and B were determined by 400 MHz ^{1}Hmr spectroscopy (see Figures 65 and 67), and



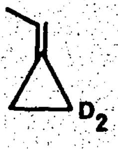
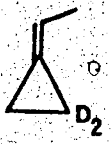
81 **82** **71**

were calculated in a manner analogous to that described above. The complete results for different thermolysis times are given in Table 29. The ratio of **81**:**82** was also determined directly from integration of the expanded 54.4 MHz ^{2}Hmr spectrum of the reaction products, **81** and **82**, (see Figures 68 and 69) without need of considering the deuterium content of **81** and **82**, and the results are given in Table 29. Each percentage in Table 29 is the average from three independent samples, and the error quoted is the 90% confidence limit.

Table 29 also indicates a degenerate rearrangement **81**⇄**82** is not likely to proceed during the thermolysis of mixtures A and B at 175.2° for an hour. Control experiments to study the interconversion of **81** to **82** were carried out in the same manner as previously described for those of **78** and **79**. However, the results as shown in Table 29 indicate that the interconversion of **81** to **82** is not only slower than that of **78** to **79**, but also the ratio of **81**:**82** appears to remain essentially constant within experimental error.

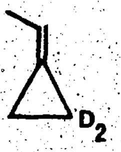
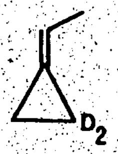
Table 29

Percentage ratios between the deuterated ethylidenecyclopropanes, 81 and 82, from the thermolysis of mixtures A and B at 175.2°C (0.7 atmosphere)

		Distribution (%)			
		 81		 82	
Reactant	Time, (min)	^{1}Hmr[a]	^{2}Hmr[a]	^{1}Hmr	^{2}Hmr
Mixture A	15	84 ± 1[b]	82 ± 1[b]	16 ± 1[b]	18 ± 1[b]
	30	83 ± 1	82 ± 1	17 ± 1	18 ± 1
	60	83 ± 1	81 ± 1	17 ± 1	19 ± 1
81:82[c] from mixture A	0	83 ± 1	81 ± 1	17 ± 1	19 ± 1
	60	82 ± 1	80 ± 1	18 ± 1	20 ± 1
	120	82 ± 1	80 ± 1	18 ± 1	20 ± 1
	300	81 ± 1	79 ± 1	19 ± 1	21 ± 1
Mixture B	15	13 ± 1	15 ± 1	87 ± 1	85 ± 1
	30	14 ± 1	15 ± 1	86 ± 1	85 ± 1
	60	14 ± 1	16 ± 1	86 ± 1	84 ± 1

continued...

Table 29 (continued)

		Distribution (%)			
		 81		 82	
Reactant	Time (min)	^{1}Hmr[a]	^{2}Hmr[a]	^{1}Hmr	^{2}Hmr
81:82[c] from mixture B	0	14 ± 1[b]	16 ± 1[b]	86 ± 1[b]	84 ± 1[b]
	60	14 ± 1	17 ± 1	86 ± 1	83 ± 1
	120	15 ± 1	17 ± 1	85 ± 1	83 ± 1
	300	15 ± 1	18 ± 1	85 ± 1	82 ± 1

---

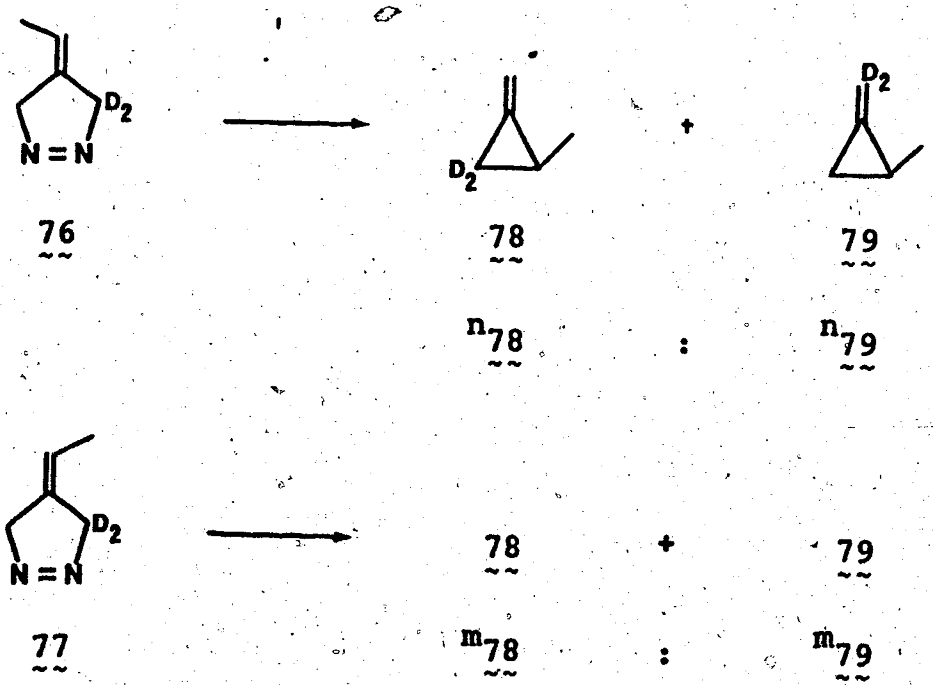
[a] Method of analysis.

[b] Errors quoted are the 90% confidence limits from three samples after separation from 2-methylmethylenecyclopropane by preparative gc.

[c] Samples from the thermolysis of mixtures A and B used as a control for the interconversion of 81 to 82 (1.1 atmosphere).

The possibility of interconversion between 2-methylmethylenecyclopropane (**70**) and ethylidenecyclopropane (**71**) was shown not to exist by Schrijver (34) from the observation that the ratio of **70**:**71** analyzed by gc remains unchanged in the thermolysis of 4-ethylidene-1-pyrazoline (**69**) at 175.1° for an hour. The thermolysis of **69** at 190.1°, however, appears to display a very slow interconversion of **70** to **71**. These results were confirmed by us by repeating the experiments.

The ratios of **78**:**79** from **76** and **77** were thus calculated by using the ^{1}Hmr data in Tables 18 and 28. If n_{78} and n_{79} represent the mole fractions of **78** and **79** from the thermolysis of **76**, and m_{78} and m_{79} represent



76 → **78** + **79**

n_{78} : n_{79}

77 → **78** + **79**

m_{78} : m_{79}

those of **78** and **79** from **77**, the following equation can be written:

$$0.75 = 0.92\ n_{78} + 0.08\ m_{78} \qquad \text{(eq. 40)}$$

or $$0.25 = 0.92\ n_{79} + 0.08\ m_{79} \qquad \text{(eq. 41)}$$

for mixture A, since it consists of a 92:8 mixture of 76:77 as in Table 18 and produced a 75:25 mixture of 78:79 as in Table 28. Also

$$0.18 = 0.07\ n_{78} + 0.93\ m_{78} \qquad \text{(eq. 42)}$$

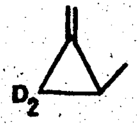
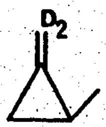
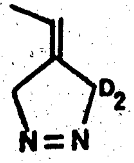
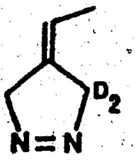
or $$0.82 = 0.07\ n_{79} + 0.93\ m_{79} \qquad \text{(eq. 43)}$$

for mixture B, since it consists of a 7:93 mixture of 76:77 as in Table 18 and was thermolyzed to give a 18:82 mixture of 78:79 as in Table 28. The simultaneous solution of equations 40 and 42 or that of equations 41 and 43 is $n_{78} = 0.80$, $n_{79} = 0.20$, $m_{78} = 0.13$ and $m_{79} = 0.87$. An analogous calculation was carried out using the ^{2}Hmr data in Tables 18 and 28. The results are detailed in Table 30. It should be noted that the results in Table 30 are believed to be more reliable than those reported previously by Crawford *et al.* (see Table 10) (11) since their results were based on the assumption that the mixture A and B consisted of only 76 and 77 respectively.

The ratios of 81:82 from the thermolysis of 76 and 77 were determined by using both the ^{1}Hmr and ^{2}Hmr data in Tables 18 and 29 in a manner similar to that used in the previous calculations of the ratios of 78:79 from

Table 30

Deuterium distribution in the deuterated 2-methylmethylenecyclopropanes produced from the thermolysis of *E*- and *Z*-ethylidene-1-pyrazoline (175.2°C, 0.7 atmosphere)

		Distribution (%)	
Reactant	Method of analysis	 78	 79
 76	^{1}Hmr ^{2}Hmr	80 ± 3* 81 ± 3	20 ± 3 19 ± 3
 77	^{1}Hmr ^{2}Hmr	13 ± 3 11 ± 3	87 ± 3 89 ± 3

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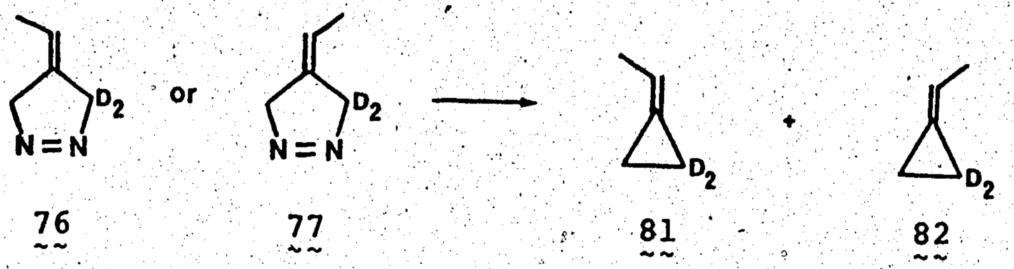
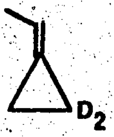
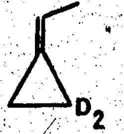
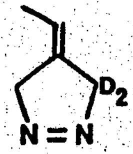
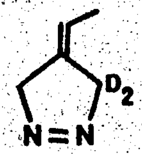
*Errors quotes are the 90% confidence limits obtained from the calculations by using the data in Table 28.



76:77. The results are presented in Table 31.

Table 31

Deuterium distribution in the deuterated ethylidenecyclopropanes produced from the thermolysis of *E*- and *Z*-ethylidene-1-pyrazoline (175.2°C, 0.7 atmosphere)

		Distribution (%)	
Reactant	Method of analysis	 81	 82
 76	^{1}Hmr	91 ± 3*	9 ± 3
	^{2}Hmr	90 ± 3	10 ± 3
 77	^{1}Hmr	7 ± 3	93 ± 3
	^{2}Hmr	8 ± 3	92 ± 3

---

*Errors quoted are the 90% confidence limits obtained from the calculations by using the data in Table 29.

DISCUSSION

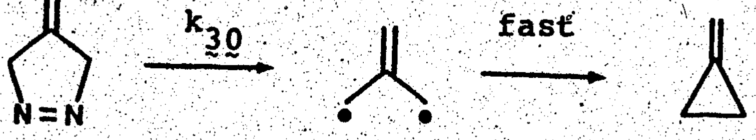
A. Thermolysis of 4-Methylene-1-pyrazoline (30) and Deuterated Derivatives

(i) Kinetic Studies

The kinetic data, at 170.0°, for the thermolysis of 30 and its deuterated derivatives are listed in Table 23. Using this data, an assessment of whether one or two carbon-nitrogen bonds are cleaving in the rate determining step (7f) will be presented. The values of $\delta\Delta G^{\ddagger}$ per deuterium can be calculated from secondary deuterium kinetic isotope effects by using the equation

$$\delta\Delta G^{\ddagger} = \frac{RT}{n} \ln (k_H/k_D) \tag{eq. 44}$$

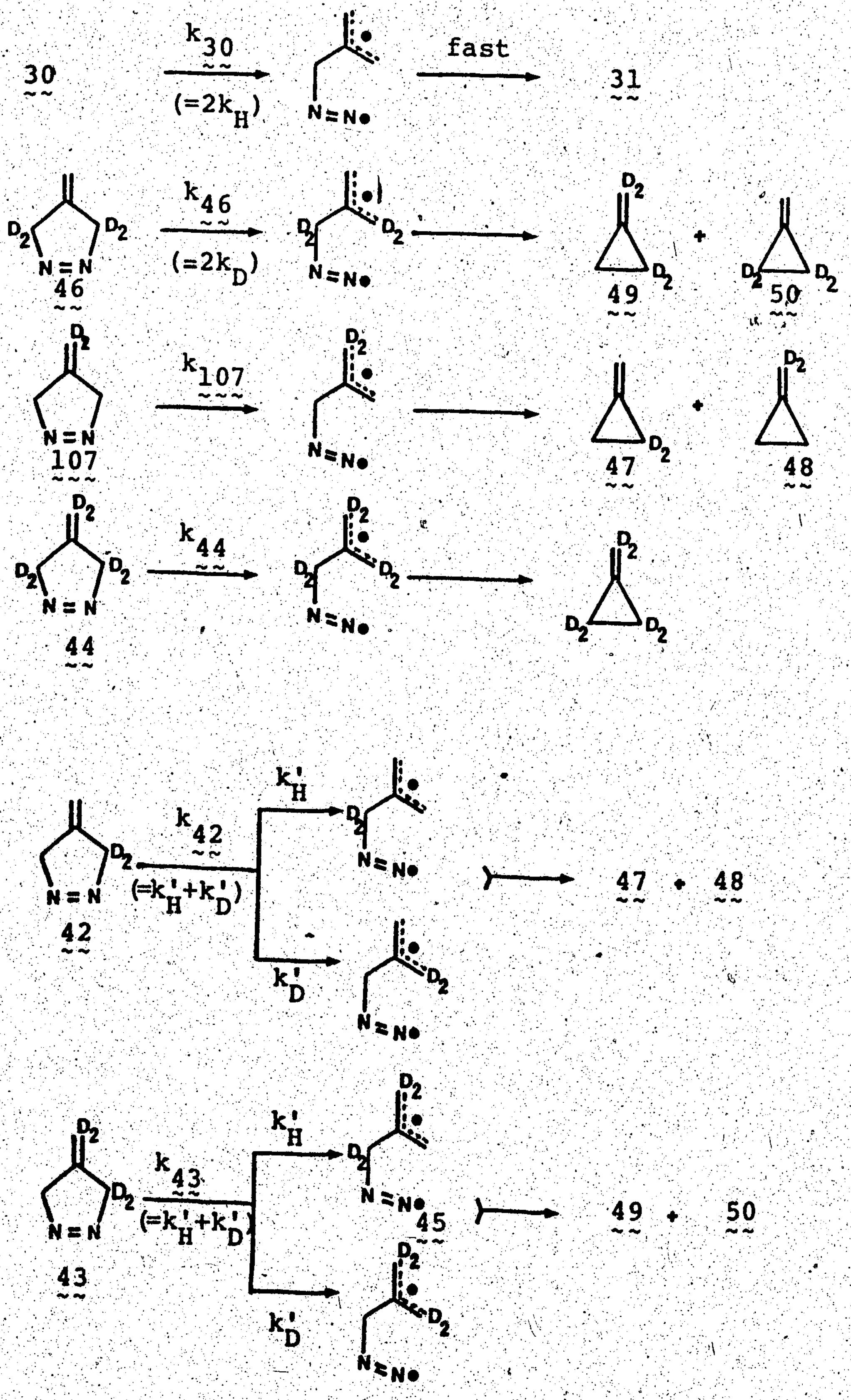
where n is the number of deuteriums. For a two-bond cleavage pathway (see Scheme 1), the observed intermolecular isotope effect in 46 (Table 23) was used to evaluate $\delta\Delta G^{\ddagger}$ in the presence of four α-deuteriums. The value of $\delta\Delta G^{\ddagger}$ was found to be 73 ± 3 cal mol^{-1} per deuterium. On the other hand, for a one-bond cleavage pathway (see Scheme 2),



30

31

Scheme 1


30
k30
(=2kH)
N=N•
fast
31
D2
N=N
46
k46
(=2kD)
49
50
107
k107
47
48
44
k44
42
k42
(=k'H+k'D)
k'H
k'D
47 + 48
43
k43
45
49 + 50

Scheme 2

assuming that deuterium substitution in the tetrahedral methylene group of the allylic diazenyl radical intermediate does not give rise to any change in rate, then the value of $\delta\Delta G^{\ddagger}$ in the presence of the α-deuteriums in 46 is calculated to be 142 ± 6 cal mol^{-1} per deuterium. For 107, we observed that the two γ-deuteriums contributed an increase of 26 cal mol^{-1} to the free energy of activation. If the reaction proceeds according to Scheme 1 then the observed isotope effect in 44 represents the the effect of four α-deuteriums plus two γ-deuteriums and we were able to calculate the effect of the four α-deuteriums in 44 as being 71 ± 3 cal mol^{-1} per deuterium. For Scheme 2, the effect of the two α-deuteriums in 44 was obtained as 141 ± 6 cal mol^{-1} per deuterium. If 42 and 43 decompose according to Scheme 1, the values of $\delta\Delta G^{\ddagger}$ per deuterium ($\delta\Delta G^{\ddagger}/n$) are calculated to be 62 ± 5 cal mol^{-1} and 64 ± 4 cal mol^{-1} respectively for the observed intermolecular isotope effects (Table 23). However, for Scheme 2, we can calculate the values of $\delta\Delta G^{\ddagger}/n$ for 42 and 43 from intramolecular isotope effects which are obtained by the equations

$$k_H/k_D \text{ (for 42)} = \frac{k_{30}}{2k_{42}-k_{30}} \quad \left(\text{or } \frac{2k_{42}-k_{46}}{k_{46}}\right) \qquad \text{(eq. 45)}$$

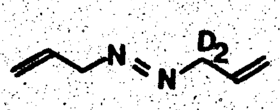
and

$$k_H/k_D \text{ (for 43)} = \frac{k_{107}}{2k_{43}-k_{107}} \quad \left(\text{or } \frac{2k_{43}-k_{44}}{k_{44}}\right) \qquad \text{(eq. 46)}$$

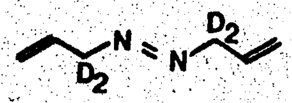
if we assume that $k'_H = k_H$ and that $k'_D = k_D$. We obtain the values of the intramolecular isotope effects and $\delta\Delta G^{\ddagger}/n$ as 1.38 ± 0.04 and 142 ± 12 cal mol^{-1} for 42, and 1.38 ± 0.03 and 142 ± 9 cal mol^{-1} for 43. The values of $\delta\Delta G^{\ddagger}/n$ obtained above for Schemes 1 and 2 are presented in Table 32.

It should be noted that for the one-bond cleavage process (see Scheme 2), the re-closure of the diazenyl species into the precursor is highly improbable since, as mentioned previously in the Historical section, Cameron (10a) observed that 43 did not rearrange to 46.

Table 32 shows that the values of $\delta\Delta G^{\ddagger}/n$, for both one-bond and two-bond cleavage pathways, are not within the frequently observed value of 90-120 cal mol^{-1} (26,27). Al-Sader and coworkers (7f) observed a $\delta\Delta G^{\ddagger}/n$ value of 135 cal mol^{-1} for the one-bond cleavage process in the gas phase thermolysis of 3,3'-azo-1-propene-3,3-d_2 (131) and 3,3'-azo-1-propene-3,3,3',3'-d_4 (132). Takagi (5) has provided kinetic evidence that strongly implicates a one bond cleavage mechanism for 3,3'-azo-propene.



131

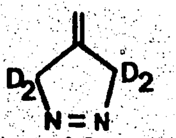
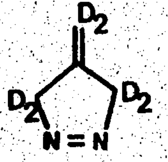
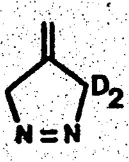
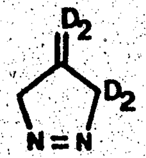
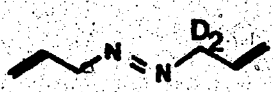
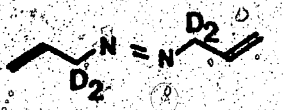


132

Interestingly, the values of $\delta\Delta G^{\ddagger}/n$ for the one-bond cleavage process (see Table 32) are more consistent with one another than the values for the two-bond cleavage.

Table 32

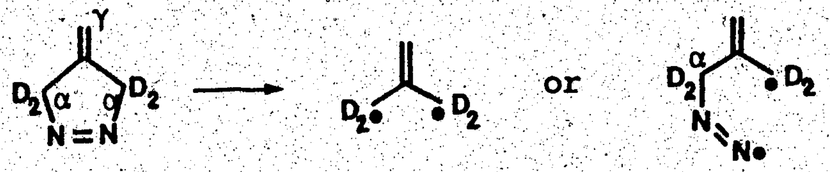
Observed values of $\delta\Delta G^{\ddagger}$ per deuterium for one-bond and two bond cleavage pathways in the thermolysis of 46, 44, 42, 43, 131 and 132

Compound	$\delta\Delta G^{\ddagger}/n$ (cal mol^{-1})	
	Two-bond cleavage	One-bond cleavage
 46	71 ± 3	142 ± 6
 44	71 ± 3	141 ± 6
 42	62 ± 5	142 ± 12
 43	64 ± 4	142 ± 9
 131	66* ± 10	135* ± 15
 132	66* ± 10	135* ± 15

*Reference 7f.

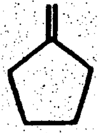
However, no real choice between the two pathways can yet be made.

In an attempt to predict the magnitude of the secondary deuterium kinetic isotope effect by the two pathways in the thermolysis of deuterated 4-methylene-1-pyrazolines, let us consider a rate-determining transition state wherein one or two carbon-nitrogen bonds are cleaving to give a trimethylenemethane (TMM) diradical or a diazenyl radical which undergoes a hybridization change to sp^2 at the α-methylene position(s). In order to calculate the isotope effect in the thermolysis of 4-methylene-1-pyrazoline-3,3,5,5-d_4 (46), we assume that changes in the infrared vibrational frequencies occur only at the α-methylene position(s) during the thermolysis. Thus, we have chosen the exomethylene group of the methylenecyclopentane (133) as a model for the re-hydridized methylene group of the transition state. It should be noted that we assume, for the one-bond cleavage pathway, that deuterium substitution in the α-position of the diazenyl radical does not change the vibrational frequencies in that position. The infrared vibrational frequencies of

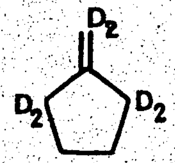


46

the α-methylene group in 4-methylene-1-pyrazoline (30) and in 46 were assigned previously as in Table 15 and the frequencies of the exo-methylene group in 133 and methylene-d_2-cyclopentane-2,2,5,5-d_4 (134) have been



133



134

reported in the literature (46). The pertinent frequencies are given in Table 33.

It has been suggested (59) that secondary kinetic isotope effects are the result of the creation, or deletion, of new, isotopically sensitive vibrational frequencies during the course of the reaction. If we make a summation over the vibration levels of our four models, the sum $\delta\Delta\omega$ is given (27) by the equation

$$\delta\Delta\omega = [\Sigma\omega(30) - \Sigma\omega(46)] - [\Sigma\omega(133) - \Sigma\omega(134)] \quad \text{(eq. 47)}$$

It should be noted that the values of $\Delta\omega_1$ and $\Delta\omega_2$ in Table 33 represent the value for four α-deuteriums in 46 and the value for two γ-deuteriums in 134 respectively. Therefore, for the two-bond cleavage pathway, $\delta\Delta\omega = \Delta\omega_1 - 2\ (\Delta\omega_2) = 313\ \text{cm}^{-1}$. Since $E_0 = hc\omega/2$ then this is an energy difference ($\delta\Delta G^{\ddagger}$) of 448 cal mol^{-1} for four α-deuteriums. For the one-bond cleavage process, $\delta\Delta\omega = \Delta\omega_1/2 - \Delta\omega_2 = 156.5\ \text{cm}^{-1}$ which gives $\delta\Delta g^{\ddagger}$ of 224 cal mol^{-1}

Table 33

Infrared frequencies used to calculate the secondary deuterium kinetic isotope effect in the thermolysis of **46**

	Frequencies[a] (cm^{-1})			Frequencies[b] (cm^{-1})	
Mode	**30**	**46**	Mode	**133**	**134**
α-CH$_2$ asym. str.	2947 2940	2217 2154	=CH$_2$ asym. str.	3084	2314
α-CH$_2$ sym. str.	2860 2849	2142 2068	=CH$_2$ sym. str.	3005	2209
α-CH$_2$ def.	1432 1418	1037 1025	=CH$_2$ def.	1405	1103
α-CH$_2$ wag[b]	1288 1261	1020 1005	=CH$_2$ twist	977	745
α-CH$_2$ twist[b]	1241 1149	973 923	=CH$_2$ rock	927	706
α-CH$_2$ rock[b]	892 789	656 612	=CH$_2$ wag	880	700
C-N str.	912 895	872 854			
$\Sigma\omega$	22873	17558	$\Sigma\omega$	10278	7777
$\Delta\omega_1$	5315		$\Delta\omega_2$	2501	

[a] Data from Table 15.

