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NAME OF AUTHOR/*NOM DE L'AUTEUR* Minoru Suda

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NAME OF SUPERVISOR/*NOM DU DIRECTEUR DE THÈSE* Prof. Satoru Masamune

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THE UNIVERSITY OF ALBERTA

THE $(CH)_4$ SPECIES

by

MINORU SUDA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
AND RESEARCH IN PARTIAL FULFILMENT OF THE
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PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1975

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

THE $(CH)_4$ SPECIES

submitted by MINORU SUDA in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

....
S.Masamune (Supervisor)

....
R.J.Crawford

R S Brown
R.S.Brown

....
W.A.G.Graham

H Baadsgaard
H.Baadsgaard

....
V.Boekelheide (External Examiner)

Date September 3 1975

To Michiko

ABSTRACT

The $(CH)_4$ system comprises only two geometrically possible isomers, [4]annulene (cyclobutadiene) and tetrahedrane (tricyclo[1.1.0.$0^{2,4}$]butane). Part I of this thesis describes a successful synthesis of a crystalline [4]annulene derivative and the matrix isolation of the parent compound. Part II concerns several approaches toward the construction of the tetrahedrane skeleton.

Low-temperature photolysis of methyl tri-tert-butylcyclopropenyldiazoacetate (46) has led to the quantitative formation of methyl tri-tert-butyl[4]annulenecarboxylate (11) which has been isolated in a crystalline form and characterized fully by use of the physical methods presently available. An X-ray analysis clearly demonstrates that this compound (11) is rectangular, consisting of two long bonds (1.547 and 1.506 A) and two short ones (1.406 and 1.376 A), and electron spin resonance (and nuclear magnetic resonance) spectroscopy leads to the conclusion that the ground state is singlet. Because of the symmetrical pattern of substitution on the [4]-annulene system, these findings can justifiably be extrapolated to the properties of the parent compound (1) itself. The generation of (1) in a matrix has also

been achieved. Its ultraviolet spectrum showing a weak absorption around 300 nm provides an additional proof for the singlet ground state of [4]annulene. These results, in addition to others, suggest that the likely geometry of (1) is a rectangle with two short bonds of approximately 1.37 A and two longer ones of the order of 1.51 A. Should [4]annulene prove to be square for reasons that are not obvious at the present moment, both square and rectangular forms must reside in a region of a flat potential energy surface.

Tri-*tert*-butyl[4]annulene (93) has also been prepared in solution and the evaluation of the chemical shift of the ring proton definitely shows that the induced magnetic current of [4]annulene is paramagnetic.

In Part II, several approaches to the synthesis of tetrahedrane derivatives have been examined. Thus far, the final goal has not been achieved using any of these methods. However, precursors themselves have revealed intriguing chemistry. Thus, 2,2,5,5-tetramethylbicyclo-[4.1.0]hept-1(6)-en-7-one (112) represents a cyclopropenone fused with the smallest ring system, and the strain thus involved in this system is reflected in the physical and chemical properties of the cyclopropenone moiety. Another precursor (155), the first homotetrahedranone derivative possessing a good leaving group at the α-position to the carbonyl group, has been synthesized. However, a hoped-for Favorskii reaction has not proceeded, but thermal rearrangement of the tricyclic skeleton to a cyclopropenyl ketene (157) has predominated under the conditions examined.

Hopefully these findings lay the foundation for further development of chemistry in this area and synthetic efforts directed at tetrahedrane will be continued.

ACKNOWLEDGEMENTS

The author expresses his gratitude;

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PART I. [4]ANNULENE.

CHAPTER I. INTRODUCTION.

A. Historical.

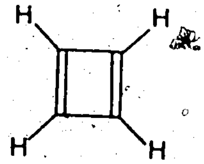
An [n]annulene[1] is a monocyclic, fully conjugated polyene. The number of CH moieties in the ring is indicated by an arabic numeral in the bracket. For instance, benzene is [6]annulene. From the moment when Kekulé[2] first formulated benzene as cyclohexatriene stating that "man könnte dann Benzol durch ein Sechseck darstellen",* the questions were immediately raised as to whether benzene was unique in exhibiting the so-called aromatic properties and further as to whether its vinylogs would show similar behavior. It was in this connection that Willstätter[3] in 1911 prepared [8]annulene (cyclooctatetraene) and found that in contrast to benzene, [8]annulene was quite reactive and had properties characteristic of polyenes. The chemical difference of these two compounds, [6]- and [8]annulene, had not been explained until 1931 when Hückel[4] applied the molecular orbital theory to the annulene system. He predicted that an annulene would possess relative electronic stability if the carbon skeleton contains $(4n+2)\pi$-electrons, whereas the $(4n)\pi$ series would behave in a manner expected

---

*) Reference 2, p.158.

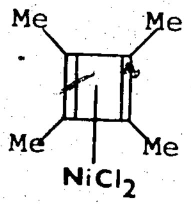
for polyenes. Guided by this simple Hückel rule, many chemists have attempted to prepare other annulenes. The first synthesis of [18]annulene[5] by Sondheimer in 1959 was indeed a significant accomplishment in annulene chemistry and successful preparations of many other [4n+2]annulenes soon followed.[6] [4n]Annulenes ([12]-,[7] [16]-,[8] and [20]-[9] annulenes) were prepared and shown to be reactive in accord with the Hückel rule.

[4]Annulene (cyclobutadiene) 1, one of the $(CH)_4$ species and also the smallest member of [4n]annulene, has been the subject of synthesis for over a century. In spite of numerous attempts made around the turn of this century, the preparation of [4]annulene was totally unsuccessful. After Hückel predicted that [4]annulene itself would be an unstable species, attempts focused on some modifications which may stabilize this intrinsically reactive 4π-electron system have met with some successes. In 1956 Longuet-Higgins[10] published an interesting result of his calculation that coordination with a transition metal would stabilize the [4]annulene system, and this prediction was indeed realized three years later by the synthesis of stable tetramethyl[4]annulenenickel chloride



1

2.[11] An iron complex (3) of the parent [4]annulene was also prepared in 1965 by Pettit.[12] A large number of [4]annulene metal complexes are now recorded, but it is obvious that they cannot be regarded as the cyclic 4π-system because the electronic structures are very much perturbed by the metal coordination.



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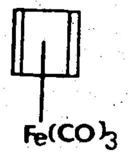

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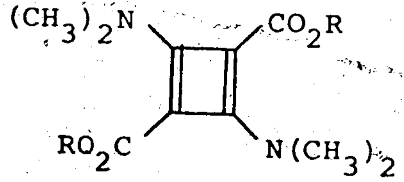
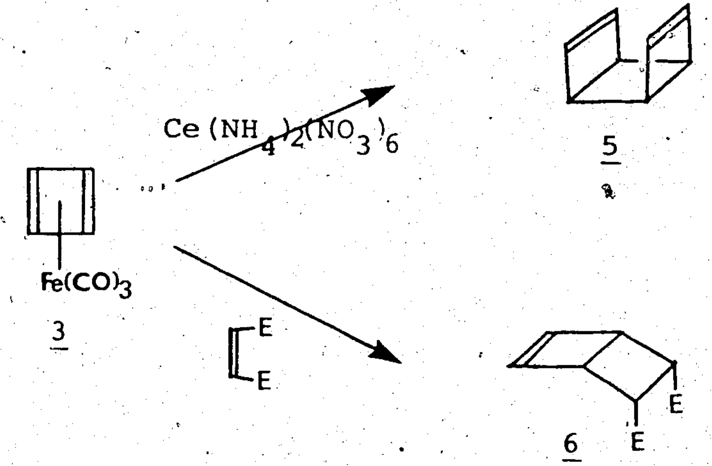
Another modification was proposed by Roberts,[13] and later by Hoffmann.[14] They predicted a greater stability for a [4]annulene derivative that possesses electron-donating and electron-accepting substituents in the proper positions, and in 1968 two groups isolated diethyl and dimethyl 2,4-bis(diethylamino)-1,3-cyclobutadiene-1,3-dicarboxylate 4, both as pale yellow crystals.[15] Again, these do not represent the true [4]annulene system, because of the extended conjugation of the double bonds with the substituents.



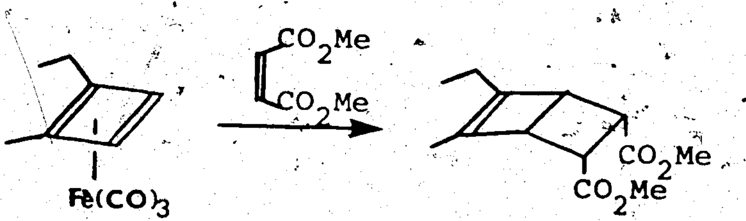
R; CH_3, C_2H_5

4

Several reactions have been recorded which may involve [4]annulene as a reaction intermediate. When [4]annulene-iron tricarbonyl 3 was oxidatively decomposed with ceric ammonium nitrate, the sole product was the syn-dimer 5 of [4]annulene, and if a dienophile was present, the corresponding Diels-Alder type adduct 6 was produced in a stereospecific manner.[16] These results indicated the intermediacy of [4]annulene 1. The life-time of 1 in the gas phase was estimated to be on the order of several msec.[17,18] Iron complex 3 was flash-photolyzed in helium and the variation of the intensity of mass peak for [4]annulene (m/e=52) with time was followed using oscillograms.[17] It was found that only the signal with m/e=52 decayed rapidly in the first 1 or 2 msec. This experiment has provided the first direct evidence that [4]annulene is a discrete entity and has a definite life-time. Although the report[16b] that claimed the successful pot-to-pot distillation of this reactive species must be incorrect



in view of the life-time measured in the gas phase, it was recently clearly shown that free [4]annulene was actually liberated from its iron complex in the above oxidative reaction.[19] When optically active methylethyl[4]annulene-iron tricarbonyl 7 was oxidatively decomposed by ceric ammonium nitrate in the presence of dimethyl maleate, a racemic adduct 8 was obtained.[19a] The only interpretation to accomodate this result is that [4]annulene 9 is free from the metal when it reacts with the dienophile.



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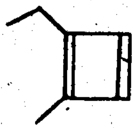

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All reports before 1967 concerning [4]annulene and related compounds are well summarized in a recent monograph.[20] When we initiated our project aimed at the characterization of the [4]annulene system, it appeared an almost hopeless venture to isolate or to detect the parent or simply substituted [4]annulenes, unless new approaches were adopted. Needless to say, no physical properties of the parent compound were known except for the life-time in the gas phase.

B. Hückel rule.

It is appropriate at this stage to elaborate on the Hückel rule. In recent years numerous experimental findings have been made which support this rule, despite the bold assumptions utilized in formulating it.[21]

Hückel's theory for a fully conjugated monocyclic polyene first assumes that the planar σ-bonded framework is completely separated from the π-system. This latter system is made up of $2p_z$ carbon orbitals which are perpendicular to the plane of the molecule. The interaction between the non-adjacent p_z orbitals is assumed to be negligible. Furthermore, the molecule is regarded as consisting of equivalent CH units which have equal carbon-carbon bond distances around the periphery. A linear combination of the p_z atomic orbitals then leads to a set of molecular orbitals (MO's), some having energies lower than those of the constituent p_z orbitals (bonding MO's) and others having higher energies (anti-bonding MO's). Only the [4n]annulenes possess doubly degenerate non-bonding MO's which have the same energy as the constituent p_z orbitals. The [4n+2]annulenes, on the other hand, do not possess such doubly degenerate non-bonding MO's. Accordingly the annulenes are divided into two groups, the [4n]- and [4n+2]annulenes.

The [4n+2]annulenes (of which benzene is a representative) have closed-shell configurations for their π-MO's (see Figure I. A). As a result, these annulenes are relatively stable; i.e. they are more stable than their corresponding acyclic polyenes. For example, the total π-electron energy of [6]annulene is ca. 18 kcal/mol lower (and hence more stable) than that of 1,3,5-hexatriene.*

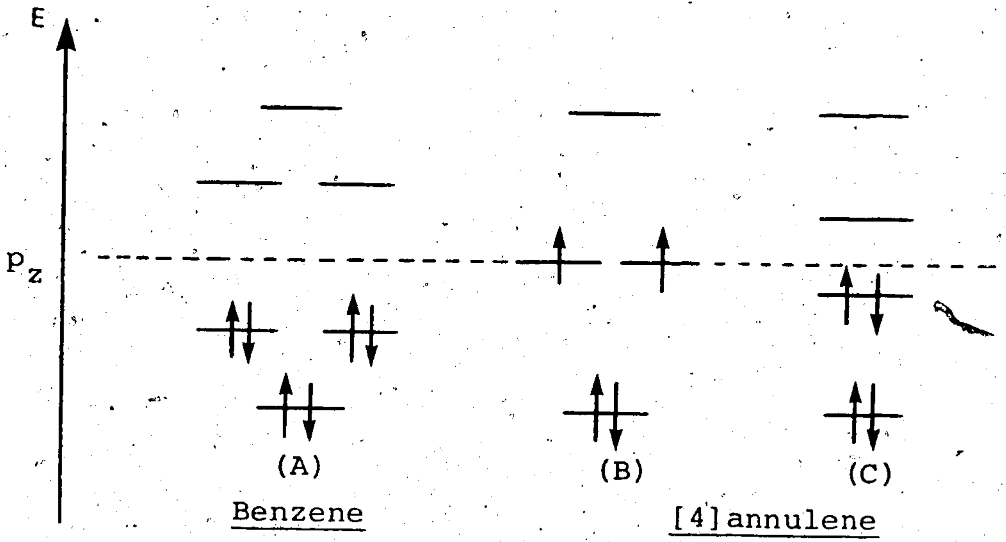

Figure I; π-Molecular orbitals for benzene and [4]annulene.

The [4n+2]annulenes exhibit diamagnetic anisotropy, showing low-field shifts for the outer-annular protons, and high-field shifts for inner-annular ones, in their proton magnetic resonance (pmr) spectra. This property is a result of the interatomic ring current[22] which is induced

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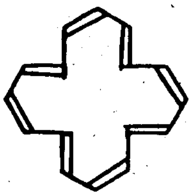
*) Total π-energies of [6]annulene and 1,3,5-hexatriene are 6α+8β and 6α+6.988β ,respectively (where α and β are Coulomb and resonance integrals, respectively). The difference of these values is hence ca. 1.0 β =18 kcal/mol.[21]

in the cyclic π-electron system when a magnetic field is applied perpendicular to the plane of the ring.

The simple Hückel MO treatment described above predicts that the [4n]annulenes, in contrast to the [4n+2]-annulenes, are relatively unstable and are thermodynamically less stable than their corresponding acyclic polyenes. This is due to the presence of the doubly degenerate non-bonding MO's. Two electrons occupy these MO's, one in each MO and having parallel spin (Hund's rule). Thus, the [4n]annulene should have a triplet ground state (Figure I. B). This unfavorable situation may be avoided by Jahn-Teller distortion which reduces the molecular symmetry and splits the degenerate orbitals. This can be achieved either by alternation of the carbon-carbon bond lengths, or by deformation of the planarity of the system. The effect of the bond-alternation is that one of the two non-bonding MO's is stabilized, while the other is destabilized. As a result, the two electrons can now form a pair in the non-degenerate MO, thus stabilizing the total π-electron system (Figure I. C). Deviation from the planarity of the system may also result in the splitting of the two non-bonding MO's. However, in the case of the [4]annulene system, it is unlikely that the four-membered ring is distorted to a non-planar conformation since the increase of strain energy involved in the σ-framework and the loss of overlap between the p_z orbitals might exceed or counterbalance the gain in energy caused by the electron pairing.

The [4n]annulenes are expected to show paramagnetic ring currents,[23] leading to high-field pmr chemical shifts for the outer-annular, and low-field pmr chemical shifts for the inner-annular protons. In the absence of bond-alternations, an infinite paramagnetic ring current is predicted by theoretical calculations.[23] This situation is not likely to occur, however, because the molecule will be distorted for the reason discussed above. For instance, [16]annulene 10 is distorted from planarity exhibiting bond alternations,[8c] and shows distinct inner and outer protons in its pmr spectrum,[8b] with the latter appearing at higher field, as predicted.



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There is however still some controversy over the ground state of the simplest annulene, [4]annulene. It may exist as a square triplet (ST), as predicted by the Hückel rule, or as a deformed, possibly rectangular, singlet (RS). A square singlet (SS) structure would be less stable than the RS structure according to the Jahn-Teller theorem. Theoretical calculations on this system have repeatedly been carried out, and the results are presented in the next section.

C. Theoretical treatment of [4]annulene.

Recent advances in computer technology have made it possible to calculate the energy levels of MO's of complicated molecules. Several calculations[24] have appeared in recent years using different approximations in order to evaluate the ground state nature of [4]annulene, and the results are listed in Table I. Except for an earlier calculation,[24b] which was later revised, all the treatment appear to agree on one point, namely that the rectangular singlet (RS) is more stable than its square counterpart (SS). In the square geometry the relative stabilities of the singlet and triplet states appear to be uncertain. A recent treatment,[24f] which was carried out apparently to confirm the result obtained from the infrared spectrum of [4]annulene, concluded that "the square singlet lies 7.7 kcal/mol above the square triplet and is unstable to a rectangular distortion". However, no mention was made as to the relative stability of the two species, ST and RS.

Allinger[24b,c] also calculated the expected ultra-

Relative stabilities (in kcal/mol) and C-C bond lengths (in A, in parentheses).

	SS	ST	RS	Ref.
SCF				
PPP	---	14.1 (1.424)	0 (1.514) (1.338)	24a
SPO	---	21.2 (1.424)	0 (1.514) (1.338)	24a
PP	22.8 (1.424)	0 (1.424)	6.1 (1.518) (1.334)	24b
PP	4.8 (1.427)	15.3 (1.422)	0 (1.498) (1.331)	24c
ab initio				
CI	10.8 (1.424)	24.4 (1.424)	0 (1.466) (1.381)	24d
SCF				
π-appro.	16.4 (1.397)	2.0 (1.425)	0 (1.512) (1.338)	24e
MINDO/2	16.6 (1.425)	---	0 (1.495) (1.319)	24e
ab initio				
GVB	7.7	0	?	24f
MINDO/3	13.1 (----)	5.9 (1.433)	0 (1.533) (1.342)	24g

Table I; Calculated relative stabilities and C-C bond lengths of possible [4]annulene structures.

violet absorption maxima of [4]annulene and predicted confidently that a singlet, whether square or rectangular, has allowed transitions around 200 nm and weak forbidden transitions at much longer wavelength in the visible region. In contrast, the triplet was predicted to absorb very strongly (ε 10^3 at 380 nm). Thus, as Allinger stated, this difference would serve to distinguish between the singlet and triplet.

The above is a brief historical description of the chemistry of [4]annulene. The following sections describe our efforts to elucidate the ground state properties and the chemistry of this intriguing species.

CHAPTER II. OUTLINE OF OBJECTIVES.

The objective of the work described in this part is the elucidation of the ground state properties of [4]annulene. The major problems associated with this system are concerned with its spin multiplicity and exact geometry.

Ordinarily, the extensive use of various spectroscopic methods helps to clarify these types of problems. However, in order to characterize [4]annulene itself, only a limited number of the spectroscopic methods can be used. This is due to its great reactivity and the resultant difficulties encountered in its isolation or detection. [4]Annulene must first be retained in a monomeric form for an extended period of time. Techniques to utilize a low-temperature matrix which is rigid enough to trap [4]annulene molecules as such appear to be most promising. As a result of the imposition of this basic experimental limitation, only electron spin resonance (esr), ultraviolet (uv), and infrared (ir) spectroscopies can be presently employed to characterize [4]annulene.

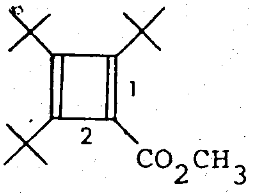
The esr spectrum of a molecule trapped in such a system clearly indicates its spin state. The uv spectrum suggests the electronic states of the π-electrons, and, as mentioned earlier, triplet and singlet [4]annulenes are predicted to have completely different uv spectra.[24b,c]

Hence the uv spectrum of [4]annulene would also provide information as to its spin state. The ir spectrum provides information about the vibrational modes of the molecule. Theoretical calculations predict the number and line positions of ir absorptions both for D_{4h} (square planar)- and D_{2h} (rectangular planar)-[4]annulenes. Thus, the ir spectrum would distinguish between the two geometries conceivable for the molecule.

Part of the present study is concerned with the characterization of matrix-isolated [4]annulene by means of its uv and esr spectra.

Although the spectroscopic means described above can provide the ground state properties of [4]annulene to a certain extent, there remains always an ambiguity as to the exact geometry of the molecule, because the methods to be employed are indirect. Obviously, the best method to obtain this information would be by an X-ray crystallographic analysis. However, to carry out such an analysis a single crystal of the molecule must be available. Furthermore, photoelectron spectroscopy, which would shed light on the energy levels of MO's, also requires at present that a compound be isolable in pure form.

Therefore our interest was also directed to the synthesis of isolable, crystalline [4]annulene derivatives. The following considerations were made in choosing an appropriate derivative: (1) that monomeric [4]annulene derivatives would be isolable if they possessed sterically bulky substituents which would serve to suppress the reactivity toward another molecule, and (2) that the substitution pattern on the ring must be such that the symmetry and the ground state properties of the derivative are as close as possible to those of the parent [4]annulene. We chose methyl tri-tert-butyl[4]annulenecarboxylate 11 as our synthetic target. Examination of a Dreiding model of this compound strongly suggests that the three tert-butyl groups would be bulky enough to retard dimerization, a major reaction that [4]annulene undergoes. Furthermore, the substitution patterns in this compound are such that bond (1) and (2) may be allowed to become equivalent (see figure above). Therefore, if a square were the energy minimum conformation of 11, bonds (1) and (2) would be of equal length.



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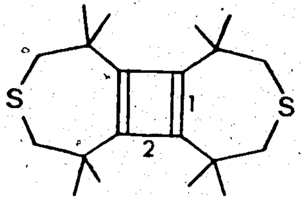
During the course of our experimental investigations, Krebs et al. reported the first isolation of a [4]annulene derivative 12.[25] Its X-ray analysis[26] was reported only after our own work had been completed. Although demonstrating that the central four-membered ring has a rectangular geometry (bond lengths are 1.340 and 1.600 Å for (1) and (2), respectively), their results do not provide any unambiguous information regarding the geometry of parent [4]annulene. This is, of course, because bonds (1) and (2) in 12 are not equivalent, as far as the substitution pattern is concerned.



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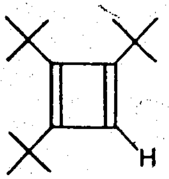
Finally, as stated in the introduction, pmr spectroscopy provides strong information about the nature of the ring current in the annulenes. ^{13}C-Nuclear magnetic resonance (cmr) spectroscopy, however, provides no such information; cmr chemical shifts are relatively insensitive to such a ring current, even when carbons are uniquely positioned in the system.[27] Thus, in order to evaluate the nature of a ring current, a proton must be directly attached to the annulene system. Analogous to 11, tri-*tert*-butyl[4]annulene 13 was expected to be isolable as such, allowing the observation of the pmr chemical shift of the unique proton in 13. A third part of our study on the [4]annulene system thus concerns the synthesis of an isolable [4]annulene derivative possessing a proton directly attached to the ring.



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In the next chapter, the syntheses and the physical properties of these [4]annulene derivatives will be presented in detail. Also included is the spectroscopic detection of parent [4]annulene isolated in a matrix.

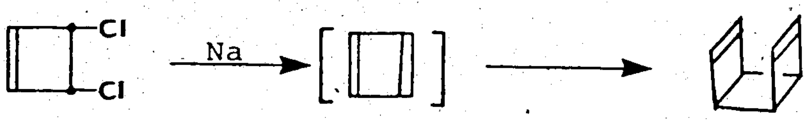
CHAPTER III. RESULTS AND DISCUSSION.

A. Preparation of highly substituted [4]annulene derivatives.

1. Preliminary attempts.

Of several conceivable approaches[20] for the construction of the [4]annulene system, the following appeared to be the most promising: (1) dehalogenation of dichlorocyclobutene derivatives by metals, (2) decomposition of [4]annulene-metal complexes, and (3) rearrangement of cyclopropenyl carbene intermediates.

The dehalogenation of dichlorocyclobutene derivatives by metals has been used rather generally in the preparation of transient [4]annulene derivatives. For instance, [4]annulene 1 itself is generated when *cis*-3,4-dichlorocyclobutene 14 is treated with sodium amalgam.[28] The product actually isolated is not 1, but the *syn*-dimer 5 owing to the extremely facile dimerization of 1.