[b] Data from ir spectra of **133** and **134** (ref. 46).

for two α-deuteriums. By using these data the values of $\delta\Delta G^{\ddagger}$ per deuterium and the kinetic isotope effects for the two pathways are calculated and presented in Table 34.

The calculated $\delta\Delta G^{\ddagger}/n$ value of 112 cal mol^{-1} in Table 34 is within the frequently observed value of 90-120 cal mol^{-1} (26,27). Therefore the data in Table 34 are best interpreted in terms of the stepwise one carbon-nitrogen bond cleavage mechanism since the values of both k_H/k_D and $\delta\Delta G^{\ddagger}/n$ calculated for this mechanism are shown to be more consistent with the observed values than are those calculated for two-bond cleavage. Thus, we would favor the one-bond cleavage pathway if forced to make a choice between the two mechanisms.

(ii) Product Studies

Inasmuch as the kinetic studies of the preceding section on the thermolysis of 4-methylene-1-pyrazoline (30) and its deuterated derivatives did not provide definitive information in assessing whether one or two carbon-nitrogen bonds are cleaving in the rate determining process, we turned to an analysis of the product distribution data in Table 26 in terms of both TMM and diazenyl radical intermediates. Our investigation of all the possible thermolysis mechanisms is described in the following paragraphs.

Table 34

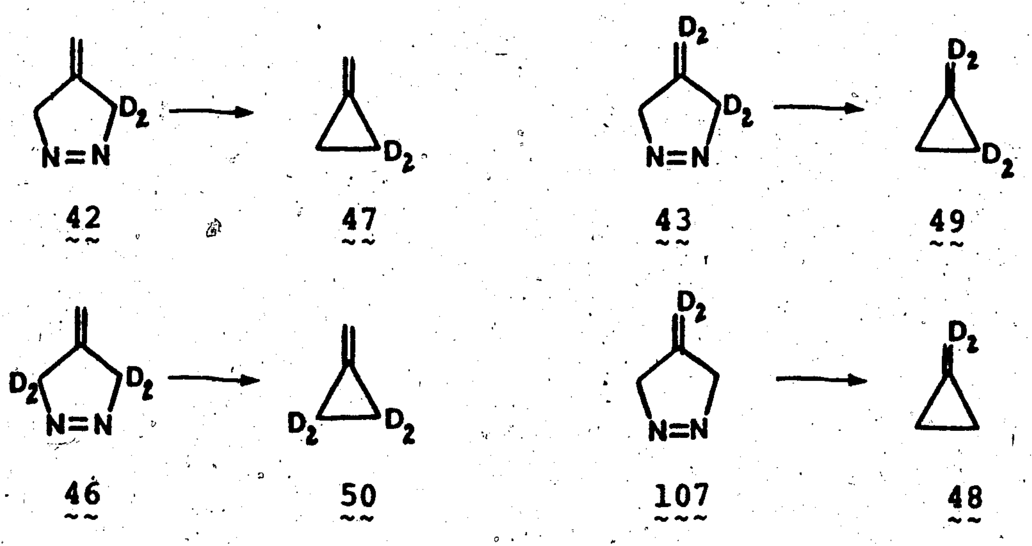
Calculated and observed values of $\delta\Delta G^{\ddagger}$ per deuterium and k_H/k_D at 170.0° for one-bond and two-bond cleavage pathways in the thermolysis of **46**

	Two-bond cleavage		One-bond cleavage	
	$\delta\Delta G^{\ddagger}/n$ (cal mol^{-1})	k_H/k_D	$\delta\Delta G^{\ddagger}/n$ (cal mol^{-1})	k_H/k_D
Calculated	112	1.66	112	1.29
Observed	71[a]	1.38[b]	142[a]	1.38[b]

[a] Data from Table 32.

[b] Date from Table 23.

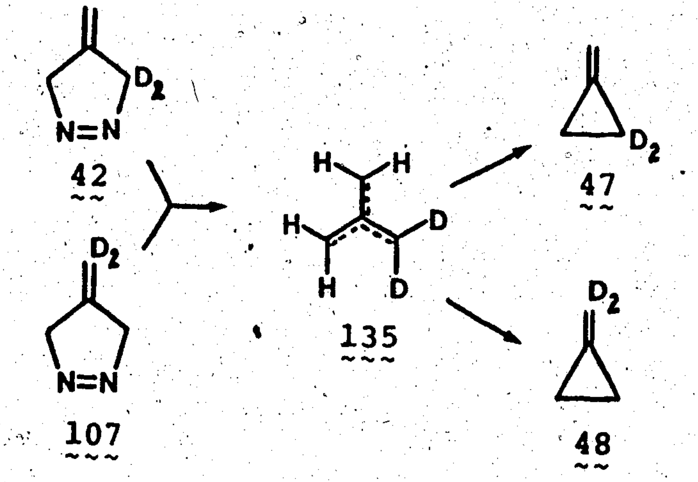
a. Fully concerted pathway: Each of the deuterated 4-methylene-1-pyrazolines (42, 43, 46 and 107) was thermolyzed to give two isomeric deuterated methylenecyclopropanes as recorded in Table 26. However, *via* a fully concerted process, only one of the two isomers would be expected to form as shown in Scheme 3 below. Thus, this Scheme can be readily dismissed.



Scheme 3

b. Concerted two C-N bond cleavage pathway: A concerted process wherein both C-N bonds are cleaving in the rate determining step may produce one of the following three TMM diradicals as an intermediate.

A planar TMM intermediate was the first to be considered. If a planar TMM 135 is an intermediate, as in Scheme 4, then the ratio of 47,48 should be the same



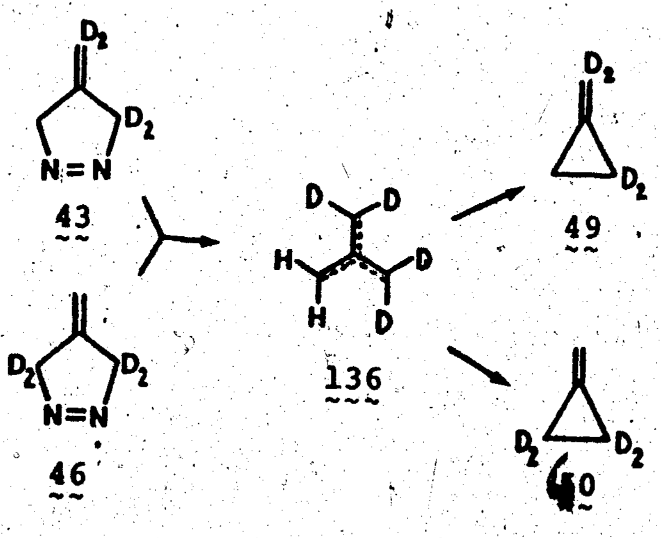
Observed

(From 42)	(From 107)
59%	66%
:	:
41%	34%

(By ^{1}Hmr)

Scheme 4

regardless of whether the precursor is 42 or 107, and clearly this is not the case. Similarly, if a planar TMM 136 is an intermediate in Scheme 5 then the ratio of



Observed

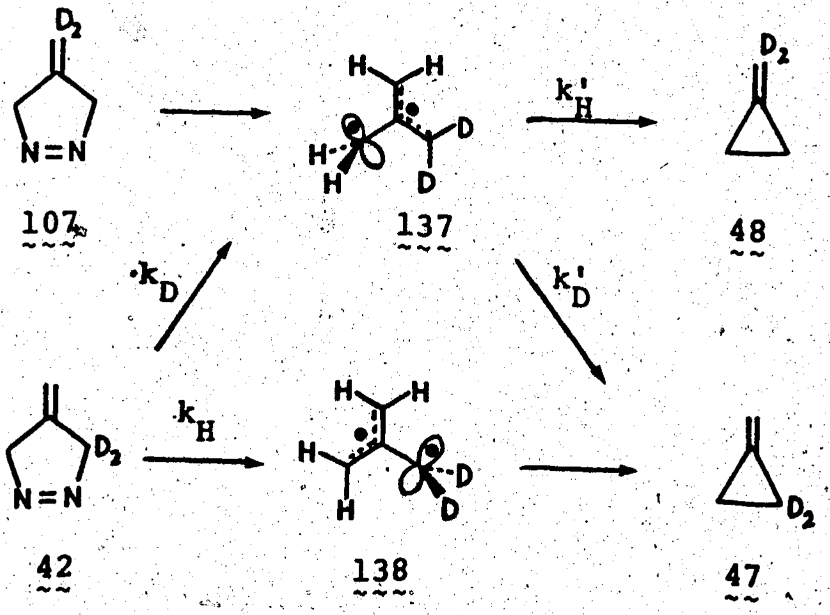
(From 43)	(From 46)
72%	77%
:	:
28%	23%

(By ^{1}Hmr)

Scheme 5

49:50 should be the same from 43 and 46 and again such is not the case.

An orthogonal TMM intermediate with the original exo-methylene planar (i.e., Chesick intermediate) was then considered (24). Scheme 6 shows that on the basis



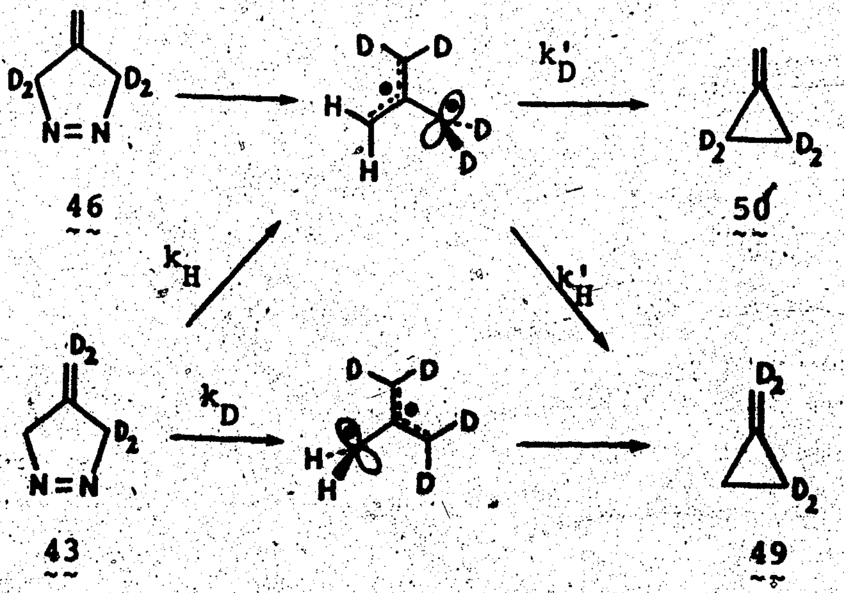
Scheme 6

of the principle of least motion (31), the thermolysis of 107 produces one orthogonal TMM 137 whereas the thermolysis of 42 gives rise to an orthogonal TMM (138) as well as 137. If k_H and k_D represent the partial rate factors (i.e., $k_H + k_D = 1$) in the formation of 138 and 137 respectively from 42 in the rate determining process, and k'_H and k'_D represent the partial rate factors (i.e., $k'_H + k'_D = 1$) giving 48 and 47 from 137 in the product forming process then we can calculate these values using the product distribution data in Table 26. It should be noted that the subscripts, D and H, of the partial rate factors denote CD_2 rotation and CH_2 rotation respectively.

Since the ratio of 48:47 from 107 is 34:66, $k'_H = 0.34$ and $k'_D = 0.66$. A value for k_H/k_D of -0.17 for 42 was then calculated by equation 48 using the ^{1}Hmr

$$\frac{[48]}{[47]} = \frac{0.41}{0.59} = \frac{k_D \cdot k'_H}{k_H + k_D \cdot k'_D} = \frac{k'_H}{(k_H/k_D) + k'_D} \qquad \text{(eq. 48)}$$

data in Table 26. The negative k_H/k_D value is unrealistic. The k'_H/k'_D of 0.51 is also improbable if it is compared with the theoretical value of 1.41 derived from classical inertial arguments (25b). Similarly, by Scheme 7, we obtained $k'_H/k'_D = 0.77/0.23 = 3.35$ and $k_H/k_D = -5.55$, the



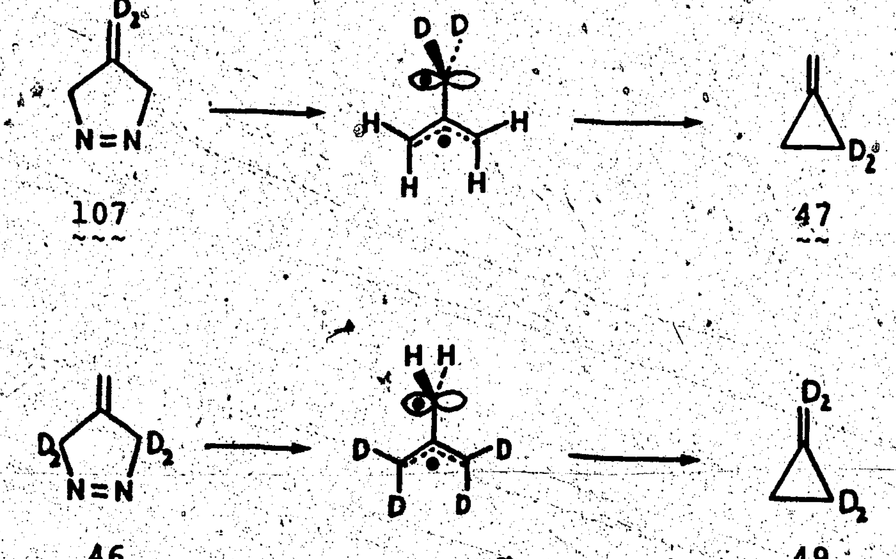
Scheme 7

former is too large and the latter unrealistic. Such results clearly indicate that this type of orthogonal TMM cannot be reconciled with the experimental data.

****

(Note) Equilibrating orthogonal TMM intermediates can also be ruled out since the product ratios from 42 and 107 will be expected to be the same and so would those from 43 and 46.

An orthogonal TMM intermediate with the original exo-methylene orthogonal was considered as a final possibility. Scheme 8 shows that *via* such an orthogonal TMM



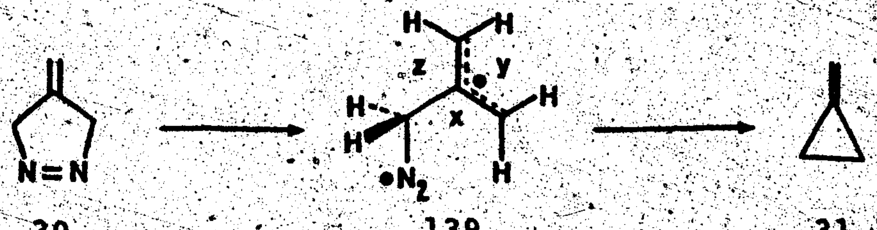
107 47

46 49

Scheme 8

intermediate, 107 produces only 47, and 46 gives only 49. Thus, this intermediate can be ruled out.

c. Stepwise one C-N-bond cleavage pathway: Allylic resonance may be effective in bringing about one-bond cleavage in the rate determining process and as a result, a tetrahedral α-methylene group of 30 will have to rotate

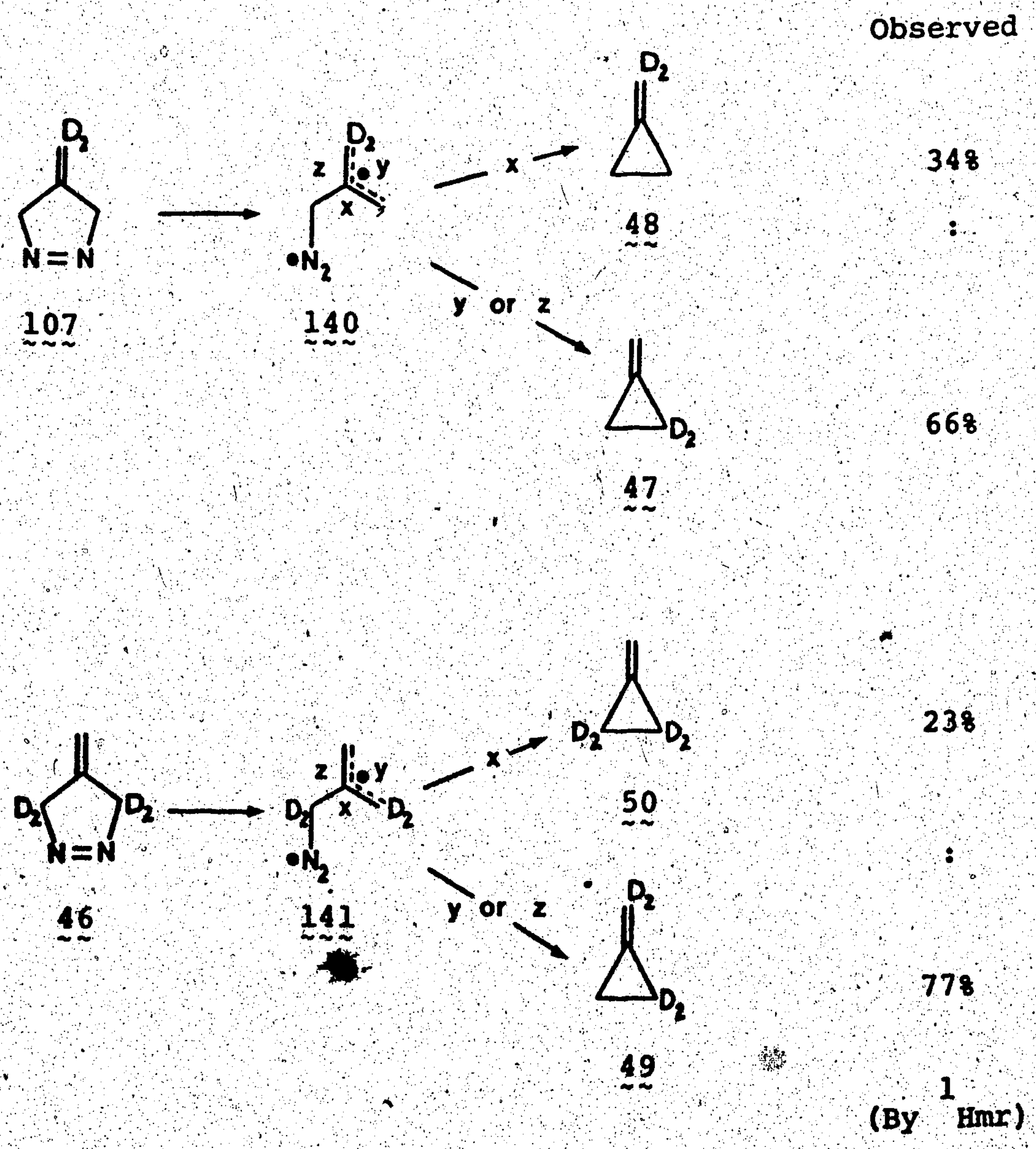


30 139 31

into the plane to give an allylic diazenyl species **139** (35,60). In order to investigate the product forming process from the diazenyl species, we will define the displacement of nitrogen by the allylic terminus which was originally the α-methylene of **30** as x-closure, the displacement of nitrogen by the allylic terminus which was the exo-methylene of **30** as z-closure, and the electrocyclic ring closure of the two allylic termini as y-closure. Then, the following mechanisms can be discussed:

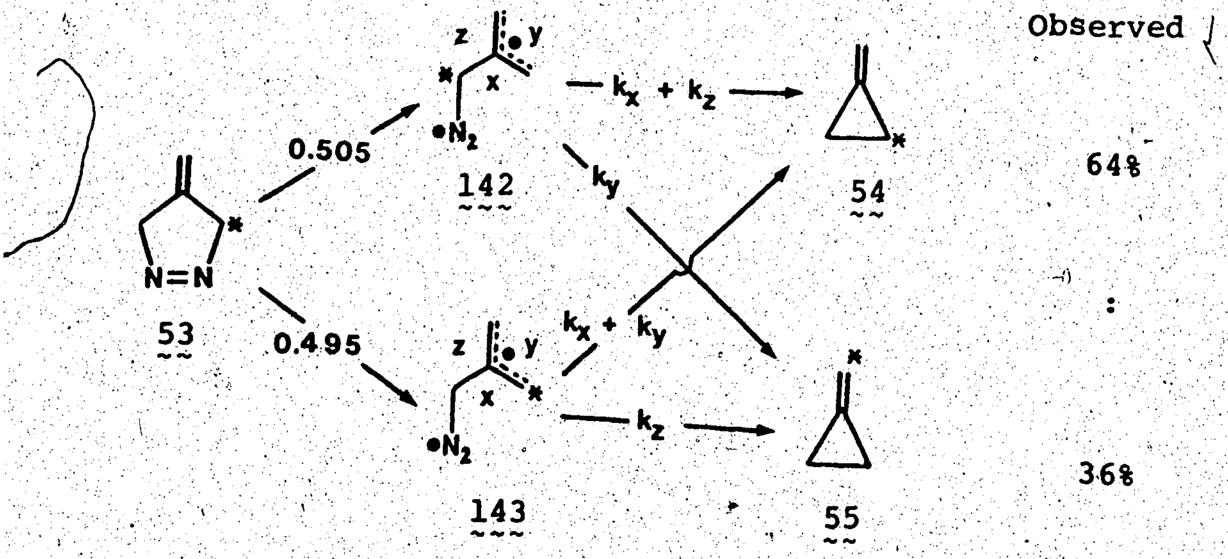
A product forming process using only x-, y- or z-closure in the intermediate diazenyl species was considered. This mechanism, as in Scheme 9, provides only a single product from each of **107** and **46** whereas two products were obtained from both **107** and **46** as in Table 26 (see also Scheme 9).

The formation of **48** and **50** respectively from **107** and **46** suggests that x-closure must be included in the product forming process but other closures are also involved to account for products **47** and **49**. It is thus necessary to consider three closures, i.e., (x+y)-, (x+z)- or (x+y+z)-closure, as possible mechanisms. It is convenient to investigate first (x+y+z)-closure as the most general case. Then, the other two closures can be treated as extreme cases of (x+y+z)-closure when z = 0 or y = 0. In order to study these mechanisms information about the relative rates of the three closures



Scheme 9

in the diazenyl species for 4-methylene-1-pyrazoline (30) is required. We chose the product distribution (10a) for 4-methylene-1-pyrazoline-3-^{13}C (53) as a model for 30.



Scheme 10

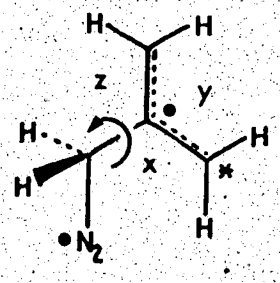
If $k_x(A)$, $k_y(A)$ and $k_z(A)$ represent the partial rate factors [i.e., $k_x(A) + k_y(A) + k_z(A)$ is 1] for x-, y- and x-closure in each diazenyl species produced from the precursor A then the lack of the ponderal effect (29,30) in the rotation of a $^{13}CH_2$ group of the diazenyl species 143 allows the ratio of $k_x(53):k_y(53):k_z(53)$ and that of $k_x(30):k_y(30):k_z(30)$ to be essentially the same. Thus, the product distribution for 53 is expected to be almost equal to that for 30. Defining k_α and k_β as the partial rate factors (i.e. $k_\alpha + k_\beta = 1$) for the faster and the slower steps respectively in the initial C-N bond breaking process and using the most normal carbon-13 isotope effect value of 1.03 (61) and the isotopic purity of 67% for 53 we are able to obtain the ratio of $k_\alpha(53):k_\beta(53)$

as 0.505:0.495. Substituting this ratio and the product ratio of 64:36 for **54**:**55** (10a) into equation 49, the ratio of $k_x(\mathbf{53}):k_y(\mathbf{53}):k_z(\mathbf{53})$ can be calculated. We cannot obtain a solution for equation 49 as it stands,

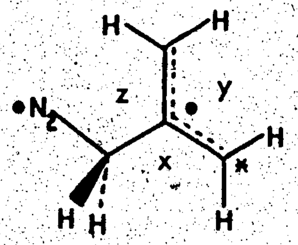
$$\frac{[\mathbf{54}]}{[\mathbf{55}]} = \frac{0.64}{0.36} = \frac{0.505[k_x(\mathbf{53})+k_z(\mathbf{53})]+0.495[k_x(\mathbf{53})+k_y(\mathbf{53})]}{0.505\cdot k_y(\mathbf{53})+0.495\cdot k_z(\mathbf{53})} \qquad \text{(eq. 49)}$$

but if we add the relationships $k_x(\mathbf{53}) + k_z(\mathbf{53}) = k_w(\mathbf{53})$ and $k_x(\mathbf{53}) + k_y(\mathbf{53}) + k_z(\mathbf{53}) \doteq 1.0$, then we have three equations and three unknowns. For the case where $k_x(\mathbf{53}) = k_z(\mathbf{53})$ the solution for $k_x(\mathbf{53}):k_y(\mathbf{53}):k_z(\mathbf{53})$ is 0.28:0.44:0.28. When the value of $k_y(\mathbf{53})$ or $k_z(\mathbf{53})$ is zero as in the extreme cases, i.e. (x+z)- or (x+y)-closure, then we obtain the ratios of $k_x(\mathbf{53}):k_y(\mathbf{53})$ as 0.27:0.73 and 0.29:0.71 respectively. These results clearly demonstrate that the value of the partial rate factor $k_x(\mathbf{53})$ is always within the range 0.27 to 0.29.

The validity of this (x+y+z)-closure mechanism can be tested by comparing the calculated ratios with the observed ratios, listed in Table 26. In order to do this, we chose, as the model, a diazenyl species whose possible rotomers (e.g. **143** and **144**) are in conformational equilibrium with one another. It is then expected that this diazenyl species will undergo both x- and z-closure with $k_x(\mathbf{53})$ and $k_z(\mathbf{53})$ having the same magnitudes. As



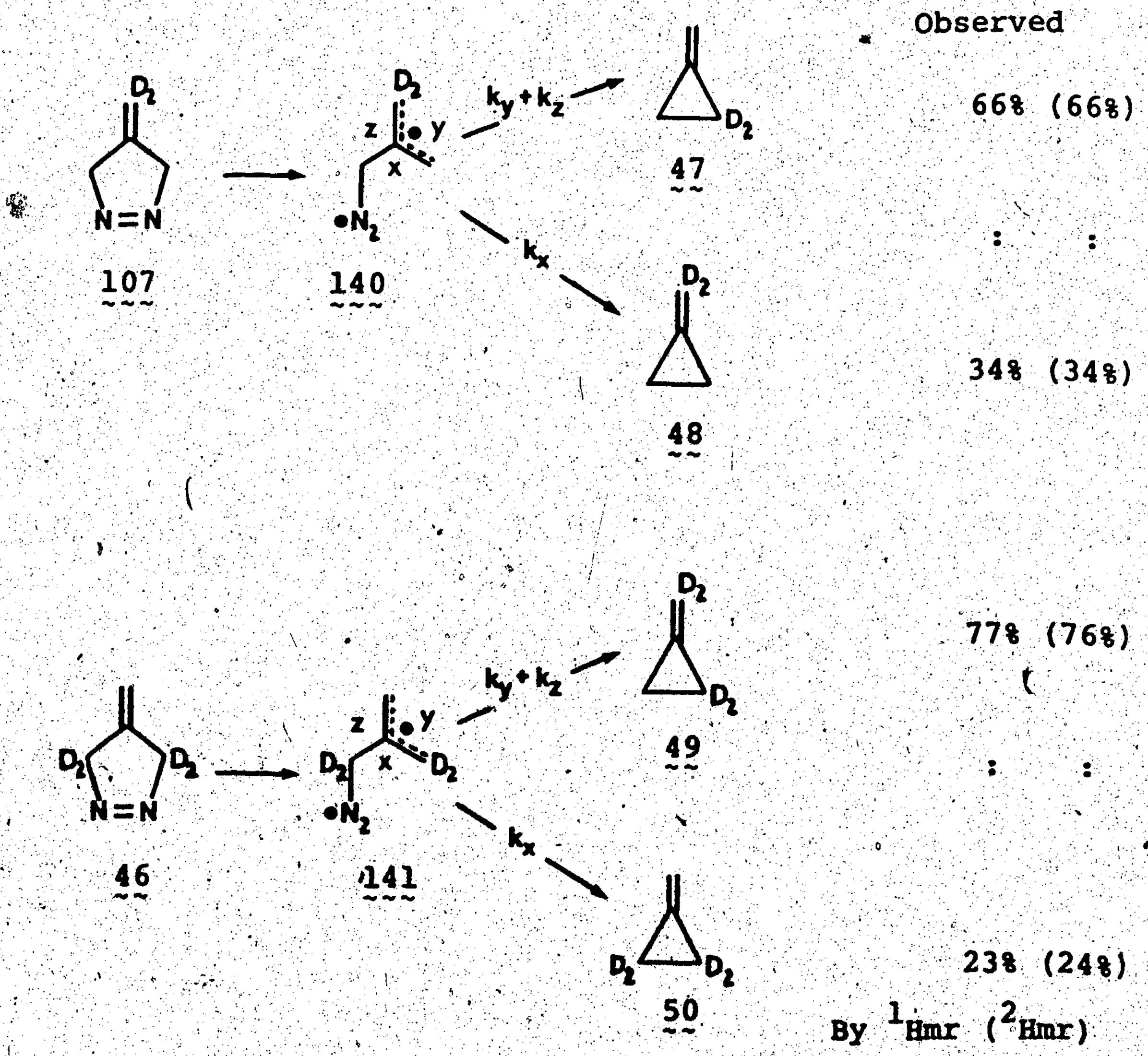
143



144

indicated previously, the ratio of k_x(53):k_y(53):k_z(53) is 0.28:0.44:0.28. It should be noted that the value of 0.28 for k_x(53) is essentially independent of the carbon-13 isotope effect even if the value of this effect is as high as 1.1.

We next calculated the product ratios for 107 and 46. As in Scheme 11, 107 going through 140 produces a 66:34 mixture of 47:48, and 46 going through 141 gives rise to a 77:23 mixture of 49:50 (see ^{1}Hmr data in Table 26 and also Scheme 11). The products, 48 and 50, can be produced only by x-closure in 140 and 141 respectively. However, the product data indicate that the ratio of 48:47 for 107 is greater than the ratio of 50:49 for 46. In other words, x-closure should be faster in 140 than it is in 141. This may imply that there exists a deuterium isotope effect in the product forming pathway since x-closure in 141 involves an allylic CD_2 rotation whereas x-closure in 140 does not. For 141, both x- and z-closure, i.e. the displacement of nitrogen by one

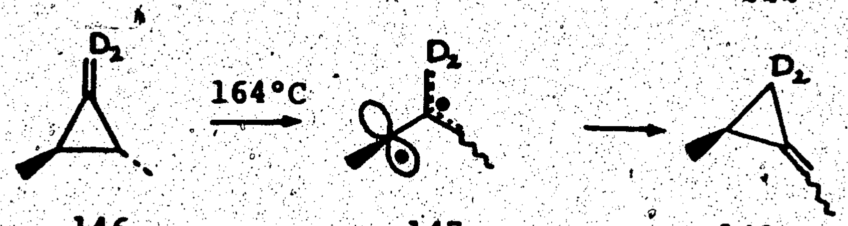


Scheme 11

of the allylic termini, are considered to be S_N2 type reactions, therefore these closures are expected not to show any significant isotope effects due to the deuterium subsitution in the tetrahedral methylene. The absence of an appreciable secondary isotope effect in such an α-deuterated substrate subjected to a direct displacement reaction is a consequence of the cancellation of the loss of an HCY bending force constant from the leaving group by the gain of an HCX bending force constant from the entering one (62). We are then left with the task of deciding which group CD_2 or CH_2 will rotate more readily, because of the isotope effect. There are two views on the origin of this isotope effect (25b). As mentioned previously in the Objective section, a classical inertial argument gives rise to a k_H/k_D value of 1.414. On the other hand, in quantum mechanical terms this isotope effect can be seen in the thermal isomerization of 48 *via* the orthogonal TMM (145) to 47. The substitution

48 145 47

of deuterium for hydrogen on the exo-methylene of methylenecyclopropane (31) will lower the zero point energy of all vibrations associated with the exo-methylene, but since the hybridization of this carbon probably changes very little from the ground state to the transition state, the torsional vibrational mode is the one on which to focus. In 31, the torsion has $\nu = 749\ cm^{-1}$, and in 48, $\nu = 537.5\ cm^{-1}$ (63). Thus, the zero point energy is lowered 106 cm^{-1} upon deuteration which corresponds to 303 cal mol^{-1}. In the formation of 47 *via* 145, the torsional vibration becomes part of the reaction coordinate motion and the zero point energy difference is lost since the vibration becomes a translation. Then, the isotope effect is calculated to be 1.41 at 170.0° which is almost identical with the value of 1.414 obtained from classical inertial argument. The work of Gajewski (25b) support this. He observed an isotope effect of 1.31 ± 0.04 in the thermal isomerization of **146** going *via* **147** to **148**.



146 **147** **148**

By using the value of 1.41 as the isotope effect (R) for the CD_2 allylic rotation (or torsion) we can calculate the percent product ratio **47**:**48** for **107** by equation 50 (see Scheme 11) as 65 ± 2:35 ± 2. This result is in good

$$\frac{[47]}{[48]} = \frac{k_y(107) + k_z(107)}{k_x(107)} = \frac{k_y(53)/R + k_z(53)/R}{k_x(53)}$$

$$= \frac{0.44/1.41 + 0.28/1.41}{0.28} = \frac{0.65}{0.35} \qquad \text{(eq. 50)}$$

agreement with the observed ratio as cited in Scheme 11 from Table 26. It should be noted that [illegible] calculated product ratio is the one normalized to satisfy [**47**] + [**48**] = 1.0.

On the other hand, for 46, assuming that the D_2C-N bond cleavage in 141 proceeds as fast as the y-closure, then there arises a question whether the D_2C-N bond cleavage can induce an isotope effect in the y-closure for 141 then Y is given as 0.81 ± 0.18 by equation 51.

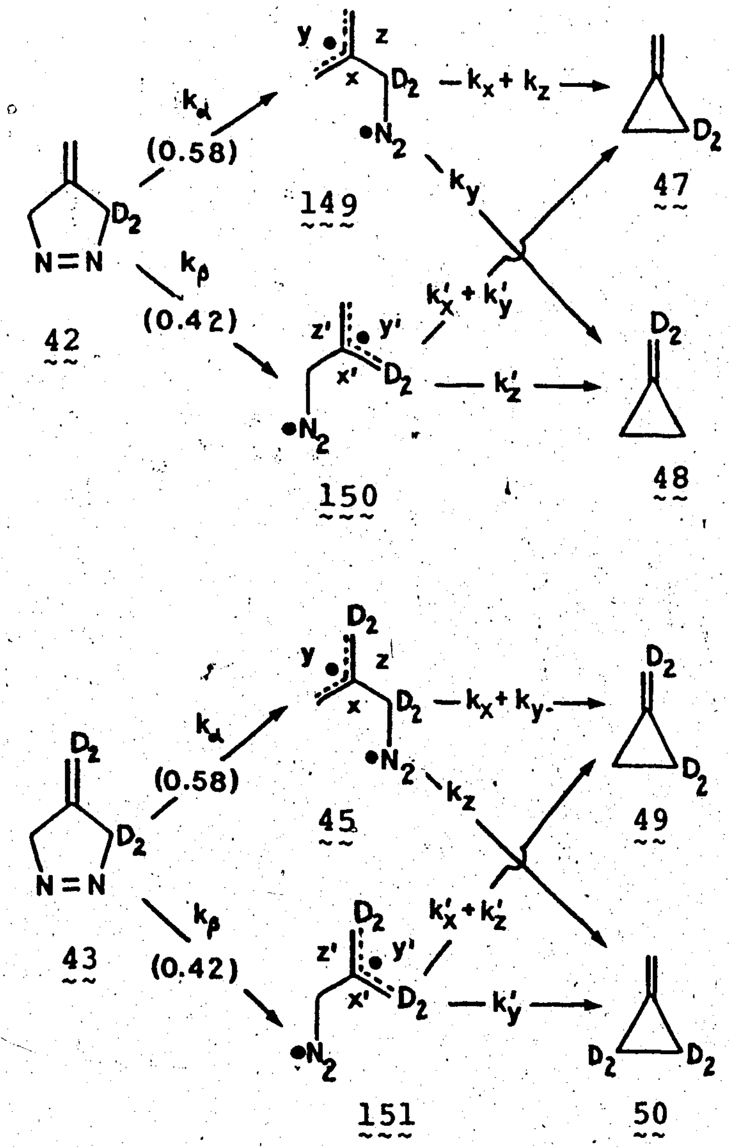
$$\frac{[49]}{[50]} = \frac{0.77}{0.23} = \frac{k_y(46) + k_z(46)}{k_x(46)} = \frac{k_y(53)/(R\cdot Y) + k_z(53)}{k_x(53)/R}$$

$$= \frac{k_y(53)/Y + k_z(53)\cdot R}{k_x(53)} \quad \frac{0.44/Y + 0.28\cdot 1.41}{0.28}$$

(eq. 51)

This value clearly indicates that there is no such isotope effect in the y-closure since an inverse isotope effect is inconceivable. Consequently, if this mechanism is the correct one we can suggest that the rotation of the two allylic termini has priority over the D_2C-N bond cleavage in the product forming y-closure process. Then, assuming Y = 1, the percent product ratio of 49:50 for 46 can be obtained as 75 ± 2:25 ± 2 by equation 51 above. This is quite consistent with the observed ratio as in Table 26 (see also Scheme 13) within the error limit of ±2%.

We then carried out the same analysis that described above on the products 42 and 43 (see Scheme 12). If k_α and k_β represent the partial rate factors in the rate determining C-N bond cleavage process, then the isotope effect allows k_β to become smaller than k_α. The observed



Observed

59% (60%)

: :

41% (40%)

72% (71%)

: :

: :

28% (29%)

By ^{1}Hmr (^{2}Hmr)

Scheme 12

secondary deuterium kinetic isotope effect of 1.38 and the isotopic purity of 97% (see Table 23) yield values of $k_\alpha : k_\beta$ of 0.58:0.42 for both 42 and 43. Scheme 12 shows that 42 produces 47 and 48 *via* two structurally different diazenyl species, 149 and 150, and also 43 gives **49** and **50** *via* **45** and **151**. It is thus expected that for either **42** or **43**, the ratio of $k_x:k_y:k_z$ in one diazenyl species should be different from the ratio in the other, since the two species display the isotope effect dissimilarly in the allylic CD_2 rotation. If k_x, k_y and k_z represent the partial rate factors for the ring closures in **149** and **45** produced by the faster α-cleavage process, and k'_x, k'_y and k'_z represent those in **150** and **151** produced by β-cleavage then their ratios for **42** and **43** can be calculated from equations 52-55 (see Scheme 12). By inserting the value of 1.41 for the rotational (or torsional) isotope effect and using the previously derived ratio of 0.28:0.44:0.28 for $k_x(\mathbf{53}):k_y(\mathbf{53}):k_z(\mathbf{53})$, we can obtain

$$k_x(\mathbf{42}) : k_y(\mathbf{42}) : k_z(\mathbf{42}) = k_x(\mathbf{53}) : k_y(\mathbf{53}) : k_z(\mathbf{53})$$

$$= \underline{0.28} : \underline{0.44} : \underline{0.28} \qquad \text{(eq. 52)}$$

$$k'_x(\mathbf{42}) : k'_y(\mathbf{42}) : k'_z(\mathbf{42}) = \frac{k_x(\mathbf{53})}{R} : \frac{k_y(\mathbf{53})}{R} : k_z(\mathbf{53})$$

$$= \underline{0.25} : \underline{0.40} : \underline{0.35} \qquad \text{(eq. 53)}$$

$$k_x(\mathbf{43}) : k_y(\mathbf{43}) : k_z(\mathbf{43}) = k_x(\mathbf{53}) : \frac{k_y(\mathbf{53})}{R} : \frac{k_z(\mathbf{53})}{R}$$

$$= \underline{0.35} : \underline{0.40} : \underline{0.25} \qquad \text{(eq. 54)}$$

$$k'_x(\mathbf{43}) : k'_y(\mathbf{43}) : k'_z(\mathbf{43}) = \frac{k_x(\mathbf{53})}{R} : \frac{k_y(\mathbf{53})}{R^2} : \frac{k_z(\mathbf{53})}{R}$$

$$= \underline{0.32} : \underline{0.36} : \underline{0.32} \qquad \text{(eq. 55)}$$

the values of the ratio for **42** and **43** and these are listed with equations 52-55. It should be noted that these ratios have been normalized to satisfy $k_x + k_y + k_z = 1$ and $k'_x + k'_y + k'_z = 1$. The product ratios for 42 and 43 can be calculated by equations 56 and 57 (see Scheme 12). The

$$\frac{[47]}{[48]} = \frac{k_\alpha \cdot [k_x(42) + k_z(42)] + k_\beta \cdot [k'_x(42) + k'_y(42]}{k_\alpha \cdot k_y(42) + k_\beta \cdot k'_z(42)}$$

$$= \frac{0.58(0.28 + 0.28) + 0.42(0.25 + 0.40)}{0.58 \cdot 0.44 + 0.42 \cdot 0.35} = \frac{0.60}{0.40} \quad \text{(eq. 56)}$$

$$\frac{[49]}{[50]} = \frac{k_\alpha \cdot [k_x(43) + k_y(43)] + k_\beta \cdot [k'_x(43) + k'_z(43)]}{k_\alpha \cdot k_z(43) + k_\beta \cdot k'_y(43)}$$

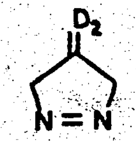
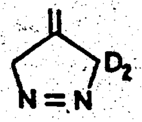
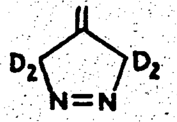
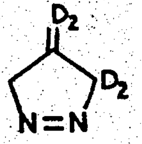
$$= \frac{0.58(0.35 + 0.40) + 0.42(0.32 + 0.32)}{0.58 \cdot 0.25 + 0.42 \cdot 0.36} = \frac{0.70}{0.30} \quad \text{(eq. 57)}$$

results obtained (see also Table 35) are in good agreement with the observed ratios quoted in Table 26 (see also Scheme 12) which were derived from ^{1}Hmr and ^{2}Hmr analyses. The ^{2}Hmr data are in good agreement with the calculated ratios, i.e. within the range of ±1%. Such results may not be surprising since the observed product ratios were obtained directly from integration of the deuterium signals, not requiring the correction for deuterium incorporation that is required for ^{1}Hmr.

The calculated product distributions obtained above are summarized in Table 35 and lead us to consider the (x+y+z)-closure mechanism as an appropriate one. However such a choice cannot be made definitively until all the

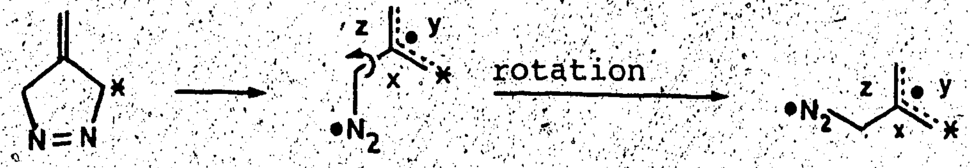
Table 35

Calculated percent product distributions for 107, 42, 46 and 43 by (x + y)-, (x + z)- (x + y + z)-closure mechanisms in the product forming process

Starting material			Product distribution, %				
			Calculated[b]			Observed[a, c]	
		Products	(x+y+z)[d]	(x+y)	(x+z)	^{1}Hmr	^{2}Hmr
107		47	65	63	66	66	66
		48	35	37	34	34	34
42		47	60	59	67	59	60
		48	40	41	33	41	40
46		49	75	71	79	77	76
		50	25	29	21	23	24
43		49	70	74	62	72	71
		50	30	26	38	28	29

[a] Data from Table 26; [b] Error in each percent distribution is ±2%; [c] Error in each percent distribution is ±1%; [d] Closure wherein $k_x(53) = k_z(53)$.

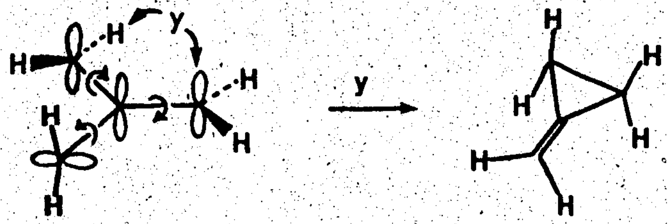
other cases, wherein k_x(53) ≠ k_z(53), are examined. If rotation in 143 leading to 144 is not as fast as either x- or z-closure then k_x(53) ≠ k_z(53) and 143 may be



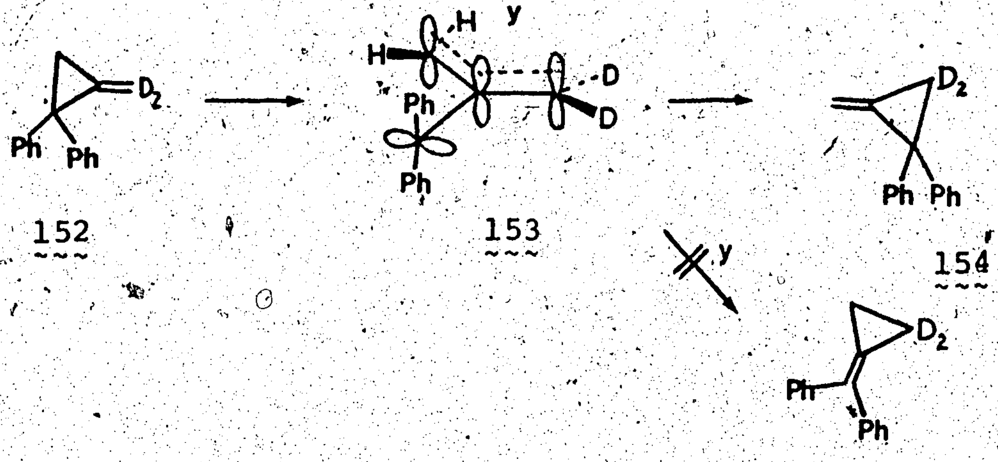
53 143 144

expected to be produced as a major species after one C-N bond cleavage. Then, x-closure will be the front-side attack by an allylic terminus (which was originally the α-methylene of 53) on the tetrahedral methylene position and z-closure the back-side attack by the allylic terminus. If we chose the two extreme cases as the examples for this: i.e. when k_z(53) = 0 [(x+y)-closure] and when k_y(53) = 0 [(x+z)-closure], then the former case represents the front-side attack for x-closure and the latter the predominant back-side attack of z-closure. The calculated product distributions for 42, 43, 46 and 107 using these two closures [(x+y)- and (x+z)-closure] by a method analogous to that demonstrated for the (x+y+z)-closure wherein k_x(53) = k_z(53) are presented in Table 35. The observed and calculated ratios are not in good agreement for 46 in the (x+y)-closure model and for 42 and 43 in the (x+z)-closure model. These results demonstrate that all three modes of ring closure (x+y+z) are involved in the product forming step. It should be noted that when the values of n, where n is the ratio of z- to x-closure for 53, are in the range of 0.8 to 1.25, the calculated product ratios are acceptable, i.e. within ±2% of the observed. The best results are obtained with n = 1.

We must ask ourselves whether the nitrogen is still involved in the product determining step, for what we have demonstrated is that one of the ring methylene groups stays stereochemically, or stoichiometrically, unique, and this could be achieved by employing the Chesick intermediate (24) and by adding in the y-closure which we did not consider in our discussion of the two-bond cleavage mechanisms. Such a y-closure requires all three methylene groups to rotate, the two that are originally in the four carbon plane to rotate out and the one that is originally orthogonal to rotate into

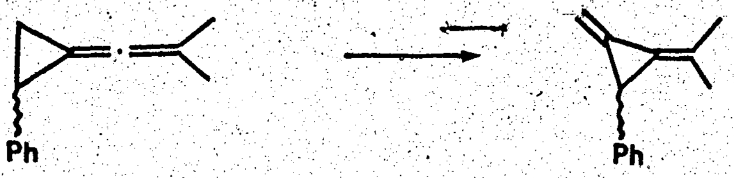


the plane; essentially maximum motion. Such a y-closure does not seem probable if we examine the isomerization of some methylenecyclopropanes (64,65). The thermolysis of 152 going through 153 equilibrates 152 and 154 by essentially x- and z-closure, and no 155 by y-closure (64). Here, the orthogonal methylene group is used as

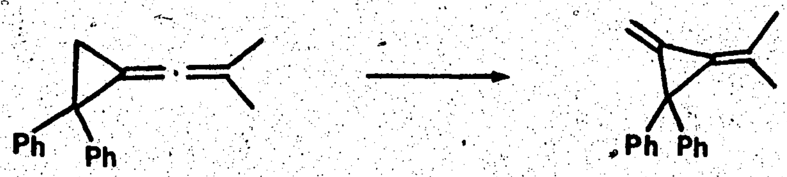


152 153 154 155

a pivot (66), and analogous results were obtained for 156 and 157 (65). We are thus encouraged to consider

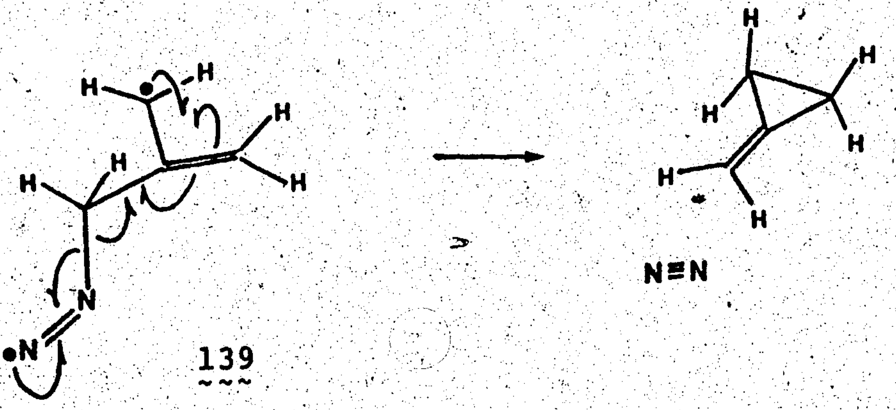


156



157

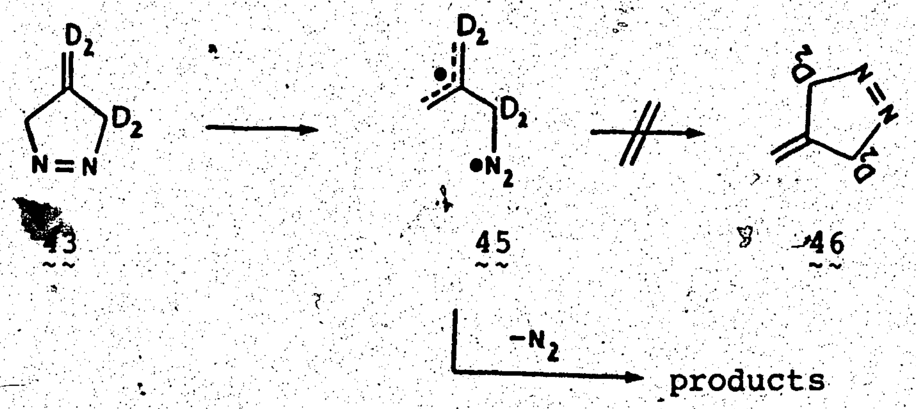
y-closure as being an electrocyclic process.