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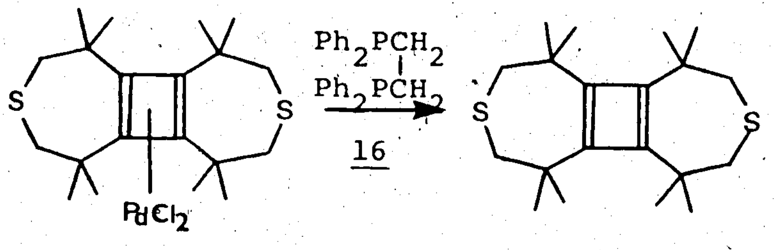
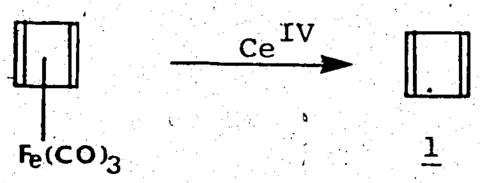
The second approach was that used in the preparation of the first isolable [4]annulene derivative 12,[25] which was obtained by the reaction of palladium complex 15 with



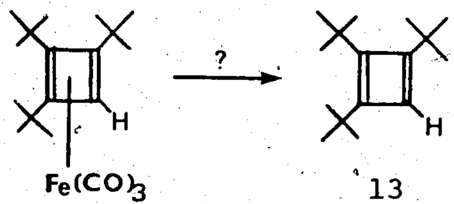
15 12

ethylenebis(diphenylphosphine) 16. The oxidative decomposition of [4]annuleneiron tricarbonyl 3[12] by ceric ammonium nitrate has been used in many reactions as the source of transient [4]annulene 1.[16,29]



3 1

We expected that decomposition of iron complex 17[30] at low temperature and under mild conditions would give rise to the desired [4]annulene derivative 13. Thus, photolysis of 17 at -60° in the presence of dimethyl acetylenedicarboxylate was carried out, and an iron-free adduct was isolated. The mass spectrum and elemental analysis indicated that the product was a 1:1:1 adduct of tri-*tert*-butyl[4]annulene, dimethyl acetylenedicarboxylate, and carbon monoxide. Its pmr spectrum revealed three different *tert*-butyl and two methyl groups. The methine proton appeared at δ 3.75. Likely structures for this adduct are bicyclo[2.2.1]heptadienone 18 and bicyclo-[3.1.0]heptadienones 19 and 20. Compound 18 would be expected to eliminate carbon monoxide easily to form a benzene derivative.[31] From the fact that the obtained adduct is fairly stable and the chemical shift of the methine proton in the pmr spectrum, we tentatively assigned structure 19 to this product. This molecule could arise if the photo-decomposition of iron complex 17 resulted in the insertion of carbon monoxide into the ring, to form a cyclopentadienone derivative 21, which further reacted



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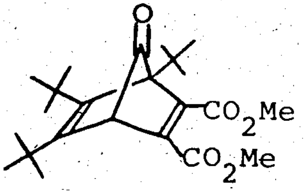

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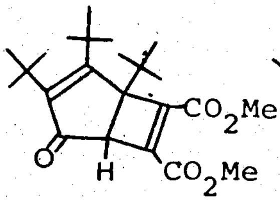

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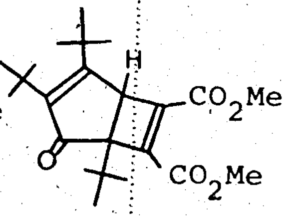

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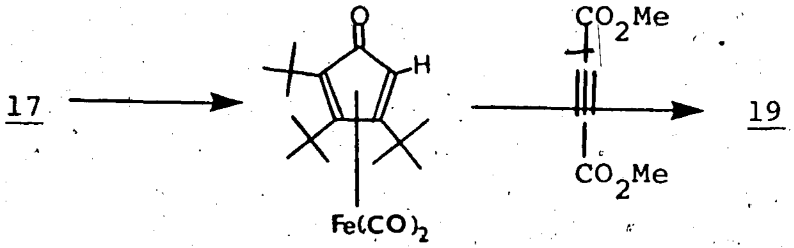
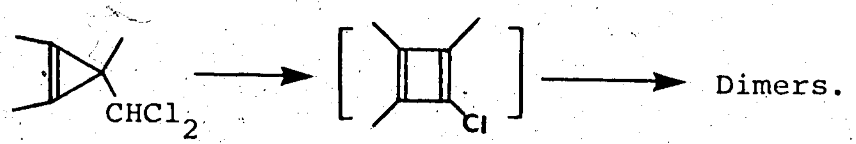
with dimethyl acetylenedicarboxylate to give 19. This approach was therefore abandoned in the light of this finding.



21

The most promising method to construct the [4]annulene system now appeared to be the rearrangement of a cyclopropenyl carbene intermediate. Closs et al. treated dichloride 22 with n-butyllithium at -20° and obtained a mixture of the dimers of chlorotrimethyl[4]annulene 23 in 85% yield.[32]



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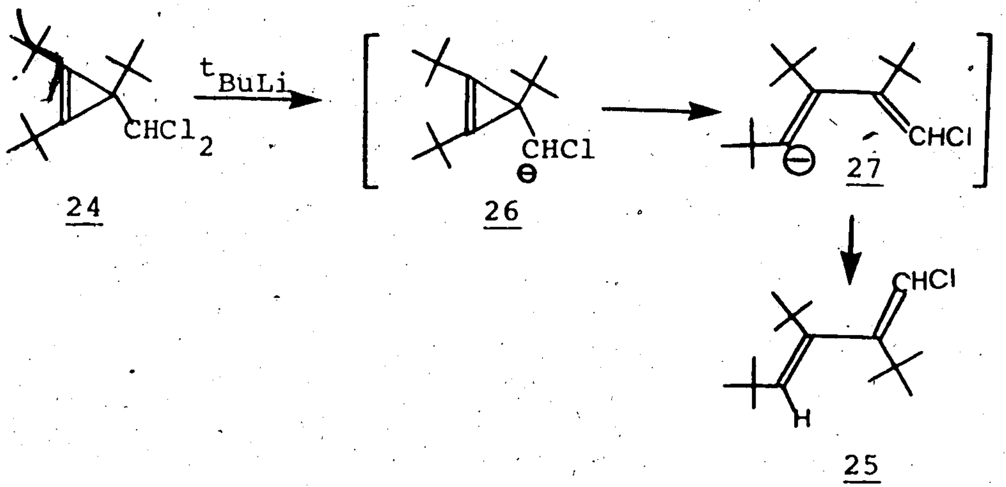
22

We performed a similar reaction using 3-dichloromethyl-1,2,3-tri-tert-butylcyclopropene 24.[30] Use of n-butyllithium yielded neither a [4]annulene derivative nor its dimer, whereas a butadiene derivative 25 was isolated when tert-butyllithium was used. It can be envisioned that tert-butyllithium could undergo a metal-halogen exchange reaction with 24 to form lithium salt 26. This anion then isomerized to the acyclic isomer 27 with a reduction of steric crowding, and finally protonation during the process of work-up led to the formation of the diene 25.



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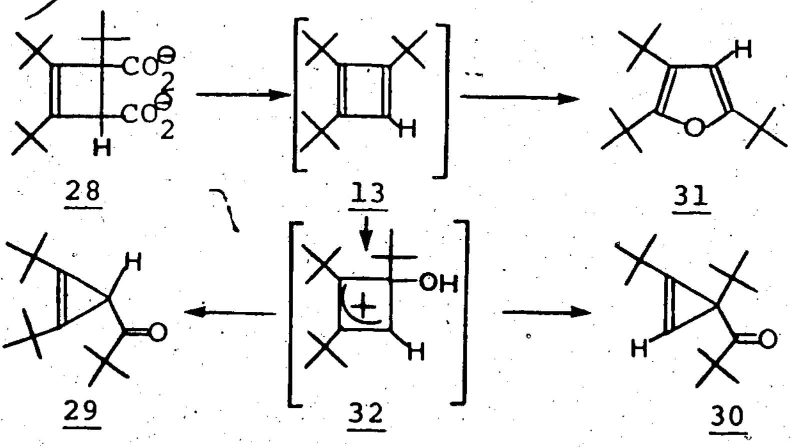
Maier et al. subjected diacid 28 to electrolysis and isolated two cyclopropenyl ketones 29 and 30, when rather drastic conditions (100 V/1 A, room temperature) were applied, while furan 31 was the sole product under mild conditions (2 V/8 mA, room temperature).[23] Importantly, the formation of 31 suggested that tri-tert-butyl-

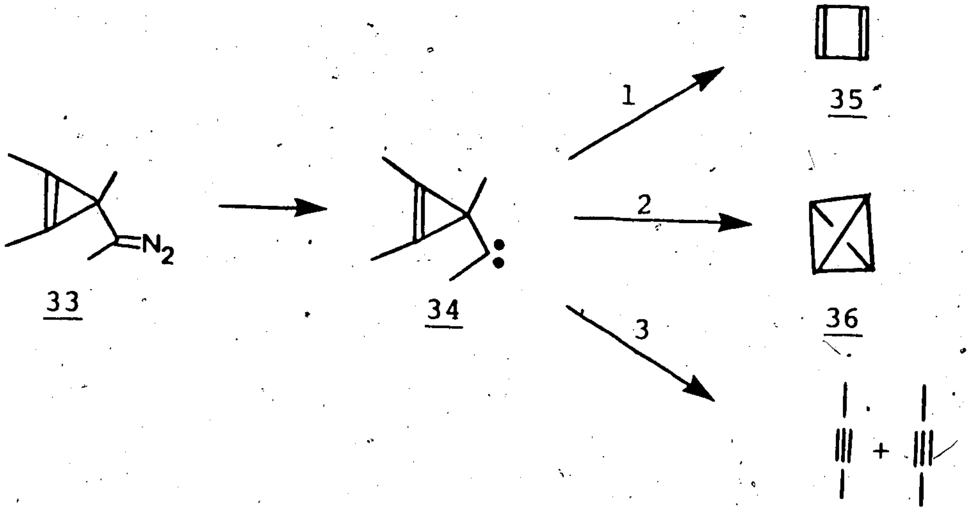


28
13
31
29
32
30

[4]annulene 13 was the intermediate which had reacted with oxygen to produce 31. It is reasonable to expect that, due to steric repulsion, the dimerization of 13 was completely prevented. That the cyclopropenyl ketones 29 and 30 were produced under drastic conditions can be explained by the over-oxidation of 13 to a cationic intermediate 32 which rearranged to 29 and 30 in order to relieve the steric repulsion of the three *tert*-butyl groups on the four-membered ring.

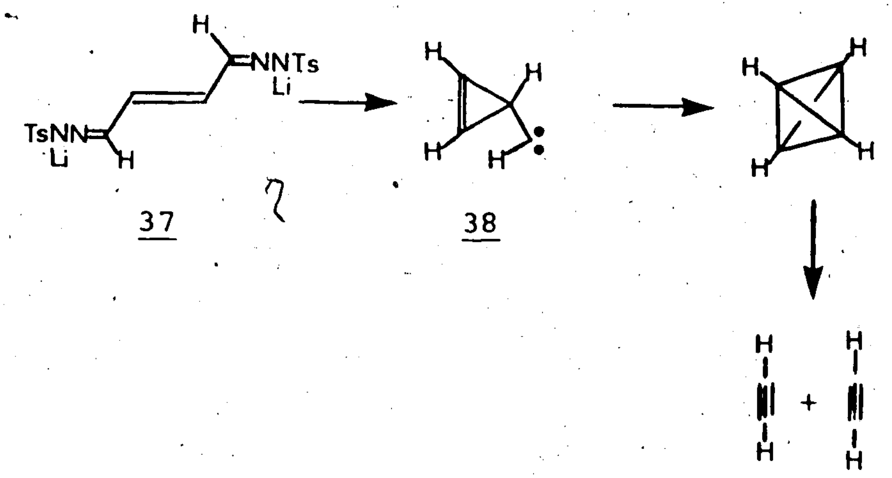
We judged from these results that the hoped-for [4]annulene derivative must be generated by a reaction, which would proceed smoothly and without side reactions and also could be performed at low temperature, so that one could examine the product by spectroscopic methods without further purification. We therefore reasoned that cyclopropenyl diazo compound 33 would serve as suitable precursors for further studies.

Photolysis of diazo compound 33 initially results in the liberation of a nitrogen molecule to form carbene intermediate 34. This carbene can undergo rearrangement in three different ways. First, the cyclopropenyl group may ring-expand to form a [4]annulene 35 (route 1). Secondly, the carbene center may insert into the double bond, forming a tetrahedrane 36 (route 2). Finally, the cyclopropenyl carbene may split into two acetylenic molecules (route 3). It is reported[34] that tetrahedrane decomposes into two acetylene molecules spontaneously. If this is indeed the case, routes 2 and 3 are indistinguishable in the case when the three-membered ring carries three identical substituents.

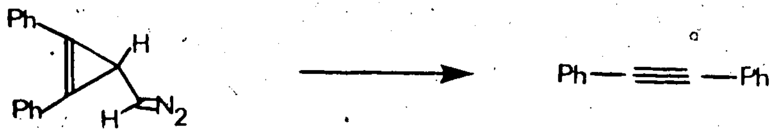


The following are some examples of the types of carbene reactions described above. First, the reaction of 22 with *n*-butyllithium (which was described on p.21)[32] to form dimers of chlorotrimethyl[4]annulene 23, exemplifies a reaction that proceeds *via* route 1.

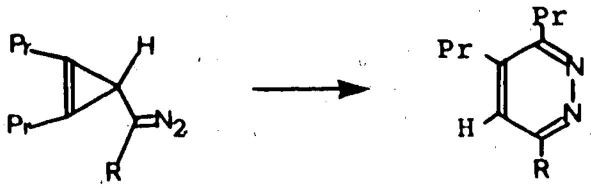
The dilithium salt of ditosylate 37, when pyrolyzed, produced acetylene as the sole volatile product in 20-30% yield.[35] Isotope labeling experiments revealed deuterium scrambling. Provided that the reaction proceeds stepwise as shown below, a cyclopropenyl carbene 38 is formed as the intermediate, which then forms tetrahedrane (route 2). Under the reaction conditions tetrahedrane reportedly splits into two acetylene molecules. The isotope labeling experiment seems to be consistent with the above mechanism.



White et al. prepared compound 39, and found that its only photolysis product was diphenylacetylene, probably formed by route 3.[36] No phenylacetylene was formed.



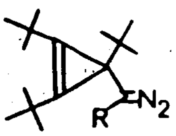
Ciabattoni et al. synthesized diazoalkanes 40 from the corresponding N-nitrosourethane or hydrazone.[37] The diazoalkanes were, however, found to be too unstable to be purified or handled further. Under aprotic conditions, these diazoalkanes isomerized to pyridazine derivatives 41.


R; H, CH_3

40 41

These results indicate that the fate of the cyclopropenyl carbene is greatly influenced by the nature of the substituents both on the ring and at the carbene center.

We anticipated that tri-tert-butylcyclopropenyl diazo compounds 42 would undergo rearrangement following route 1. The presence of three tert-butyl groups on the ring of 42 would affect its reaction course. Firstly, the isomerization to form a pyridazine derivative would be blocked, because the resultant pyridazine would possess three tert-butyl groups on three adjacent carbons, and this structure is sterically very unfavorable. Furthermore it is known that trimethylcyclopropenyl azide 43[38] isomerizes to triazine 44 slowly at room temperature, whereas tri-tert-butylcyclopropenyl azide 45[39] does not show any tendency toward a similar isomerization, and it can even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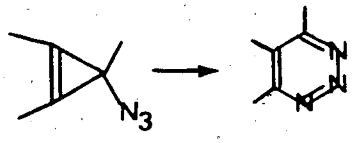
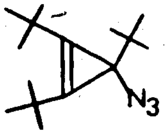
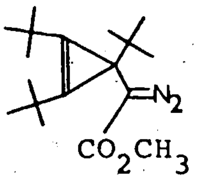

43 44


45

be distilled at 40-50°/0.03-0.05 mmHg. Secondly, the tert-butyl groups would destabilize the single bond of the cyclopropenyl moiety. As a result, the ring-expansion pathway to form the [4]annulene system should be favored over the other two possible pathways.

We further considered the stabilization of the diazo groups by use of an α-carbonyl group. The α-diazo esters usually possess a certain degree of stability, allowing purification and isolation,[40] whereas diazoalkanes are very often too unstable to be isolated and purified. We therefore expected that tri-tert-butylcyclopropenyl diazoacetate (42, $R=CO_2R'$) could be isolated in a pure form.

With all these reasons in mind, we first approached the synthesis of methyl tri-tert-butylcyclopropenyl diazoacetate 46, the potential precursor of 11, and studied its photochemical behavior. Next, we focused upon the synthesis of tri-tert-butylcyclopropenyl diazomethane 47, the potential precursor of tri-tert-butyl[4]annulene 13. Although 47 might not be stable at room temperature, we at least hoped that 47, upon photolysis, would produce 13. This compound is important in that it can provide information about the paramagnetic ring current of the [4]annulene system.



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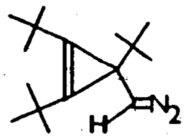
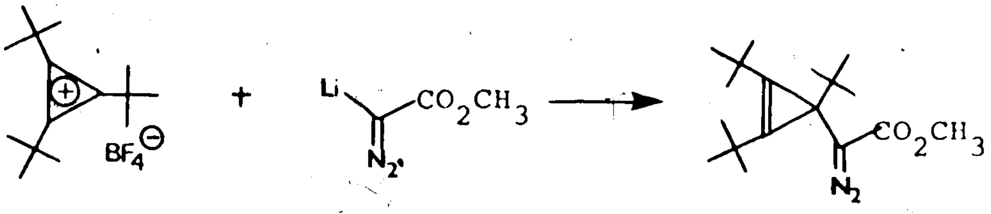


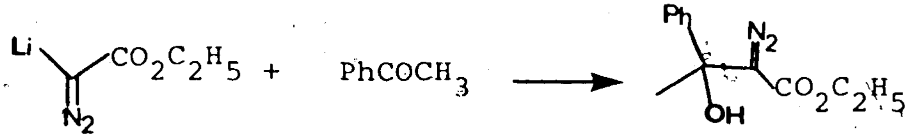
47

2. Methyl tri-*tert*-butyl[4]annulenecarboxylate (11).[41]

A precursor of the title compound is methyl tri-*tert*-butylcyclopropenyldiazoacetate 46. In order to obtain 46, we have examined the direct condensation of anion 48, derived from methyl diazoacetate, with tri-*tert*-butylcyclopropenium fluoroborate 49.[42] The lithium salt of ethyl diazoacetate was first prepared by Fransnelli *et al.*[43] in 1970 by the reaction of ethyl diazoacetate with *n*-butyllithium at -110°. They found that the salt was reactive toward many electrophilic functional groups, and obtained, for instance, ethyl 2-diazo-3-hydroxy-3-phenylbutyrate 50 in 50% yield on reaction with acetophenone.



49 48 46



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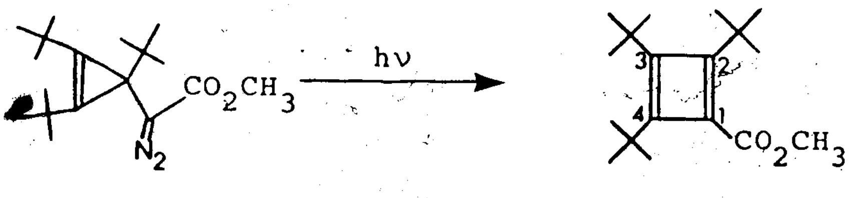
Tri-*tert*-butylcyclopropenium fluoroborate 49 has been known to react easily with nucleophilic reagents despite the presence of bulky substituents, to form the corresponding coupled products.[30,39,42a] We have reacted 49 with the lithium salt 48 of methyl diazoacetate in ether/tetrahydrofuran at -110°. As anticipated, the reaction proceeded smoothly and after chromatography on neutral alumina,[43b] the pure diazoacetate 46 was obtained in 88% yield as yellow crystals, mp 46.0-47.5°. Both the pmr and ir spectra are consistent with the assigned structure 46. The former showed singlets at δ 0.93 (9H), 1.26 (18H), and 3.72 (3H), while the latter exhibited strong absorptions at 2080 cm^{-1} attributable to the diazo stretching, and at 1698 cm^{-1} due to the carbonyl stretching. Diazoester 46 was found to be rather stable and, as reasoned earlier, showed no tendency toward isomerization to form the corresponding pyridazine derivative. Thus, the first task of this approach was completed, and the photochemical reaction of 46 was examined.

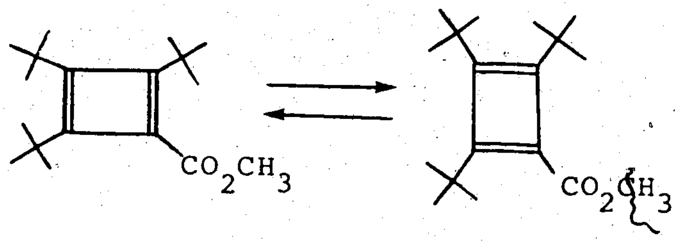
A solution of diazoester 46 in methylcyclohexane-d_{14} was degassed and sealed in an nmr tube, and irradiated at -78° by a high-pressure mercury lamp with a Pyrex filter. After several hours' irradiation, light brown crystals began to form. When the photolysate, after the completion of irradiation, was warmed to room temperature, the precipitated brown crystals dissolved and the solution became dark brown. The solution decolorized rapidly, however, when oxygen was bubbled into the solution. The formation



46 11

of this new product (11) from 46 was almost quantitative, as judged from the pmr spectrum of the photolysate.

The pmr spectrum showed absorptions at δ 1.13 (18H,s), and 1.19 (9H,s) for the tert-butyl groups, and at δ 3.45 (3H,s) for the O-methyl group. The appearance of two different tert-butyl groups easily eliminates the tetrahedrane structure for the photo-product. Within the limit of the nmr time scale, two of the three tert-butyl groups are equivalent. This suggests two possibilities for the geometry of the four-membered ring: one is a square, and the other is a rectangular equilibrating very rapidly between two forms 51 and 52, as shown below.



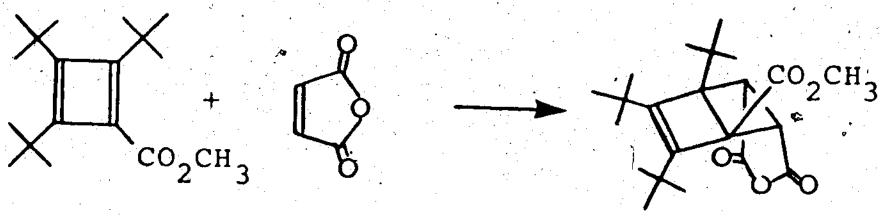
51 52

The cmr spectrum exhibited signals at δ 147.0 and 154.5 for olefinic carbons, in addition to others, supporting the [4]annulene structure. The relative intensities of these signals for olefinic carbons are ca. 1:3, therefore the weaker absorption at δ 147.0 was tentatively assigned as being due to C(3) and the other to the remaining three carbons, C(1),C(2), and C(4), those of C(1) and C(2) being coincidentally overlapped. Although these chemical shift values for the olefinic carbons appear to be somewhat lower than normally expected,[44] they are not exceptional if one considers the presence of the substituents and the unique geometry of the molecule.

Compound 11 was also characterized by a weak and broad uv absorption at λ_{max} 425 nm (ϵ 50) (Figure II.). This weak absorption in the visible region is in good agreement with the prediction that singlet [4]annulene would possess a forbidden absorption in this region.[24b,c]

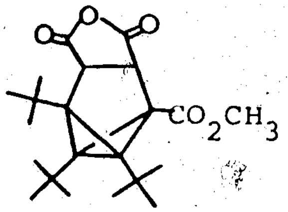
These spectral data thus permit us to assign the [4]annulene structure 11 to the crystalline photolysate.

Chemical transformations of this air-sensitive [4]-annulene derivative provided further support for its structure. Maleic anhydride reacted with 11 to form Diels-Alder adduct 53. The presence of two olefinic carbons in the cmr spectrum of adduct 53 indicated the structure to be as shown, and not dihydrobenzvalene derivative 54. This



11

53



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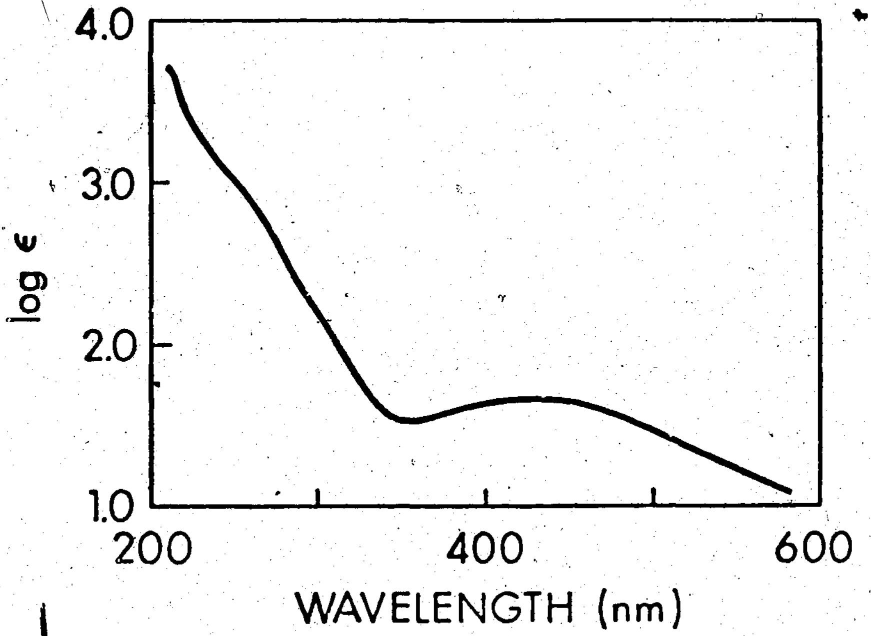
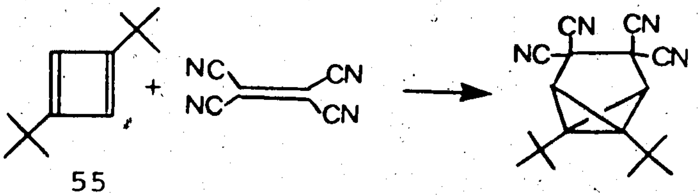


Figure II; Uv spectrum of methyl tri-tert-butyl[4]-annulenecarboxylate 11 in pentane.

behavior is in contrast with an earlier report that 1,3-di-tert-butyl[4]annulene 55, generated in situ from its iron carbonyl complex, reacted with tetracyanoethylene to form 56.[45]



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56

The pmr spectrum of 53 is temperature-dependent (Figure III.). At 70°, the spectrum exhibits three singlets for tert-butyl groups at δ 1.10, 1.20, and 1.30, a sharp singlet for OCH_3 at δ 3.64, and two doublets at δ 4.23 and 3.65. As the temperature is lowered, the absorption for the tert-butyl groups appearing at the highest field starts to broaden and almost disappears at 0°. At this temperature, the second tert-butyl signal, as well as the OCH_3 singlet and the two doublets, show line-broadening. Below -60°, the spectrum does not show any further change, exhibiting a complex pattern in the tert-butyl region. The OCH_3 group and the doublets split into two pairs (ratio ca. 3:1). These spectral changes indicate that the rotation of the carbomethoxy group is completely frozen at -60° resulting in a ca. 3:1 mixture of rotational isomers, and that the

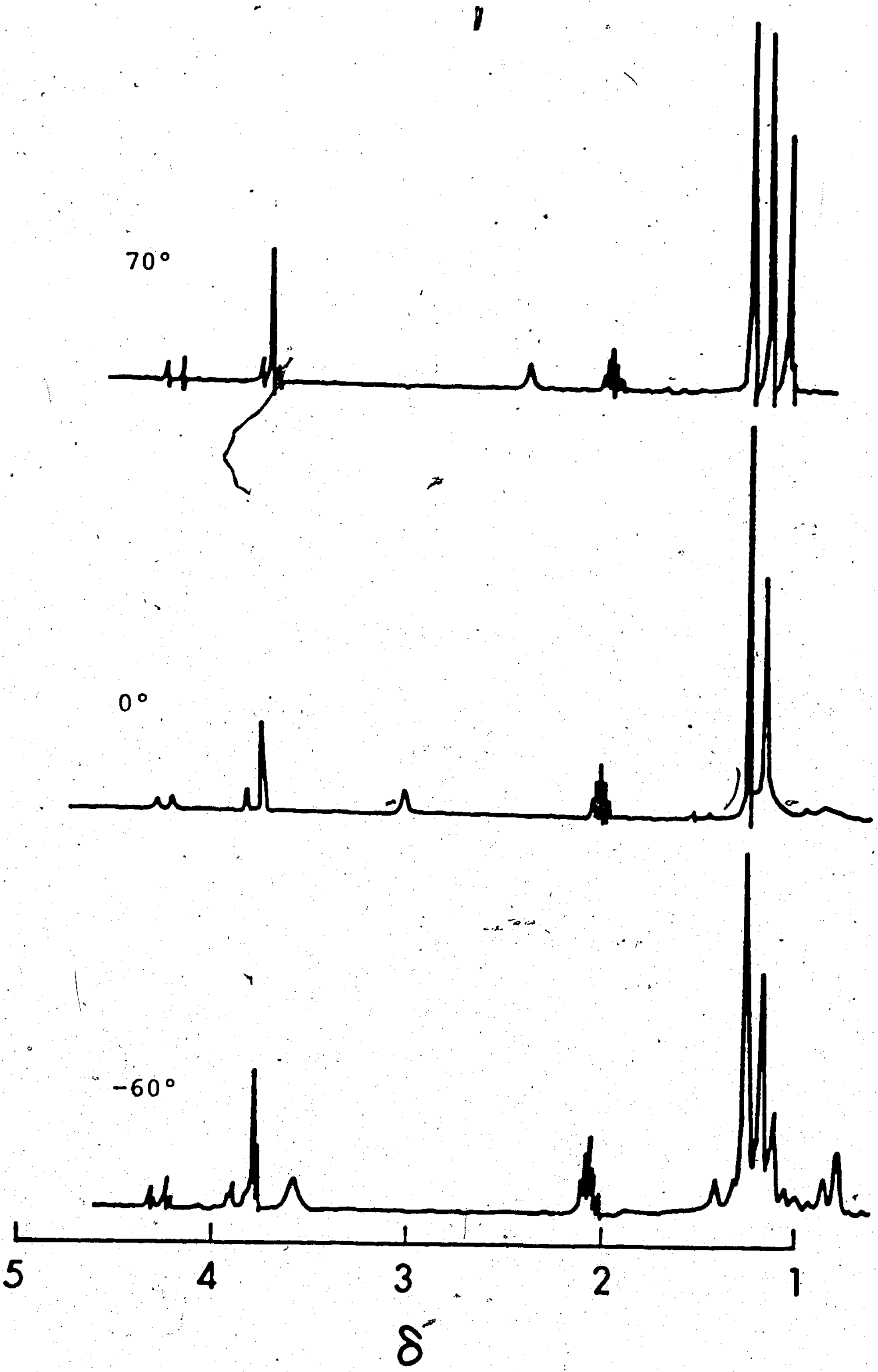
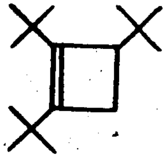


Figure III; Temperature dependent pmr spectrum of 53.

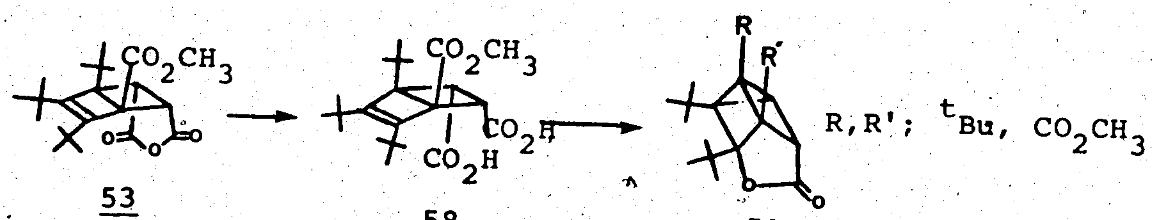
rotation of two tert-butyl groups is also frozen.*

Similarity of the uv spectra of 53 {λ_{max} 215 nm (ϵ 3240), 225 (1665), 235 (680)}, and 1,2,3-tri-tert-butylcyclobutene 57[30b] {λ_{max} 215 (2640), 225 (294), 235 (61)} suggests that the carbomethoxy group is located at a bridge-head position.



57

The stereochemistry of this adduct 53 was established by the following reactions. Hydrolysis to diacid 58 followed by electrolysis, afforded lactone 59. The ir spectrum of 59 showed peaks at 1785 and 1735 cm^{-1} in the carbonyl region, indicating the presence of a five-membered lactone ring. The formation of an intramolecular lactone ring leads to the assignment that the initial adduct 53 has the endo-configuration.



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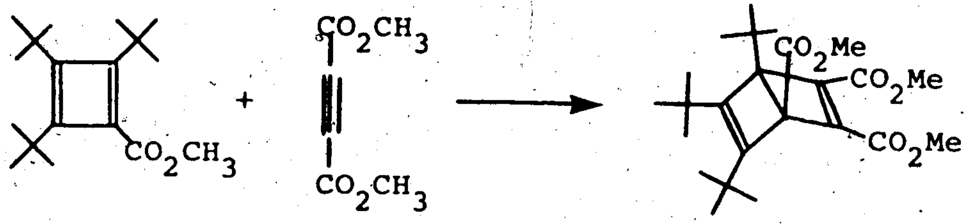
*) Restricted rotation along an axis of C(sp^3)-C(sp^3) single bond was first observed by Brewer et al.,[46] and reviewed by Kessler.[47] The isolation of rotational isomers was also achieved by Ōki et al..[48]

The Diels-Alder adduct 60 of 11 with dimethyl acetylenedicarboxylate was also obtained as colorless crystals, mp 99.5-100.5°. The cmr spectrum of this adduct exhibits four olefinic carbons, thus the adduct has the Dewar-benzene structure. Not surprisingly, attempts to ring-open (at 160°) this Dewar-benzene derivative to the corresponding benzene derivative failed.



11

60

The [4]annulene derivative 11 could be recrystallized at -78° from pentane and sublimed at 50°/0.01 mmHg without decomposition. After sublimation it had a mp of 70°.

With a crystalline derivative in our hands, an X-ray crystallographic analysis was undertaken.[49] A single crystal was placed in a capillary tube, using a dry-box to ensure that the crystal was in an inert atmosphere. This seemingly simple process demanded extraordinary care because of the sensitivity of 11 to oxygen, and was executed by Dr. Nakamura of this laboratory. The X-ray analysis was performed by Drs. James and Delbaere of the Biochemistry

Department. Figure IV shows the geometry of this molecule.[49] It is quite clear that the chemically equivalent bonds C(1)-C(2), C(1)-C(4), and C(2)-C(3), C(3)-C(4) are of <u>unequal</u> length. The two short bonds, C(1)-C(2), and C(3)-C(4) are in the range of the aromatic bond length of 1.394A,[50] therefore definitely much longer than normal double bonds (1.335A).[50] Of the two longer bonds, only C(2)-C(3) is of single bond character whereas C(1)-C(4) has a length similar to that of a bond between C(sp^2) and C(sp^3){<u>viz</u>. C(2)-C(7), C(3)-C(11), and C(4)-C(15)}. Even though there appears to be over-crowding of the <u>tert</u>-butyl groups, the closest H-H approach in this conformation is 2.13A, not significantly shorter than the van der Waals contact distance of 2.2-2.3A expected for hydrogen atoms.

The four carbon atoms of the ring are strictly co-planar. Also, the four non-hydrogen atoms of the carbomethoxy group are co-planar, and the dihedral angle between the plane of this group and that of the ring is 84.1°. Steric interactions with the neighboring <u>tert</u>-butyl groups clearly imposes this conformation on the C(1)-C(5) bond, thus little or no π-electron overlap from the C(5)-C(1) bond with the ring is possible.

Because of the substitution pattern of <u>11</u>, the two bonds C(1)-C(4) and C(1)-C(2) would be of equal length, if a square conformer were the true energy minimum of this

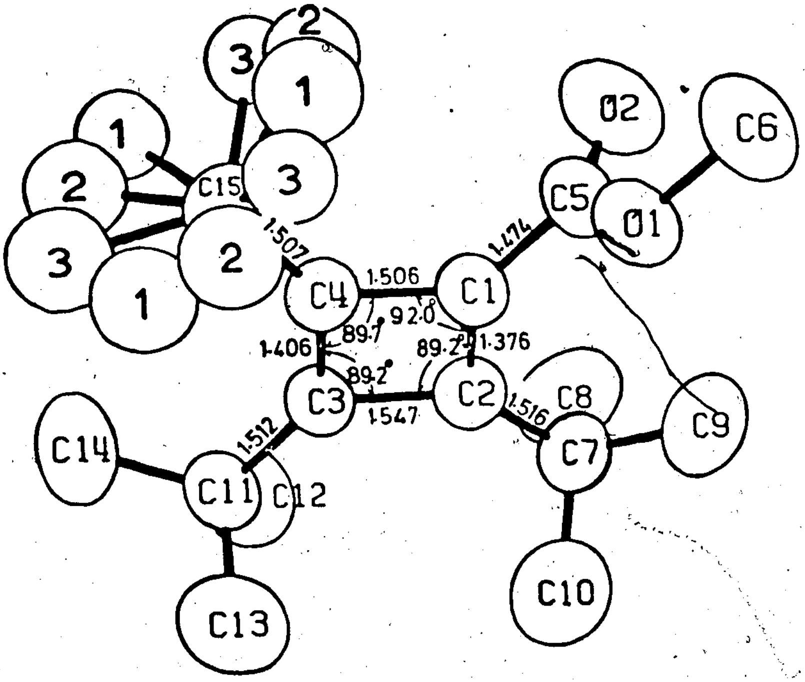


Figure IV; Molecular structure of methyl tri-tert-butyl[4]annulenecarboxylate 11. (The three sites (occupancies 0.51, 0.32, 0.17) of the disordered methyl group bonded to C-15 are designated as 1,2, and 3, respectively.)

particular system. Our result therefore represents the first clear, direct evidence to demonstrate that a rectangle, distorted slightly by the substituents, corresponds to the most stable conformation of this [4]annulene system.

The photoelectron spectrum (pes) of 11 was recorded,[51] by Dr. Brown of this department. Figure V. shows the spectra of diazoester 46, of 11, and of the final oxygenated material 61.* The first vertical ionization potential (vip) of 11 was 6.90 eV and would be assigned to the removal of an electron from π_2 of the [4]annulene system.** At first glance, this vip value appears to correlate well with that reported for 12 (6.89 eV).[52] However, due to the presence of the inductively electron-withdrawing carbomethoxy group which lies nearly perpendicular to the plane of the ring,[49] the value for 11 would be expected to be

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*) As yet, the product(s) of oxygenation have not been identified. It would be a mixture of the initially formed dioxetane derivative and/or its decomposition products.

**) A linear combination of two π molecular orbitals (LCMO) gives a bonding orbital ($\pi_a+\pi_b$) and an anti-bonding orbital ($\pi_a-\pi_b$) both of which are occupied. The latter orbital is referred to as π_2.

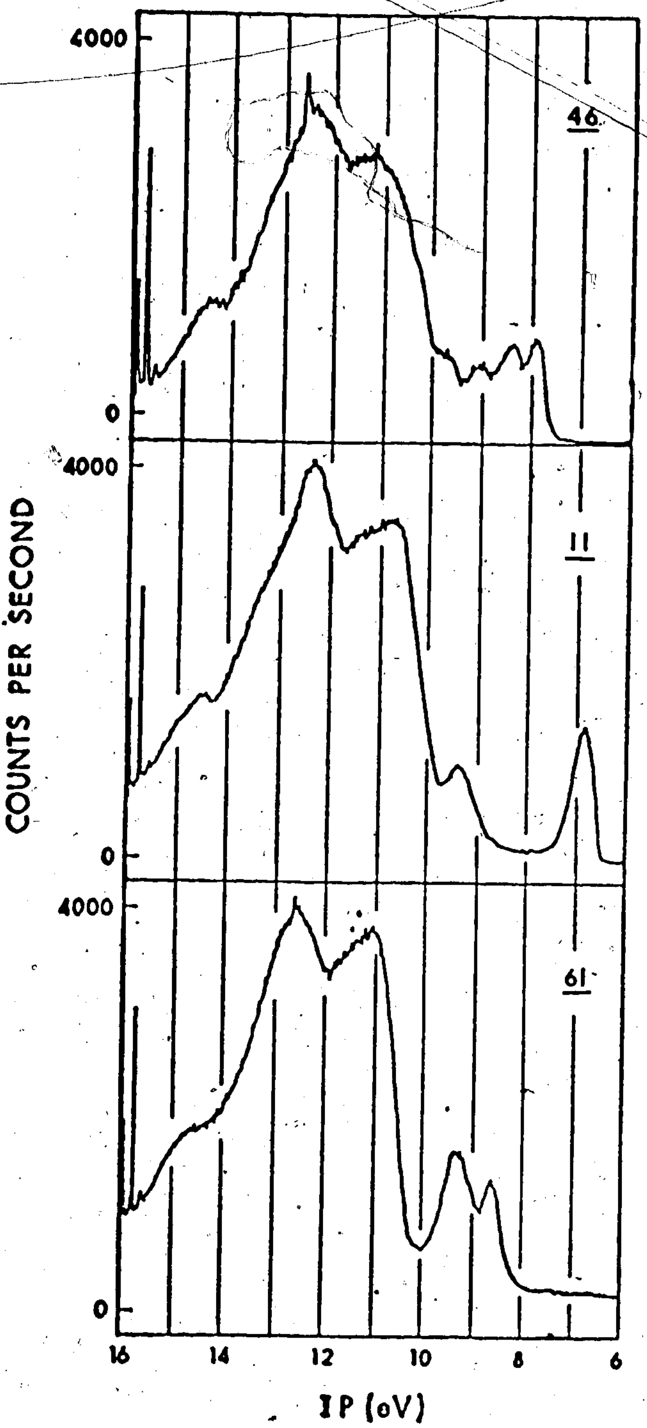
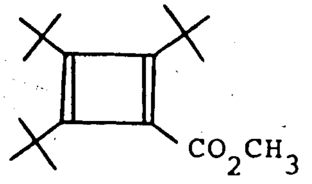
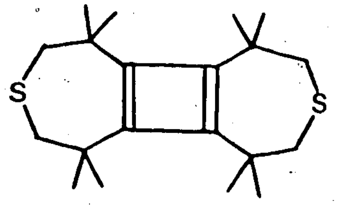


Figure V; Photoelectron spectra of 46, 11, and 61.

somewhat higher than that of 12. We feel that two fused rings in 12 would restrict the geometry in such a way that the two double bonds would become more localized and interact less. Indeed, the single bonds in 12 are found



11



12

to be 1.60 A long,[26] and hence the first vip assigned to π_2 in 12 should appear at somewhat higher energies than in unrestricted tetra-tert-butyl[4]annulene. In contrast, 11 contains somewhat shorter single bonds of 1.506 and 1.547 A.[49] It appears as though the presence of the carbomethoxy group in 11 counterbalances the effect of distortion in 12 and hence the vip's are the same.

The value reported for the first vip of tri-tert-butyl[4]annulene 13 of 6.83 eV[53] indicates a lower value in the absence of the carbomethoxy group, which is in agreement with the above reasoning.

The ionization pertaining to the second band in the photoelectron spectrum of 11 (9.45 eV) cannot be assigned with absolute certainty at this time. While we cannot rigorously exclude the possibility that this band is due to some impurity,[*] careful and repeated experiments have shown no diminution of band 2 with time. If one is allowed to use CNDO/2 calculations as an aid, then this band can be assigned to removal of an electron from a σ-orbital located primarily on the [4]annulene ring. That the ionization occurs simply from the carbomethoxy group can be ruled out since the values reported for methyl acetate[54] are 10.45 eV (n_0) and 11.16 (π_0).[**]

Due to the presence of the substituents, the above first vip values of <u>11</u> is expected to be roughly 1.5 eV[***] lower than that for parent [4]annulene. The value reported by Hedaya <u>et</u> <u>al</u>.[18] of 8.2 eV based upon the appearance potential of the molecular ion stands as the best present value for the first vip of [4]annulene.

---

[*]) We can be certain that this peak is not due to either the starting material <u>46</u> or the final oxygenated product <u>61</u>, since the photoelectron spectra of these two are quite different from that of <u>11</u> as shown in Figure V.

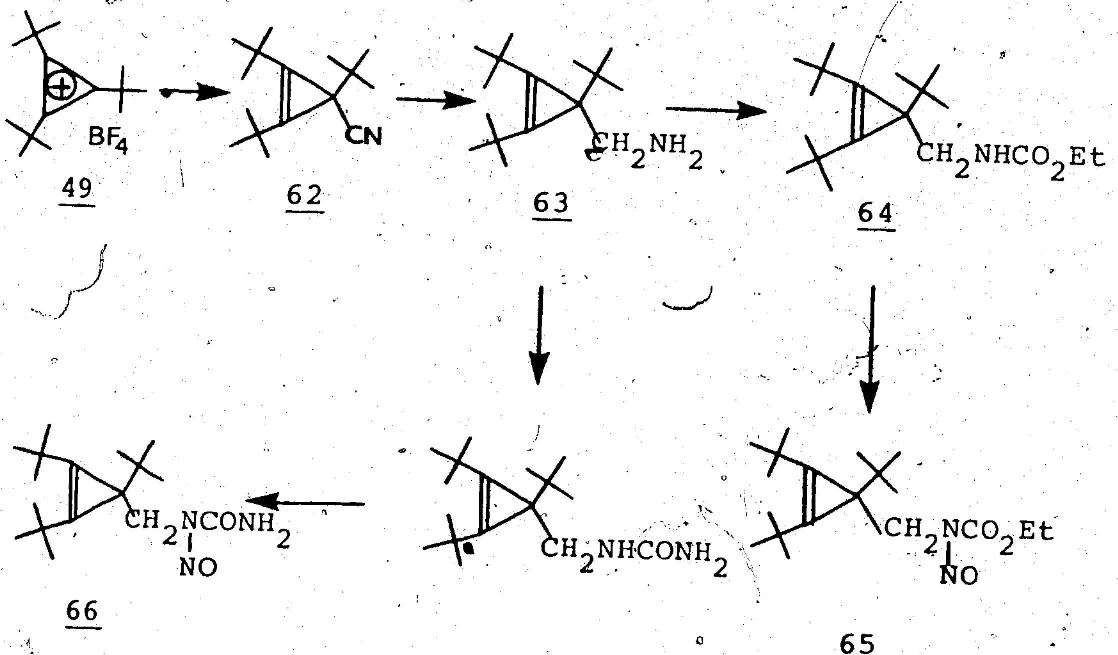
[**]) The reported photoel[illegible] spectrum[53] of <u>13</u> shows the second band at <u>ca</u>. 9.0 eV. This would thus be due to the impurity in the sample.

[***]) The effect of substituting a <u>tert</u>-butyl group for a hydrogen in ethylene is to lower the observed ip from 10.51 eV to 9.7 eV.[55]

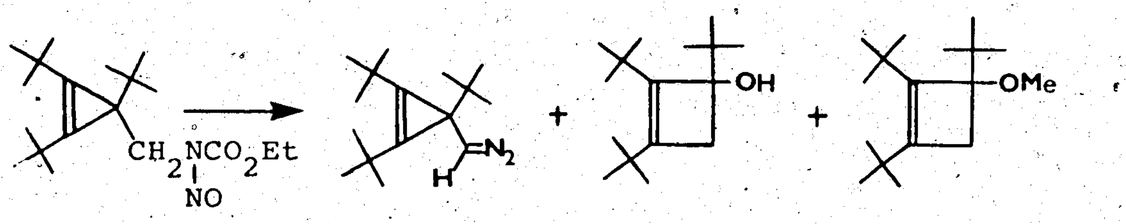
The above presents a full account of our findings on methyl tri-_tert_-butyl[4]annulenecarboxylate 11. The compound has now been fully characterized and has provided important information concerning the ground state properties of the [4]annulene system.

3. Tri-*tert*-butyl[4]annulene (13).[41]

We next embarked upon the synthesis of tri-*tert*-butyl[4]annulene 13, which would elucidate the nature of the magnetic ring current induced in the [4]annulene system. The synthesis involved the use of conventional methods. Thus, tri-*tert*-butylcyclopropenium fluoroborate 49 was treated with sodium cyanide to form the corresponding cyano compound 62 in 99% yield. Reduction with lithium aluminium hydride produced amine 63 (98% yield), which was then transformed to urethane 64. The N-nitrosourethane 65 was formed by the reaction of 64 with N_2O_4. The N-nitrosourea 66 was also prepared by a similar sequence. Although

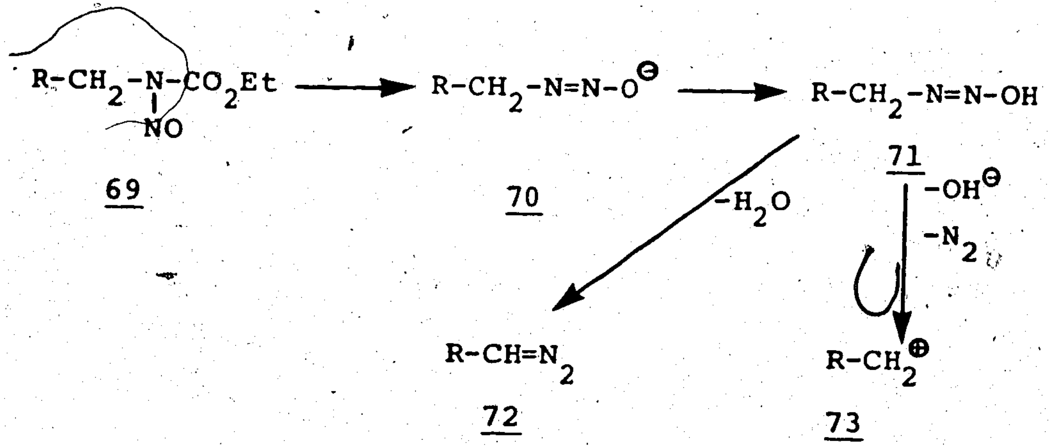


base treatment of 66 did not afford any desired diazo compound, the N-nitrosourethane 65, upon treatment with sodium methoxide, provided the expected diazoalkane 47 in addition to variable amounts of the cyclobutene derivatives 67 and 68. The formation of the diazo compound was indicated by the pink color of the reaction mixture and an ir absorption at 2030 cm^{-1}. The pmr spectrum of the mixture showed peaks attributable to the diazo compound at δ 0.98 (9H), 1.17 (18H), and 4.07 (1H).