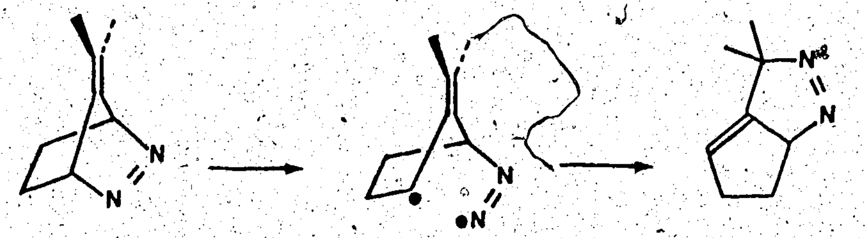


139

We conclude that all of the data can be rationalized on the basis of a diazenyl intermediate, 139, and that ring closure modes x, y and z vary in their role depending upon the position of deuterium substitution.

One possibility which has to be considered is re-closure of the diazenyl intermediate into the precursor. The activation energy for dissociation of the intermediate to the products is informative in this regard. Baird (67) has predicted, using *ab initio* molecular orbital calculations, that the activation energy for the reaction H-N=N· to H· + N_2 is 22.6 kcal mol^{-1}. It is expected that this would be smaller for a more stable hydrocarbon radical and from bond dissociation energies (BDE) we would predict that for $RCH_2\cdot$ the barrier may be reduced by 6 kcal mol^{-1} (compare H-H BDE of 104 with RCH_2-H BDE of 98 kcal mol^{-1} when R = Me or Et). If allylic resonance is of importance then this could be further reduced (BDE of $H-CH_2CH=CH_2$ is 88 kcal mol^{-1}) to a value of approximately 6 kcal mol^{-1} i.e. to a value of the order of the rotational energy barrier. Cameron (10a) observed that 43 did not rearrange





36 41

to 46. However, Berson (6a) did observe the re-closure of the diazenyl radical. As mentioned previously in the Historical section (11), for the more planar monocyclic pyrazoline 43, cleavage of the C-N bond in the diazenyl species 45 may be easier than rotation and rebonding to the exocyclic CD_2. On the other hand, recombination to 41 can be facilitated in the bicyclic system 36 since the exocyclic isopropylidene group is much closer to the diazenyl nitrogen because of folding.

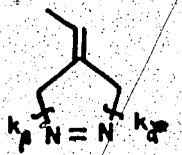
B. Thermolysis of 4-Alkylidene-1-pyrazolines

(i) Kinetic Studies

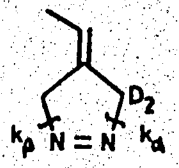
a. Thermolysis of 4-ethylidene-1-pyrazoline (69) and its deuterated derivatives (76, 77 and 128)

Prior to the presently described investigation, Schrijver and Godard (11,34) studied the ratios of products from 69, 76 and 77. They were unable to obtain kinetic data due to interference from tautomerism, but by using the stainless steel reaction vessel we have been able to minimize the tautomerism to such an extent that a kinetic study of these molecules, and of **128**, appeared profitable. Since they had rationalized the product proportions in terms of an asymmetric cleavage of the C-N bond, the asymmetry should be reflected in the secondary deuterium kinetic isotope effects for these molecules.

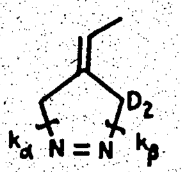
Using the kinetic data from Table 25 we have recorded, in the second column of Table 36, the values of $\delta\Delta G^{\ddagger}$ per deuterium for each of the deuterated 4-ethylidene-1-pyrazolines. We have also considered the model wherein the bonds α (the faster) and β are breaking competively in the rate determining step. Using equations 58-61, and



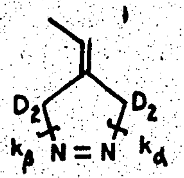
69



76



77



128

Obs. 10^3k (sec^{-1})	1.94	1.63	1.82	1.51

assuming that deuterium substitution at the *syn*-methylene group does not affect the rate constant for cleavage of the α-bond [i.e. $k_\alpha(\mathbf{77}) = k_\alpha(\mathbf{69})$] and that substitution at the anti-methylene does not affect the rate constant for cleavage of the β-bond [i.e. $k_\beta(\mathbf{76}) = k_\beta(\mathbf{69})$] we have

$$k_\alpha(\mathbf{69}) + k_\beta(\mathbf{69}) = 1.94 \times 10^{-3} \qquad \text{(eq. 58)}$$

$$k_\alpha(76) + k_\beta(76) = k_\alpha(69)/(k_H/k_D) + k_\beta(69) = 1.63 \times 10^{-3} \quad \text{(eq. 59)}$$

$$k_\alpha(77) + k_\beta(77) = k_\alpha(69) + k_\beta(69)/(k_H/k_D) = 1.82 \times 10^{-3} \quad \text{(eq. 60)}$$

$$k_\alpha(128) + k_\beta(128) = [k_\alpha(69) + k_\beta(69)]/(k_H/k_D) = 1.51 \times 10^{-3} \quad \text{(eq. 61)}$$

calculated $\delta\Delta G^{\ddagger}$ per deuterium and the proportions of the thermolysis putatively going by α-bond cleavage and β-bond cleavage. These results are listed in the third and fourth columns of Table 36.

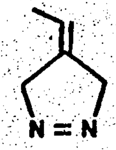
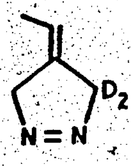
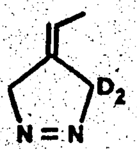
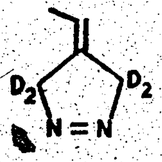
It is apparent that the one-bond cleavage mechanism gives a value for $\delta\Delta G^{\ddagger}$ per deuterium in good agreement with the generally accepted range of 90-120 cal mol^{-1} (26,27).

b. Thermolysis of 4-alkylidene-1-pyrazolines

Earlier attempts in this laboratory to measure the rate of the thermolysis of several 4-alkylidene-1-pyrazolines had failed, the reason being the intervention of tautomerism possibly due to surface catalysis. Having been successful with 4-methylene- and 4-ethylidene-1-pyrazoline we turned our attention to other compounds previously prepared by Tokunaga and Schrijver (10a,11,48). The relative rates for these compounds along with those of 62 (32) and 65 (33) are listed in Table 37. The

Table 36

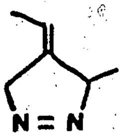
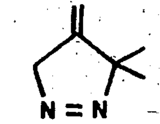
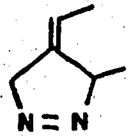
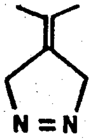
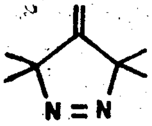
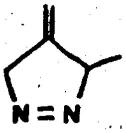
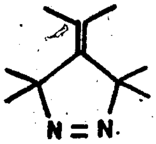
Observed values of $\delta\Delta G^{\ddagger}$ per deuterium for one- and two-bond cleavage pathways and ratios of $k_{\alpha}(A):k_{\beta}(A)$ for one-bond cleavage in the thermolysis of 69, 76, 77 and 128

	Two-bond cleavage	One-bond cleavage	
(A)	$\delta\Delta G^{\ddagger}/n$ (cal mol^{-1})	$\delta\Delta G^{\ddagger}/n$ (cal mol^{-1})	$k_{\alpha}(A):k_{\beta}(A)$*
 69			0.72:0.28
 76	78 ± 3	110 ± 4 (k_H/k_D=1.29)	0.67:0.33
 77	30 ± 1	110 ± 4 (k_H/k_D=1.29)	0.77:0.23
 128	57 ± 2	110 ± 3 (k_H/k_D=1.29)	0.72:0.28

*See Scheme 13.

Table 37

The relative rates, at 170.0°, for the gas phase thermolysis of some 4-alkylidene-1-pyrazolines

Compound	Relative rate[a]	Compound	Relative rate[a]
 89	2.30	 56	0.70
 90	2.21	 57	0.55
 69	2.17	 62	0.020[b]
 68	1.04	 65	0.00065[c]
 30	1.00		

[a] Calculated from the data in Table 20.

[b] Reference 32.

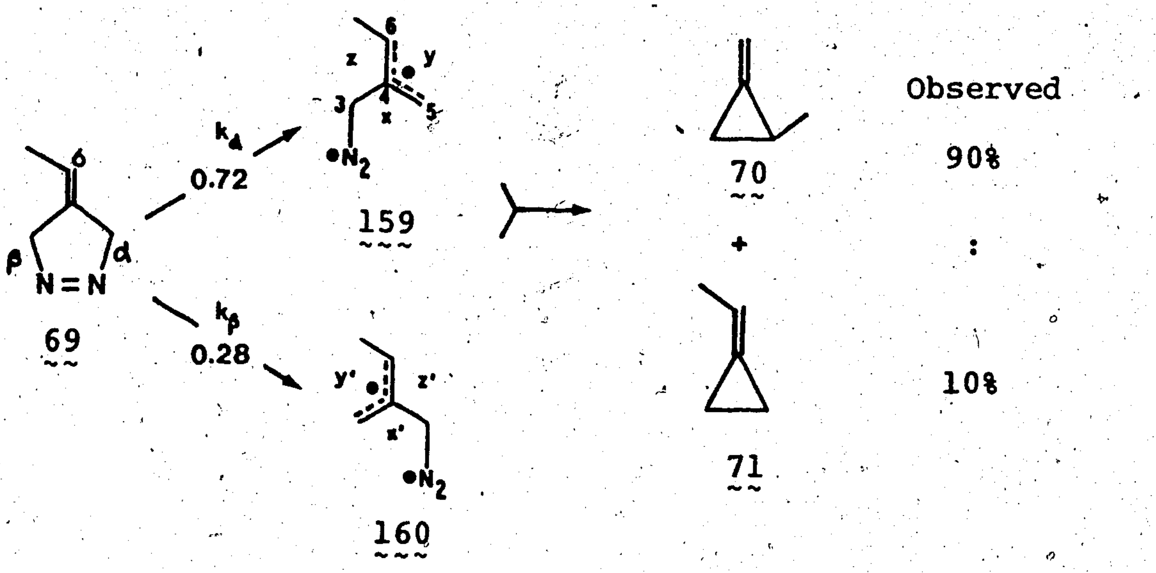
[c] Reference 33.

results are noteworthy only in that methylation results in such a small change in the thermolysis rate. Only compounds 62 and 65 have the thermolysis rates which differ significantly from the others. This suggests that the methyl groups are indeed manifesting steric factors which decrease the thermolysis rate constant, probably by steric crowding in the transition state.

(ii) Product Studies

a. Thermolysis of 4-ethylidene-1-pyrazoline (69) and its deuterated derivatives (76 and 77)

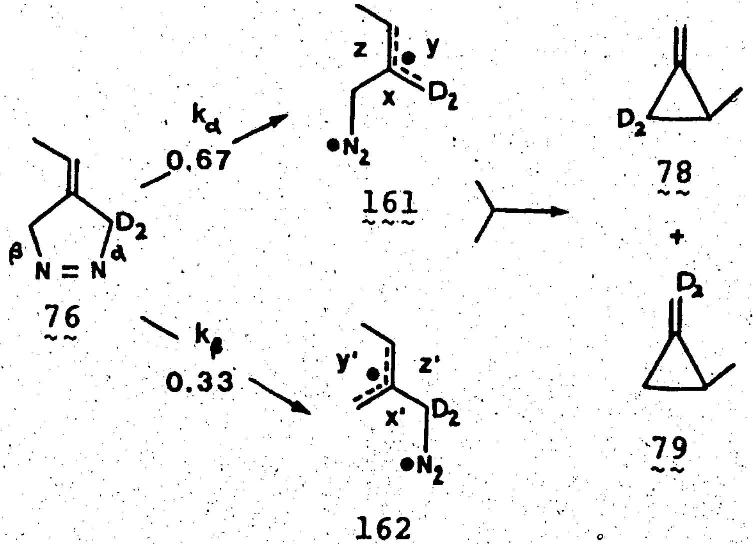
Table 9 (11) shows that 69 gives rise to a 90:10 mixture of 70:71. This can be rationalized qualitatively in the following manner. As noted previously in Table 36, the ratio of k_α(69):k_β(69) was found to be 0.72:0.28. This indicates that 159 should be the major intermediate



species and will thus control the product ratio. Product 70 can be obtained by (y+z)-closure in 159, and (y'+z')-closure in 160. The product ratio of 90:10 for 70:71 indicates that (y+z)-closure has increased at the expense of x-closure. One possible reason for the decrease of x-closure in 159, the major intermediate, is that back-side attack (4a,68) by the allylic terminus on the tetrahedral methylene is favored over front-side attack. Then, in 159, restriction in the rotation of the azo group around the C_3-C_4 single bond due to the steric effect of the methyl group on C_6 would increase z- and y-closure at the expense of x-closure.

Further insight can be gained by examining the products from the thermolysis of the dideuterated derivatives of 69, i.e. 76 and 77. From the ^{1}Hmr (^{2}Hmr) data in Table 30, for the deuterated 2-methylmethylenecyclopropanes, we see that 76 produces an 80:20 (81:19) mixture of 78:79. This implies that y-closure predominates in the major intermediates (161 and 163) and that more of the major product (78 for 76, and 79 for 77) can be produced from 77 than from 76. Such a result can be explained by the observation (see Table 36) that 77 forms 163 to a greater extent than 76 forms 161 (i.e. k_α is faster in 77 than in 76) and also the deuterium isotope effect for CD_2 rotation (torsion) can slow down y-closure

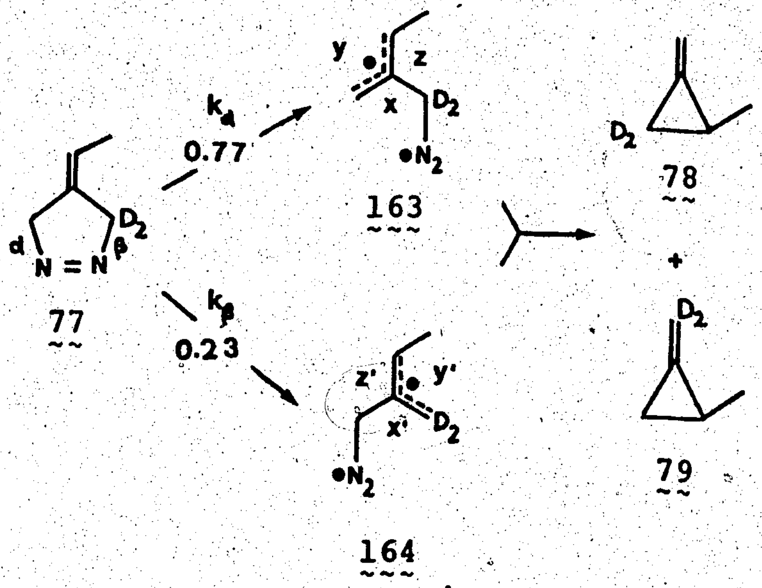
Observed ratio



80 (81)

: :

20 (19)



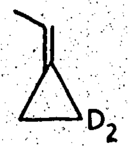
13 (11)

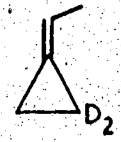
: :

87 (89)

By ^{1}Hmr (^{2}Hmr).

in **161** and y'-closure in **164**. It should be noted that from the ^{1}Hmr (^{2}Hmr) data in Table 31, for the deuterated ethylidenecyclopropanes, **76** produces 91:9 (90:10) mixture of **81**:**82** and **77** gives rise to a 7:93 (8:92) mixture of **81**:**82**. This could imply that approximately 10% of the


81

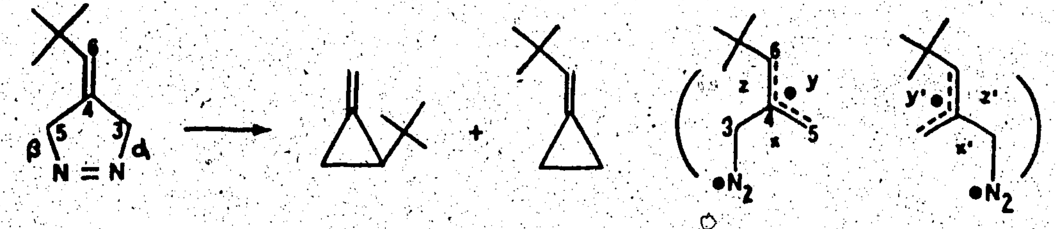

82

major diazenyl species, **161** and **163**, convert into **164** and **162** respectively. It should be noted however that **82** constitutes only 1% of the total product from **76** and that **81** represents less than 0.8% of the total hydrocarbon derived from **77**.

b. Thermolysis of other 4-alkylidene-1-pyrazolines

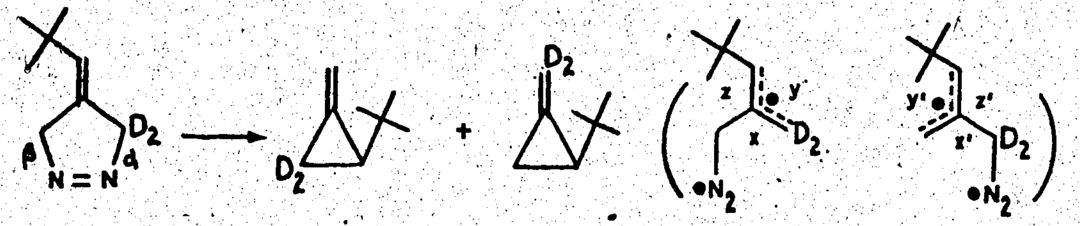
In order to further test the one-bond cleavage mechanism which we have proposed, analyses similar to that in the preceding section were performed to explain the products from the thermolysis of some 4-alkylidene-1-pyrazolines which had been reported previously from this laboratory (10a,11,32).

As an analogy to **69**, the products from **83** (see Table 11) were examined. Compared to the methyl group in **69** the much bulkier *t*-butyl group on C_6 in **83** resulted in mainly α-cleavage to produce 165. In 165, the steric



83 85 86 165 166

Observed 95.8% : 4.2%

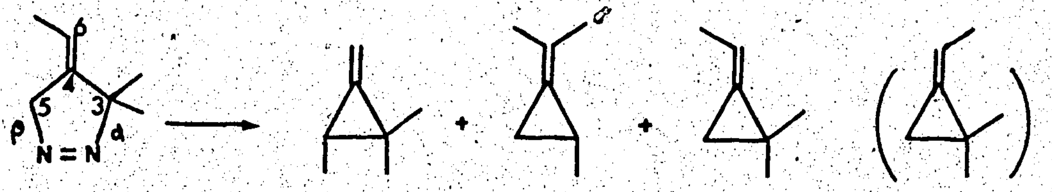


84 87 88 167 168

Observed ratio 70 : 30

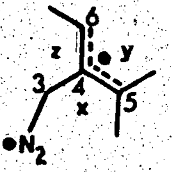
hindrance due to the *t*-butyl group can suppress x-closure *via* the back-side displacement of the allylic terminus (C_5). The major product, 85, will form predominantly *via* (y+z)-closure. This can be confirmed by analyzing the deuterated 2-*t*-butylmethylenecyclopropane products from 84. We suggest that 87 will be obtained principally *via* y-closure in 167.

The products from 98 are presented in Table 13. Due to the steric effect of the methyl group on C_6, α-cleavage is expected to give mainly 169 as the diazenyl intermediate.

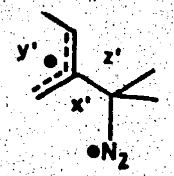


98 99 100 101 102

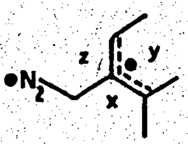
Observed 71.5% : 16.0% : 12.5% None



169



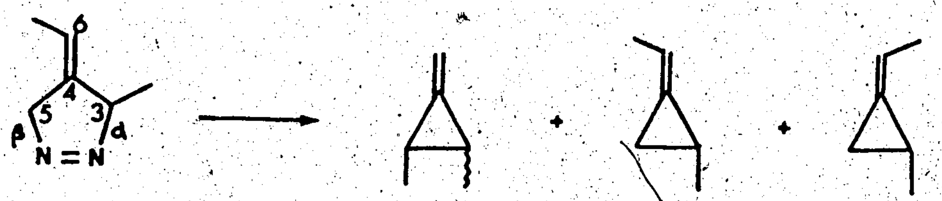
170



171

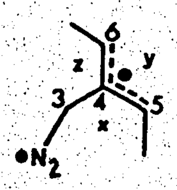
Then y-closure in 169 gives rise to 99 as the major product. The minor products, 101 and 100, can be produced *via* x- and z-closure respectively in 169, and by x'- and y'closure in 170. It should be noted that the steric effect of the methyl group on C_5 in 169 may prevent 169 from converting into 171. However, such a conversion might have occurred for 76 and 77 and could account for the trace components 82 and 81, respectively.

The products from 89 are listed in Table 12. Because of the steric effect of the methyl on C_6 173 is expected

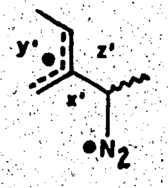


89 172 93 94

Observed 77.6% : 20.0% : 2.4%



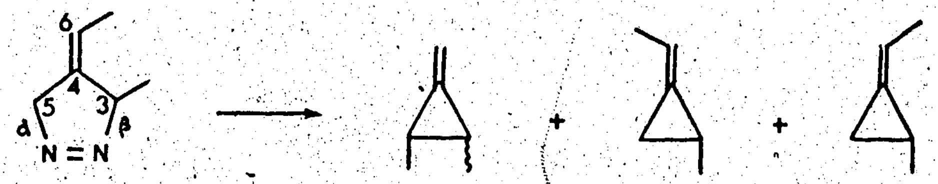
173



174

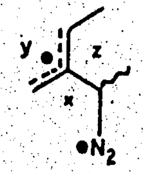
to be the major diazenyl species. In 173, the steric hindrance for x- and z-closure by the methyls on C_5 and C_6 can suppress x- and z-closure and y-closure is expected to be much faster. Thus, y-closure in 173 will give rise to 172 as the major product. The x- and z-closure in 173 as well as some of the y'-closure in the minor diazenyl species, 174, (*via* β-cleavage) produces 93 in moderate yield, whereas only some of y'-closure in 174 gives rise to 94 in very low yield.

The products for 90 (see Table 12) can be rationalized *via* the diazenyl species, 175 and 176. Considering the steric effect of the methyl on C_6 in 90 then the major species will be 175 *via* α-cleavage. In fact, the product

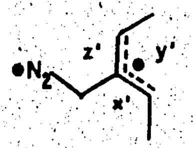


90 172 93 94

Observed : 33% : 31.5% : 35.5%



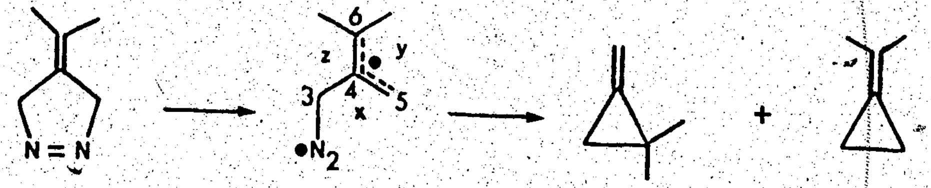
175



176

ratio of 33:67 for 172:93+94 indicates that x- and y-closure in 175 mainly give rise to 93 and 94 as the major products. The z-closure in 175 and y'-closure in the minor species, 176, produce 172 as the minor product.

Thermolysis of 57, going *via* 177, produces a 63:37 mixture of 58:59 (see Table 7). This implies that the ratio of $(k_y+k_z):k_x$ for 177 is 0.63:0.37. This ratio

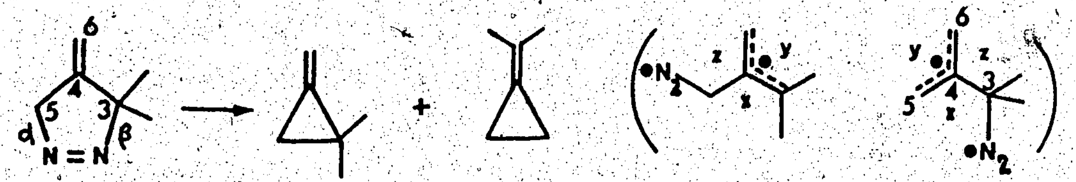


57 177 58 59

Observed 63% : 37%

indicates a fairly large magnitude of x-closure in spite of the restriction to x-closure because of the steric effect of the methyl on C_6. This can be rationalized by considering that y- and z-closure are also suppressed due to the steric effect by the methyl on C_6, i.e. the tertiary radical is either a poor nucleophile or there is a ponderal effect.

The products for 56 are presented in Table 7. If the C_3-N bond in 56 cleaves first due to an inductive effect, to produce 177 as the major diazenyl species

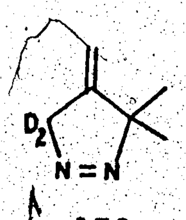


56 58 59 177 178

Observed 82% : 18%

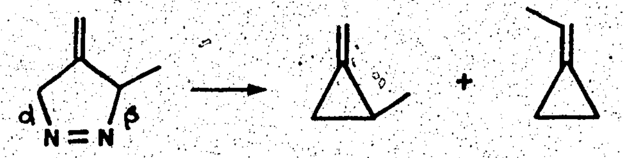
then this is the very same species produced from 57. However, if 177 is greater than 50% of the total intermediate species (18/37 th's) then it is not possible to account for the products from 56. Since the relative rate data in Table 36 show that the methyl groups have slowed down the absolute rate relative to 30 we may choose the C_5-N bond in 56 as α which will cleave to give rise to 178 as the major diazenyl species. In any event 178 has to give principally 58 *via* x- and z-closure.

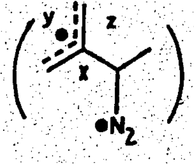
This can be rationalized by assuming that the C_3-N bond in 178 cleaves, prior to ring closure, to produce a Chesick intermediate (24) presumably because of the inductive effect of the methyls on C_3. In order to confirm this, synthesis and thermolysis of 179 is needed.



179

Similarly, the products from 68 (see Table 9) can be rationalized by considering 180 as the major diazenyl



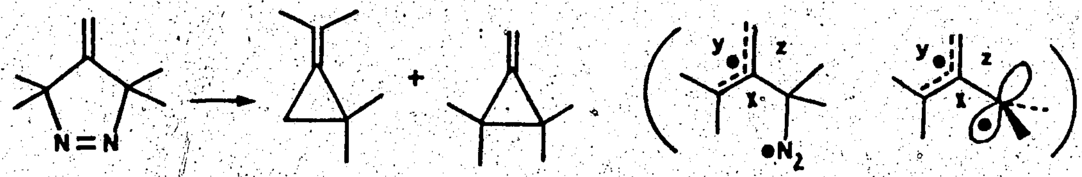


68 70 71 180

Observed 80% : 20%

species, which undergoes exclusive x- and z-closure to give 70 as the major product.

A possible Chesick intermediate, 182, which is produced from 181 can also explain the products from 62 if the magnitudes of x- and z-closure are comparable to one another.



62 63 64 181 182

Observed 48% : 52%

The products for the thermolysis of the 4-alkylidene-1-pyrazolines studied could qualitatively be rationalized and thus, this may be considered as additional evidence supporting the one-bond cleavage process for the thermolysis of 4-alkylidene-1-pyrazolines in general.

EXPERIMENTAL

All boiling points are uncorrected.

Gas chromatographic separations on a preparative scale were achieved on a Nester Faust Model 850 "Prepkromat" connected to an Elecktronik 18* strip chart contact recorder.

The proton nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer, a Varian HA-100 spectrometer and a Bruker WH-400 high field cryospectrometer. The deuterium nuclear magnetic resonance analyses were carried out on a Bruker HFX 90 spectrometer in the Fourier transform mode, and a Bruker WH-400 high field cryospectrometer.

Exact masses were determined on an A.E.I. MS9 mass spectrometer. The mass spectra analyses at low ionization potential were performed on an A.E.I. MS2 instrument.

The Fourier transform infrared spectra were obtained using a Nicolet 7199 Transform Interferometer.

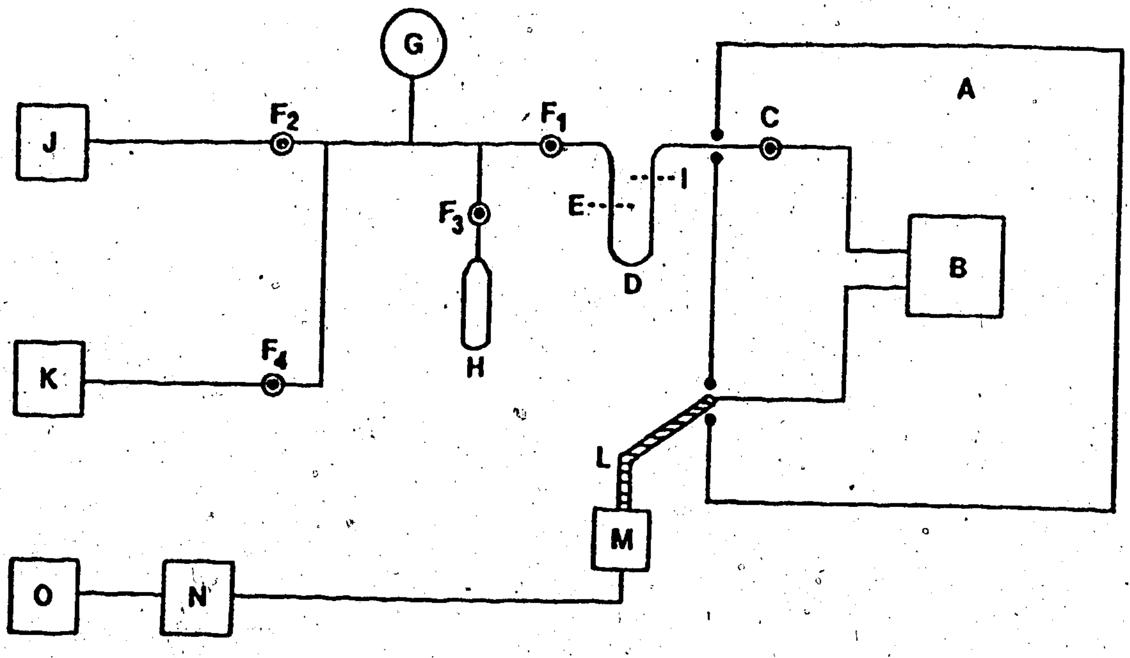
Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, University of Alberta.

A. Air Bath System

The kinetic experiments in the thermolysis of the 4-alkylidene-1-pyrazolines were conducted in the static vacuum system shown in the schematic diagram (Figure 49). Transducer emf was shown to be directly proportional to the pressure used (0-200 Torr) by plotting emf against the pressure as recorded on a mercury manometer. The system was equipped with Hoke stainless steel diaphragm and bellow valves. A 250-ml cylindrical type stainless steel reaction vessel (6.5 cm x 7.0 cm i.d.) was situated in a well-insulated air bath (69) with fast air circulation provided by a high-speed fan located at the bottom of the bath. The main heater, controlled by a Variac variable resistance, was used to bring the temperature to about 20°C below the desired operating temperature, and a secondary heater controlled by a Melabs Model CTCIA proportional temperature controller was used to maintain the desired temperature.

The temperature was measured by a Hewlett-Packard (HP) Model 2802A thermometer system calibrated against an ice-point reference. The temperature of the system was monitored by an HP Model 3470A digital display system, and the long term stability of the temperature was better than ±0.1°C.

The measurement of the transducer emf was performed using an HP Model 34701A DC voltmeter coupled to an HP Model 34721B BCD module which was connected to a National Semi-conductor LX 1702A transducer functional in the pressure range of 0-1 atm. The emf was monitored



A: air bath

B: reaction vessel

C: high temperature Hoke valve

D: injection port

E: point of sealing

F: Hoke valve

G: Pirani gauge

H: sample tube

I: cut

J: Pumps

K: argon tank

L: tubing with silicone oil

M: transducer

N: voltmeter

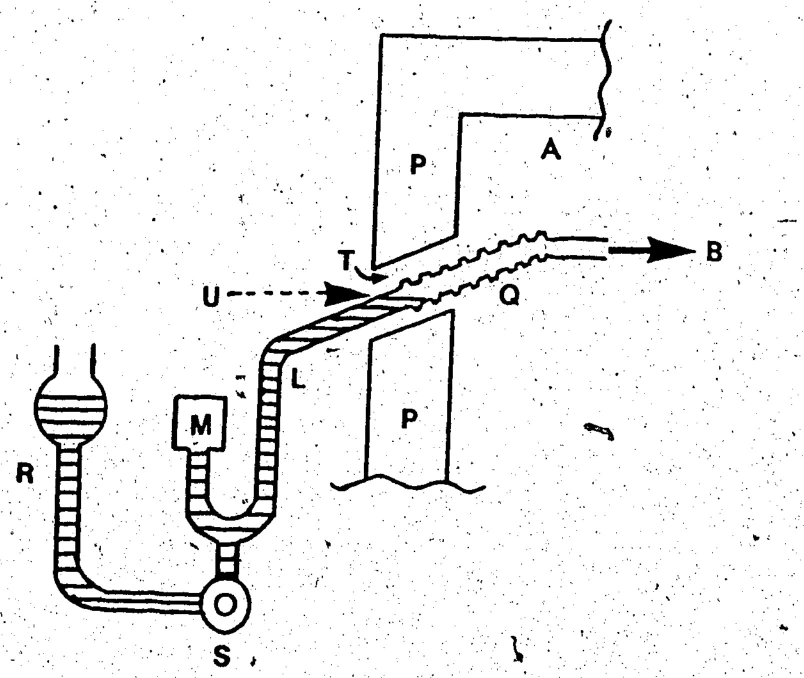
O: recorder

Figure 49. Schematic diagram of the apparatus used for the kinetic studies in the thermolysis of 4-alkylidene-1-pyrazolines.

by an HP Model 3470A digital display system and was then recorded as a function of time by an HP Model 5150A thermal printer. The stability of the emf was better than ±0.002 volt during the measurements.

In order to avoid condensation of the pyrazolines, the Pyrex tubing "L" (see Figure 70), connecting the reaction vessel (B) and the transducer (M), was filled with high boiling GE Silicon Oil 710. During thermolysis the oil level "U" was maintained just inside the insulating wall (P) of the bath (A). It should be noted that the oil slowly evaporates into the vacuum system, when the oil level is raised into the air bath (A). The oil level was adjusted by controlling the pressure in the vacuum system while the three-way vacuum stopcock (S) connected to the silicon oil reservoir (R) was open, and then by completely degassing the oil in the tubing "L" with the stopcock "S" closed. The Hoke model 4213Q6Y high temperature valve (C) located inside the air bath (A) as well as the silicon oil in the tubing "L" play a role of eliminating any dead-space effects during the measurements. The hole "T" in the insulating wall (P) was filled with glass wool to prevent loss of heat from the bath (A).

The vacuum manifold valves (F_1, F_2, F_3 and F_4) were Hoke Model 4251N6Y stainless steel bellows valves.



A: air bath

L: Pyrex tubing with silicon oil

M: transducer

R: reservoir of silicon oil

T: hole in the wall (P)

B: reaction vessel

P: insulating wall

Q: flexible stainless steel tubing

S: vacuum stopcock

U: oil level

Figure 70. Detailed schematic diagram of the silicon oil tubing system.

All the sample was injected into the reactor as gases over a period of 5-15 seconds depending upon the thermolysis temperatures and the reaction rates.

The method of operation of the apparatus (Figure 49) is described in the following paragraphs.

After evacuating the system using an oil pump with the valve "F_4" closed, the valves "C", "F_1", "F_2" and "F_3" were closed and dry argon was flushed through with the valves "F_4" open. A pure liquid sample (80 μl) was placed into the sample tube (H), and degassed at least three times according to a standard procedure. The degassed sample was then transferred into the bottom of the U-shaped Pyrex tubing (D) with the aid of liquid nitrogen. After sealing the tubing at "E" using a torch, the sample was injected as a gas into the reaction vessel (B) by plunging the tubing "D" into boiling water contained in a Dewar bottle while the valve "C" was open. The valve "C" was then closed 5-15 seconds later, and the recorder (O) was started at the same time. During the thermolysis, the left-over sample remaining in the line between the tubing "D" and the valve "C" was condensed at "D" by the aid of liquid nitrogen, and discarded by cutting the tubing at "I". This avoided any difficulties in the subsequent glass blowing. A new U-shaped Pyrex tubing was connected at "D" by glass blowing, and evacuated. It should be noted that two flexible stainless steel tubings were placed between "C" and "D" and between "D" and "F_1" to prevent breakage of the Pyrex tubing during the glass cutting and blowing operations. After the thermolysis, the products in the reactor (B) were transferred by evacuation to the short Pyrex tubing which had been connected at the bottom of "D". The short tubing was sealed using a torch, and the whole system was then evacuated with all the valves open (except "F_4") for at least half a day to be ready for the next run. In this way the apparatus was kept clean throughout more than one hundred runs, and the results were reproducible.

The nondeuterated and deuterated methylenecyclopropanes formed in the thermolysis of the corresponding 4-methylene-1-pyrazolines were collected in the following manner. After the thermolysis, the products trapped in the tubing "D" were transferred to a new tube or a breakseal at "H" which was cooled in liquid nitrogen, while warming the tubing "D" in an ice-water bath. In this way the tautomers of the pyrazolines would remain at "D". Chloroform-d or carbon tetrachloride was added to the products trapped in the tube at "H", and the resulting solution was used in the nmr analysis of the products. The products trapped in the breakseal at "H" were analyzed by mass spectrometry to determine the deuterium content of the pyrazolines.

B. Oil Bath System

Nondeuterated and deuterated 2-methylmethylenecyclopropanes and ethylidenecyclopropanes were obtained by the thermolysis of the corresponding 4-ethylidene-1-pyrazolines sealed in breakseals in a well insulated oil bath. The temperature of the oil bath was controlled by a Melabs Model CTCIA proportional temperature controller, and measured by an HP Model 2801A quartz thermometer calibrated by the National Bureau of Standards. The long term stability of the system was better than ±0.1°C.

The thermolyses of the pyrazolines were conducted in breakseals of approximately 80 ml volume. The initial pressure inside the breakseal was kept at approximately 1 atomosphere at the reaction temperature of 175.2°C by filling each breakseal with about 200 μl of the pure pyrazoline by vapor transfer. After thermolysis, the breakseal was put quickly into ice-water to quench the reaction. The contents of each breakseal were vapor transferred into the trap. The trapped products were dissolved in 300 μl benzene or in chloroform, and separated by preparative gc.

The gas chromatographic separations of the products were performed by injecting up to 100 μl of the sample solution into a 50 ft x 0.25 in. column packed with 20% SF-96 on Chromosorb W. The column was kept at 60°C and the injection port at 100°C with a helium flow rate of

100 ml/min. The retention times were 24 min. for 2-methylmethylenecyclopropanes and 34 min. for ethylidenecyclopropanes. The separated products were then analyzed by nmr.

C. Preparations

4-Methylene-1-pyrazoline (30) from Allene and Diazomethane

The procedure was essentially that of Crawford and Cameron (10a). A solution of diazomethane (6 g, 0.14 mol) in absolute ether (400 ml) was prepared from N-methyl-N-nitroso-p-toluenesulfonamide by the method of de Boer and Backer (70) and carefully distilled at 33-34°C to give a concentrated solution of diazomethane (60 ml) (35). Allene (30 ml) was then condensed into a 200 ml pressure bottle cooled in a Dry Ice-acetone bath. The solution of diazomethane was added to the pressure bottle, it was sealed and allowed to warm to room temperature. After a day or two the yellow color disappeared, the bottle was recooled, opened, and the excess allene and ether were distilled under atmospheric pressure. The residue distilled to give the product (7.5 g, 92 mmol, 65% yield), bp 25°C/6.0 Torr (lit. 49-50°C/33 Torr).

The 60 MHz ^{1}Hmr spectrum δTMS (benzene-d_6) showed: 4.47 (triplet, J = 2.3 Hz, 4H) and 4.70 (pentet, J = 2.3 Hz, 2H).

4-Methylene-1-pyrazoline-3,3-d_2 (42)

The procedure was similar to that described above for the synthesis of 4-methylene-1-pyrazoline from allene and diazomethane. A solution of diazomethane-d_2 (3.2 g, 73 mmol) in absolute ether (30 ml) was prepared by the method of Gassman and Greelee (71) and reacted with allene (15 ml) to give the product (2.9 g, 34 mmol, 47% yield).

The 100 MHz ^{1}Hmr spectrum δTMS (benzene-d_6) showed: 4.47 (triplet, J = 2.3 Hz, 2H) and 4.70 (pentet, J = 2.3 Hz, 2H); and indicated 97 ± 1% isotopic purity. The mass spectrum indicated 97.0 ± 0.1% isotopic purity (D_0 = 0.6, D_1 = 4.8, D_2 = 94.6).

4-Methylene-1-pyrazoline-3,3,6,6-d_4 (43)

The procedure was similar to that described previously for the synthesis of 4-methylene-1-pyrazoline from allene and diazomethane. Allene-d_4 was prepared from hexachloropropene according to the method of Morse and Leitch (72) with the modification that most of the propyne-d_4 was removed by passing the mixture of allene-d_4 and propyne-d_4 through two portions of an ammonical silver nitrate solution (35) stirred vigorously by a magnetic stirrer. A solution of diazomethane (3 g, 71 mmol) in absolute ether (30 ml) reacted with allene-d_4 (5 g, 114 mmol) to give the product (2.7 g, 32 mmol, 45% yield).

The 100 MHz ^{1}Hmr spectrum δTMS (benzene-d_6) showed: 4.47 (singlet); and indicated 97 ± 1% isotopic purity. The mass spectrum indicated 97.1 ± 0.1% isotopic purity (D_0 = 0.3, D_1 = 0.2, D_2 = 1.6, D_3 = 6.7, D_4 = 91.2).

4-Methylene-1-pyrazoline-3,3,5,5,6,6-d_6 (44)

The procedure was similar to that described previously for the synthesis of 4-methylene-1-pyrazoline from allene and diazomethane. A solution of diazomethane-d_2 (3.2 g, 73 mmol) in absolute ether (30 ml) reacted with allene-d_4 (5 g, 114 mmol) to give the product (2.7 g, 31 mmol, 42% yield).

The mass spectrum indicated 96.8 ± 0.1% isotopic purity (D_0 = 0, D_1 = 0, D_2 = 0.3, D_3 = 0.1, D_4 = 1.5, D_5 = 14.4, D_6 = 83.7).

5-Nitro-5-(hydroxymethyl)-2-phenyl-1,3-dioxan (108)

The procedure was essentially that of Scattergood and MacLean (38). Tris-(hydroxymethyl)nitromethane (755 g, 5.0 mol) was added to distilled water (500 ml) and methylcellosolve (500 ml) in a 3-ℓ three-necked round-bottom flask fitted with a reflux condenser, a dropping funnel and a mechanical stirrer. Benzaldehyde 531 g, 5.0 mol) and conc. hydrochloric acid (400 ml) were added to the flask. The reaction mixture was kept at room temperature with mechanical stirring for 3 days.

The solid products were filtered, washed with distilled water until neutral and unreacted aldehyde had been removed; and air-dried. Recrystallization of the crude product (886 g) from ethanol and water was followed by drying over phosphorous pentoxide in a vacuum dessicator to give a white crystalline product (850 g, 3.56 mol, 7.12% yield), mp 124-125°C (lit. 124.8°C).

The 100 MHz ^{1}Hmr spectrum δTMS (DMSO-d_6) showed: 3.69 (doublet, J = 12 Hz, 2H), 4.18 (doublet of slight multiplets, J = 12 Hz, 2H), 4.77 (doublet of slight multiplets, J = 12 Hz, 2H), 5.54 (triplets, J = 6 Hz, 1H), 5.63 (singlet, 1H) and 7.37 (singlet, 5H).

5-Amino-5-(hydroxymethyl)-2-phenyl-1,3-dioxan (109)

The procedure used was essentially that of Marei and Raphael (39). A solution of 5-nitro-5-(hydroxymethyl)-1,3-dioxan (57.0 g, 0.24 mol) in absolute ethanol (1.0 l) was shaken with a small quantity of Raney-nickel (73) and filtered. The filtrate was stirred vigorously with fresh Raney-nickel (10 g) under 1,500 psi of hydrogen at 80°C for 5 hr in an autoclave. Filtration of the solution and evaporation of the solvent using a rotatory evaporator was followed by trituration of the residue with skellysolve B to give crude product. The crude product recrystallized in needles from ethyl acetate to give a white solid product (48.0 g, 0.23 mol, 95.8% yield), mp 117.5-118.5°C (lit. 117-118°C).

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 2.67 (singlet, 3H), 3.36 (singlet, 2H), 3.88 (singlet, 4H), 5.40 (singlet, 1H) and 7.38 (complex multiplet, 5H).

5-Oxo-2-phenyl-1,3-dioxan (111)

The method of synthesis by Marei and Raphael (39) was modified to improve the yield considerably and to achieve a one-step synthesis of the product without the intermediate formation of 5,5-dihydroxy-2-phenyl-1,3-dioxan. A mixture of 5-amino-5-(hydroxymethyl)-2-phenyl-1,3-dioxan (70.6 g, 0.338 mol) and pH 6 buffer solution (2.0 l) (74) in a 3-l round-bottomed flask was stirred mechanically at room temperature. When sodium metaperiodate (72.3 g, 0.338 mol) was added all at once with vigorous stirring, the reaction mixture initially became homogeneous, and then a white solid began to appear. After 15 min of stirring, the product was extracted with dry dichloromethane (3 x 2.0 l), the extract was dried over anhydrous sodium sulfate and the solvent was evaporated using a rotatory evaporator at less than 20°C. A slightly yellow solid (55.7 g) was produced. The solid was dissolved in boiling dry pentane (6.0 l). Decantation of the clear solution was followed by cooling and evaporation of the solvent using a rotatory evaporator at less than 20°C to give a white solid (50.7 g, 0.285 mol, 84.3%

yield) which was pure, judging from the ^{1}Hmr spectrum, and mp 68-69°C (lit. 69-71°C). The product should be stored in a freezer below -20°C to prevent it from decomposing slowly into a yellow oil. The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 4.47 (singlet, 4H), 5.87 (singlet, 1H) and 7.42 (complex multiplet, 5H).

Methyltriphenylphosonium Bromide

The procedure used was similar to that of Wittig and U. Schoellkopf (75). In a 200 ml pressure bottle, triphenylphosphine (55 g, 0.21 mol) was dissolved in dry benzene (50 ml). The solution was cooled in an ice-salt bath and methyl bromide (33.3 g, 0.351 mol) was added. The bottle was then sealed and kept at room temperature for a day with occasional shaking. After the bottle ha[illegible]oled in a Dry Ice-acetone bath for 30 min., it[illegible]ed and the white solid was filtered. The sol[illegible] ground to a fine powder and washed with hot benz[illegible] (0.5 l each) until the washings became colorless. The p[illegible]uct recrystallized from dichloromethane-ether and d[illegible]d at 100°C under high vacuum in an electrical vacuu[illegible] oven over phosphorous pentoxide for 2 days to give a white-colored product (71 g, 0.20 mol, 95.2% yield). The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 3.26 (doublet, J = 13.5 Hz, 3H) and 7.72 (complex multiplet, 15H).