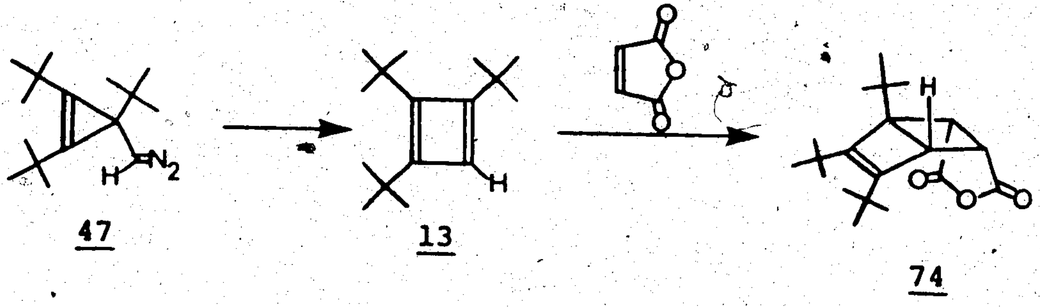


65 47 67 68

Generally,[56] when N-nitrosourethane 69 is treated with base, diazotate salt 70 is formed, which is stable in the absence of a proton source. Protonation of a diazotate salt 70 by the addition of water, affords a diazotic acid 71, which partitions between formations of diazoalkane 72 and carbonium ion 73, depending on the structure of the compound and reaction conditions. In the present case, the formation of cyclobutene derivatives 67 and 68 is rationalized by the formation of the carbonium ion intermediate 73.



Because of the instability of diazoalkane 47, we photolyzed the crude mixture directly at low temperature. The progress of the photolysis at -70° was monitored by low-temperature pmr spectroscopy, and it was observed that a new signal at δ 5.[illegible] (1H) and additional two singlets at δ 1.05 (18H) and 1.22 (9H) appeared at the expense of those ascribed to diazoalkane 47. These new signals disappeared almost instantly either on exposure to air or warming to room temperature. The reactivity of the photo-product precluded further purification, nevertheless the pmr signals are evidently due to the desired tri-*tert*-butyl-[4]annulene 13. Further confirmation of the structure was obtained



chemically. Maleic anhydride was added to the crude photolysate at −78°, and the adduct 74 was obtained as colorless crystals, mp 123.0-124.5°. The pmr spectrum showed three *tert*-butyl groups, and the cmr spectrum exhibited two olefinic carbons. These results indicate that the adduct has a [2.2.0]bicyclohexane ring system, similar to adduct 53. The presence of an ABC system at δ 3.1-3.5 in the pmr spectrum suggests that a proton is attached at the bridgehead position. Although the stereochemistry of the anhydride moiety is not unambiguously established, it is tentatively assigned the *endo*-configuration by analogy with 53.

This compound 13 is the first [4]annulene derivative which possesses a proton directly attached to the π-system. Using the C-2 proton (δ 6.42) of cyclopentadiene as a reference, the difference, Δδ=1.04=6.42−5.38, may be taken as the paramagnetic contribution of the induced ring current. If one neglects the perturbation of the electronic structure of 13 caused by the three *tert*-butyl substituents and adopts, (i) the equation (1)* advanced by Pople and Untch,[23]

---

*) The equation (1) is;[23]

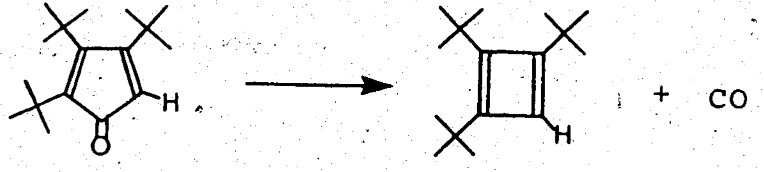
$$I=-(\pi^2 e^2 \beta_0/h^2 c)S(32^{1/2}M^2)\sum_{j}^{occ}[1+2\lambda\cos(4\pi j/M)+\lambda^2]^{-3/2} \times$$

$$[\lambda+(1+\lambda^2)\cos(4\pi j/M)+\lambda\cos^2(4\pi j/M)]$$

where I, S, λ and β_0 are induced ring current per unit magnetic field, area of the ring, the degree of bond alternation, and β value for benzene respectively. Δδ=I x spacial factor (Biot-Savart law).

to calculate the induced ring current in an [M]annulene, (ii) the reactangular geometry predicted by Dewar,[24e] (these values are quite close to those of compound 11), and (iii) Coulson and Golebiewski's equation for the estimate of λ,[57] one obtains a paramagnetic contribution of 1.18 ppm for [4]-annulene (the calculation was done by Mr. Morio of this department). The agreement between the experimental and calculated values is excellent. Thus, one can conclude that the ring current induced in the [4]annulene system is paramagnetic, but not diamagnetic.

Maier et al. were able to synthesize 13 by an independent route.[58] Tri-tert-butylcyclopentadienone 75, upon photo-irradiation at -198°, loses carbon monoxide and forms 13, which exhibits a pmr spectrum identical to that of our compound. They also succeeded in obtaining the photoelectron spectrum of 13.[53] The first vip was found to be 6.83 eV, leading them to the conclusion that 13 is rectangular and having a geometry similar to that of 12. (However,



75

13

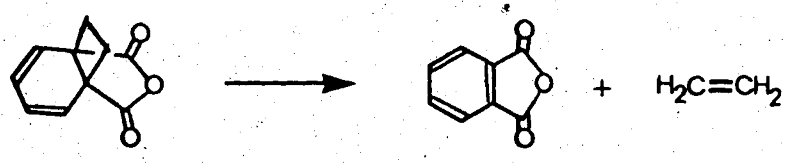
see footnote** on page 42.)

We have thus succeeded in preparing tri-*tert*-butyl[4]annulene *13*, the first example of [4]annulene derivative with a proton directly attached to the ring ~~and~~ have demonstrated the existence of a paramagnetic ring current, the degree of which is in good agreement with the theoretically calculated value.

B. Spectroscopic detection of parent [4]annulene.[59]

Our attention was next turned toward the detection of parent [4]annulene itself, trapped in a matrix, by means of its uv and esr spectra. The ideal precursor required for this purpose is a compound which generates [4]annulene by a photochemical reaction, one of very few chemical transformations which can be induced in a low temperature matrix. Another requirement is that the side products which are formed must be transparent in the uv region of interest, and also must not interact chemically with [4]annulene.

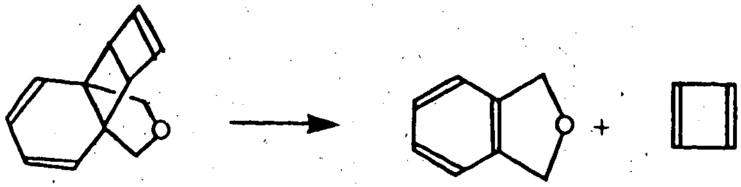
It is known that anhydride 76 photochemically produces phthalic anhydride and ethylene quantitatively.[60] We



76

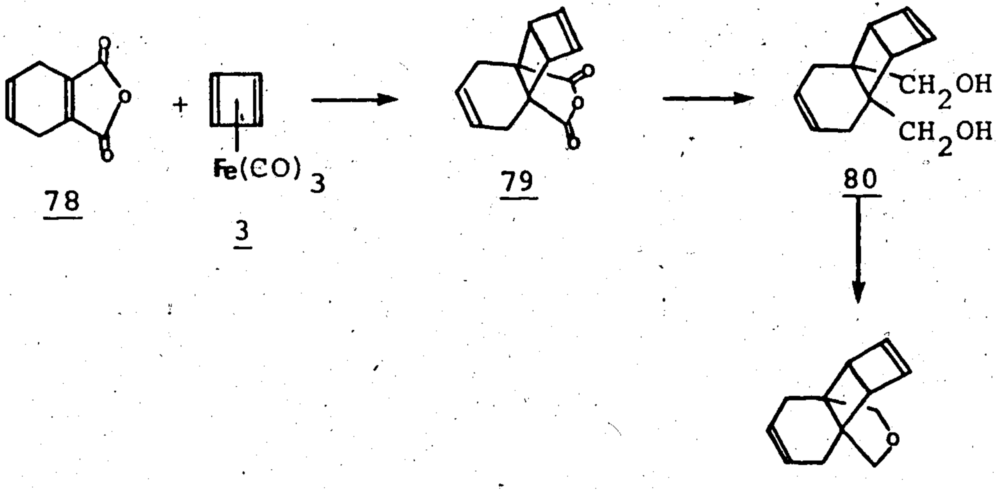
therefore anticipated that the tetracyclic triene 77 would photochemically generate [4]annulene 1 together with phthalan, which has no uv absorption above 280 nm and would be expected to form no charge-transfer complex with

[4]annulene.



77 1

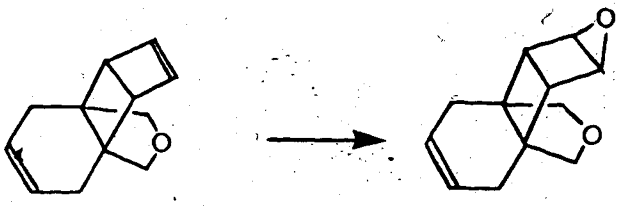
The synthesis of 77 was accomplished by the following route. A Diels-Alder reaction of anhydride 78[61] and "cyclobutadiene" which was generated in situ by the oxidative decomposition of iron complex 3, afforded a mixture of the desired adduct 79 and unreacted starting anhydride 78. The excess reagent 78 could be selectively hydrolyzed in methanol, and the neutral product was isolated. The stereochemistry of this adduct is very likely to be as shown below, based on the general mode of the Diels-Alder reaction.



78 3 79 80 81

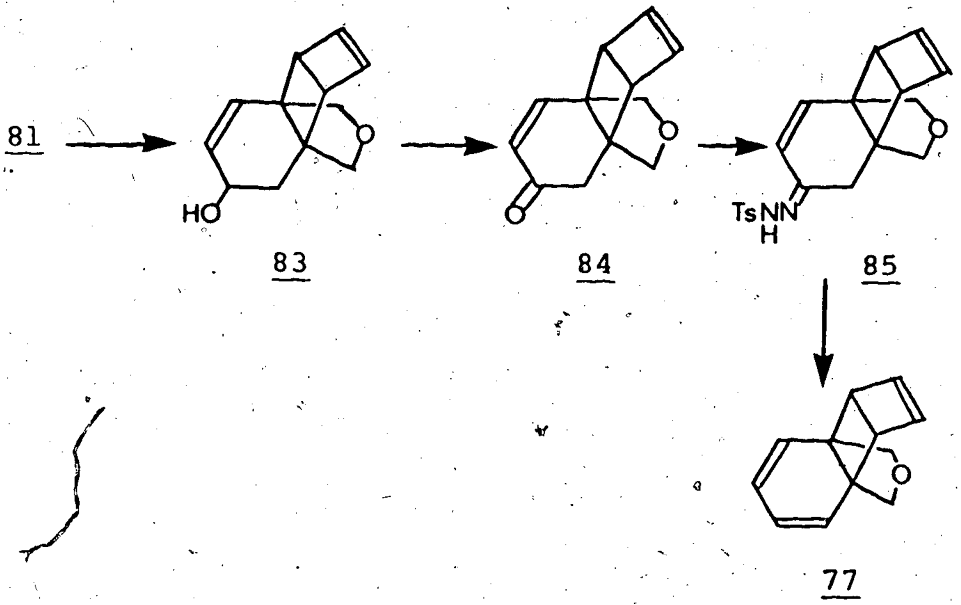
The anhydride 79 was reduced by lithium aluminium hydride to the diol 80 in 88% yield. Cyclization to ether 81 was achieved by treatment with one equivalent of tosyl chloride. The initially formed mono-tosylate appeared to cyclize relatively slowly in competition with the formation of the ditosylate of 80. Therefore, after a small portion of tosyl chloride was added, the cyclization step was forced to completion by increasing the reaction temperature. Then this process was repeated until one equivalent of tosyl chloride was added. In this way the formation of the ditosylate was minimized. No detectable amount of the ditosylate was obtained, and the expected ether 81 was obtained in 75% yield.

We attempted to convert the cyclohexene moiety to the corresponding cyclohexadiene by a bromination-debromination sequence. Thus, the ether 81 was treated with bromine; however, only a complex mixture was obtained. Epoxidation of 81 with m-chloroperbenzoic acid produced only the undesired epoxide 82.



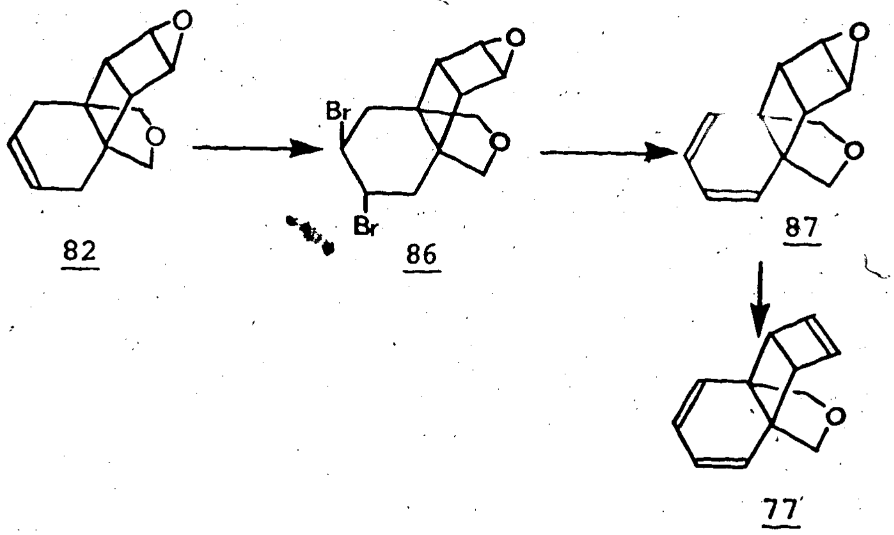
81 82

However, oxidation[62] by singlet oxygen produced the fruitful result. Diene 81 was irradiated in methanol with a high pressure mercury lamp in the presence of methylene blue as a sensitizor, while oxygen gas was bubbled through the reaction mixture. The crude allylic hydroperoxide was reduced directly with lithium aluminium hydride to give allylic alcohol 83 in 60% yield.



Oxidation with manganese dioxide converted alcohol 83 to the corresponding α,β-unsaturated ketone 84. The tosylhydrazone 85, formed by reaction with tosylhydrazine in methanol, was reacted with two equivalents of methyllithium[63] to produce the expected triene 77 in yields of 10-50%. The triene was purified by preparative glpc (UCW-98). It is known,[63] however, that carvone tosylhydrazone forms the corresponding diene in very high yield. The low yield of triene 77 is rationalized by the fact that the proton which must be abstracted in 77 is in a very hindered position, compared with the corresponding proton in carvone.

Sharpless *et al*. has reported a successful deoxygenation of an epoxide using a WCl_6-*n*-butyllithium reagent.[64] Although the actual reacting species as well as the reaction methanism is not clear, we examined a different scheme leading to triene 77, which could use this deoxygenation reaction in the final step. The epoxide 82 was treated with bromine in dichloromethane to form the dibromide 86, which was used directly for the dehydrobromination step. Treatment of crude 86 with potassium *tert*-butoxide in dimethyl sulfoxide produced diene 87 in 80% overall yield from epoxide 82. Deoxygenation of 87 with WCl_6-*n*-BuLi[64] was carried out at room temperature and the expected triene 77 was obtained in 72% yield.



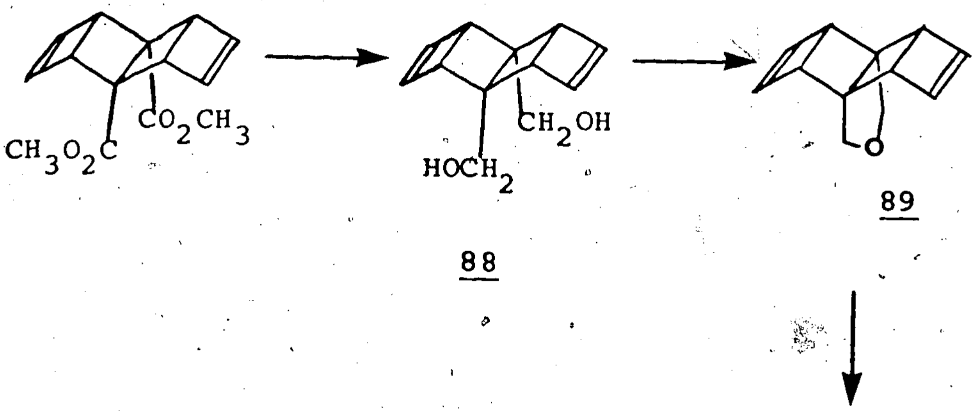
82

86

87

77

The structure of this triene 77 is confirmed by its pmr, uv, ir, and mass spectra. After the above results were printed, Martin and Hekman reported the preparation of this triene through an alternative route, as shown below.[65]

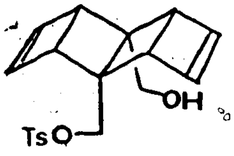


88

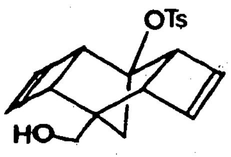
89

77

This sequence has a serious drawback in that the cyclization of 88 proceeds only in poor yield. Treatment of diol 88 with tosyl chloride, as reported,[65] produced ether 89 and a substantial amount of by-product, to which the authors assigned the structure 90. We expected to be able to obtain the ether 89 by cyclization of this



90



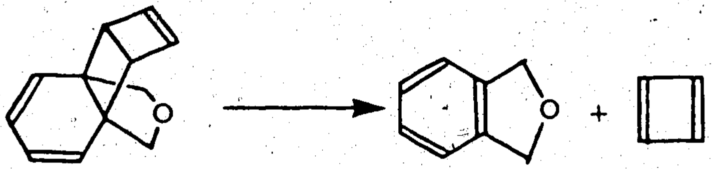
91

mono-tosylate, and treated 90 with bases such as pyridine, sodium hydride, sodium amide, and potassium tert-butoxide. However, the starting material was invariably recovered unchanged. This unexpected stability and the pmr spectrum of this compound led us to doubt the correctness of the proposed structure 90. The pmr absorptions for the two CH_2 groups are at δ 2.00 and 3.53. The corresponding absorptions in diol 88 and ether 89 are at δ 3.60 and 3.59, respectively. Structure 91 explains the large chemical shift difference between these two methylene signals, and should be assigned to this by-product.

The cyclization step to form 89 has the lowest yield (21%) reported[65] for this sequence. We examined several modifications in order to improve the yield, and found that initial formation of the dianion of diol 88, followed by cyclization by means of tosyl chloride raised the yield of 89 to 55%.

As expected, triene 77 has a broad uv absorption at 250-260 nm. This region is ideal for the subsequent photoreaction using a low pressure mercury lamp which emits mainly the light of 253.7 nm. When triene 77 was irradiated at -90°, the pmr spectrum of the photo-products showed peaks only for phthalan (δ 4.96, 7.16) and the [4]annulene syn-dimer (δ 3.05, 5.94). These two products were also identified by glpc analysis (UCW-98). This indicated that the reaction took place in the expected manner to form

[4]annulene 1 as a reaction intermediate.



77 1

In order to record the uv spectrum of [4]annulene 1 in a matrix, low-temperature photolysis was carried out. 2-Methyltetrahydrofuran was used to form a transparent matrix at near liquid-nitrogen temperature. A solution of triene 77 in 2-methyltetrahydrofuran, under an argon atmosphere, was placed in a 1-cm quartz uv cell. The cell was cooled to below -170° with nitrogen gas, which was pre-cooled in a liquid-nitrogen bath. Irradiation by a low pressure mercury lamp was continued for 1-2 hours and the uv spectrum recorded. The matrix was then melted and subsequently cooled to the same temperature as before, and the uv spectrum again recorded. The difference of the two spectra was taken to be the spectrum of [4]annulene, which was found to have a maximum at 300 nm (ϵ 100), (Figure VI.).

The esr spectrum of the photolyzed matrix was recorded, but no esr signal attributable to a triplet species was observed. These results indicate that the triplet state of [4]annulene is neither the ground state nor a low-lying excited state. The weak absorption at 300 nm agrees espe-

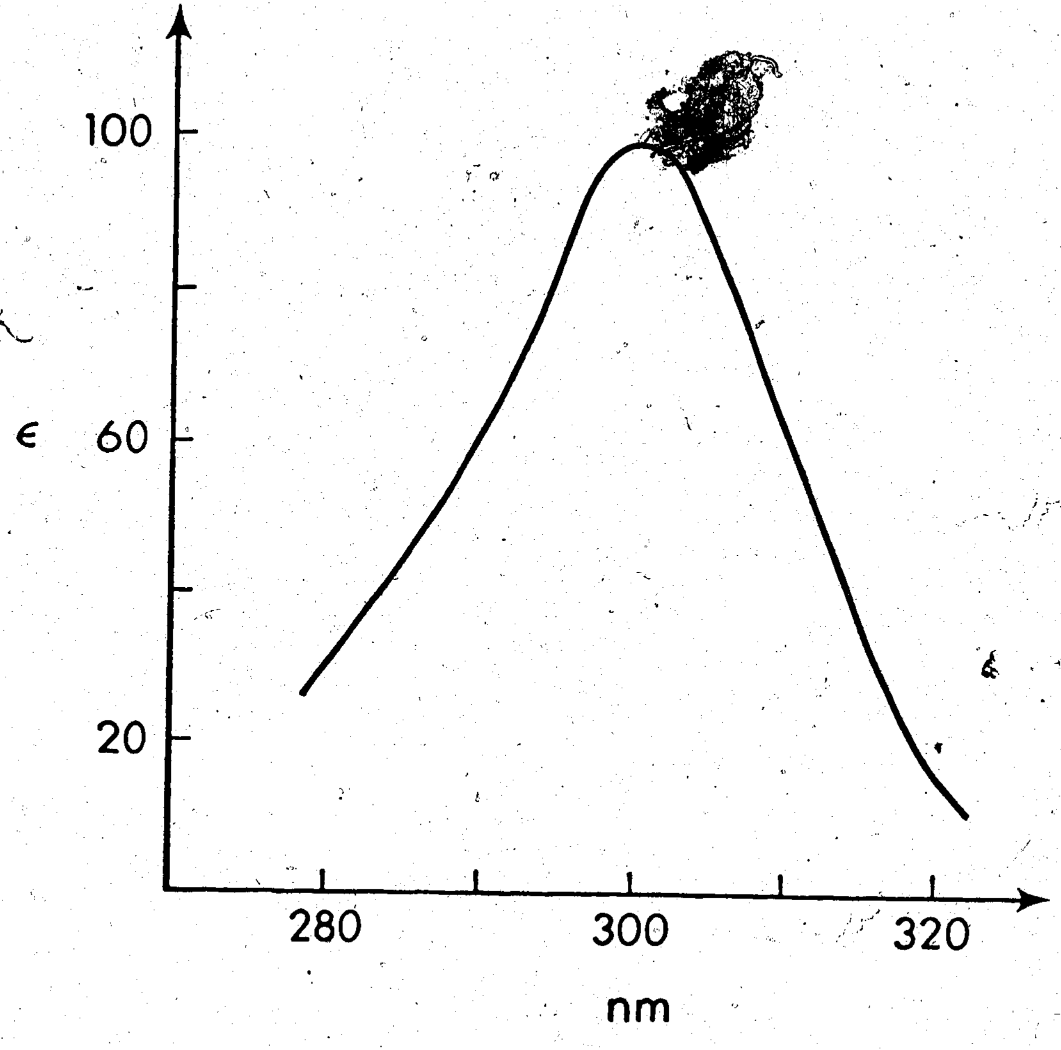
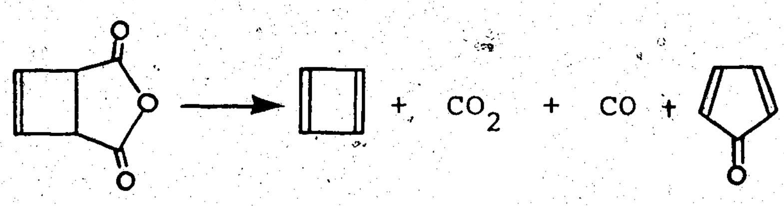


Figure VI; Uv spectrum of [4]annulene.

cially well with the calculated result for the singlet [4]annulene, which was predicted[24b,c] to have a weak absorption in the visible [illegible].