5-Methylene-2-phenyl-1,3-dioxan

The procedure was a modification of that of Malloy, Hedges and Fisher (40). A 3-l three-necked round-bottomed flask was fitted with a reflux condenser, a dropping funnel, a mechanical stirrer and a gas inlet tube. A gentle flow of dry argon through the apparatus was maintained throughout the reaction. Dry 1,2-dimethoxyethane (1.2 l, freshly distilled three times from lithium aluminum hydride) and methyltriphenylphosphonium bromide (151 g, 0.423 mol) were added to the flask which was cooled in an ice-water bath. While stirring vigorously, a hexane solution (166.5 ml) of 2.29 M n-butyllithium (76) was added dropwise through a dropping funnel. The temperature of the reaction mixture was then raised to 65°C over a period of 2 hr and maintained at this temperature for 3 hr to give a yellowish or brownish solution of methylenetriphenylphosphorane. This solution was cooled in an ice-water bath and 5-oxo-2-phenyl-1,3-dioxan (60.9 g, 0.342 mol; freshly purified from n-pentane before use) in dry 1,2-dimethoxyethane (0.6 l) was added dropwise through a dropping funnel while stirring vigorously. The temperature of the reaction mixture was then gradually increased over 3 hr until the solvent began to reflux. After refluxing for a day, the reaction mixture was cooled to room temperature. Acetone (75 ml) was added and the mixture was stirred for 30 min. This was followed by the addition of ether (1.5 l) and stirring was continued for a further 30 min. Solids were removed by gravity-filtration and the solvents including benzene and 1,2-dimethoxyethane were almost completely evaporated using a rotatory evaporator. The residual solution was extracted with n-pentane (3 x 0.75 l). After evaporating the n-pentane from the combined extracts, the residual solution distilled at reduced pressure to give the product (49.2 g. 0.280 mol, 81.9% yield), bp 68-69°C/0.15 Torr (lit. 76-78°C/3 Torr) (77).

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 4.47 (triplet, J = 1.3 Hz, 4H), 4.94 (pentet, J = 1.3 Hz, 2H), 5.57 (singlet, 1H) and 7.37 (complex multiplet, 5H).

Methyl-d_3-triphenylphosphonium bromide

The procedure was a slight modification of that of Malloy, Hedges and Fisher (40). Methyltriphenylphosphonium bromide (150 g, 0.420 mol) was dissolved in deuterium oxide (>99 at % D; 300 ml) by warming, and the solution was filtered. To the filtrate, 1% sodium deuteroxide solution (17 ml; prepared by adding 0.5 g of sodium to 50 ml of deuterium oxide under nitrogen) was added with stirring. After stirring for 10 min, the solution was extracted immediately with distilled dichloromethane (3 x 250 ml). The combined dichloromethane layers were separated, dried over anhydrous sodium sulfate, and concentrated using a rotatory evaporator to give a light yellow-colored solid. This solid was subjected to the same reaction conditions twice more. Recrystallization of the solid from dichloromethane-ether and drying at 100°C under high vacuum over phosphorous pentoxide for 2 days gave a white-colored product (114 g, 0.317 mol, 75.5% yield).

The 100 MHz ^{1}Hmr spectrum ($CDCl_3$) indicated greater than 97 at % D at the methyl group.

5-Methylene-2-phenyl-1,3-dioxan-7,7-d_2 (112)

The procedure used was that described previously for the synthesis of 5-methylene-2-phenyl-1,3-dioxan from 5-oxo-2-phenyl-1,3-dioxan. From methyl-d_3-triphenylphosphonium bromide (101.4 g, 0.282 mol) in dry 1,2-dimethoxyethane (0.8 l), a hexane solution of 2.29 M n-butyllithium (111 ml, 0.254 mol) and 5-oxo-2-phenyl-1,3-dioxan (40.6 g, 0.228 mol) in dry 1,2-dimethoxyethane (0.4 l), was obtained a colorless liquid product (32.5 g, 0.183 mol, 80.2% yield).

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 4.47 (singlet, 4H), 5.57 (singlet, 1H) and 7.37 (complex multiplet, 5H); and indicated 95 ± 1% isotopic purity. The mass spectrum indicated 95 ± 1% isotopic purity (D_0 = 0.9, D_1 = 7.9, D_2 = 91.2). The 13.6 MHz ^{2}Hmr spectrum (CCl_4) indicated >99.8% of total deuterium at the exo-methylene position.

Diethyl Methylenemalonate

The procedure was essentially that of Bachman and Tanner (41). Paraformaldehyde (120 g), malonic ester (160 g, 1.0 mole), copper acetate (10 g) and potassium acetate (10 g) were added to glacial acetic acid (800 g) in a 2-l round-bottomed flask. The mixture was heated with stirring until clear, and then for an hour longer. It was distilled until the boiling point reached 80°C at 35 Torr. At this point, the contents of the distilling flask began to thicken to a paste. The receiver was changed, and the distillation continued. The blue-colored paste foamed and appeared to decompose, the product being evolved during the decomposition. When the paste turned dark brown, distillation was discontinued. The greenish yellow distillate was redistilled to give almost pure product (75 g, 0.436 mol , 43.6% yield), bp 200-212°C at atmospheric pressure (lit. 205-215°C). The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 1.33 (triplet, J = 7.0 Hz, 6H), 4.34 (quartet, J = 7.0 Hz, 4H) and 6.57 (singlet, 2H).

5,5-Dicarbethoxy-2-norbornene (118)

Freshly prepared cyclopentadiene (60.0 g, 0.910 mol) was added slowly to diethyl methylenemalonate (110.0 g, 0.640 mol) which had been cooled in an ice-water bath.

The reaction mixture was warmed to room temperature and kept at this temperature for an hour. It was then heated to 100°C over a period of 1 hr and kept at this temperature for 3 hr. Distillation of the mixture gave a colorless liquid (122.6 g, 0.516 mol, 80.6%), bp 107-108.5°C/2.5 Torr. Exact mass calcd. for $C_{13}H_{18}O_4$: 238.2828; found: 238.2206.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61; O, 26.86. Found: C, 65.34; H, 7.75; O, 26.91.

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 1.21 (triplet, J = 7.3 Hz, 3H), 1.23 (triplet, J = 7.3 Hz, 3H), 1.57 (multiplet, 2H), 2.04 (multiplet, 2H), 2.89 (singlet, 1H), 3.37 (singlet, 1H), 4.10 (quartet, J = 7.3 Hz, 2H), 4.17 (quartet, J = 7.3 Hz, 2H), 5.95 (multiplet, 1H) and 6.24 (multiplet, 1H). The i.r. spectrum ν_{max} 1733 cm^{-1} (C=O).

5,5-Bis-(hydroxymethyl)-2-norbornene

The procedure was an adaptation of that of Moffet (78). In a 2-l three-necked round-bottomed flask fitted with a reflux condenser, a dropping funnel, a gas inlet tube and a mechanical stirrer, pulverized lithium aluminum hydride (10.63 g, 0.280 mol) in absolute ether (600 ml) was refluxed overnight in an oil bath under a gentle flow of dry argon. After the oil bath had been removed, 5,5-dicarbethoxy-2-norbornene (54.7 g, 0.230 mol) in dry ether (100 ml) was added with vigorous stirring at such a rate that the solvent refluxed gently. When the initial reaction had subsided, the reaction mixture was refluxed for 4 hr longer, and cooled. Distilled water (12 ml), 15% sodium hydroxide solution (12 ml) and distilled water (36 ml) were added successively to destroy the excess lithium aluminum hydride, and the mixture was stirred for 5 hr. Dry ether (500 ml) was added, and the solution was warmed almost to boiling, since the product is quite soluble in hot ether but not in cold. After filtration by vacuum, the residue was extracted with hot ether (2 x 0.5 l) and the combined ethereal solutions were evaporated to dryness on a rotatory evaporator under reduced pressure (0.1 Torr) overnight. Recrystallization from hot benzene (ca. 300 ml) and washing with cold skelly B gave the product (28.0 g, 0.182 mol, 79.1% yield) in needles, mp 112-112.5°C (77,42).

The 100 MHz ^{1}Hmr spectrum δTMS (DMSO-d_6) showed: 0.46-1.60 (multiplet, 4H), 2.59 (slight multiplet, 1H), 2.61 (slight multiplet, 1H), 3.18 (multiplet, 2H), 3.54 (multiplet, 2H), 4.20 (triplet, J = 5.0 Hz, 1H), 4.44 (triplet, J = 5.0 Hz, 1H) and 6.08 (slight multiplet, 2H).

5,5-Bis-(hydroxymethyl-d_2)-2-norbornene (119)

The procedure was that described previously for the synthesis of 5,5-bis-(hydroxymethyl)-2-norbornene from

5,5-dicarbethoxy-2-norbornene. From lithium aluminum deuteride (13.5 g, 0.321 mol; minimum isotopic purity: 95 atom % D from Merck, Sharp & Dohme, Canada, Ltd.) and 5,5-dicarbethoxy-2-norbornene (63.0 g, 0.264 mol), was obtained a white solid product (34.3 g, 0.216 moles, 81.8% yield), mp 111.5-112.5°C.

The 100 MHz ^{1}Hmr spectrum δTMS (DMSO-d_6) showed: 0.46-1.60 (multiplet, 4H), 2.59 (slight multiplet, 1H), 2.61 (slight multiplet, 1H), 4.16 (singlet, 1H), 4.40 (singlet, 1H) and 6.08 (slight multiplet, 2H).

2-Methylene-1,3-propanediol

(a) From 5-methylene-2-phenyl-1,3-dioxan

5-Methylene-2-phenyl-1,3-dioxan (45.0 g, 0.256 mol) in methanol (1.5 l) was added to ammonium chloride (240 g) in distilled water (580 ml) in a 3-l three-necked round-bottomed flask fitted with a reflux condenser and a mechanical stirrer. The mixture was vigorously stirred at 40°C for three days and then neutralized with 5% sodium bicarbonate solution. After evaporation of solvents using a rotatory evaporator, acetone (1.0 l) was added to the residue. The solid was filtered and the solvents were evaporated using a rotatory evaporator. The residue was extracted with acetone (0.5 l) and the solvent was evaporated completely under reduced pressure (1 Torr) at room temperature. The residue was then extracted with ether (3 x 0.4 l) and the extracts were dried over anhydrous magnesium sulfate. The ether was evaporated to give yellowish crude product. The crude product was washed with freshly distilled chloroform (3 x 5 ml), and kept at room temperature under reduced pressure (0.35 Torr) overnight. Distillation of the remaining solution gave a colorless liquid (19.2 g, 0.218 mol, 85.2% yield), bp 96.5-97.5°C/3.5 Torr (lit. 127-129°C/32 Torr) (79). The 100 MHz ^{1}Hmr spectrum δTMS (DMSO-d_6) showed: 3.91 (doublet of triplets; J = 5.5 Hz, J = 1.3 Hz; 4H), 4.68 (triplet, J = 5.5 Hz, 2H) and 4.97 (pentet, J = 1.3 Hz, 2H).

(b) From 5,5-bis-(hydroxymethyl)-2-norbornene

The procedure was an adaptation of that of Corey and Suggs (42). A 22 cm quartz column (2.54 cm i.d.) was packed with Pyrex beads which were heated to 480-520°C by a heating tape wrapped around the column. The tape was covered by an outer Pyrex jacket. The temperature was measured by an iron-constantan thermocouple and a potentiometer (Minneapolis-Honeywell Reg. Co.). To the column was added neat 5,5-bis-(hydroxymethyl)-2-norbornene (25.0 g, 0.162 mol) in small portions. Argon was passed through the apparatus so that the contact time of the vaporized reagent with the column was 7-10 sec. The crude product was collected in two successive traps cooled to -78°C under slightly reduced pressure

(500 Torr). Water was added to the crude product, and the aqueous solution was washed once with n-pentane. After concentration of the aqueous extract using a rotatory evaporator, distillation gave the colorless liquid (10.1 g, 0.115 mol, 70.8% yield).

2-(Methylene-d_2)-1,3-propanediol (113)

The procedure was that described previously for the synthesis of 2-methylene-1,3-propanediol from 5-methylene-2-phenyl-1,3-dioxan. 5-Methylene-2-phenyl-1,3-dioxan-7,7-d_2 (31.1 g, 0.175 mol) in methanol (1.0 l) and ammonium chloride (165 g) in distilled water (0.4 l) were stirred at 40°C for 3 days to give the product (13.0 g, 0.145 mol, 82.9% yield).

The 100 MHz ^{1}Hmr spectrum δTMS (DMSO-d_6) showed: 3.91 (doublet, J = 5.5 Hz, 4H) and 4.66 (triplet, J = 5.5 Hz, 2H; and indicated 95 ± 1% isotopic purity.

2-Methylene-1,3-propanediol-1,1,3,3-d_4 (120)

The procedure was that described previously for the synthesis of 2-methylene-1,3-propanediol from 5,5-bis-(hydroxymethyl)-2-norbornene. 5,5-Bis-(hydroxymethyl-d_2)-2-norbornene (32.9 g, 0.208 mol) was thermolyzed to give the product (14.0 g, 0.152 mol, 73.1% yield).

The 100 MHz ^{1}Hmr spectrum δTMS (DMSO-d_6) showed: 4.64 (singlet, 2H) and 4.97 (singlet, 2H); and indicated

96 ± 1% isotopic purity.

3-Chloro-2-(chloromethyl)propene (124)

The procedure was a modification of that of Hooz and Gilani (43). Freshly prepared dry triphenylphosphine (dried at room temperature at 0.2 Torr overnight; 217.0 g, 0.827 mol) was added to a mechanically stirred solution of 2-methylene-1,3-propanediol (28.0 g, 0.318 mol) in dry tetrahydrofuran (250 ml; distilled twice from lithium aluminum hydride) and carbon tetrachloride (580 ml; distilled from phosphorous pentoxide) in a 2-l three-necked round-bottomed flask fitted with a mechanical stirrer, a reflux condenser and a gas inlet tube. A gentle flow of dry argon through the apparatus was maintained throughout the reaction. The reaction mixture was then refluxed for approximately 2 hr, until a light reddish solution formed and a large quantity of white solid appeared. n-Pentane (1.5 l) was added, and the reaction mixture was stirred for 10 min. The solid was filtered and washed with n-pentane (500 ml). The solvents were slowly removed from the combined n-pentane solutions by means of distillation below 37°C under reduced pressure (40 Torr). To the residue, n-pentane (200 ml) was added, and the mixture was stirred. The solid was filtered, and the filtrate distilled below 37°C under reduced pressure (40 Torr) to remove the solvent. Distillation of the residue yielded the product (20.3 g, 0.162 mol, 50.9% yield), bp 57.0-58.0°C/40 Torr (lit. 137-138°C/756 Torr) (80).

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 4.19 (triplet, J = 0.6 Hz, 4H) and 5.32 (pentet, J = 0.6 Hz, 2H).

3-Chloro-2-(chloromethyl)propene-1,1-d_2 (114)

The procedure was that described previously for the synthesis of 3-chloro-2-(chloromethyl)propene from 2-methylene-1,3-propanediol. 2-(Methylene-d_2)-1,3-propanediol (12.6 g, 0.140 mol) in dry tetrahydrofuran (110 ml), carbon tetrachloride (255 ml) and freshly purified triphenylphosphine (95.5 g, 0.365 mol) reacted to give the product (9.3 g, 0.0732 moles, 52.3% yield).

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 4.19 (singlet); and indicated 95 ± 1% isotopic purity. The mass spectrum indicated 94 ± 1% isotopic purity (D_0 = 1.8, D_1 = 9.0, D_2 = 89.2). The 13.6 MHz ^{2}Hmr spectrum (CCl_4) indicated >99.8% of total deuterium at the exo-methylene position.

3-Chloro-2-(chloromethyl-d_2)-propene-3,3-d_2 (121)

The procedure was that described previously for the synthesis of 3-chloro-2-(chloromethyl)propene from 2-methylene-1,3-propanediol. 2-Methylene-1,3-propanediol-1,1,3,3-d_4 (13.2 g, 0.143 mol) in dry tetrahydrofuran

(113 ml), carbon tetrachloride (262 ml) and freshly purified triphenylphosphine (98.0 g, 0.374 mol) reacted to give the product (9.2 g, 71.3 mmol, 49.9% yield).

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 5.32 (singlet); and indicated 96 ± 1% isotopic purity. The mass spectrum indicated 96 ± 1% isotopic purity (D_0 = 0, D_1 = 0, D_2 = 6.5, D_3 = 1.6, D_4 = 91.9) based on the molecular ion peak.

1,2-Dicarbethoxy-4-methylenepyrazolidine (125)

The procedure was adapted from that used by Rubottom and Chabala (44). A solution of *sym*-dicarbethoxyhydrazine (15.2 g, 86.4 mmol; purified by recrystallization from 95% ethanol and drying under high vacuum) (81) in hexamethylphosphoramide (HMPA; 100 ml; dried over Molecular Sieves 4A) was placed in a 500 ml three-necked round-bottomed flask fitted with a reflux condenser, a mechanical stirrer and a gas inlet tube. A gentle flow of dry argon was maintained in the apparatus during the reaction. The reaction mixture was cooled in an ice-salt bath. Sodium hydride (57% dispersion, 3.64 g, 86.4 mmol) which had been washed three times to remove protective oil, was added to the reaction mixture in small portions with the aid of n-pentane. The mixture was allowed to warm to room temperature, and stirred mechanically for 6 hr. After cooling in an ice-salt bath, 3-chloro-2-(chloromethyl)propene (10.5 g, 84.0 mmol) was added dropwise.

Again, the mixture was allowed to warm to room temperature and kept at this temperature for 3 days. After cooling in an ice-salt bath, sodium hydride (57% disperions; 3.6 g, 85.5 mmol; washed with n-pentane) was slowly added in small portions with the aid of n-pentane. Once more, the reaction mixture was allowed to warm to room temperature and kept at this temperature for a day. After cooling in an ice-water bath, distilled water (150 ml) was slowly added, and the mixture was stirred vigorously for 30 min. Extraction of the product with absolute ether (5 x 200 ml), and evaporation of the solvent using a rotatory evaporator followed by distillation of the residue yielded the liquid product (13.3 g, 58.3 mmol, 69.4% yield), bp 88-89°C/0.08 Torr. Exact mass calcd. for $C_{10}H_{16}O_4N_2$: 228.2474; found: 228.2112.

Anal. Calcd. for $C_{10}H_{16}O_4N_2$: C, 52.62; H, 7.07; O, 28.04; N, 12.27. Found: C, 52.91; H, 7.11; O, 27.81; N, 12.17.

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 1.20 (triplet, J = 7.3 Hz, 6H), 4.15 (quartet + broad peak, J = 7.3 Hz, 8H; ester CH_2 + ring methylene) and 5.04 pentet, J = 2.3 Hz, 2H). The i.r. spectrum ν_{max} 1709 and 1733 cm^{-1} (C=O).

1,2-Dicarbethoxy-4-methylenepyrazolidine-6,6-d_2 (**115**)

The procedure was that described previously for the synthesis [illegible] 2-dicarbethoxy-4-methylenepyrazolidine from 3-c[illegible]chloromethyl)propene. A solution of *sym*-dicar[illegible]ydrazine (12.1 g, 68.8 mmol) in hexamet[illegible]phos[illegible]ide (80 ml), sodium hydride (57% dispersion [illegible].80 [illegible] 137.7 mmol) and 3-chloro-2-(chloromethyl)-prope[illegible]-1[illegible]-d_2 (8.5 g, 66.9 mmol) reacted to give the produc[illegible].9 g, 47.4 mmol, 70.9% yield).

T[illegible]00 MHz ^{1}Hmr apsectrum δTMS ($CDCl_3$) showed: 1.20 (t[illegible]let, J = 7.3 Hz, 6H) and 4.16 (quartet + broad peak, J [illegible]7.3 Hz, 8H; ester CH_2 + ring methylene); and indi[illegible]ed 94 ± 1% isotopic purity. The mass spectrum indicated 94.8 ± 0.1% isotopic purity (D_0 = 0.7, D_1 = 9.1, D_2 = 90.2) based on the molecular ion peak. The 13.6 MHz ^{2}[illegible] spectrum (CCl_4) indicated >99.8% of total deuterium [illegible] the exo-methylene position.

1,2-Dicarbethoxy-4-methylenepyrazolidine-3,3,5,5-d_4 (**122**)

The procedure was that described previously for the synthesis of 1,2-dicarbethoxy-4-methylenepyrazolidine from 3-chloro-2-(chloromethyl)propene. A solution of *sym*-dicarbethoxyhydrazine (12.1 g, 68.8 mmol) in hexamethylphosphoramide (80 ml), sodium hydride (57% dispersion, 5.80 g, 137.7 mmol) and 3-chloro-2-(chloromethyl-d_2)-propene-3,3-d_2 (8.6 g, 66.7 mmol) reacted to give the product (11.1 g, 47.8 mmol, 71.7% yield).

The 100 MHz ^{1}Hmr spectrum δTMS ($CDCl_3$) showed: 1.20 (triplet, J = 7.3 Hz, 6H), 4.15 (quartet, J = 7.3 Hz, 4H, ester CH_2), and 5.04 (singlet, 2H); and indicated 95 ± 1% isotopic purity. The mass spectrum indicated 95 ± 1% isotopic purity (D_0 = 0, D_1 = 0, D_2 = 10.1, D_3 = 1.8, D_4 = 88.1) based on the molecular ion peak.

4-Methylenepyrazolidine hydrochloride (127)

The procedure was an adaptation of that of Crawford and Tokunaga (10a). Ethylene glycol (70 ml), distilled water (17 ml) and potassium hydroxide (16.7 g, 300 mmol) were added to a 250 ml three-necked round-bottomed flask fitted with a reflux condenser, a magnetic stirrer and a gas inlet tube. A gentle flow of dry argon was maintained in the apparatus throughout the reaction. 1,2-Dicarbethoxy-4-methylenepyrazolidine (10.1 g, 44.2 mmol) was added to the solution. The reaction mixture was heated at 110°C for 8 hr and distilled at approximately 55°C/0.12 Torr. The distillate was trapped in a flask cooled in a Dry Ice-acetone bath. The flask was transferred to an ice-salt bath and conc. hydrochloric acid (4.4 ml, 53.0 mmol) was added. The solvent was removed using a rotatory evaporator. The residual solution was distilled and the fraction distilling below 50°C/0.12 Torr was collected. It solidified in the distilling flask and was ground to a fine powder. After washing with dry ether, the solid was dried over phosphorous pentoxide under high vacuum to give the product (4.7 g, 39.0 mmol, 88.2% yield), mp 112-114°C.

Anal. Calcd. for $C_4H_9N_2Cl$: C, 39.85; H, 7.52; N, 23.23; Cl, 29.40. Found: C, 39.80; H, 7.56; N, 22.97; Cl, 29.67.

The 60 MHz ^{1}Hmr spectrum δ external TMS (D_2O) showed: 4.04 (triplet, J = 2.3 Hz, 4H), 4.88 (singlet, 3H) and 5.43 (J = 2.3 Hz, 2H).

4-Methylenepyrazolidine-6,6-d_2 hydrochloride (116)

The procedure was that described previously for the synthesis of 4-methylenepyrazolidine hydrochloride from 1,2-dicarbethoxy-4-methylenepyrazolidine. Ethylene glycol (70 ml), distilled water (17 ml), potassium hydroxide (16.4 g, 295 mmol), 1.2-dicarbethoxy-4-methylenepyrazolidine-6,6-d_2 (10.0 g, 43.5 mmol), and conc. hydrochloric acid (4.3 ml, 51.8 mmol) reacted to give the product (4.8 g, 39.2 mmol, 90.1% yield).

The 60 MHz ^{1}Hmr spectrum, δ external TMS (D_2O) showed: 4.04 (singlet, 4H) and 4.88 (singlet, 3H); and indicated 94 ± 1% isotopic purity.

4-Methylenepyrazolidine-3,3,5,5-d_4 hydrochloride (123)

The procedure was that described previously for the synthesis of 4-methylenepyrizolidine hydrochloride from

1,2-dicarbethoxy-4-methylenepyrazolidine. Ethylene glycol (70 ml), distilled water (17 ml), potassium hydroxide (16.9 g, 303 mmol), 1,2-dicarbethoxy-4-methylenepyrazolidine-3,3,5,5,-d_4 (10.4 g, 44.8 mmol) and conc. hydrochloric acid (4.5 ml, 54.2 mmol) reacted to give the product (5.0 g, 40.2 mmol, 89.7% yield).

The 60 MHz ^{1}Hmr spectrum, δ external TMS (D_2O) showed: 4.88 (singlet, 3H) and 5.43 (singlet, 2H); and indicated 95 ± 1% isotopic purity.