Maier et al. have developed an independent route to [4]annulene derivatives.[66] Irradiation of anhydrides 92 having simple alkyl substituents was expected to result in the elimination of carbon dioxide and carbon monoxide, forming [4]annulene derivatives. In most experiments carried out to date, cyclopentadienones, which possess strong uv absorptions, are formed together with the desired [4]annulene derivatives. Consequently, the observation of the desired weak uv absorption of [4]annulene was not achieved.



92

After the publication of our result, the same group reported the result of the photolysis of the parent and mono-tert-butyl substituted cyclobutenedicarboxylic anhydrides.[66b,67] In both cases, the desired [4]annulene, which was generated in an ether/tetrahydrofuran/isopentane matrix, exhibited a uv absorption at 301 nm. No cyclopentadienone was formed. These results corroborate our observation that [4]annulene possesses a weak uv absorption at 300 nm.

They also prepared tetramethyl[4]annulene 93 in a matrix from a number of precursors 94-98.[66b,68] It should be pointed out that compound 97 has the same basic ring structures as our precursor 77. When 96 was irradiated in a matrix, a deep coloration was observed due to a maximum at 495 nm, and a dimer of tetramethyl[4]annulene and phthalic anhydride were isolated from the reaction products. On cleavage of 97 neither coloration nor a maximum above 300 nm was observed, although a dimer of tetramethyl[4]annulene and phthalan were produced. Similarly, 94, 95, and 98 were

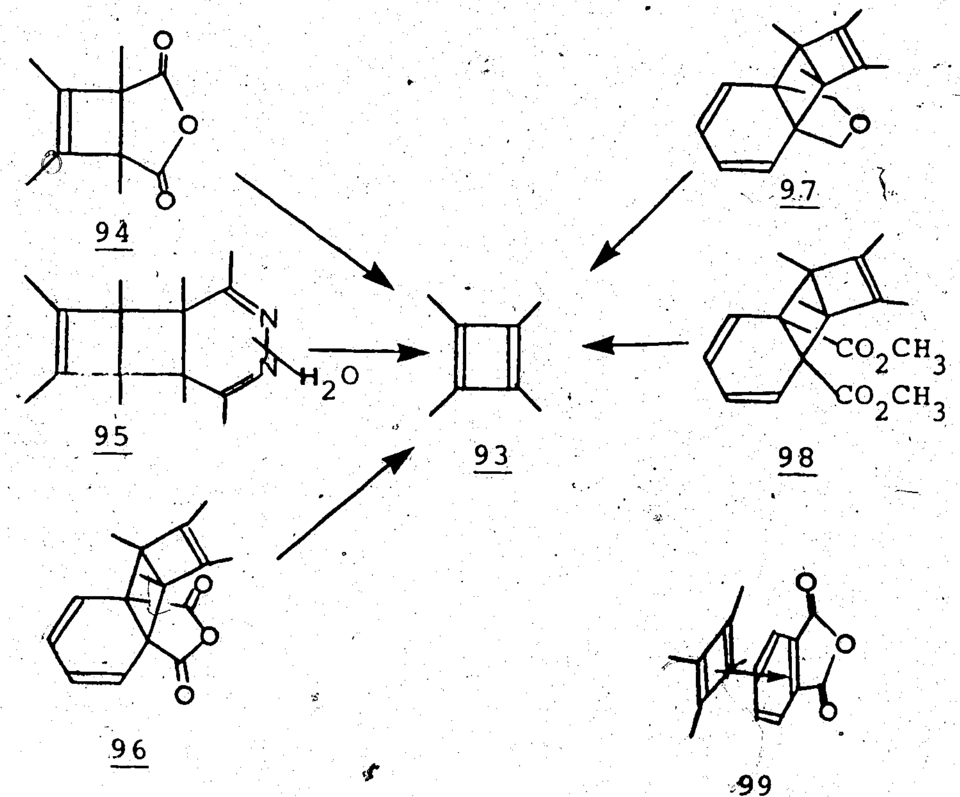
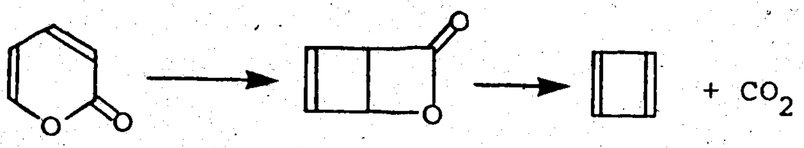


photo-cleaved generating tetramethyl[4]annulene 93 in a matrix. However, a different uv spectrum was recorded for each one of these fragmentations. These inconsistent results were explained by the formation of a charge-transfer complex between tetramethyl[4]annulene and the other cleavage product. For instance, cleavage of 96 generates 93 and phthalic anhydride simultaneously. The necessary geometric arrangement to form a charge-transfer complex 99 is already provided by the starting material. On the other hand, the maximum at 423 nm observed upon cleavage of 94 is solely due to tetramethylcyclopentadienone. Only the fragmentation of 97 generates free tetramethyl[4]-annulene since phthalan is not prone to act as electron-acceptor, and no appreciable absorption above 300 nm was observed. These experimental results support our own finding that the observed absorption of the product formed by the photolysis of 77 is indeed that of [4]annulene itself.

All of these results obtained from the matrix uv spectra suggested that the ground state of [4]annulene has a singlet spin state, as supported by theoretical predictions.

However, contrary to this, the ir spectrum of [4]-annulene was characterized in an argon matrix by two independent groups,[24f,69] leading to the conclusion that [4]-annulene has a square geometry suggesting a triplet (ground) state. Upon irradiation, α-pyrone, isolated in an argon matrix at 8°K, converts slowly to the β-lactone 100. Further irradiation gives rise to [4]annulene 1 and carbon dioxide. Group theory predicts four ir active fundamentals for D_{4h} (square planar)- and seven for D_{2h} (rectangular)-[4]annulenes. The simplicity of the observed [4]annulene ir spectrum, which consisted of four absorptions, led the authors to conclude that [4]annulene has D_{4h} symmetry. The location of the bands is also in good agreement with those obtained by the theoretical calculations. They also prepared mono-, 1,2-di-, and 1,3-dideutero[4]annulenes from appropriately deuterated α-pyrones. The inspection of these spectra supported the authors' conclusion. This result is apparently in contradiction with other findings, all of which support the rectangular singlet ground state of [4]annulene.



100 1

Recently, Dewar published a suggestion for this discrepancy.[70] According to his MINDO/3 calculations a rectangular singlet (RS) is the ground state of [4]annulene, lying 3.6 kcal/mol below the square triplet (ST). A square singlet (SS) is predicted to be unstable by 13.1 kcal/mol relative to the ST. The intersection of the singlet and triplet states therefore lies above ST in energy. Since spin-orbit coupling is expected to be unimportant, conversion of ST to RS should require activation, with the transition state corresponding to the lowest point along the intersection of the singlet and triplet surfaces. Dewar calculated that the transition state for this conversion lies 2.3 kcal/mol above ST. He further concluded that the activation energy from ST to RS is at least 3.5 kcal/mol, and suggested that the species obtained from α-pyrone would have been the triplet and not the ground state.

C. Conclusions.

As described above, the century-old problem concerning the ground state properties of [4]annulene has almost reached its final solution. The following is a summary of our experimental results.

1) Methyl tri-tert-butyl[4]annulenecarboxylate 11 was obtained in pure crystalline form. The X-ray analysis revealed that the four-membered ring has a rectangular geometry with rather extensive bond-alternation. We are now almost certain that the ground state of [4]annulene system is a singlet. The likely geometry is a rectangle with two short bonds of approximately 1.37 A and two longer ones of the order of 1.51 A. Should [4]annulene prove to be square for reasons that are not obvious at the present moment, both square and rectangular must reside in a region of a flat potential surface.

2) Tri-tert-butyl[4]annulene 13 was prepared in solution and its pmr spectrum indicated the presence of a paramagnetic ring current.

3) Parent [4]annulene 1 isolated in a matrix exhibits a weak uv absorption at 300 nm.

CHAPTER IV. EXPERIMENTAL.

General

All melting points and boiling points were uncorrected.

The pmr and cmr spectra were measured with Varian Associate A-60 or HA-100 spectrometers and a Bruker HFX-10 spectrometer, respectively. Tetramethylsilane was used as internal standard, unless otherwise stated. All coupling constants are reported in Hz. In reporting pmr spectral data, the following abbreviations are used.

s ; singlet
d ; doublet
t ; triplet
q ; quartet
m ; multiplet

The ir spectra were obtained on a Perkin-Elmer model 257 infrared spectrometer. In reporting ir spectral data, the following abbreviations are used.

s ; strong
m ; medium
w ; weak
b ; broad

The uv spectra were determined using Cary model 14 and 15 spectrometers.

The mass spectra were obtained with A.E.I. MS-2 and

MS-9 mass spectrometers.

Glpc analyses were performed with an F&M modle 5750 with 1.8 m columns (packing is indicated in the text).

The following abbreviations are used for chemical names.

LAH ; lithium aluminium hydride
THF ; tetrahydrofuran
HMPA ; hexamethylphosphoric triamide
DMSO ; dimethyl sulfoxide

The pH 7 buffer solution was prepared by dissolving KH_2PO_4 (9.1 g) and Na_2HPO_4 (18.9 g) in water (1000 ml). All experiments were conducted under nitrogen or argon atmospheres. A rotary evaporator (water aspirator) was used for the removal of solvents from all reaction mixtures, unless otherwise specified.

Photolysis of tri-tert-butyl[4]annuleneiron tricarbonyl (17) in the presence of dimethyl acetylenedicarboxyalte.

A solution of 17 (355 mg, 0.99 mmol) and dimethyl acetylenedicarboxylate (430 mg, 3.0 mmol) in ether (90 ml) was irradiated with a high pressure mercury lamp (Pyrex filter) at -60° for 2 hr. Evaporation of the solvent and chromatography on silicic acid (25 g) gave a mixture (220 mg) of dimethyl acetylenedicarboxylate and an iron-free adduct, presumably dimethyl 3,4,5-tri-tert-butylbicyclo[3.1.0]hepta-

3,6-dien-2-one-6,7-dicarboxylate 19 (*ca.* 10:1), and a brown solid (259 mg). The latter product exhibits strong ir absorptions at 2030, 1985, and 1965 cm^{-1} suggesting that it is an iron carbonyl complex. Pure adduct 19 was obtained by chromatography on silicic acid (25 g) using chloroform as the eluent.

pmr δ ($CDCl_3$); 1.12 (9H,s), 1.17 (9H,s), 1.22 (9H,s), 3.75 (1H,s), 3.83 (3H,s), 3.90 (3H,s).

ir ($CHCl_3$); 1730 cm^{-1} (s).

mass spectrum; 390 (M^+).

elemental analysis; Calcd for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78.
Found: C, 70.75; H,8.72.

The brown solid (88 mg), produced in the above reaction, was dissolved in acetone (10 ml) and ceric ammonium nitrate (634 mg) was added at 0°. Stirring was continued at 0° for 30 min, and the solvent was removed. Chromatrography on a small amount of silicic acid using chloroform as the eluent gave an oil (77 mg). The pmr spectrum indicated that the major product was 19.

Reaction of 3-dichloromethyl-1,2,3-tri-*tert*-butylcyclopropene (24) with *tert*-butyllithium.

To a solution of dichloromethane (339 mg, 4.0 mmol) in THF (20 ml) was added at -78° a hexane solution of *n*-butyllithium (1.5 *M*, 2.66 ml, 4.0 mmol). After stirring for 15 min at -78°, tri-*tert*-butylcyclopropenium fluoroborate **49** (1.0 g, 3.4 mmol) was added in small portions. Stirring was continued for 2 hr at -78°, then the reaction mixture was warmed to -25° and to this was added in dropwise a pentane solution of *tert*-butyllithium (2.2 *M*, 1.8 ml, 4.0 mmol). After 2 hr stirring at -25°, the reaction mixture was poured into ice. The organic layer was washed with brine (3x10 ml), and dried over $MgSO_4$. Removal of the solvent followed by a molecular distillation (bath temperature 24-27°/0.05 mmHg) afforded an oil (660 mg), which contained chloro-tri-*tert*-butylbutadiene **25** in *ca.* 90% purity. Pure diene **25** was obtained by preparative glpc (UCW-98, 135°).

pmr δ ($CDCl_3$); 1.08 (9H,s), 1.20 (9H,s), 1.25 (9H,s), 5.42 (1H,s), 6.07 (1H,s).

mass spectrum; 256,258 (M^+ calcd for $C_{16}H_{29}Cl$, 3:1).

Methyl tri-*tert*-butylcyclopropenyldiazoacetate (**46**).

To a vigorously stirred solution of methyl diazoacetate (903 mg, 9.03 mmol) in ether (40 ml) and THF (40 ml) was added dropwise at -110° a hexane solution of *n*-butyllithium (1.6 *M*, 6.0 ml, 9.6 mmol). After the addition was complete, the mixture was stirred for 40 min at -110°. Finely ground tri-*tert*-butylcyclopropenium fluoroborate (2.358 g, 8.00 mmol) was added in small portions. After 3 hr of stirring at -110°, the reaction mixture was allowed to warm very slowly to room temperature, poured into brine (200 ml), washed with brine (100 ml), and dried over Na_2SO_4.

Filtration and solvent removal left a brown oil, which was chromatographed on neutral alumina (activity grade III, 75 g) using pentane/ether (100:3,v/v) as the eluent. Yellow crystals, 2.19 g ([illegible] obtained, mp 46.0-47.5°.
pmr δ $(CDCl_3)$; 0.93 (9H,s), 1.26 (18H,s), 3.72 (3H,s).
ir$(CHCl_3)$; 2080 cm^{-1} (s), 1698 (s).

Methyl tri-*tert*-butyl[4]annulenecarboxyate (11).

Diazoester 46 (336 mg), dissolved in methylcyclohexane-$\underline{d}_{14}$ (1.6 ml), was irradiated with a high pressure mercury lamp (Pyrex filter) at -78° for 13 hr. After 3 hr of irradiation, light brown crystals began to precipitate. When the phtolysate, after completion of irradiation, was warmed to room temperature, the precipitated crystals dissolved. The conversion to 11 was almost quantitative.
pmr δ (methylcyclohexane-$\underline{d}_{14}$); 1.13 (18H,s), 1.19 (9H,s), 3.45 (3H,s).
cmr δ (methylcyclohexane-$\underline{d}_{14}$); 29.7 $(H_3\underline{C}\text{-}C)$, 31.6,31.8 (quart.-$\underline{C}$), 50.4 (OCH_3), 147.0, 154.5 (olefinic-$\underline{C}$), 165.7 (C=O).
ir (pentane); 1716 cm^{-1}(s).
uv λ_{max} (pentane); 425 nm (ϵ 47).

The photolysate was cooled to -78°, and after crystals had appeared, the mother liquor was removed by syringe. Recrystallization from pentane at -78° was repeated twice and the pure crystals were dried under vacuum. The crystals sublimed at 50°/0.01 mmHg and had a melting point of 70.0°.

A single crystal was mounted manually in a capillary tube for X-ray analysis. This operation was carried out in a rigorously anhydrous dry-box under an oxygen- free nitrogen atmosphere.

Adduct of <u>11</u> with maleic annhydride. (53)

Irradiation of diazoester <u>46</u> (428 mg, 1.4 mmol) in ether (30 ml) as before at -78° for 2 hr afforded a light brown solution, to which was added a solution of maleic anhydride (137 mg, 1.40 mmol) in ether (1.5 ml) and THF (1.5 ml). The mixture was allowed to warm to room temperature Removal of the solvent gave a colorless crystalline product (479 mg, 89%), which, after sublimation at 80° under high vacuum, had a melting point of 213.0-215.0° (ether).

pmr δ ($CDCl_3$); 1.08 (9H,bs), 1.22 (9H,s), 1.30 (9H,s), 3.73 (3H,s), 3.50 (1H,d,J=8.3), 4.20 (1H,d,J=8.3).

cmr δ (dioxane-d_8); 27.8,31.0, 32.8 ($H_3\underline{C}$-C), 33.7, 34.4, 34.9 (quart.-$\underline{C}$), 40.9, 41.4 (tert.-$\underline{C}$), 57.2, 68.6 (other quart.-$\underline{C}$), 152.8,157.4 (olefinic-$\underline{C}$) 171.7,172.5,172.7 ($\underline{C}$=O).

ir (nujol); 1865 cm^{-1} (m), 1796 (s), 1715(s).

uv (ether); 215 nm (ε 3240), 225 (1665), 235 (680).

mass spectrum; Calcd for $C_{22}H_{32}O_5$: m/e=376.2250

Found: m/e=376.2241.

Conversion of anhydride 53 to lactone 59.

A mixture of anhydride 53 (102 mg, 0.27 mmol), sodium carbonate (28.5 mg), water (3 ml) and dioxane (2 ml) was stirred at 70° for 15 min. At the end of this time, a clear solution was obtained. The reaction mixture was filtered, acidified with 2 N HCl, and extracted three times with dichloromethane (60 ml in total). The combined extracts were washed with brine (50 ml) and dried over Na_2SO_4. Filtration and evaporation of the solvent left diacid 58 (110 mg), which was used directly in the next step.

pmr δ (CD_3OD); 1.09 (9H,s), 1.26 (9H,s), 1.34 (9H,s), 3.58 3.93 (2H, AB, J=11.2), 3.69 (3H,s).

A solution of diacid 58 (110 mg, 0.27 mmol) in water (2.5 ml) containing triethylamine (0.3 ml) was added to pyridine (20 ml) in an electrolysis cell, which was cooled with an ice-bath to maintain the solution at about 20°. The solution was electrolyzed with a current of 600 mA (70 V), which after 1 hr decreased to less than 100 mA. The reaction mixture was diluted with water (40 ml) and extracted with pentane (6x30 ml). The combined pentane extracts were washed with cold 2 N HCl (3x10 ml), 5% $NaHCO_3$ (3x20 ml), brine (30 ml) and dried over Na_2SO_4. The solvent was removed to leave a white crystalline product, 37.9 mg (46%), mp 200° (dec.).

pmr δ (hexamethyldisilane, chlorobenzene, 150°); 0.96 (9H,s), 1.11 (9H,s), 1.22 (9H,s) 3.45 (3H,s), 3.12 , 3.53 (2H, AB, J=11.2).

ir ($CHCl_3$); 1785 cm^{-1} (s), 1735 (s).

Adduct of 11 with dimethyl acetylenedicarboxylate. (60).

After the irradiation of diazoester 46 (306 mg, 1.00 mmol) in ether (25 ml) at -78° for 85 min, a solution of dimethyl acetylenedicarboxylate (116 mg, 0.82 mmol) in ether (2.5 ml) was added. The mixture was allowed to warm to room temperature. After standing at room temerature for 2.5 hr, the solvent was removed to leave a yellow solid (329 mg), which was chromatographed on silicic acid (15 g) using pentane/ether (10:1, v/v) as the eluent. Pure crystalline adduct 60 was obtained , 240 mg (70%), mp 99.5-100.5° (pentane).

pmr δ ($CDCl_3$); 1.16 (9H,s), 1.23 (9H,s), 1.26 (9H,s), 3.36 (3H,s), 3.79 (6H,s).

cmr δ ($CDCl_3$); 28.6, 30.6, 31.5 (CH_3), 33.8, 34.4, 34.6 (quart.-C of tert-butyls), 51.1,51.8 (OCH_3), 61.2, 73.7 (quart.-C), 144.4, 152.7, 153.1, 157.9 (olefinic-C), 162.3, 164.8, 171.8 (C=O).

ir ($CHCl_3$); 1740 cm^{-1} (s), 1635 (s).

uv (ether); λ_{sh} 238 nm (ϵ 2800).

mass spectrum; 420 (M^+).

elemetal analysis; Calcd for $C_{24}H_{36}O_6$: C,68.54: H, 8.65.

Found: C,68.58: H,8,63.

1,2,3-Tri-*tert*-butylcyclobutene. (57)

This compound was prepared as reported[30b] from 3,4-dichloro-1,2,3-tri-*tert*-butylcyclobutene.

cmr δ ($CDCl_3$); 28.3, 31.0 ($H_3\underline{C}$-C), 29.4 (CH_2), 32.6,32.7 (quart.-$\underline{C}$), 49.8 (tert-$\underline{C}$), 148.1,148.3 (olefinic-$\underline{C}$).

uv (ether); 215 nm (ε 2640), 225 (294), 235 (61).

3-Cyano-1,2,3-tri-*tert*-butylcyclopropene. (62)

A mixture of tri-*tert*-butylcyclopropenium fluoroborate (10 g, 34 mmol), NaCN (32 g, 0.65 mol) and water (500 ml) was stirred at room temperature for 1.75 hr. Ether (150 ml) was added and stirring was continued for a further 1.5 hr. The ether layer was separated, and the aqueous layer was vigorously stirred for 2 hr with ether (200 ml), after which the ether was separated. The combined ether layers were dried over $MgSO_4$ and evaporated to give pure cyano compound 62, 7.9 g (99%).

pmr δ ($CDCl_3$); 1.02 (9H,s), 1.29 (18H,s).

ir (neat); 2220 cm^{-1} (s).

mass spectrum; Calcd for $C_{16}H_{27}N$; m/e=233.2144.

Found; m/e=233.2138.

3-Aminomethyl-1,2,3-tri-*tert*-butylcyclopropene. (63)

To a 2-l,three-necked flask, equipped with a dropping funnel, a reflux condenser, and a mechanical stirrer was added cyano compound 62 (7.335 g, 31.4 mmol) and THF (550 ml). With stirring, a THF solution of LAH (0.60 M, 150 ml, 90 mmol) was slowly added at room temperature. After 23 hr stirring at room temperature, excess LAH was carefully decomposed at 0° with a mixture of water (20 ml) and THF (30 ml). Filtration to remove the insoluble salts and washing of the salts with ether (500 ml) was followed by evaporation of the solvents. A pure amine, 7.34 g (98%) was obtained as a colorless oil.

pmr δ ($CDCl_3$); 0.96 (9H,s), 1.28 (18H,s), 2.88 (2H,s).
ir (neat); 3330 cm^{-1}.
mass spectrum; No molecular peak. m/e 207 (base peak, $M^{+}-CH_2NH_2$). Calcd for $C_{15}H_{27}$: m/e=207.2113.
Found: m/e=207.2109.

Urethane of 63. (64)

To a suspension of amine 63 (1.0 g, 4.2 mmol) and K_2CO_3(350 mg) in benzene (10 ml) was added dropwise a solution of ethyl chloroformate (550 mg, 5.06 mmol) in benzene (5 ml) at room temperature and the mixture was stirred for 1 hr. Sufficient ice was added to dissolve the inorganic salts and the benzene layer was separated. The aqueous layer was extracted twice with benzene (10 ml in total). The combined benzene layers were washed with brine (20 ml) and dried over Na_2SO_4. Removal of the solvent followed by distillation (bath temperature 80°/0.02 mmHg)

yielded urethane 64, 1.1 g (98%).
pmr δ ($CDCl_3$); 0.95 (9H,s), 1.20 (3H,t,J=7.2), 1.22 (18H,s), 3.43 (2H,d,J=5.4), 4.08 (3H,overlapped with NH,q,J=7.2).
ir (CCl_4); 3450 cm^{-1}(m), 1815 (w), 1725(s).

Urea of 63.

To a suspension of amine 63 (1.0 g, 4.2 mmol) and hydrochloric acid (1.44 N, 2.9 ml, 4.2 mmol) in water (30 ml) was added KCNO (1.02 g, 12.6 mmol) at room temperature and the mixture was stirred for 30 min at room temperature, and then for 1 hr at 55°. The white precipitate was removed by filtration, washed with water (200 ml) and dried under vacuum to give the urea, 1.044 g (88%).
pmr δ ($CDCl_3$); 0.95 (9H,s), 1.23 (18H,s), 3.39 (2H,d, J=5), 3.90 (1H,b), 4.60 (2H,b).
ir ($CHCl_3$); 1670 cm^{-1}(s).