4-Methylene-1-pyrazoline (30) from 4-methylenepyrazolidine hydrochloride (127)

The procedure was adapted from that used by Crawford and Tokunaga (10a). 4-Methylenepyrazolidine hydrochloride (4.4 g, 36.5 mmol) was slowly added to a well stirred slurry of red mercuric oxide (50 g) and anhydrous sodium sulfate (50 g) in absolute ether (100 ml). The reaction mixture was mechanically stirred for 15 hr at room temperature. Filtration of the solid and removal of the ether at room temperature and reduced pressure were followed by rapid distillation of the residue at 25°C/1 Torr with the receiver being cooled in a Dry Ice-acetone bath. The distillate redistilled to give a colorless liquid (1.4 g, 17.1 mmol, 46.8% yield), bp 25°C/6.0 Torr (lit. 49-50°/33 Torr).

The 60 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 4.47 (triplet, J = 2.3 Hz, 4H) and 4.70 (pentet, J = 2.3 Hz, 2H).

4-Methylene-1-pyrazoline-6,6-d_2 (107)

The procedure was that described previously for the synthesis of 4-methylene-1-pyrazoline from 4-methylenepyrazolidine hydrochloride. 4-Methylenepyrazolidine-6,6-d_2 hydrochloride (4.4 g, 36.7 mmol), red mercuric oxide (50 g) and anhydrous sodium sulfate (50 g) in absolute ether (100 ml) reacted to give the product (1.4 g, 16.7 mmol, 45.5% yield).

The 100 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 4.47 (singlet); and indicated 95 ± 1% isotopic purity. The mass spectrum indicated 95.0 ± 0.1% isotopic purity (D_0 = 0.4, D_1 = 9.2, D_2 = 90.4). The 13.6 MHz ^{2}Hmr spectrum (CCl_4) indicated >99.8% of total deuterium at the exomethylene position.

4-Methylene-1-pyrazoline-3,3,5,5-d_4 (46)

The procedure was that described previously for the synthesis of 4-methylene-1-pyrazoline from 4-methylenepyrazolidine hydrochloride. 4-Methylenepyrazolidine-3,3,5,5-d_4 hydrochloride (4.7 g, 37.8 mmol), red mercuric oxide (52 g) and anhydrous sodium sulfate (52 g) in absolute ether (100 ml) were reacted to give the product (1.4 g, 16.3 mmol, 43.1% yield).

The 100 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 4.70 (singlet); and indicated 95 ± 1% isotopic purity. The mass spectrum indicated 95.4 ± 0.1% isotopic purity (D_0 = 0.6, D_1 = 0.0, D_2 = 7.0, D_3 = 2.0, D_4 = 90.4). The 13.6 MHz ^{2}Hmr spectrum (CCl_4) indicated >99.8% of total deuterium at the 3- and 5-methylene (ring methylene) positions.

4-Ethylidene-1-pyrazoline (69)

The procedure was essentially that of Crawford and Tokunaga (48). 1,2-Butadiene was prepared according to the method of Hurd and Meinert (82,83). Thus, 1-bromo-2-butene, prepared from 2-buten-1-ol with hydrobromic acid, was converted into 1,2,3-tribromobutane by the addition of bromine in carbon tetrachloride. The tribromide was dehydrobrominated with sodium hydroxide to give a mixture of 1,2-dibromo-2-butene and 2,3-dibromo-1-butene. This mixture was then debrominated with zinc dust to give 1,2-butadiene. A solution of diazomethane (6 g, 0.14 mol) in absolute ether (60 ml), prepared from N-methyl-N-nitroso-p-toluenesulfonamide according to the method of de Boer and Backer (70), was placed in a 200 ml pressure bottle at Dry Ice-acetone temperature, and 1,2-butadiene (11 g, 0.20 mol) was added. The bottle was sealed, allowed to warm to room temperature and left until the yellow color disappeared (ca. 12 days). The ether and the excess 1,2-butadiene were distilled off under atmospheric pressure, and the residue distilled to give the product (5.0 g, 52 mmol, 37% yield), bp 25°C/2.0 Torr (lit. 44-45°C/10 Torr).

The 400 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 1.16 (doublet of slight multiplets, J = 6.70 Hz, 3H), 4.40 (doublet of quartets, J = 1.65 and 2.20 Hz, 2H), 4.48 (pentet, J = 2.25 Hz, 2H) and 4.96 (multiplet, 1H).

E-4-ethylidene-1-pyrazoline-3,3,-d_2 (76)

The procedure was that described previously for the synthesis of 4-ethylidene-1-pyrazoline except that diazomethane-d_2 was used. A solution of diazomethane-d_2 (6.4 g, 0.15 mol) in absolute ether (60 ml), prepared according to the method of Gassman and Greenlee (71), reacted with 1,2-butadiene (11 g, 0.20 mol) to give the product (4.7 g, 48 mmol, 32% yield).

The 400 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 1.16 (doublet of slight multiplets, J = 6.70 Hz, 3H), 4.40 (doublet of quartets, J = 1.65 Hz and 2.20 Hz, 1.84H), 4.48 (pentet, J = 2.25 Hz, 0.16H) and 4.95 (multiplet, 1H). The mass spectrum indicated 96 ± 1% isotopic purity (D_0 = 0.9, D_1 = 5.8, D_2 = 93.3). The expanded 400 MHz ^{1}Hmr spectrum indicated that the % ratio of *E*- *vs*. *Z*-4-ethylidene-1-pyrazoline-3,3-d_2 was 92 ± 1 : 8 ± 1, and the 54.4 MHz ^{2}Hmr spectrum (benzene-d_6) showed the % ratio between the *E* and *Z* was 90 ± 1 : 10 ± 1.

Z-4-Ethylidene-1-pyrazoline-3,3-d_2 (77)

The procedure was that described previously for the preparation of 4-ethylidene-1-pyrazoline except that 1,2-butadiene-1,1-d_2 was used. The 1,2-butadiene-1,1-d_2 was prepared according to the method of Hurd and Meinert (83) except that 2-buten-1-ol-1,1-d_2 was produced by lithium aluminum deuteride reduction of crotonyl chloride (48,84). A solution of diazomethane (6 g, 0.14 mol) in absolute ether (60 ml) reacted with 1,2-butadiene-1,1-d_2 (9 g, 0.17 mol) to give the product (4.5 g, 46 mmol, 33% yield).

The 400 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 1.18 (doublet of slight multiplets, J = 6.70 Hz, 3H), 4.37 (doublet of quartets, J = 1.65 and 2.20 Hz, 0.14H), 4.43 (pentet, J = 2.25 Hz, 1.86H) and 4.91 (multiplet, 1H). The mass spectrum indicated 97 ± 1% isotopic purity (D_0 = 0.7, D_1 = 4.8, D_2 = 94.5). The % ratio between *E*- and Z-4-ethylidene-1-pyrazolines-3,3-d_2 were 7 ± 1 : 93 ± 1 by the expanded 400 MHz ^{1}Hmr spectrum and 9 ± 1 : 91 ± 1 by the expanded 54.4 MHz ^{2}Hmr spectrum (benzene-d_6).

4-Ethylidene-1-pyrazoline-3,3,5,5-d_4 (128)

The procedure was that described previously for the synthesis of 4-ethylidene-1-pyrazoline except that 1,2-butadiene-1,1-d_2 and diazomethane-d_2 were used. A

3,3-Dimethyl-4-methylene-1-pyrazoline (56)

The procedure was a slight modification of that of Crawford and Tokunaga (10a). A solution of 2-diazopropane (12 g, 0.17 mol) in ether (90 ml), prepared from acetone hydrazone (87) by mercuric oxide oxidation according to the method of Andrews, Day, Raymond and Whiting (88), was added at Dry Ice-acetone temperature to allene (30 ml) contained in a 200 ml pressure bottle. The mixture was allowed to warm to 0°C. After 3 hr the solution became colorless. Removal of the excess allene and the ether followed by distillation of the residual solution gave a mixture (7 g), bp 25°C/6 Torr, which proved to be 58% product, 13% acetone hydrazone and 29% acetone azine by the nmr spectrum (benzene-d_6). This mixture was dissolved in ether (50 ml), and the resulting solution was extracted with water (3 x 5 ml) to remove the acetone hydrazone. Distillation of ether followed by careful distillation of the residue gave a mixture (2.5 g, 87% product, and 13% acetone azine; calculated yield, 2.2 g, 20 mmol, 12% yield), bp 25°C/6 Torr.

The 100 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 1.17 (singlet, 6H), 1.82 (doublet, acetone azine) and 4.65 (slight multiplet, 4H, ring methylene + exo-methylene).

4-Isopropylidene-1-pyrazoline (57)

The procedure was a slight modification of that of Crawford and Tokunaga (10a). Diethyl isopropylidene malonate, prepared from acetone and diethyl malonate, was reduced to 2-isopropylidene-1,3-propanediol by lithium aluminum hydride, and the diol was converted into 2-isopropylidene-1,3-dibromopropane by bromination with phosphorous tribromide (89). The cyclization of the dibromide with *sym*-dicarbethoxyhydrazine in the presence of sodium hydride was followed by hydrolysis with potassium hydroxide and subsequent treatment with hydrochloric acid to give 4-isopropylidenepyrazolidine hydrochloride (10a). The hydrochloride (5.4 g, 36 mmol) was added slowly to a well-stirred slurry of red mercuric oxide (50 g) and anhydrous sodium sulfate (50 g) in absolute ether (100 ml). The reaction mixture was stirred mechanically for 5 hr at room temperature. Filtration of the solid, and distillation of ether at room temperature under reduced pressure were followed by fast distillation of the residue at 25°C/0.05 Torr. The distillate was trapped at Dry Ice-acetone temperature. It redistilled to give the product (2.0 g, 18 mmol, 50% yield), bp 25°C/0.1 Torr (lit. 37°C/0.1 Torr).

The 100 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 1.26 (pentet, J = 2.0 Hz, 6H) and 4.54 (heptet, J = 2.0 Hz, 6H).

E-3-Methyl-4-ethylidene-1-pyrazoline (89)

The procedure used was essentially that of Crawford and Tokunaga (48). 1,2-Butadiene was prepared according to the method of Hurd and Meinert (83) which has been described earlier in the synthesis of 4-ethylidene-1-pyrazoline. A solution of diazoethane (0.06 mol) in ether and n-propanol (60 ml), prepared from ethyl N-nitroso-N-ethylcarbamate (12.5 g, 86 mmol) according to the procedure of Wilds and Meader (86), was added to 1,2-butadiene (5 g, 93 mmol) in a 200 ml pressure bottle cooled in a Dry Ice-acetone bath. The mixture was allowed to warm to room temperature and left undisturbed for two days until the orange color of diazoethane disappeared. Removal of the ether, the n-propanol and the excess 1,2-butadiene followed by distillation of the residual solution gave the product (2.7 g, 25 mmol, 42% yield), bp 25°C/1.5 Torr (lit. 30-33°C/3 Torr).

The 100 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 1.24 (doublet and multiplet, J = 7.0 Hz, 6H; 3-methyl and 6-methyl), 4.57 (multiplet, 3H) and 5.01 (multiplet, 1H).

Z-3-Methyl-4-ethylidene-1-pyrazoline (90)

The procedure was essentially that of Crawford and Tokunaga (48). 1,1-Dibromo-2,3-dimethylcyclopropane (90) prepared from 2-butene, bromoform and potassium t-butoxide were allowed to react with methyllithium according to the procedure of Doering and LaFlamme (91). Distillation of the reaction mixture using a spinning band column gave 2,3-pentadiene. A solution of diazomethane (3 g, 71 mmol) in absolute ether (30 ml), and 2,3-pentadiene (5.5 g, 81 mmol) were placed in a 200 ml pressure bottle at Dry Ice-acetone temperature, and allowed to warm to room temperature. The mixture was left undisturbed for 12 days. Removal of the ether and the excess 2,3-pentadiene followed by distillation of the residual solution gave the product (2.5 g, 23 mmol, 32% yield), bp 25°C/1.5 Torr (lit. 30-33°C/3 Torr).

The 100 MHz ^{1}Hmr spectrum δ TMS (benzene-d_6) showed: 1.11 (doublet, J = 7.0 Hz, 3H; 3-methyl), 1.33 (multiplet, 3H; 6-methyl), 4.62 (multiplet, 3H) and 5.07 (multiplet, 1H).

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APPENDIX

Kinetic data for the thermolysis of the 4-alkylidene-1-pyrazolines

1. Rate constants and activation parameters for the thermolysis of the 4-alkylidene-1-pyrazolines were obtained from the data presented on pages 253 and 273.
2. Secondary deuterium kinetic isotope effects for the deuterated 4-methylene-1-pyrazolines and the deuterated 4-ethylidene-1-pyrazolines were obtained from the data on pages 274 and 281.
3. Each individual rate constant (k_i) was obtained by a least squares analysis, and the average (k) of the individual rate constants was taken.
4. σ and ρ represent the standard deviation and the correlation coefficient respectively.

Thermolysis of 4-Methylene-1-pyrazoline (30) at 165.0°C

Time (sec)	$E_\infty - E_t$ (volt) Run #1	Run #2	Run #3
300	0.353	0.374	0.407
360	0.334	0.353	0.384
420	0.316	0.333	0.363
480	0.299	0.314	0.342
540	0.283	0.296	0.322
600	0.267	0.280	0.304
660	0.253	0.264	0.287
720	0.239	0.249	0.271
780	0.226	0.235	0.257
840	0.214	0.223	0.244
900	0.202	0.211	0.231
960	0.191	0.200	0.219
1020	0.180	0.189	0.207
1080	0.170	0.179	0.196
1140	0.161	0.170	0.185
E_∞	1.074	1.142	1.219
$10^3(k_i \pm \sigma k_i)$ (sec^{-1})	0.936 ±0.0055	0.942 ±0.0060	0.934 ±0.0047
ρ	0.99978	0.99976	0.99983
$10^3(k \pm \sigma_k)$ (sec^{-1})		0.937 ± 0.0042	

Thermolysis of 4-Methylene-1-pyrazoline (30) at 170.0°C

Time (sec)	$E_\infty - E_t$ (volt)				
	Run #1	Run #2	Run #3	Run #4	Run #5
210	0.267	0.237	0.399	0.230	0.246
240	0.256	0.227	0.383	0.220	0.236
270	0.246	0.218	0.367	0.211	0.226
300	0.236	0.209	0.352	0.202	0.217
330	0.226	0.200	0.337	0.194	0.208
360	0.217	0.192	0.323	0.186	0.199
390	0.208	0.184	0.308	0.178	0.191
420	0.199	0.176	0.296	0.171	0.183
450	0.191	0.169	0.283	0.164	0.175
480	0.183	0.162	0.271	0.157	0.168
510	0.175	0.155	0.259	0.150	0.161
540	0.168	0.148	0.248	0.144	0.154
570	0.161	0.142	0.237	0.138	0.147
600	0.154	0.136	0.227	0.132	0.141
630	0.147	0.130	0.217	0.126	0.135
660	0.141	0.124	0.208	0.121	0.129
690	0.135	0.119	0.199	0.116	0.123
720	0.129	0.114	0.191	0.111	0.118
750	0.123	0.109	0.183	0.106	0.113
780	0.118	0.104	0.175	0.101	0.108
810	0.113	0.099	0.168	0.097	0.103
840	0.108	0.095	0.161	0.093	0.099
870	0.103	0.091	0.154	0.089	0.095
900	0.098	0.087	0.147	0.085	0.091
930	0.094	0.083	0.141	0.081	0.087
E_∞	0.797	0.715	1.197	0.687	0.762
$10^3(k_i \pm \sigma k_i)$ (sec^{-1})	1.450 ±0.0093	1.458 ±0.0107	1.450 ±0.0086	1.443 ±0.0070	1.451 ±0.0095
ρ	0.99976	0.99971	0.99978	0.99984	0.99975
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.450 ± 0.0053				

Thermolysis of 4-Methylene-1-pyrazoline (30) at 175.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
140	0.352	0.286	0.245
180	0.322	0.262	0.224
220	0.295	0.239	0.206
260	0.270	0.219	0.188
300	0.246	0.200	0.172
340	0.225	0.183	0.157
380	0.205	0.167	0.144
420	0.187	0.153	0.132
460	0.171	0.140	0.121
500	0.157	0.128	0.111
540	0.144	0.117	0.102
580	0.132	0.107	0.093
620	0.121	0.098	0.085
660	0.111	0.090	0.078
700	0.102	0.082	0.071
E_∞	1.007	0.847	0.712
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	2.222 ±0.0116	2.230 ±0.0177	2.203 ±0.0135
ρ	0.99982	0.99968	0.99977
$10^3(k \pm \sigma_k)$ (sec^{-1})	2.218 ± 0.0139		

Thermolysis of 3-Methyl-4-methylene-1-pyrazoline (68) at 164.0°C

Time (sec)	$E_\infty - E_t$ (volt) Run #1	Run #2	Run #3
300	0.271	0.321	0.350
360	0.258	0.304	0.333
420	0.245	0.289	0.317
480	0.233	0.275	0.301
540	0.221	0.262	0.286
600	0.210	0.249	0.271
660	0.199	0.237	0.257
720	0.189	0.225	0.243
780	0.179	0.214	0.230
840	0.170	0.203	0.217
900	0.161	0.192	0.205
960	0.152	0.182	0.194
1020	0.144	0.172	0.183
1080	0.136	0.162	0.173
1140	0.128	0.153	0.163
1200	0.121	0.144	0.154
E_∞	0.836	0.990	1.107
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	0.894 ±0.0062	0.880 ±0.0098	0.917 ±0.0069
ρ	0.99973	0.99951	0.99970
$10^3(k \pm \sigma_k)$ (sec^{-1})		0.897 ± 0.0187	

Thermolysis of 3-Methyl-4-methylene-1-pyrazoline (**68**) at 170.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
210	0.415	0.270	0.400
240	0.396	0.258	0.382
270	0.378	0.247	0.365
300	0.361	0.236	0.349
330	0.345	0.226	0.334
360	0.330	0.216	0.320
390	0.315	0.207	0.306
420	0.301	0.198	0.293
450	0.288	0.189	0.280
480	0.275	0.181	0.268
510	0.263	0.173	0.256
540	0.251	0.165	0.245
570	0.240	0.158	0.234
600	0.229	0.151	0.224
630	0.219	0.144	0.214
660	0.209	0.138	0.205
690	0.200	0.132	0.196
720	0.191	0.126	0.187
750	0.182	0.120	0.179
780	0.174	0.115	0.171
810	0.166	0.110	0.163
840	0.158	0.105	0.156
870	0.151	0.100	0.149
900	0.144	0.096	0.142
930	0.137	0.092	0.136
E_∞	1.290	0.869	1.240
$10^3(k_i \pm \sigma_{k_i})$	1.530	1.501	1.495
(sec^{-1})	±0.0095	±0.0119	±0.0096
ρ	0.99977	0.99968	0.99976
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.509 ± 0.0187		

Thermolysis of 3-Methyl-4-methylene-1-pyrazoline (68) at 175.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
210	0.307	0.317	0.258
240	0.287	0.296	0.241
270	0.268	0.276	0.225
300	0.250	0.258	0.210
330	0.233	0.241	0.196
360	0.218	0.225	0.183
390	0.204	0.210	0.171
420	0.191	0.196	0.160
450	0.179	0.183	0.150
480	0.167	0.171	0.140
510	0.156	0.160	0.131
540	0.145	0.150	0.122
570	0.135	0.140	0.114
600	0.126	0.131	0.106
630	0.117	0.122	0.099
660	0.109	0.114	0.092
E_∞	1.100	1.132	0.907
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	2.289 ±0.0167	2.269 ±0.0109	2.278 ±0.0155
ρ	0.99971	0.99984	0.99976
$10^3(k \pm \sigma_k)$ (sec^{-1})	2.279 ± 0.0100		

Thermolysis of 3,3-Dimethyl-4-methylene-1-pyrazoline (56) at 170.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
360	0.129	0.118	0.103
420	0.121	0.111	0.097
480	0.114	0.104	0.091
540	0.107	0.098	0.085
600	0.101	0.092	0.080
660	0.095	0.087	0.075
720	0.089	0.082	0.070
780	0.084	0.077	0.066
840	0.079	0.072	0.062
900	0.074	0.068	0.058
960	0.070	0.064	0.055
1020	0.066	0.060	0.052
1080	0.062	0.057	0.049
1140	0.058	0.054	0.046
1200	0.055	0.051	0.044
E_∞	0.475	0.449	0.390
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.016 ±0.0084	1.005 ±0.0051	1.027 ±0.0101
ρ	0.99960	0.99983	0.99958
$10^3(k \pm \sigma_k)$ (sec^{-1})		1.016 ± 0.0110	

Thermolysis of 3,3-Dimethyl-4-methylene-1-pyrazoline (**56**) at 175.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
240	0.115	0.098	0.120
270	0.110	0.093	0.114
300	0.105	0.089	0.109
330	0.100	0.085	0.104
360	0.095	0.081	0.099
390	0.090	0.077	0.094
420	0.086	0.073	0.090
450	0.082	0.070	0.086
480	0.078	0.067	0.082
510	0.074	0.064	0.078
540	0.071	0.061	0.074
570	0.068	0.058	0.071
600	0.065	0.055	0.068
630	0.062	0.052	0.065
660	0.059	0.050	0.062
690	0.056	0.048	0.059
720	0.054	0.046	0.057
E_∞	0.400	0.370	0.440
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.590 ±0.0120	1.589 ±0.0091	1.564 ±0.0138
ρ	0.99970	0.99979	0.99963
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.581 ± 0.0147		

Thermolysis of 3,3-Dimethyl-4-methylene-1-pyrazoline (56) at 180.0°C

Time (sec)	$E_\infty - E_t$ (volt)		
	Run #1	Run #2	Run #3
150	0.117	0.107	0.112
180	0.108	0.099	0.105
210	0.100	0.092	0.098
240	0.093	0.085	0.091
270	0.087	0.079	0.085
300	0.081	0.073	0.079
330	0.075	0.068	0.073
360	0.070	0.063	0.068
390	0.065	0.059	0.063
420	0.060	0.055	0.058
450	0.056	0.051	0.054
480	0.052	0.047	0.050
510	0.048	0.044	0.046
540	0.045	0.041	0.043
570	0.042	0.038	0.040
E_∞	0.402	0.376	0.402
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	2.438 ±0.0173	2.454 ±0.0231	2.485 ±0.0137
ρ	0.99972	0.99960	0.99980
$10^3(k \pm \sigma_k)$ (sec^{-1})	2.459 ± 0.0239		

Thermolysis of 4-Ethylidene-1-pyrazoline (**69**) at 160°C

Time (sec)	$E_\infty - E_t$ (volt)		
	Run #1	Run #2	Run #3
300	0.149	0.139	0.121
330	0.143	0.133	0.116
360	0.137	0.128	0.111
390	0.131	0.123	0.106
420	0.126	0.118	0.102
450	0.121	0.113	0.098
480	0.116	0.108	0.094
510	0.111	0.104	0.090
540	0.106	0.100	0.086
570	0.102	0.096	0.082
600	0.098	0.092	0.079
630	0.094	0.088	0.076
660	0.090	0.084	0.073
690	0.086	0.091	0.070
720	0.082	0.078	0.067
750	0.079	0.075	0.064
780	0.076	0.072	0.061
810	0.073	0.069	0.059
840	0.070	0.066	0.057
870	0.067	0.063	0.055
900	0.064	0.061	0.053
E_∞	0.522	0.484	0.423
$10^3(k_i \pm \sigma k_i)$ (sec^{-1})	1.405 ±0.0120	1.377 ±0.0077	1.391 ±0.0094
ρ	0.99965	0.99980	0.99974
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.391 ± 0.0140		

Thermolysis of 4-Ethylidene-1-pyrazoline (69) at 164.0°C

Time	$E_\infty - E_t$ (volt)				
(sec)	Run #1	Run #2	Run #3	Run #4	Run #5
300	0.155	0.142	0.159	0.126	0.166
330	0.147	0.134	0.150	0.119	0.157
360	0.139	0.127	0.141	0.112	0.148
390	0.132	0.120	0.133	0.106	0.140
420	0.125	0.113	0.125	0.100	0.132
450	0.118	0.107	0.118	0.094	0.124
480	0.112	0.101	0.111	0.089	0.117
510	0.106	0.095	0.105	0.084	0.110
540	0.100	0.090	0.099	0.079	0.104
570	0.094	0.085	0.093	0.075	0.098
600	0.089	0.079	0.088	0.071	0.092
630	0.084	0.075	0.083	0.067	0.087
660	0.079	0.071	0.078	0.063	0.082
690	0.075	0.067	0.074	0.059	0.077
720	0.071	0.063	0.070	0.056	0.073
750	0.067	0.059	0.066	0.053	0.069
780	0.062	0.056	0.062	0.050	0.065
810	0.058	0.052	0.059	0.047	0.061
840	0.055	0.050	0.056	0.044	0.058
870	0.052	0.047	0.052	0.041	0.055
900	0.049	0.044	0.050	0.039	0.052
E_∞	0.623	0.555	0.628	0.495	0.648
$10^3(k_i+\sigma_{k_i})$	1.928	1.950	1.931	1.948	1.952
(sec^{-1})	±0.0168	±0.0176	±0.0120	±0.0158	±0.0097
ρ	0.99964	0.99962	0.99977	0.99967	0.99983