N-Nitrosourethane from 64. (65)

To a suspension of urethane 64 (1.199 g, 3.87 mmol) and sodium acetate (324 mg) in THF (30 ml) was added 1.2 equivalents of N_2O_4 in ether (4.8 ml) at -30°. The pale yellow solution was stirred for 40 min while allowing the temperature to reach 0°. The yellow reaction mixture was then stirred for 5 hr at 0°. After filtration through a Celite-$NaHCO_3$ pad, which was then washed twice with THF (30 ml in total), the solvent was removed at 0°. The residue was dissolved in dichloromethane (30 ml), washed with 5% $NaHCO_3$, and brine. After drying over Na_2SO_4, the solvent was removed to give 1.33 g (100%) of N-nitrosourethane.

pmr δ ($CDCl_3$); 0.96 (9H, s), 1.16 (18H, s), 1.43 (3H, t, J=7.2), 4.04 (2H, s), 4.50 (2H, q, J=7.2).

ir (CCl_4); 1815 cm^{-1} (w), 1745 (s).

mass spectrum; No molecular peak. m/e 281 (M^+-*tert*-butyl).

Calcd for $C_{15}H_{25}N_2O_3$: m/e=281.1865.

Found: m/e=281.1873.

N-Nitrosourea. (66)

To a mixture of urea (539 mg, 1.92 mmol) and sodium acetate (160 mg) in dry THF (55 ml) was added 1.0 equivalent of N_2O_4 in ether (0.45 ml) at -30°. The temperature was allowed to reach 0° over a 1 hr period. The solution was filtered through a pad of Celite and $NaHCO_3$, which was washed with ether (100 ml). The fi[illegible] concentrated, diluted with dichlo[illegible]e (100 ml), washed with 5% $NaHCO_3$ and dried over Na_2S[illegible]trosourea 66 was obtained in 87% yield (516 mg) afte[illegible] solvent was removed.

pmr δ ($CDCl_3$); 0.93 (9H, s), 1.25 (18H, s), 3.58 (2H, s).

ir ($CHCl_3$); 1735 cm^{-1} (s).

Reaction of N-nitrosourea 66 w[illegible] base.

To a slurry of sodium methoxide (30 mg, 0.55 mmol) in ether (5 ml) was added N-nitrosourea 66 (133 mg, 0.43 mmol) at -30°. The mixture was stirred at -30° for 1.5 hr.

The original yellow color disappeared soon after the addition, and then the yellow color re-appeared. The mixture was filtered through a sintered-glass funnel at -78°. The ir spectrum showed peaks at 2215, 2105 and 1735 cm^{-1}, but no peak at 2030 cm^{-1}.

Tri-tert-butyl[4]annulene (13) from N-nitrosourethane 65.

To a mixture of sodium methoxide (23 mg, 0.43 mmol) in ether (5 ml) was added N-nitrosourethane 65 (126 mg, 0.36 mmol) in ether (1 ml). The mixture was stirred for 30 min at -30°. Methanol (10 ml) was added and stirring was continued for 1 hr at -30°. The mixture was cooled to -40° and to this was added ethylene glycol-water (1:1,v/v, 1 ml). The organic layer was then dried over $MgSO_4$ at -78°, and filtered through a Celite pad. The ir spectrum of this product exhibited a strong absorption at 2030 cm^{-1}. Methylcyclohexane-d_{14} (1.1 ml) was added and the bulk of the solvent carefully removed under vacuum at -30°. The residual solution was transferred to a nmr tube. The pmr spectrum showed peaks for the diazo compound and the by-products 67 and 68. After irradiation at -[illegible] with a high pressure mercury lamp for 4 hr, the diazo peaks had completely disappeared. A new peak at δ 5.38 (1H) appeared as well as two singlets at δ1.05 (18H) and 1.22 (9H). These absorptions and the yellow color of the solution disappeared almost instantly upon warming to room temperature or by bubbling oxygen into the nmr tube.

The methoxy compound 68 was collected by preparative glpc (UCW-98). The pmr spectrum showed peaks at δ ($CDCl_3$); 0.99 (9H,s), 1.15 (9H,s), 1.20 (9H,s), 2.17 (1H,d,J=10), 2.25 (1H,d,J=10), and 3.20 (3H,s).

Adduct of 13 with maleic anhydride. (74)

N-Nitrosourethane 65 (4.5 g, 13.3 mmol) was treated with sodium methoxide (3.6 g, 66.7 mmol) in ether (300 ml) and methanol (3 ml), and was then worked-up as above. The crude mixture was irradiated in THF (35 ml) at -78° for 2 hr. To this photolysate was added maleic anhydride (870 mg, 8.9 mmol). Removal of volatile impurities, followed by chromatography on silicic acid (100 g) using chloroform as the eluent gave a mixture (239 mg) of the adduct and alcohol 67. The latter was removed by sublimation at 25-30°/0.05 mmHg, to give pure adduct 74, 175 mg (4%), which was recrystallized from hexane, mp 123.0-124.5°.

pmr δ ($CDCl_3$); 0.96 (9H,[illegible]), 1.12 (9H,s)1.16 (9H,s), 3.1-3.5 (3H,m).

cmr δ ($CDCl_3$); 27.0, 32.1,36.6 (CH_3), 32.8, 33.2,33.5 (tert-C), 61.9 (quart-C), 153.7,154.8 (olefinic-C), 172.5 172.7 (C=O).

ir (CCl_4); 1847 cm^{-1} (w), 1777 (s).

elemental analysis; Calcd for $C_{20}H_{30}O_3$: C,75.43; H,9.50.

Found: C, 75.55; H,9.46.

Alcohol 67 was obtained by sublimation, mp 43.0-44.0°.

pmr δ ($CDCl_3$); 1.06 (9H,s), 1.17 (9H,s), 1.25 (9H,s), 1.60 (1H,s), 1.92 (1H,d,J=12), 2.55 (1H,d,J=12).
ir (CCl_4); 3610 cm^{-1} ,3550, 3400.
mass spectrum; m/e 238 (M^+).

Tricyclo[6.2.0]deca-4,9-diene-2,7-dicarboxylic anhydride. (79)

To a solution of anhydride 78 (5.0 g, 33 mmol) and cyclobutadieneiron tricarbonyl 3 (5.0 g, 26 mmol) in acetone (170 ml) was added ceric ammonium nitrate (85 g, 155 mmol) in portions over a 1 hr period at 0°. After additional stirring for 2 hr, ether (500 ml) was added to the reaction mixture, which was then filtered through a Celite pad. The insoluble salts were washed three times with THF (100 ml in total). The filtrate was washed with 5% $NaHCO_3$ (100 ml), brine (100 ml) and dried over Na_2SO_4. The solvent was removed and the resulting solid (a mixture of the starting material and the adduct) was dissolved in methanol (100 ml) and refluxed for 30 min. Dichloromethane (400 ml) was added and the organic layer was washed with 5% $NaHCO_3$ (50 ml) , and with brine (50 ml). Removal of the solvent gave a crystalline residue, which was sublimed under high vacuum at 70-75° to afford the pure adduct 79, 2.4 g (46%), mp 157.0-158.0° (ether).
pmr δ ($CDCl_3$); 2.55 (4H), 3.32 (2H), 5.98 (2H), 6.35 (2H).

2,7-Bis(hydroxymethyl)tricyclo[6.2.0]deca-4,9-diene. (80)

A solution of LAH in THF (0.7 M, 34 ml, 24 mmol) was slowly added to anhydride 79 (2.4 g, 11.9mmol) dissolved in THF (20 ml) and the mixture was refluxed for 7 hr. Decomposition of excess LAH by wet ether, filtration through Celite and removal of the solvent gave a crude product, which was recystallized from ether to afford the pure diol, 2.0 g (88%), mp 132.5-134.5°.

pmr δ($CDCl_3$); 1.90 (4H), 2.67 (2H), 3.43 (2H,d,J=11), 4.00 (2H,d,J=11), 5,95 (2H), 6.12 (2H).

elemental analysis; Calcd for $C_{12}H_{16}O_2$: C,74.97; H,8.39.
Found: C, 74.68; H,8.23.

12-Oxatetracyclo[4.4.3.$0^{2,5}$]trideca-3,8-diene. (81)

To a solution of diol 80 (2.07 g, 10.8 mmol) in dry pyridine (30 ml) was added tosyl chloride (700 mg, 3.6 mmol, 1/3 equivalent) at 0°. Stirring was continued for 1.5 hr at 0°, then for 30 min at room temperature. Another 1/3 equivalent of tosylchloride was added and the reaction mixture was stirred similarly. The last 1/3 equivalent of tosyl chloride was added and the reaction mixture was kept at 0° overnight. Pentane (200 ml) and ether (50 ml) were added to the mixture, which was then washed with water (50 ml), 2% HCl (30 ml), and 5% $NaHCO_3$ (50 ml). After dring over Na_2SO_4, the solution was concentrated, and molecular-distillation at 50°/0.1 mmHg afforded the diene, 1.41 g

(75%).

pmr δ ($CDCl_3$); 2.17 (4H,d,J=2.5), 2.80 (2H), 3.37 (2H,d,J=9), 3.90 (2H,d,J=9), 5.97 (2H,t,J=2.5), 6.25 (2H).

3,4-Epoxy-12-oxatetracyclo[4.4.3.$0^{2,5}$]tridec-8-ene. (82)

A solution of diene 81 (205 mg, 1.17 mmol) and *m*-chloroperbenzoic acid (85%, 286 mg, 1.41 mmol) in dichloromethane (4 ml) was stirred at room temperature for 1 hr. The mixture was washed with 5% Na_2SO_3 (5 ml), 5% $NaHCO_3$ (5 ml), brine (5 ml) and dried over Na_2SO_4. Removal of the solvent and molecular distillation at 80°/0.3 mmHg afforded an oil, 145 mg (65%).

pmr δ ($CDCl_3$); 2.12 (4H,m), 2.38 (2H,d,J=3), 3.32 (2H,d,J=10), 3.98 (2H,d,J=3), 4.27 (2H,d,J=10), 5.95 (2H,m).

9-Hydroxy-12-oxatetracyclo[4.4.3.$0^{2,5}$]trideca-3,7-diene. (83)

Diene 81 (721 mg, 4.1 mmol) and methylene blue (30 mg) were dissolved in methanol (200 ml). The solution was irradiated with a high pressure mercury lamp (Pyrex filter), while oxygen was bubbled into the solut[illegible] Irradiation was continued until almost no starting material was detected by glpc (about 5 hr). Removal of the solvent gave an oily residue, which was dissolved in ether (40 ml). To this solution was added an ether solution of LAH (1 *M*, 10 ml, 10 mmol) at 0°. After 10 min, wet ether (10 ml) was added and the insoluble salts were filtered. Removal of the solvent gave an oil, which was distilled to afford the α,β-unsaturated alcohol, 465 mg (60%), bp 67°/0.03 mmHg. pmr δ ($CDCl_3$); 1.7-2.2 (2H,m), 2.92 (2H,m), 3.42 (2H,bd, J=10), 3.94 (1H,d,J=10), 3.97 (1H,d,J=10), 5.87 (2H,m), 6.23 (2H,m).

12-Oxatetracyclo[4.4.3.$0^{2,5}$]trideca-3,7-dien-9-one. (84)

Alcohol 83 (201 mg, 1.06 mmol) and manganese dioxide (1.9 g, 22 mmol) were stirred in dichloromethane (20 ml) at room temperature for 3 hr. Filtration through Celite and removal of the solvent were followed by molecular distillation to yield ketone 84, 156 mg (78%).
pmr δ ($CDCl_3$); 2.57 (2H,m), 3.05 (2H,m), 3.43 (1H,d,J=9), 3.52 (1H,d,J=9), 4.07 (1H,d,J=9), 4.12 (1H.d,J=9), 6.12 (1H, d,J=10), 6.82 (1H,d,J=10), 6.37 (2H,m).
ir ($CHCl_3$); 1672 cm^{-1} (s).

12-Oxatetracyclo[4.4.3.$0^{2,5}$]trideca-3,7,9-tiene. (77)

A solution of ketone 84 (82 mg, 0.44 mmol) and tosyl hydrazine (82 mg, 0.44 mmol) in methanol (o.4 ml) was kept at room temperature for 2 hr. The solvent was removed and toluene (2 ml) was added and then evaporated to dryness. To the slurry of the residue in dry benzene (4 ml) was added at 0° an ether solution of methyllithium (1.6 M,1.1 ml, 1.8 mmol). Stirring was continued for 1[illegible]hr at room temperature. Wet ether was then added to the reaction mixture, which was then washed with water, and dried over Na_2SO_4. Removal of the solvent gave an oil (72 mg), which contained the desired trien[illegible]7 in about 50% purity. Preparative glpc (UCW-98, 105°) afforded pure triene.

pmr δ ($CDCl_3$); 3.23 (2H,m), 3.49 (2H,d,J=10), 4.09 (2H, d,J=10), 5.76 (4H,m), 6.27 (2H,m).

ir (neat); 3020 cm^{-1} (m), 2950 (m), 2840 (m), 1580 (w), 1294 (m), 1074 (m), 1033 (m), 917 (m), 783 (m), 723 (s), 708 (m).

mass spectrum; m/e 172 (M^+, 7%), 171 (5), 143 (9), 142 (32), 141 (35), 128 (14), 119 (100), 115 (24), 91 (42).

Calcd for $C_{12}H_{12}O$: m/e=172.0888

Found: m/e=172.0886.

8,9-Dibromo-3,4-epoxy-12-oxatetracyclo[$4.4.3.0^{2,5}$]tridecane. (86)

To a solution of epoxide 82 (145 mg, 0.76 mmol) in dichloromethane (5 ml) at 0° was added bromine (135 mg, 0.84 mmol) in dichloromethane (2 ml). After stirring at 0° for 10 min, the reaction mixture was warmed to room temperature. The solvent was removed to afford the white crystalline dibromide, 257 mg (97%). This crude product was used in the next step.

3,4-Epoxy-12-oxatetracyclo[$4.4.3.0^{2,5}$]trideca-7,9-diene. (87)

To a solution of the dibromide (257 mg, 0.734 mmol) in DMSO (3 ml) was added potassium *tert*-butoxide (260 mg, 2.3 mmol). The reaction was stirred at room temperature for 40 min, and then poured into ice-water, extracted twice with pentane (100 ml in total). The pentane layers were combined and washed twice with water and once with brine. After dring over Na_2SO_4, the solvent was removed to afford white crystals, 113 mg (82%), which were sublimed at 65°/ 0.25 mmHg, mp 58-68°.

pmr δ ($CDCl_3$); 2.73 (2H,d,J=3), 3.32 (2H,d,J=10), 3.98 (2H,d,J=3), 4.45 (2H,d,J=10), 5.73 (4H,m).

Deoxygenation of 87.

To a suspension of tungsten chloride* (624 mg, 1.57 mmol) in THF (13.5 ml), maintained at -78°, was added *n*-butyllithium (hexane solution, 1.6 *M*, 1.88 ml, 3.01 mmol). The mixture was allowed to warm to room temperature over a period of 20-30 min. During this period the tungsten chloride completely dissolved and the solution became green-brown.

To this solution was added epoxide 87 (117 mg, 0.623 mmol) in THF (3.9 ml). The reaction mixture changed to

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*) Dark-blue crystals obtained by sublimation of the commercial product (Pressure Chemical Co.) *in vacuo* were collected and used in this reaction. The crystals were stored in a desiccater.

dark-brown. After stirring at room temperature for 2 hr, the mixture was poured into 20% NaOH and extracted with pentane (2x20 ml). After removal of the solvent, the residue was distilled to give triene 77, 77 mg (72%).

12-Oxapentacyclo[4.4.3.$0^{2,5}$.$0^{7,10}$]trideca-3,8-diene. (89)

To a solution of diisopropylamine (121 mg, 1.2 mmol) in THF (2 ml) cooled with dry-ice/acetone bath, was added dropwise *n*-butyllithium (hexane solution, 1.45 *M*, 0.83 ml, 1.2 mmol). The solution was warmed to room temperature and stirred for 10 min, and then cooled in a dry-ice/acetone bath. Diol 88 (95 mg, 0.5 mmol) in HMPA (1 ml) was added dropwise. The mixture was stirred for 15 min at room temperature. The mixture was cooled to 0°, and to this was added a 0.25 ml portion of a solution of tosyl chloride (142 mg, 0.74 mmol) in THF (3 ml). After stirring at room temperature for 15 min, this procedure was repeated, until all the tosyl chloride solution was added. The mixture was then poured into ice, extracted with ether and dried over $MgSO_4$. Removal of the solvent, followed by chromatography on silica gel, using dichloromethane as the eluent, afforded cololess crystals. Recrystallization from pentane at dry-ice temperature gave needles, mp 66.0-67.0°, in 50-55% yield.

Detection of [4]annulene 1 in a matrix.

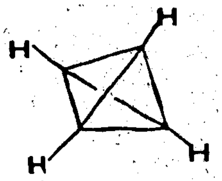
A solution of triene 77 in tetrahydrofuran-d_8 was placed in an nmr tube, degassed and sealed. At -90°, This solution was irradiated with a low pressure mercury lamp for 20 min. The pmr spectrum showed no starting material and new peaks appeared corresponding to phthalan (δ 4.96, 7.16) and the [4]annulene *syn*-dimer (δ 3.05, 5.94). Also photolysis products {irradiated in isopentane/2-methyltetrahydrofuran (2.8/0.5, v/v) in liquid nitrogen bath} were shown by glcp (UCW-98, 130°) to be a mixture of these two compounds.

[4]Annulene 1 in a matrix was detected by uv spectroscopy in the following experiment. In a quartz uv cell was placed a 3.1 x 10^{-3} M solution of the triene in 2-methyltetrahydrofuran under an argon atmosphere. The cell was placed in a quartz Dewar bottle, which had quartz windows through which the spectrum could be measured. The cell was cooled below -170° by cold nitrogen gas, which was pre-cooled in liquid nitrogen bath. During the whole experiment the cell was kept at about -175°. Irradiation with a low pressure mercury lamp was continued for 1-2 hours, and the uv spectrum was recorded. A background spectrum was taken after thawing the matrix for a short time and re-cooling to the same temperature as before. The difference in the two spectra was taken as the spectrum of [4]annulene 1, which had an absorption at λ_{max} 300 nm (ε 100), (Figure VI.).

PART II. TETRAHEDRANE.

CHAPTER I. INTRODUCTION.

Tetrahedrane 101, the second possible isomer of the $(CH)_4$ species, has long been held in the mind of organic chemists as the most strained polycyclic small-ring system. Moreover, it represents the simplest of the five possible regular polyhedra.* The strain energy of this system is calculated to be about 130 kcal/mol,[34,75] and if this energy is as great as that predicted, tetrahedrane 101



101

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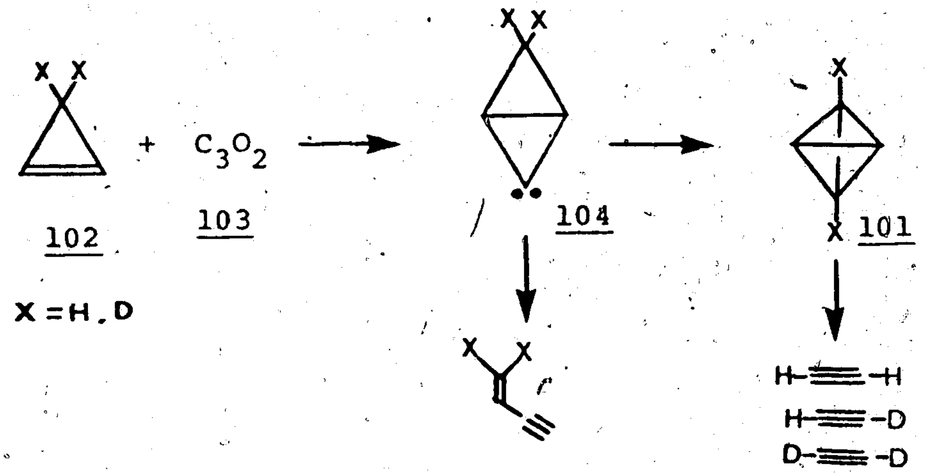
*) Of these five possible polyhedra, only three can be constructed using the carbon skeleton; tetrahedron (tetrahedrane), hexahedron (cubane), and dodecahedron (dodecahedrane). Cubane was first synthesized by Eaton[71] in 1964. Two independent syntheses[72,73] of cubane soon followed. Attempted synthesis[74] of dodecahedrane by photo-dimerization of triquinacene appears to have met with no success thus far.

is very unlikely to exist as a stable species except at very low temperatures. It may undergo spontaneous disruption via the diradical into two molecules of acetylene or possibly into [4]annulene with extreme ease. A number of theoretical treatments[34,75] have been reported on this interesting system. The most recent one,[75] which used an *ab initio* SCF method, predicted some physical properties of tetrahedrane. Interestingly, calculations show that this species is a local minimum point on the C_4H_4 potential energy surface. A barrier of at least 18 kcal/mol has been calculated for homolytic cleavage of the single bond. This barrier seems to be high enough to allow at least the spectroscopic detection of this species.

Some experimental results[76,77] support the intermediacy of tetrahedrane, although the evidence is gleaned from the labeling pattern of acetylenes obtained as cleavage products. Photolysis of a mixture of cyclopropene 102 and carbon suboxide 103 produced acetylene (24%) together with vinyl acetylene (33%).[76] The appreciable

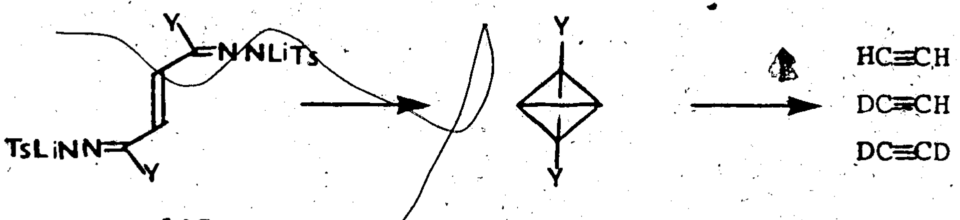


102 103 104 101

X = H, D

yield of acetylene suggested the presence of tetrahedrane as an intermediate. Photolysis of carbon suboxide produces ketocarbene which reacts with cyclopropene to give an adduct leading to a bicyclic carbene 104 intermediate. This carbene may either rearrange to give vinyl acetylene or undergo intramolecular carbon-hydrogen insertion to give tetrahedrane 101. In order to determine if the acetylene could arise from the decomposition of a tetrahedrane intermediate, isotope labeling experiments were carried out. Photolysis of cyclopropene-3,3-$\underline{d}_2$ (87.1 ± 3.2% D) with C_3O_2 produced acetylenes, which were analyzed by mass spectroscopy. The relative yields of C_2H_2, C_2HD, and C_2D_2 were 23.7 ± 2.5, 63.6 ± 1.2, and 12.8 ± 1.4%, respectively. The corresponding calculated yields, based on the decomposion of a symmetrical tetrahedrane, are 25.0, 62.4, and 12.6%, respectively. It thus seems that tetrahedrane is an intermediate of this reaction. Further support was obtained by a double-labeling experiment using cyclopropene-3,3-$\underline{d}_2$ and carbon 2-^{14}C-suboxide.

Similarly, the dilithium salt of ditosylhydrazone 105, when pyrolyzed, produced acetylene (20-30% yield) as the sole volatile product.[35] Deuterium labeling experiments



105

Y = H, D

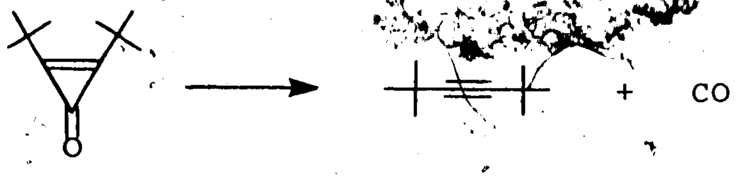
indicated that 37-47% of the acetylene was produced via tetrahedrane or its diradical equivalent.

To date, no experimantal result has been reported which indicates that tetrahedrane is an isolable species. In the following section, several attempts toward the synthesis of tetrahedrane derivatives are presented.

CHAPTER II. RESULTS AND DISCUSSION.

A. Attempted synthesis from a bicyclic cyclopropenone.

Cyclopropenones are known to decarbonylate either by photolysis or by pyrolysis. For instance, di-*tert*-butylcyclopropenone 106 produces di-*tert*-butylacetylene quantitatively when irradiated at 2537 A or when pyrolyzed at 320-327°.[42a] Pyrolysis of cycloheptenocyclopropenone 107 at 250° produced carbon monoxide and triscycloheptenobenzene 108,[78] which presumably arose *via* an intermediate cycloheptyne 109.



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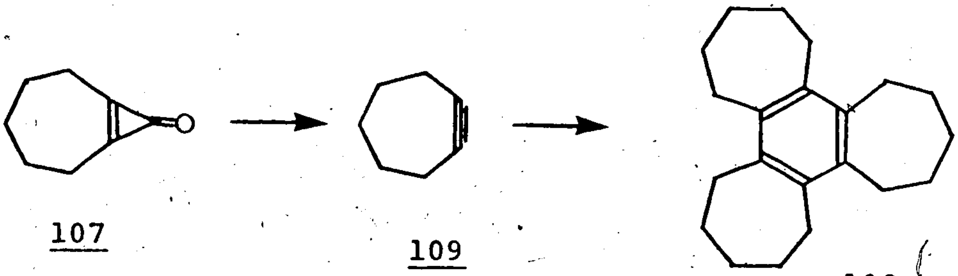
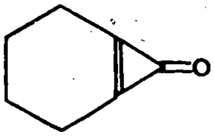


107

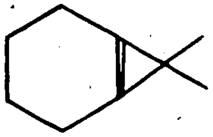
109

108

An attempted synthesis[79] of the buteno derivative 100 of cyclopropenone met with no success. Also, 7,7-dimethyl-bicyclo[4.1.0]hept-1(6)-ene 111[80] is stable only below -20°. We thought that the high reactivity of the cyclopropenone moiety in 110 was responsible for the earlier

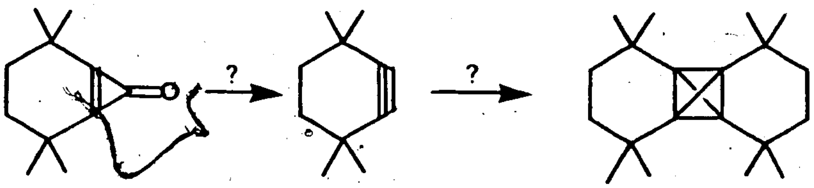


110



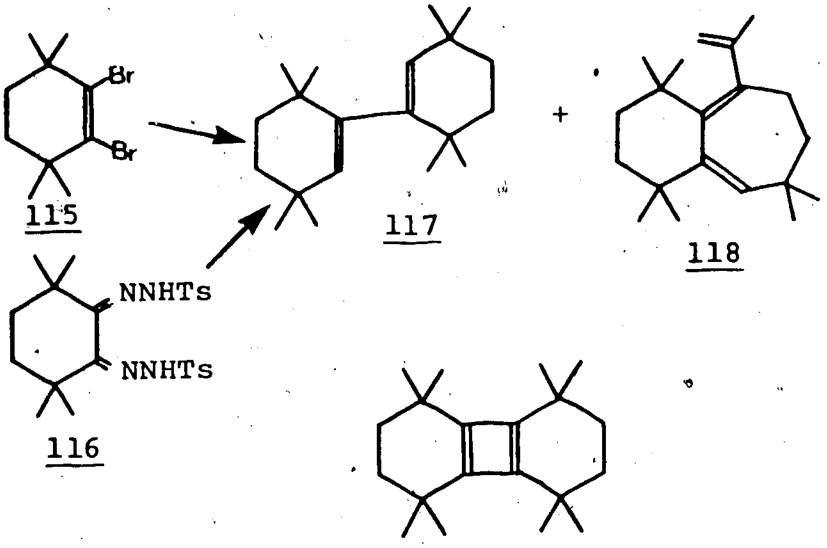
111

failure at isolation. Introduction of four methyl groups at the α-position should suppress the reactivity of this bicyclic molecule. We anticipated that tetramethylbutenocyclopropenone 112 would be much less reactive than 110, allowing its isolation, and furthermore that tet[illegible]cyclohexyne 113, if produced from 112 by photolysis, would form a tetrahedrane derivative 114, rather than its benzene counterpart due to the steric hindrance expected in the latter



112 113 114

Applequist *et al*. tried to generate tetramethylcyclohexyne 113 from dibromide 115 and from bishydrazone 116.[81] When the dibromide was treated with sodium at room temperature, two dimeric hydrocarbons 117 and 118 were obtained in 90% total yield. Oxidation of bishydrazone 116 with silver oxide also gave these products in low yields.

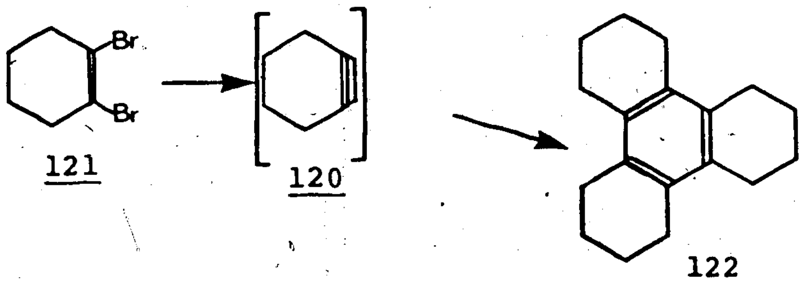


115 116 117 118

119

Formation of dimeric products indicated the intermediacy of cyclobutadiene derivative 119. The latter product 118, the authors explained, was formed by a $[2_s+2_s+2_s]$cycloaddition reaction of 119.

As described above, our anticipation was that, although cyclohexyne 120 generated from dibromide 121 was known to produce the trimer 122,[82] tetramethyl cyclohexyne 113 would not di- or trimerize in a similar manner, due to the steric repulsion of the methyl groups. Also, the advan-

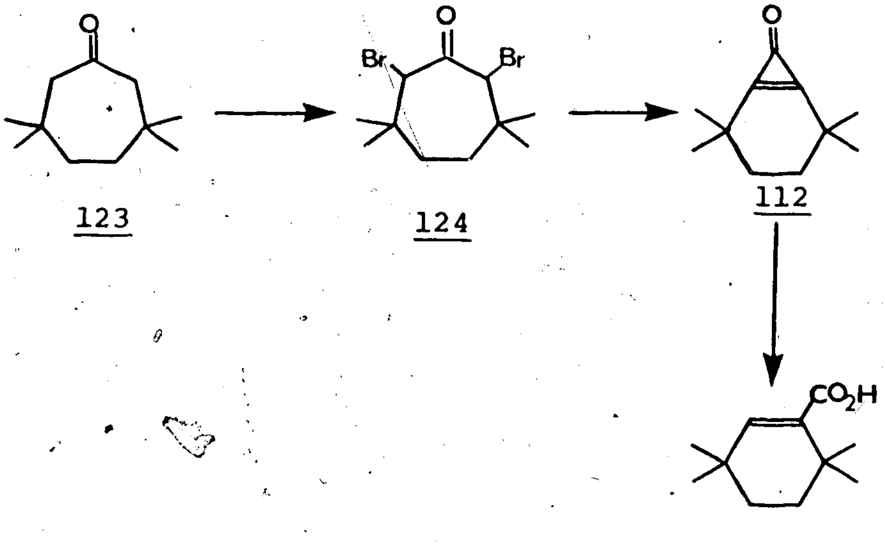


121 120 122

tage of our approach over the earlier one is that the decarbonylation reaction can be performed at low temperature, even in a matrix, without the need for any work-up procedures,

Thus, our first approach involved the synthesis of tetramethylcyclohexenocyclopropenone 112,[83] in order to examine its photochemical behavior.

We attacked this seemingly reactive cyclopropenone derivative starting from the known 3,3,6,6-tetramethylcycloheptanone 123.[84] Treatment with two equivalents of bromine provided dibromide 124. The simplicity of its pmr spectrum indicated that the product was a single isomer, but no further work was conducted to rigorously establish the stereochemistry.



123

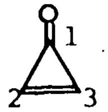
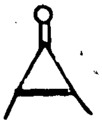
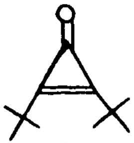
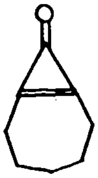
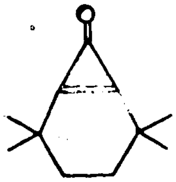
124

112

125

When dibromide 124 was reacted with potassium tert-butoxide, followed by an acidic work-up, carboxylic acid 125 was obtained in 48% yield. The formation of acid 125, rather than the tert-butyl ester, indicated that the desired cyclopropenone 112 was actually formed, but 112 reacted with water under the acidic conditions to yield acid 125. Dibromide 124 was then treated with potassium tert-butoxide and the reaction mixture was quenched with aqueous monobasic sodium phosphate. Usual work-up followed by sublimation at room temperature afforded the desired cyclopropenone 112 in 41% yield. As later found, this cyclopropenone derivative is very sensitive to both acid and base. Consequently, careful handling was necessary to obtain 112 as pure white crystals, mp 89.0-89.5°. Spectroscopic properties as well as elemental analysis support the proposed structure, and are summarized in Table II, together with data for related compounds of 112 for comparison.

The ir spectrum of 112 exhibits strong absorptions at 1852, 1790, and 1617 cm^{-1}. All cyclopropenones show characteristic absorptions at 1800-1870 and 1600-1660 cm^{-1}.[89,90] Although these two modes of vibrations are undoubtedly tightly coupled, the higher frequency band may safely be ascribed mainly to carbonyl stretching and the other band to C=C stretching.[90] The large shifts for both absorptions in compound 112 indicate that the cyclopropenone system is perturbed by the fused six-membered ring to a much greater

	Infrared (cm^{-1}; CCl$_4$)		Ultraviolet (nm, ε; cyclohexane)	cmr (δ; CDCl$_3$)	
				C-1	C-2&3
	1833 1864	--[85]	276 (31)[86]	155.1	158.3[87]
	1848 1866	1657[88]	272 (43)[89]		
	1820 1855	1640[42a]		159.5	164.8*
	1840	1640[88,89]	267 (79)[89]	154.6	164.2*
	1790 1852	1617*	263 (95)*	146.7	169.0*

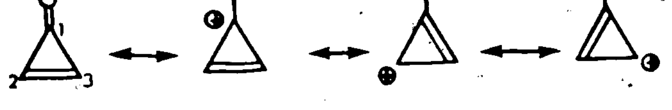
*) present work

Table II: Spectral properties of cyclopropenone derivatives.

extent than in the compound with a seven-membered ring.

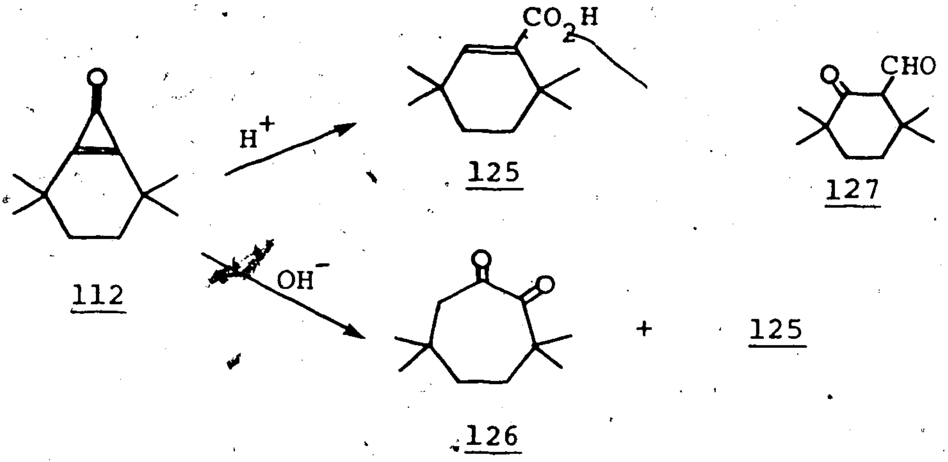
The uv spectrum of 112 has an absorption at 263 nm (ϵ 95) and the hypsochromic shift of the n-π^* absorption is clearly observable when compared with other less constrained compounds.

In the cmr spectra, the C=O absorption shifts upfield (with allowance of substituents effects) as the fused ring size becomes smaller, while the olefinic carbons show the reverse trend. These trends are interpreted as an indication of change in the electronic structure of the system; cyclopropenones are represented as a mixture of resonance structures A-D, and the contribution of each structure varies with the nature of the fused ring. Thus, in 112, C and D become more important than they are in the parent compound. As a result, the double bond becomes more exocyclic in nature with respect to the fused ring system, thus relieving strain in the system as much as possible. Furtheremore, C-2 and C-3 in 112 now carry a slightly more positive charge than in other compounds. The above interpretation is only tentative and is obviously a subject for further study.

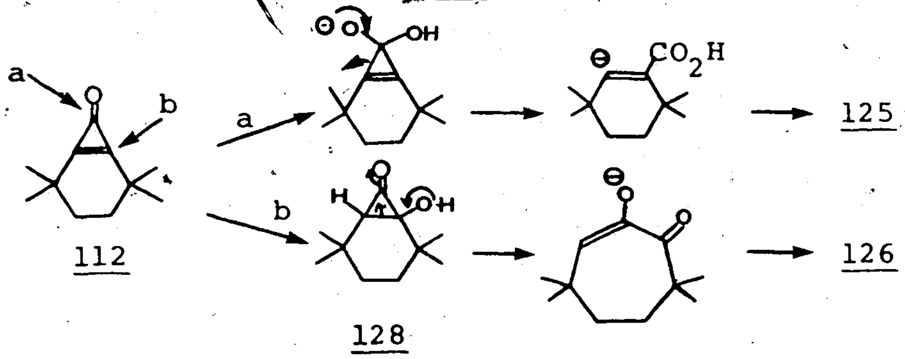


A B C D

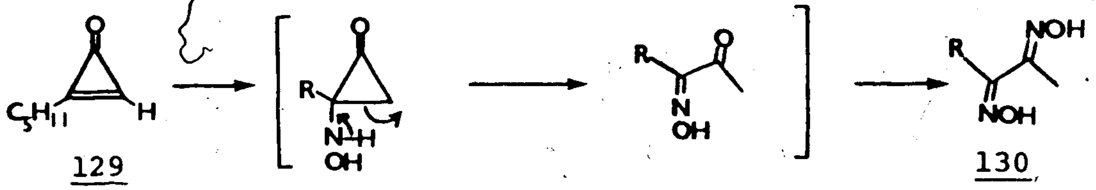
As already described, cyclopropenone 112 is very sensitive to acid, whereas other known cyclopropenones are stable in acidic media; cycloheptenocyclopropenone 107 was actually purified by extracting it with 75% H_2SO_4.[78] In contrast, compound 112 decomposed completely upon brief treatment with 0.1 N H_2SO_4 at room temperature giving a quantitative yield of acid 125. This acid was expected to be produced under basic conditions in a manner analogous to those acids produced from other known cyclopropenones.[78] However, compound 112 ring-opened with 0.05 N NaOH at room temperature, and a diketone 126 was formed as the major product in addition to acid 125. The structure of 126 was assigned from its spectroscopic properites. The pmr spectrum showed two singlets for the methyl groups, a multiplet for the CH_2CH_2 unit, and a singlet for the isolated CH_2 group. A sharp singlet at δ 2.25 indicated the presence of a methylene unit at a postion α to a ketone function. No absorption was observed in the low-field region, thus excluding structure 127 . The mass spectrum



showed a molecular ion peak (m/e 183, 14%), and fragmentation peaks at 154 (M^+-CO, 3%), 139 (M^+-CO-CH_3, 5%), 110 (100%), and 83 (56%). The hydroxide anion can attack two different sites of the cyclopropenone system; attack on the carbonyl carbon produces the acid 125 (route a), while attack on the double bond first produces hydrate 128, which ring-opens to form the diketone 126 (route b). Although many

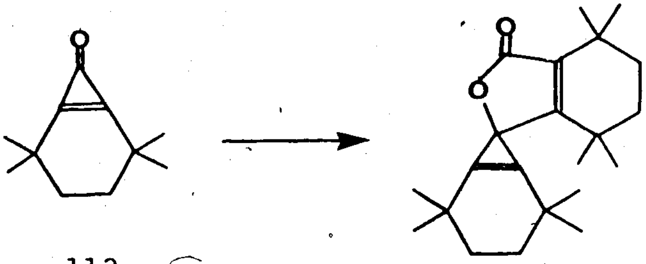


examples are known[91] in which a nucleophile attacks the double bond of cyclopropenone derivatives, the formation of a diketone has only one precedent.[92] When pentylcyclopropenone 129 was treated with excess hydroxylamine, a glyoxime 130 was formed,[92] presumably through the mechanism depicted below. Conjugate addition followed by ring-opening produces a monoxime of the α-diketone, which in turn produces the product. The difference in reactivity of 112 from other known cyclopropenone derivatives is a reflection of the extra ring-strain in the system and may be in line with the



above interpretation of the cmr spectrum.

In the hope that photolysis of 112 would cause decarbonylation to generate tetramethylcyclohexyne 113 as a reactive intermediate, an irradiation experiment was carried out. Photolysis of 112 at 0° produced a dimeric compound 131 as the sole product. Spectroscopic data are fully consistent with this structure. The ir spectrum has a strong carbonyl absorption at 1720 cm^{-1}, and the pmr spectrum shows four singlets for the methyl groups and also two singlets for the methylenes. The mass spectrum shows a parent peak (m/e 328) and strong fragments at m/e 313 (M^+-CH_3) and 285 (M^+-CH_3-CO). The structure of this dimer is related to those proposed for the dimers 132[93] of diphenyl- and methylcyclopropenone.[88]



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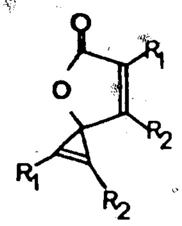
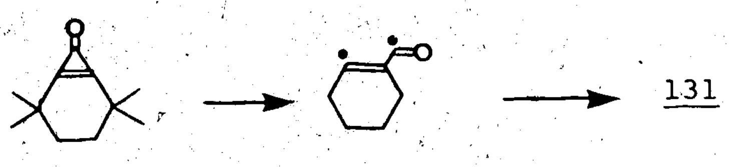
131



132

$R_1=R_2=Ph$
and
$R_1=CH_3$,
$R_2=H$

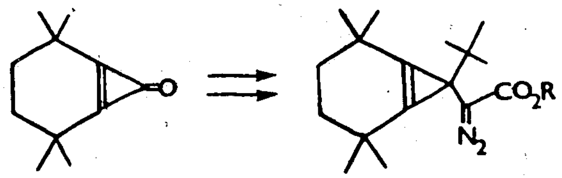
The formation of compound 131 probably proceeds in the following manner. Irradiation causes the formation of a diradical 133 which in other cases easily loses carbon monoxide to lead to the corresponding acetylenic product. In this case, however, the strain expected in the cyclohexyne system may disfavor the loss of CO and consequently the life-time of this intermediate is long enough to allow the formation of 131.



112 133

The fact that the irradiation of 112 in a matrix of 2-methyltetrahydrofuran at -198° produced the same dimer astonished us. A tentative explanation is that due to the high polarity of the cyclopropenone moiety, the molecule exists in a paired form even in a matrix. Consequently, in every solvent cage there is more than one guest molecule, which can react with the diradical 133 to form the dimer 131.

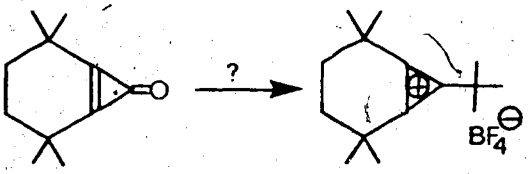
Initially, this approach was started with the expectations not only that cyclopropenone 112 would form a tetrahedrane derivative photochemically, but also that 112 would provide another tetrahedrane presursor, for instance, diazoester 134, which would be synthesized from 112 in a similar manner to the preparation of 46. The presence of



112 134

a fused six-membered ring in 134 would activate the C=C bond, in order to release the extra strain involved in the bicyclic system. Thus, we anticipated that photolysis of 134 would yield a tetrahedrane derivative, instead of a [4]annulene derivative.

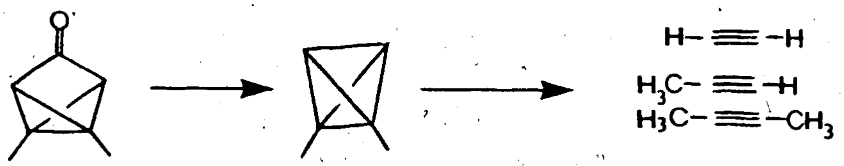
In the hope of obtaining 135, a precursor of 134, 112 was treated with tert-butyllithium; however, no desired product was obtained as a precipitate. The failure of this reaction may be due to the high reactivity of the intermediate cyclopropenyl alcohol or its lithium salt. Thus, we abandoned this approach.



112 135

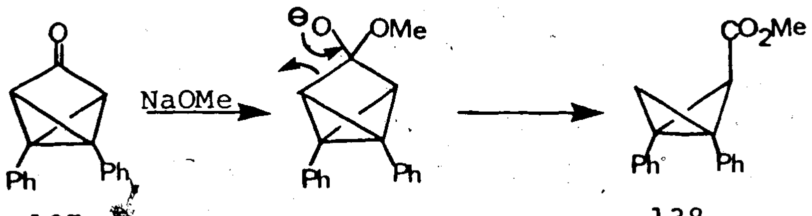
B. Attempted synthesis from homotetrahedrane derivatives.

Homotetrahedrane (tricyclo[2.1.0.$0^{2,5}$]pentane) derivatives appear to be a good precursor for the synthesis of tetrahedrane in that part of the ring system of tetrahedrane has already been constructed. When dimethylhomotetrahedranone 136 was photolyzed in the gas phase, small amounts of acetylene, propyne, and butyne were formed,[94] indicating the existence of a tetrahedrane intermediate.



136

When diphenylhomotetrahedranone 137 was treated with sodium methoxide, bicyclobutane derivative 138 was formed.[95]



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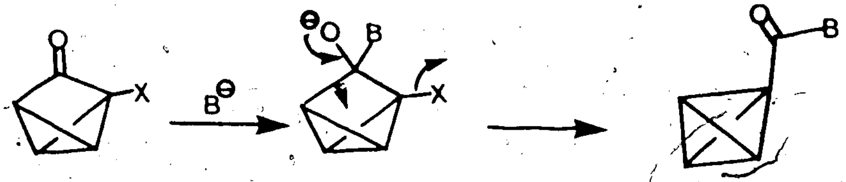
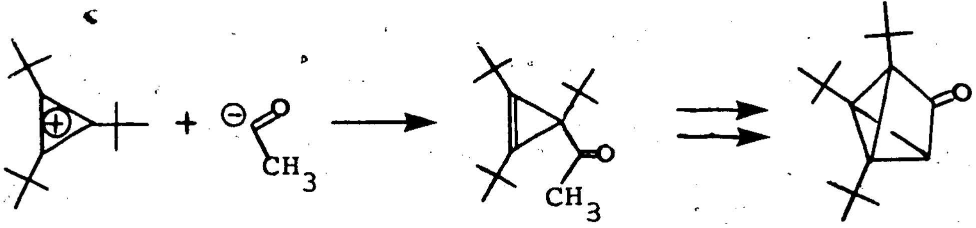
138

This result suggests that a homotetrahedranone, which possesses a good leaving group at the α-position to the carbonyl, might produce a tetrahedrane derivative upon treatment with base, as schematically indicated below.



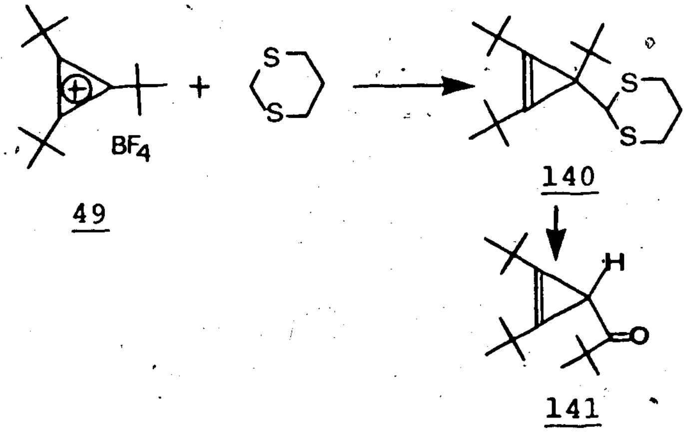
From these expectations, tri-*tert*-butylhomotetrahedranones and related compounds were synthesized and their chemical reactivities examined.

We expected that methyl ketone 139 would be a good synthetic intermediate, which could then be diazotized and cyclized to the homotetrahedranone system. Schematically, reaction of a tri-*tert*-butylcyclopropenium salt with an acyl anion produces the desired ketone 139.