$10^3(k\pm\sigma_k)$ (sec^{-1})	1.942 ± 0.0114

Thermolysis of 4-Ethylidene-1-pyrazoline (**69**) at 170.0°C

Time (sec)	$E_\infty - E_t$ (volt)		
	Run #1	Run #2	Run #3
210	0.117	0.125	0.131
240	0.106	0.113	0.118
270	0.096	0.102	0.106
300	0.087	0.092	0.096
330	0.079	0.084	0.087
360	0.072	0.077	0.079
390	0.066	0.070	0.072
420	0.060	0.064	0.066
450	0.055	0.058	0.060
480	0.050	0.053	0.055
510	0.046	0.048	0.050
E_∞	0.481	0.510	0.550
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	3.111 ±0.0227	3.157 ±0.0180	3.186 ±0.0313
ρ	0.99971	0.99979	0.99958
$10^3(k \pm \sigma_k)$ (sec^{-1})		3.151 ± 0.0378	

Thermolysis of *E*-3-Methyl-4-ethylidene-1-pyrazoline (89) at 160.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
300	0.115	0.133	0.159
330	0.110	0.127	0.152
360	0.105	0.121	0.145
390	0.100	0.116	0.138
420	0.095	0.111	0.132
450	0.091	0.106	0.126
480	0.087	0.101	0.120
510	0.083	0.097	0.115
540	0.079	0.093	0.110
570	0.075	0.089	0.105
600	0.072	0.085	0.100
630	0.069	0.081	0.096
660	0.066	0.077	0.092
690	0.063	0.074	0.088
720	0.060	0.071	0.084
750	0.057	0.068	0.080
780	0.055	0.065	0.076
810	0.053	0.062	0.073
840	0.051	0.059	0.070
870	0.049	0.057	0.067
900	0.047	0.055	0.064
E_∞	0.430	0.492	0.605
$10^3(k_i \pm \sigma_{k_i})$	1.507	1.485	1.516
(sec^{-1})	±0.0163	±0.0118	±0.0102
ρ	0.99953	0.99968	0.99974
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.503 ± 0.0160		

Thermolysis of *E*-3-Methyl-4-ethylidene-1-pyrazoline (**89**) at 164.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
270	0.138	0.118	0.125
300	0.130	0.111	0.118
330	0.122	0.104	0.111
360	0.115	0.098	0.104
390	0.108	0.092	0.098
420	0.102	0.086	0.092
450	0.096	0.081	0.086
480	0.090	0.076	0.081
510	0.085	0.071	0.076
540	0.080	0.067	0.071
570	0.075	0.063	0.067
600	0.070	0.059	0.063
630	0.066	0.056	0.059
660	0.062	0.053	0.055
690	0.058	0.050	0.052
720	0.054	0.047	0.049
750	0.051	0.044	0.046
780	0.048	0.042	0.043
E_∞	0.565	0.478	0.516
$10^3(k_i \pm \sigma_{k_i})$	2.076	2.042	2.100
(sec^{-1})	±0.0168	±0.0131	±0.0215
ρ	0.99967	0.99976	0.99956
$10^3(k \pm \sigma_k)$ (sec^{-1})		2.073 ± 0.0291	

Thermolysis of *E*-3-Methyl-4-ethylidene-1-pyrazoline (89) at 170.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
150	0.149	0.140	0.156
180	0.135	0.125	0.141
210	0.122	0.112	0.127
240	0.110	0.101	0.115
270	0.099	0.091	0.103
300	0.089	0.082	0.093
330	0.080	0.074	0.084
360	0.072	0.067	0.076
390	0.066	0.061	0.069
420	0.062	0.056	0.062
450	0.055	0.051	0.056
480	0.050	0.047	0.051
510	0.045	0.043	0.046
E_∞	0.555	0.490	0.578
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	3.329 ±0.0300	3.278 ±0.0233	3.396 ±0.0221
ρ	0.99962	0.99972	0.99975
$10^3(k \pm \sigma_k)$ (sec^{-1})	3.334 ± 0.0592		

Thermolysis of *Z*-3-Methyl-4-ethylidene-1-pyrazoline (**90**) at 160.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
300	0.156	0.175	0.164
330	0.150	0.168	0.157
360	0.144	0.161	0.151
390	0.138	0.154	0.145
420	0.132	0.148	0.133
450	0.127	0.142	0.133
480	0.122	0.136	0.128
510	0.117	0.130	0.123
540	0.112	0.125	0.118
570	0.107	0.120	0.113
600	0.103	0.115	0.108
630	0.099	0.110	0.104
660	0.095	0.105	0.100
690	0.091	0.100	0.096
720	0.087	0.096	0.092
750	0.083	0.092	0.088
780	0.079	0.088	0.084
810	0.076	0.084	0.080
840	0.[illegible]73	0.080	0.077
870	0.070	0.077	0.074
900	0.067	0.074	0.071
E_∞	0.568	0.650	0.592
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.412 ±0.0109	1.445 ±0.0086	1.397 ±0.0108
ρ	0.99969	0.99978	0.99969
$10^3(k \pm \sigma_k)$ (sec^{-1})		1.418 ± 0.0246	

Thermolysis of Z-3-Methyl-4-ethylidene-1-pyrazoline (**90**) at 164.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
270	0.171	0.141	0.152
300	0.161	0.133	0.143
330	0.152	0.125	0.135
360	0.144	0.118	0.127
390	0.136	0.111	0.120
420	0.129	0.105	0.113
450	0.122	0.099	0.107
480	0.115	0.093	0.101
510	0.109	0.088	0.095
540	0.103	0.083	0.090
570	0.097	0.078	0.085
600	0.091	0.073	0.080
630	0.086	0.069	0.075
660	0.081	0.065	0.071
690	0.076	0.061	0.067
720	0.071	0.057	0.063
750	0.066	0.054	0.059
780	0.062	0.051	0.056
E_∞	0.678	0.596	0.589
$10^3(k_i \pm \sigma_{k_i})$	1.964	2.001	1.954
(sec^{-1})	±0.0267	±0.0138	±0.0166
ρ	0.99938	0.99973	0.99965
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.973 ± 0.0248		

Thermolysis of Z-3-Methyl-4-ethylidene-1-pyrazoline (**90**) at 170.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
150	0.155	0.171	0.162
180	0.140	0.155	0.147
210	0.127	0.140	0.134
240	0.115	0.127	0.122
270	0.104	0.115	0.111
300	0.094	0.105	0.101
330	0.085	0.095	0.092
360	0.077	0.086	0.084
390	0.070	0.078	0.076
420	0.064	0.071	0.069
450	0.059	0.064	0.063
480	0.054	0.058	0.057
510	0.049	0.053	0.052
E_∞	0.536	0.605	0.565
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	3.203 ±0.0301	3.258 ±0.0238	3.156 ±0.0310
ρ	0.99960	0.99971	0.99958
$10^3(k \pm \sigma_k)$ (sec^{-1})	3.206 ± 0.0511		

Thermolysis of 4-Isopropylidene-1-pyrazoline (57) at 175.0°C

Time (sec)	$E_\infty - E_t$ (volt) Run #1	Run #2	Run #3
240	0.149	0.106	0.199
300	0.139	0.099	0.185
360	0.129	0.092	0.172
420	0.120	0.086	0.160
480	0.112	0.080	0.149
540	0.104	0.074	0.139
600	0.097	0.069	0.129
660	0.090	0.064	0.120
720	0.083	0.059	0.111
780	0.077	0.055	0.103
840	0.071	0.051	0.095
900	0.066	0.047	0.088
960	0.061	0.044	0.081
1020	0.056	0.041	0.075
1080	0.051	0.038	0.069
1140	0.047	0.035	0.064
1200	0.043	0.032	0.059
E_∞	0.497	0.350	0.639
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.286 ±0.0188	1.241 ±0.0107	1.266 ±0.0090
ρ	0.99933	0.99964	0.99972
$10^3(k \pm \sigma_k)$ (sec^{-1})		1.264 ± 0.0225	

Thermolysis of 4-Isopropylidene-1-pyrazoline (57) at 180.0°C

Time	$E_\infty - E_t$ (volt)		
(sec)	Run #1	Run #2	Run #3
120	0.088	0.134	0.101
180	0.079	0.120	0.091
240	0.071	0.108	0.082
300	0.064	0.096	0.073
360	0.057	0.086	0.065
420	0.051	0.076	0.058
480	0.045	0.068	0.052
540	0.040	0.060	0.046
600	0.035	0.053	0.041
660	0.031	0.047	0.036
720	0.027	0.042	0.032
780	0.024	0.037	0.028
840	0.021	0.033	0.025
900	0.019	0.029	0.022
E_∞	0.260	0.388	0.299
$10^3(k_i \pm \sigma k_i)$ (sec^{-1})	2.000 ±0.0260	1.969 ±0.0209	1.963 ±0.0167
ρ	0.99941	0.99954	0.99965
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.977 ± 0.0199		

Thermolysis of 4-Isopropylidene-1-pyrazoline (57) at 185.0°C

Time (sec)	$E_\infty - E_t$ (volt)		
	Run #1	Run #2	Run #3
90	0.051	0.082	0.154
120	0.047	0.075	0.154
150	0.043	0.069	0.129
180	0.040	0.063	0.117
210	0.037	0.058	0.107
240	0.034	0.053	0.098
270	0.031	0.048	0.089
300	0.028	0.044	0.081
330	0.025	0.040	0.074
360	0.023	0.036	0.068
390	0.021	0.033	0.062
420	0.019	0.030	0.057
450	0.017	0.027	0.052
E_∞	0.150	0.240	0.430
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	3.044 ±0.0216	3.078 ±0.0250	3.027 ±0.0318
ρ	0.99972	0.99967	0.99954
$10^3(k \pm \sigma_k)$ (sec^{-1})	3.050 ± 0.0260		

Thermolysis of 4-Methylene-1-pyrazoline-6,6-d_2 (107) at 170.0°C

Time	$E_\infty - E_t$ (volt)				
(sec)	Run #1	Run #2	Run #3	Run #4	Run #5
210	0.404	0.241	0.272	0.250	0.234
240	0.388	0.231	0.261	0.240	0.224
270	0.372	0.222	0.251	0.230	0.215
300	0.357	0.213	0.241	0.221	0.206
330	0.342	0.204	0.231	0.212	0.198
360	0.328	0.196	0.222	0.203	0.190
390	0.314	0.188	0.213	0.195	0.182
420	0.301	0.180	0.204	0.187	0.175
450	0.288	0.173	0.196	0.179	0.168
480	0.276	0.166	0.188	0.172	0.161
510	0.264	0.159	0.180	0.165	0.154
540	0.253	0.152	0.173	0.158	0.148
570	0.242	0.146	0.166	0.151	0.142
600	0.232	0.140	0.159	0.145	0.136
630	0.222	0.134	0.152	0.139	0.130
660	0.213	0.128	0.146	0.133	0.125
690	0.204	0.123	0.140	0.127	0.120
720	0.196	0.118	0.134	0.122	0.115
750	0.188	0.113	0.128	0.117	0.110
780	0.180	0.108	0.123	0.112	0.105
810	0.173	0.103	0.118	0.107	0.101
840	0.166	0.099	0.113	0.103	0.097
870	0.159	0.095	0.108	0.099	0.093
900	0.152	0.091	0.103	0.095	0.089
930	0.146	0.087	0.099	0.091	0.085
E_∞	1.238	0.696	0.807	0.751	0.681
$10^3(k_i \pm \sigma k_i)$ (sec^{-1})	1.420 ±0.0084	1.417 ±0.0093	1.405 ±0.0071	1.411 ±0.0103	1.401 ±0.0077
ρ	0.99978	0.99975	0.99983	0.99971	0.99980
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.411 ± 0.0080				

Thermolysis of 4-Methylene-1-pyrazoline-3,3-d_2 (**42**) at 170.0°C

Time	$E_\infty - E_t$ (volt)				
(sec)	Run #1	Run #2	Run #3	Run #4	Run #5
240	0.386	0.349	0.394	0.281	0.392
270	0.371	0.336	0.379	0.271	0.379
300	0.357	0.323	0.365	0.261	0.364
330	0.343	0.311	0.351	0.251	0.350
360	0.330	0.299	0.338	0.242	0.337
390	0.317	0.288	0.325	0.233	0.324
420	0.305	0.277	0.313	0.224	0.312
450	0.293	0.267	0.301	0.216	0.300
480	0.282	0.257	0.290	0.208	0.289
510	0.271	0.247	0.279	0.200	0.278
540	0.261	0.238	0.269	0.193	0.268
570	0.251	0.229	0.259	0.186	0.258
600	0.242	0.220	0.249	0.179	0.248
630	0.233	0.220	0.240	0.172	0.239
660	0.224	0.204	0.231	0.166	0.230
690	0.216	0.196	0.222	0.160	0.221
720	0.208	0.189	0.214	0.154	0.213
750	0.200	0.182	0.206	0.148	0.205
780	0.193	0.175	0.198	0.142	0.197
810	0.186	0.168	0.191	0.137	0.190
840	0.179	0.162	0.184	0.132	0.183
870	0.173	0.156	0.177	0.127	0.176
900	0.167	0.150	0.171	0.122	0.169
930	0.161	0.144	0.165	0.117	0.163
960	0.155	0.139	0.159	0.113	0.157
E_∞	1.129	1.069	1.158	0.829	1.058
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.267 ±0.0098	1.279 ±0.0083	1.264 ±0.0075	1.266 ±0.0078	1.274 ±0.0069
p	0.99969	0.99975	0.99978	0.99977	0.99981
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.270 ± 0.0063				

Thermolysis of 4-Methylene-1-pyrazoline-3,3,6,6-d_4 (43) at 170.0°C

Time	$E_\infty - E_t$ (volt)				
(sec)	Run #1	Run #2	Run #3	Run #4	Run #5
240	0.373	0.196	0.215	0.348	0.287
270	0.358	0.189	0.207	0.336	0.277
300	0.344	0.182	0.199	0.324	0.267
330	0.332	0.175	0.192	0.313	0.257
360	0.320	0.169	0.185	0.302	0.248
390	0.309	0.163	0.178	0.291	0.239
420	0.298	0.157	0.171	0.281	0.230
450	0.297	0.151	0.165	0.271	0.222
480	0.277	0.145	0.159	0.261	0.214
510	0.267	0.140	0.153	0.252	0.206
540	0.257	0.135	0.147	0.243	0.199
570	0.248	0.130	0.142	0.234	0.192
600	0.239	0.125	0.137	0.226	0.185
630	0.230	0.120	0.132	0.218	0.178
660	0.222	0.116	0.127	0.210	0.172
690	0.214	0.112	0.122	0.202	0.166
720	0.206	0.108	0.118	0.195	0.160
750	0.198	0.104	0.114	0.188	0.154
780	0.191	0.100	0.110	0.181	0.148
810	0.184	0.096	0.106	0.174	0.143
840	0.177	0.093	0.102	0.168	0.138
870	0.170	0.090	0.098	0.162	0.133
900	0.164	0.087	0.095	0.156	0.128
930	0.158	0.084	0.092	0.150	0.123
960	0.152	0.081	0.089	0.145	0.119
E_∞	1.012	0.569	0.633	1.053	0.878
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.239 ±0.0081	1.235 ±0.0067	1.233 ±0.0089	1.220 ±0.0077	1.224 ±0.0082
ρ	0.99975	0.99981	0.99969	0.99976	0.99974
$10^3(k \pm \sigma_k)$ (sec^{-1})			1.230 ± 0.0079		

Thermolysis of 4-Methylene-1-pyrazoline-3,3,5,5,-d_4 (46)
at 170.0°C

Time (sec)	$E_\infty - E_t$ (volt) Run #1	Run #2	Run #3	Run #4	Run #5
260	0.223	0.285	0.234	0.197	0.421
300	0.214	0.274	0.224	0.189	0.404
340	0.205	0.263	0.215	0.181	0.388
380	0.196	0.252	0.205	0.173	0.372
420	0.188	0.242	0.197	0.166	0.357
460	0.180	0.232	0.189	0.159	0.342
500	0.172	0.222	0.191	0.152	0.328
540	0.165	0.212	0.173	0.146	0.314
580	0.158	0.204	0.166	0.140	0.301
620	0.151	0.195	0.159	0.134	0.288
660	0.145	0.187	0.152	0.128	0.276
700	0.139	0.179	0.146	0.123	0.264
740	0.133	0.171	0.140	0.118	0.253
780	0.127	0.164	0.134	0.113	0.242
820	0.122	0.157	0.128	0.108	0.232
860	0.117	0.150	0.123	0.104	0.222
900	0.112	0.144	0.118	0.100	0.213
940	0.107	0.138	0.113	0.096	0.204
980	0.103	0.132	0.108	0.092	0.196
1020	0.099	0.127	0.103	0.088	0.188
E_∞	0.627	0.837	0.668	0.557	1.240
$10^3(k_i \pm \sigma k_i)$ (sec^{-1})	1.076 ±0.006	1.075 ±0.0070	1.075 ±0.0064	1.060 ±0.0052	1.069 ±0.0087
ρ	0.99977	0.99975	0.99978	0.99984	0.99967
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.071 ± 0.0067				

Thermolysis of 4-Methylene-1-pyrazoline-3,3,5,5,6,6-d_6 (44) at 170.0°C

Time (sec)	$E_\infty - E_t$ (volt) Run #1	Run #2	Run #3	Run #4	Run #5
260	0.272	0.224	0.241	0.316	0.360
300	0.261	0.215	0.231	0.304	0.346
340	0.251	0.206	0.222	0.292	0.332
380	0.241	0.198	0.213	0.281	0.319
420	0.231	0.190	0.204	0.270	0.306
460	0.222	0.182	0.196	0.259	0.294
500	0.213	0.175	0.188	0.249	0.282
540	0.204	0.168	0.180	0.239	0.271
580	0.196	0.161	0.173	0.229	0.260
620	0.188	0.154	0.166	0.220	0.250
660	0.180	0.148	0.159	0.211	0.240
700	0.173	0.142	0.153	0.202	0.230
740	0.166	0.136	0.147	0.194	0.221
780	0.159	0.130	0.141	0.186	0.212
820	0.153	0.125	0.135	0.178	0.203
860	0.147	0.120	0.130	0.171	0.195
900	0.141	0.115	0.125	0.164	0.187
940	0.136	0.110	0.120	0.157	0.179
980	0.131	0.106	0.115	0.151	0.172
1020	0.126	0.102	0.111	0.145	0.165
E_∞	0.787	0.650	0.676	0.903	1.049
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.022 ±0.0073	1.042 ±0.0064	1.024 ±0.0050	1.033 ±0.0072	1.027 ±0.0091
ρ	0.99972	0.99977	0.99985	0.99973	0.99963
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.030 ± 0.0081				

Thermolysis of *E*-4-Ethylidene-1-pyrazoline-3,3-d_2 (**76**) at 164.0°C

Time (sec)	$E_\infty - E_t$ (volt)				
	Run #1	Run #2	Run #3	Run #4	Run #5
300	0.188	0.200	0.145	0.184	0.169
330	0.179	0.190	0.138	0.175	0.161
360	0.170	0.181	0.132	0.167	0.153
390	0.162	0.172	0.126	0.159	0.145
420	0.154	0.164	0.120	0.151	0.138
450	0.146	0.156	0.114	0.144	0.131
480	0.139	0.148	0.109	0.137	0.124
510	0.132	0.141	0.104	0.130	0.118
540	0.125	0.134	0.099	0.124	0.112
570	0.119	0.128	0.094	0.118	0.106
600	0.113	0.122	0.089	0.112	0.101
630	0.107	0.116	0.085	0.107	0.096
660	0.102	0.110	0.081	0.102	0.091
690	0.097	0.105	0.077	0.097	0.087
720	0.092	0.100	0.073	0.092	0.083
750	0.088	0.095	0.069	0.088	0.079
780	0.084	0.090	0.066	0.084	0.075
810	0.080	0.086	0.063	0.080	0.072
840	0.076	0.082	0.060	0.076	0.069
870	0.073	0.078	0.057	0.072	0.066
900	0.071	0.074	0.054	0.069	0.063
E_∞	0.643	0.667	0.535	0.675	0.625
$10^3(k_i \pm \sigma k_i)$ (sec^{-1})	1.671 ±0.0139	1.661 ±0.0160	1.649 ±0.0094	1.639 ±0.0117	1.662 ±0.0153
ρ	0.99966	0.99959	0.99979	0.99972	0.99961
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.656 ± 0.0125				

Thermolysis of Z-4-Ethylidene-1-pyrazoline-3,3-d_2 (77) at 164.0°C

Time	$E_\infty - E_t$ (volt)				
(sec)	Run #1	Run #2	Run #3	Run #4	Run #5
300	0.093	0.109	0.167	0.120	0.148
330	0.088	0.103	0.158	0.114	0.140
360	0.083	0.098	0.150	0.108	0.133
390	0.079	0.093	0.142	0.103	0.126
420	0.075	0.088	0.135	0.098	0.120
450	0.071	0.083	0.128	0.093	0.114
480	0.067	0.079	0.121	0.088	0.108
510	0.063	0.075	0.115	0.083	0.103
540	0.060	0.071	0.109	0.079	0.098
570	0.057	0.067	0.103	0.075	0.093
600	0.054	0.063	0.098	0.071	0.088
630	0.051	0.060	0.093	0.067	0.083
660	0.048	0.057	0.088	0.063	0.079
690	0.045	0.054	0.083	0.060	0.075
720	0.043	0.051	0.079	0.057	0.071
750	0.041	0.048	0.075	0.054	0.067
780	0.039	0.045	0.071	0.051	0.063
810	0.037	0.043	0.067	0.048	0.059
840	0.035	0.041	0.063	0.045	0.056
870	0.033	0.039	0.059	0.043	0.053
900	0.031	0.037	0.056	0.041	0.050
E_∞	0.373	0.437	0.655	0.468	0.557
$10^3(k_i \pm \sigma k_i)$	1.820	1.817	1.806	1.811	1.797
($\sec^{-1}$)	±0.0148	±0.0108	±0.0125	±0.0107	±0.0173
ρ	0.99967	0.99978	0.99973	0.99978	0.99959
$10^3(k \pm \sigma_k)$ ($\sec^{-1}$)	1.810 ± 0.0092				

Thermolysis of 4-Ethylidene-1-pyrazoline-3,3,5,5-d_4 (128) at 164.0°C

Time	$E_\infty - E_t$ (volt)				
(sec)	Run #1	Run #2	Run #3	Run #4	Run #5
330	0.109	0.091	0.097	0.114	0.101
360	0.104	0.087	0.093	0.109	0.097
390	0.099	0.083	0.089	0.104	0.093
420	0.094	0.079	0.085	0.100	0.089
450	0.090	0.076	0.081	0.096	0.085
480	0.086	0.073	0.077	0.092	0.081
510	0.082	0.070	0.074	0.088	0.077
540	0.078	0.067	0.071	0.084	0.074
570	0.074	0.064	0.068	0.080	0.071
600	0.071	0.061	0.065	0.076	0.068
630	0.068	0.058	0.062	0.073	0.065
660	0.065	0.055	0.059	0.070	0.062
690	0.062	0.052	0.056	0.067	0.059
720	0.059	0.050	0.053	0.064	0.056
750	0.056	0.048	0.051	0.061	0.053
780	0.053	0.046	0.049	0.058	0.051
810	0.051	0.044	0.047	0.055	0.049
840	0.049	0.042	0.045	0.052	0.047
870	0.047	0.040	0.043	0.050	0.045
900	0.045	0.038	0.041	0.048	0.043
930	0.043	0.036	0.039	0.046	0.041
E_∞	0.393	0.342	0.370	0.427	0.361
$10^3(k_i \pm \sigma_{k_i})$ (sec^{-1})	1.558 ±0.0085	1.536 ±0.0116	1.521 ±0.0102	1.527 ±0.0121	1.516 ±0.0140
ρ	0.99981	0.99970	0.99974	0.99968	0.99961
$10^3(k \pm \sigma_k)$ (sec^{-1})	1.532 ± 0.0165				

VITA

The author was born in Seoul, Korea on July 13, 1945. He entered Kyunggi High School, Seoul in 1961, and in 1964 was accepted by Seoul National University, Seoul. After serving for Korean Army from 1966 to 1970, he graduated with a B.Sc. in Chemistry in 1972. Upon graduation he was employed by Miwon Industrial Company Ltd. in its laboratory. In 1975 he entered the Faculty of Graduate Studies at the University of Alberta, Edmonton, Canada, where he served as a Graduate Teaching Assistant in Chemistry while completing his Ph.D. program.

In 1977 he married Sung S. Chang and is now the father of one boy.