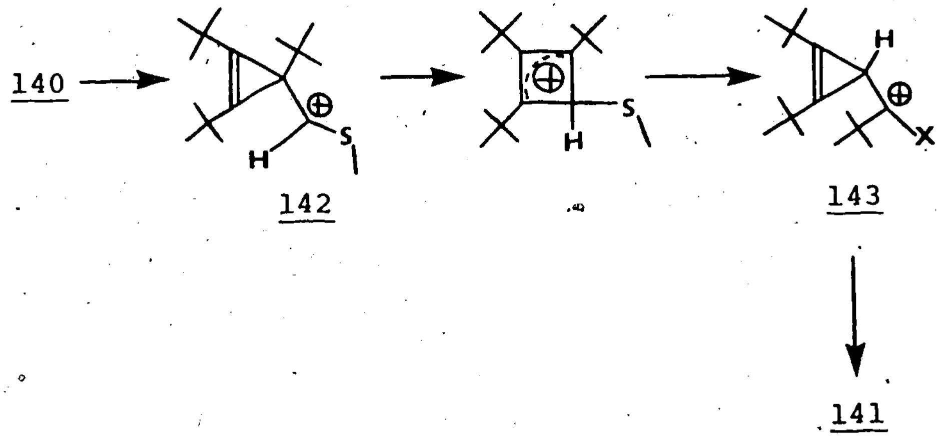


139

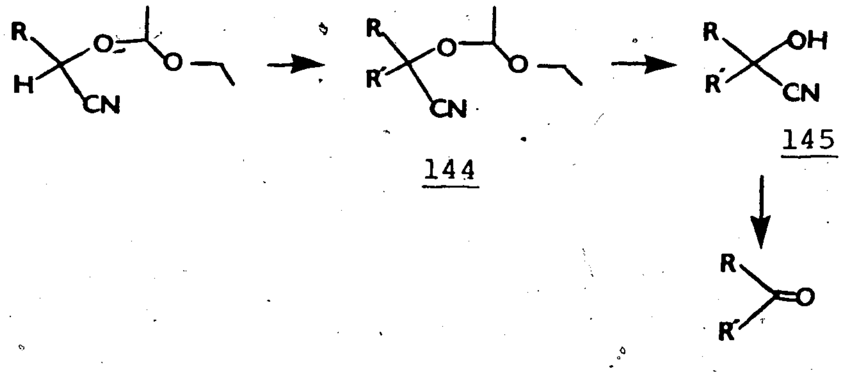
When tri-*tert*-butylcyclopropenium fluoroborate 49 was reacted with the lithium salt of dithiane, the expected product 140 was formed. Unfortunately, however, hydrolysis of this product using any known methods,[96] even under neutral conditions (methyl iodide and sodium carbonate)[96] produced only the rearranged ketone 141. This observation



is explained by the fact that the carbonium ion intermediate 142, inevitably produced in this hydrolytic process, will rearrange to the thermodynamically more stable isomer 143 containing a *tert*-butyl group in the side chain. This result indicated that the step to regenerate the ketone must not involve an intermediate which may develop a positive charge on the carbon α to the cyclopropenyl system.



Stork's method[97] utilizes a protected cyanohydrin as the source of an acyl anion. The advantage of this method is that the carbonyl group is regenerated from its protected form under basic conditions. The sequence is depicted below. After the reaction to form a new C-C bond is carried out, the cyanohydrin ketal 144 is converted under acidic conditions to the corresponding cyanohydrin 145, which in turn is treated with base to produce ketone 146.

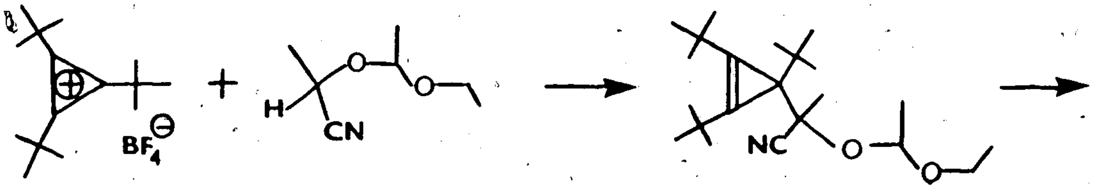


144

145

146

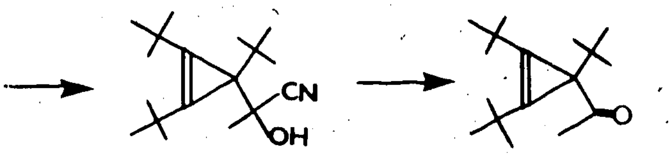
Thus, the anion of acetaldehyde cyanohydrin ketal 147[98] was reacted with fluoroborate 49 to give 148, which was hydrolyzed in acidic conditions to cyanohydrin 149. Finally, base treatment afforded the desired ketone 139 in 81% overall yield from the fluoroborate 49. No rear-



49

147

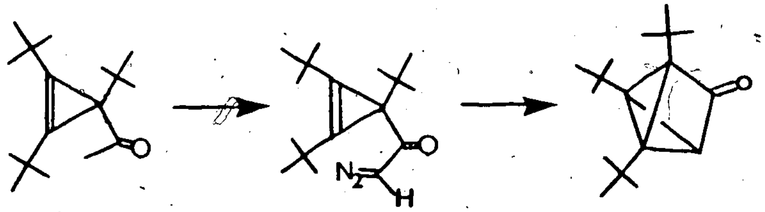
148



149 139

ranged ketone was produced. Hydrolysis of 149 under basic conditions would proceed by deprotonation of the hydroxy group, followed by the removal of the nitrile moiety. No positive charge developed on the carbon α to the cyclopropenyl system, and therefore no skeletal rearrangement occured.

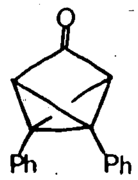
Since the introduction of an α-formyl group was unsuccessful, direct diazotization[99] of 139 was tried using such bases as sodium methoxide and potassium *tert*-butoxide. The results had not been encouraging until we used a stronger base, *n*-butyllithium. Diazoketone 150 was obtained in 89% yield by the treatment of the anion of 139 with tosyl azide. The spectroscopic data of this product strongly support the structure. The ir spectrum



139 150 151

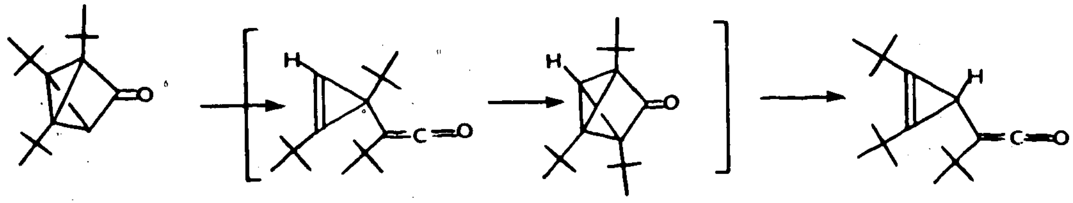
shows a diazo stretching at 2120 cm^{-1} and a band at 1615 cm^{-1} due to the carbonyl stretching. The low frequency shift from 1660 cm^{-1} in 139 to 1615 cm^{-1} in 150 is characteristic for α-diazotization. The pmr spectrum has two peaks for the *tert*-butyl groups and a singlet for the methine.

Photolysis of diazoketone 150 produced a ketone 151 in 31% yield. The high ir frequency, 1765 cm^{-1}, for the carbonyl stretching indicates the formation of this tricyclic system. Also, a large ^{13}C-H coupling constant was observed for the methine moiety. In diphenyl compound 137,[100] the ir spectrum shows $\nu_{C=O}$ at 1785 cm^{-1} and a $J(^{13}C\text{-}H)$ of 190 Hz.



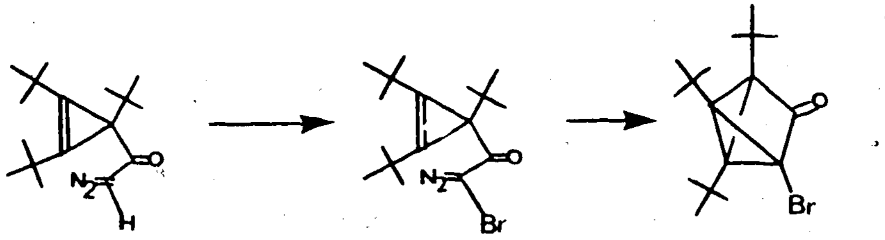
137

This ketone 151 is quite stable compared with 137. After either treatment with base (sodium methoxide in methanol, refluxing for 1 hr) or with acid (0.2 N HCl, room temperautre for 24 hr), ketone 151 was recovered unchanged. Also, ketone 151 was found to survive photolysis. Thermally, 151 isomerized slowly at 95° to a single compound which was believed to be ketene 152, on the basis of its spectral behavior; ir (2110 cm^{-1}) and pmr {δ 0.94 (9H), 1.24 (18H), 2.87 (1H)} spectra. A plausible mechanism is shown below. The isomeric ketene 153 is initially formed and rearranges to the isomeric tricyclic ketone 154, which further isomerizes to the more stable isomer 152.



151 153 154 152

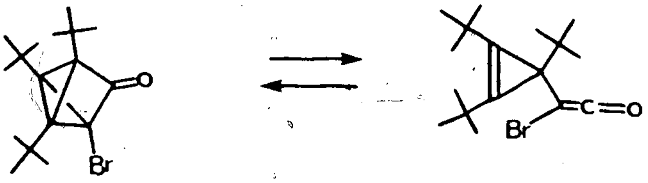
With the above encouraging results, we proceeded to prepare the next target molecule, tricyclic ketone 155, which contains a good leaving group at the position α to the carbonyl. It was hoped that the bromoketone 155, if obtained, would undergo a Favorskii-type reaction to yield a tetrahedrane derivative. Diazoketone 150 was treated with methylmercuric ethoxide to give the corresponding mercuridiazoketone,[101] which was directly reacted with



150 156 155

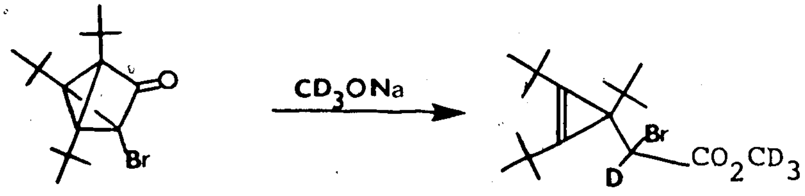
bromine.[102] Produced bromodiazoketone <u>156</u> was found to lose nitrogen spontaneously at 40° (<u>cf.</u> ethyl bromodiazoacetate is stable for several days at 0-5°),[102] and the desired bromoketone <u>155</u> was isolated in 52% overall yield from the diazoketone <u>150</u>. The ir (1780 cm^{-1}) and pmr (δ 1.36, 1.23) spectra are consistent with the structure.

Thermolysis of <u>155</u> at 60° produced an equilibrated mixture of <u>155</u> and probably ketene <u>157</u> (<u>ca.</u>2:1), as judged from the ir spectrum, which showed an absorption at 2120 cm^{-1} for <u>157</u> , in addition to an absorption at 1780 cm^{-1} for <u>155</u>.



<u>155</u> <u>157</u>

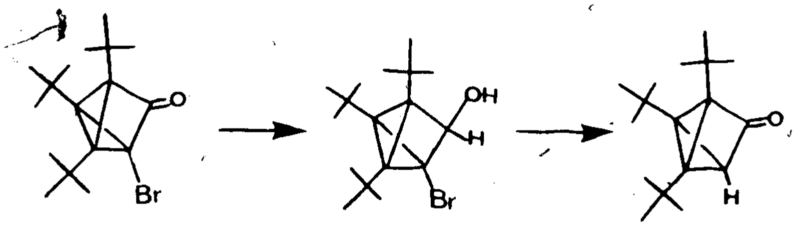
Treatment of <u>155</u> with sodium methoxide in perdeuteromethanol gave a single product, presumably ester <u>158</u>. The pmr spectrum showed three <u>tert</u>-butyl peaks of equal intensity and the ir spectrum had an absorption at 1710 cm^{-1}. It is not clear whether <u>158</u> was formed from ketene <u>157</u>.



<u>155</u> <u>158</u>

Bromoketone 155 was also found to be stable toward photolysis. The anticipated reaction to produce a tetrahedrane derivative was not observed.

Bromoketone 155 was successfully transformed into the corresponding bromohydrin 159 by reduction with lithium aluminium hydride. Although methyllithium did not give a clean product, lithium aluminium hydride reacted smoothly to form 159, which was isolated in 54% yield. Although 159 was stable under basic conditions, a purified sample of 159 isomerized to ketone 151 with the liberation of HBr, which presumably catalyzed the isomerization. An analogous rearrangement reaction is known for a tricyclopentane derivative.[103] 1,5-Dimethyltricyclo[2.1.0.$0^{2,5}$]-pent-3-yl benzoate 160 undergoes a very fast skeletal rearrangement via an ion pair to afford a new isomer 161.



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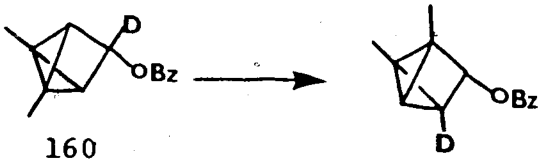
159

151



160

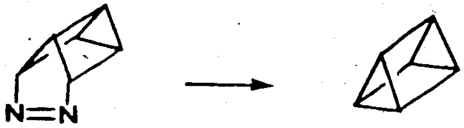
161

When bromohydrin 159 was treated with sodium hydride, only a complex mixture was formed and none of the products of this reaction could be identified.

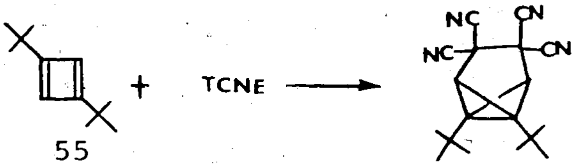
C. Other attempts.

Another promising precursor of tetrahedrane is diazabenzvalene 162, which upon irradiation may form tetrahedrane *via* a diradical, in a manner analogous to the formation of prismane 163 from 164.[104] Pettit reported that the reaction between 1,3-di-*tert*-butyl[4]annulene 55 (generated *in situ*) and tetracyanoethylene (TCNE) afforded not bicyclic adduct but instead tricyclic one 56.[45] We anticipated that other highly substituted [4]annulenes may react in a similar manner with dienophiles to form the diazabenzvalene system. We carried out the reaction of 11 with N-phenyltriazolinedione and with diethyl azodicarboxylate. In each case, a single adduct was isolated. The pmr spec-

162



164 163



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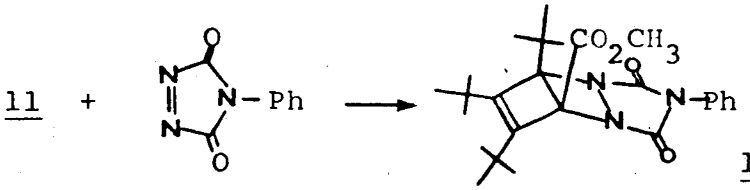

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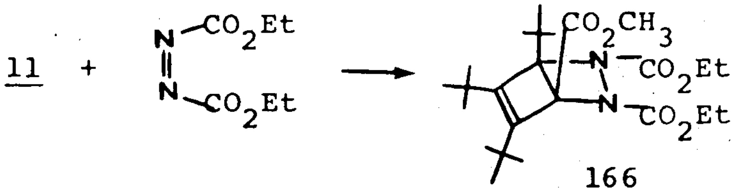
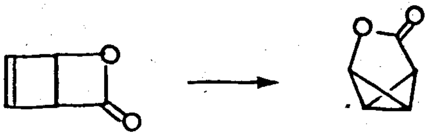


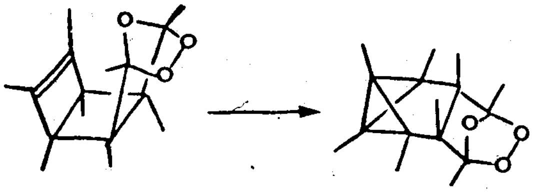
166

tra of the adducts indicated the presence of three tert-butyl groups. The pmr spectrum of the tricyclic species should exhibit only two tert-butyl absorptions. Therefore, the product cannot have a benzvalene structure, but may be formulated as 165 and 166.

Photo-α-pyrone 100 is known to isomerize to the corresponding tricyclic lactone 167 upon standing in aprotic solvents at room temperature.[105] Also a similar isomerization reaction of 168 to bicyclobutane derivative 169 was observed,[106] when 168 was treated with silver fluoroborate at 20°.

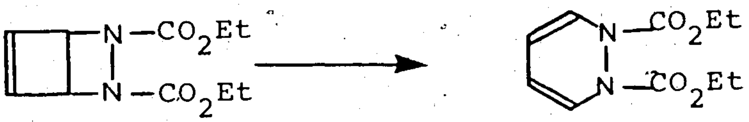


100 167



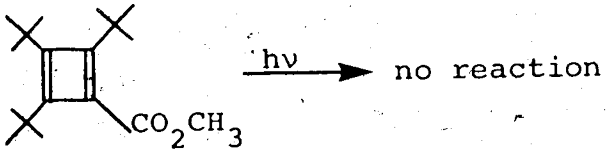
168 169

In the hope of obtaining a diazabenzvalene derivative by a similar rearrangement, diethyl 2,3-diazabicyclo[2.2.0]-hex-5-ene-2,3-dicarboxylate 170[107] was treated with silver perchlorate. The pmr spectrum of the crude product exhibited new peaks at δ 5.50 (m) and 6.35 (m), in addition to absorptions due to the starting material. This result clearly shows that the rearranged compound is not the one we are after, but rather dihydropyridazinedicarboxylate 171.



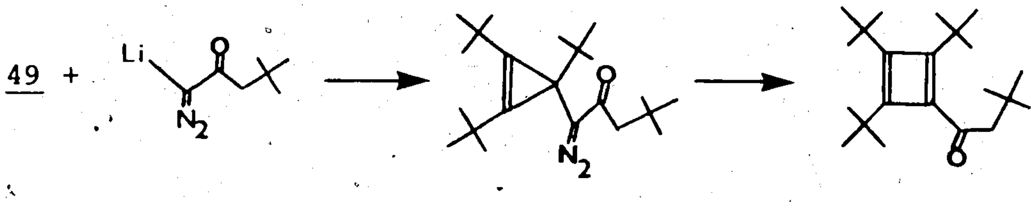
170 171

Isomerization of cyclobutadiene to tetrahedrane is a photochemically allowed process. Photolysis of 11 was attempted, again in the hope of obtaining the corresponding tetrahedrane derivative. No observable photochemical reaction took place, either in solution or in a matrix.



11

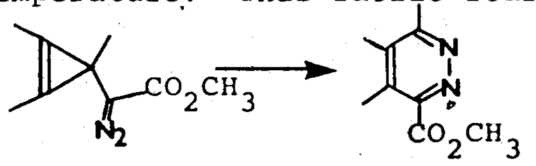
Neopentyl tri-*tert*-butyl[4]annulenyl ketone 172 was also prepared by the photolysis of the corresponding diazoketone 173, which was obtained in a similar manner to diazoester 46. Photolysis of diazoketone 173 with a high pressure mercury lamp through a Pyrex filter cleanly produced the [4]annulene derivative 172, which in turn was irradiated either with a low-pressure mercury lamp or with a high pressure mercury lamp through a Vycor filter. However, no pmr (at room temperature) and ir (at -140°) spectral changes were observed.



173 172

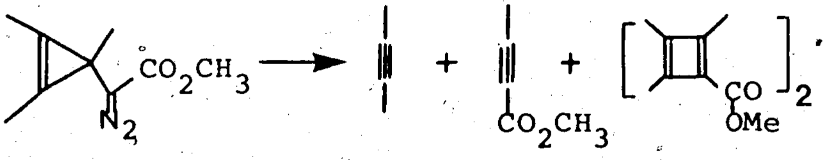
As mentioned in Part I, cyclopropenyl diazo compounds may have produced tetrahedrane derivatives, which subsequently rearranged to the corresponding [4]annulenes. In order to gain further information about this possibility, several other cyclopropenyl diazoacetates were prepared in order to examine the effect of the substituents on the reaction course of the cyclopropenyl carbene.

Methyl trimethylcyclopropenyldiazoacetate 174 was prepared in an analogous fashion to 46. Diazoester 174 rearranges to the corresponding pyridazine derivative 175 at room temperature. This facile rearrangement supports



174 175

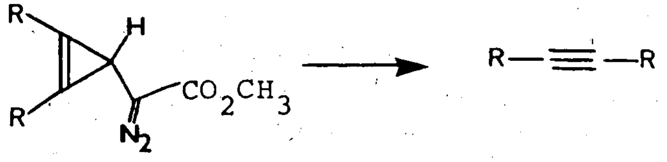
our initial expectation that the three tert-butyl groups contributed toward the stability of 46. Consequently, all further reactions were carried out well below room temperature. When a matrix containing 174 was irradiated at -198°, the matrix turned dark brown. The color disappeared instantly when the sample was melted. An esr spectrum of this brown matrix did not show any signal attributable to a triplet species. This indicates that the colored intermediate is probably a singlet species. The photolysis products were 2-butyne, methyl 2-butyrate, and dimers of the corresponding [4]annulene derivative, in ca. 1:2:2 ratio, respectively, as judged from the glpc-mass spectrum analysis.



174

The photolysis of 174 was carried out either in the presence of cyclopentene or butadiene and the products in both cases were identical with those obtained in the absence of these trapping reagents. No adduct with the solvent was detected. These experimental results show that an intermediate, perhaps a carbene, has a long life-time in the matrix, but cannot be trapped by an external reagent. Instead, the intermediate either isomerizes to a [4]annulene derivative or collapses into two acetylenic molecules. From this experiment, it is not clear if the carbene isomerized to two acetylenes via a tetrahedrane intermediate.

Methyl diphenylcyclopropenyldiazoacetate 176 was prepared similarly and was irradiated. Diphenylacetylene was formed but no phenylacetylene was detected in the product mixture by glpc analysis. A similar result was obtained using methyl dipropylcyclopropenyldiazoacetate 177. These results would indicate that the acetylenes are formed directly from the carbene intermediate, and not through a tetrahedrane, although the latter possibility is not absolutely excluded.



176; R=Ph
177; R=Pr

The easily accessible azide 45[39] was also irradiated. The obvious aim is to prepare either the aza[4]annulene* or azatetrahedrane derivative. Trimethylcyclopropenyl azide

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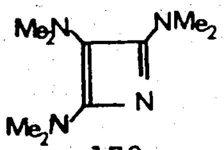
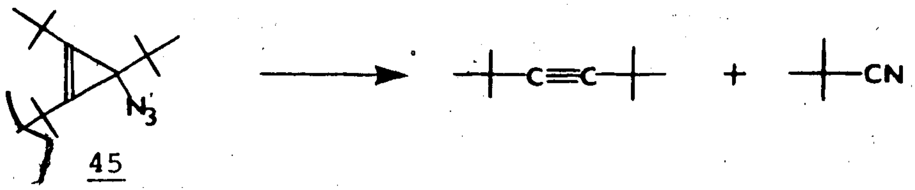
*) A successful preparation of aza[4]annulene derivative 178 has been reported.[108]

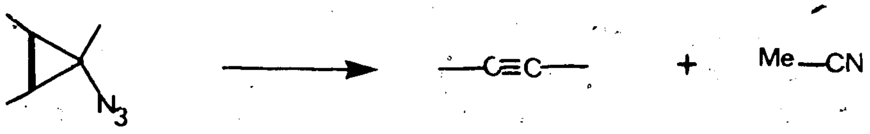


178

43 is reported to yield only butyne and acetonitrile upon photolysis.[38] Irradiation of 45 at -110° resulted in the



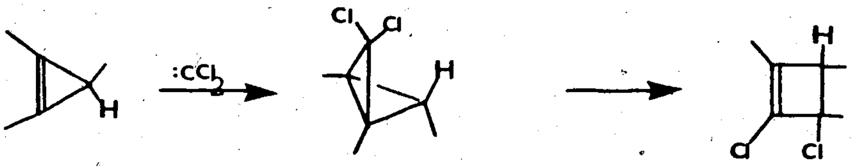
45



43

evolution of nitrogen. The pmr spectrum at -50° and glpc analysis, however, showed that the products were only di-*tert*-butylacetylene and pivalonitrile. Irradiation in a matrix at -198° produced the identical products.

Trost *et al.* approached tetrahedrane in a different way.[109] They tried to prepare a bicyclobutane derivative 179, which was substituted with halogens in the methylene position. They expected that a carbene derived from 179 would insert into the C-H bond to form tetrahedrane. Reaction of dichlorocarbene with trimethylcyclopropene,

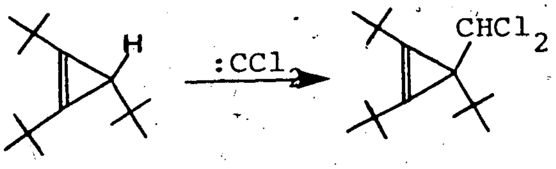


179

180

however, produced cyclobutene derivative 180, which was believed to be derived from 179. The latter compound could not be detected even at -73°.

We attempted a similar reaction using tri-*tert*-butylcyclopropene 181.[42a] When 181 was treated with dichlorocarbene, generated from chloroform and *n*-butyllithium, a mixture of starting material and known dichloride 24,[30] which was formed by the carbene insertion into the C-H bond on the ring, was obtained. The two *tert*-butyl groups attached to the double bond thus appear to retard the attack of the reagent on the double bond.



181

24

D. Conclusions.

Tetrahedrane, the isomer of [4]annulene, has been the target molecule of several synthetic approaches. Unfortunately, there has been obtained no indication that this reactive species is formed, even as an intermediate. In the course of this study, however, a strained bicyclic cyclopropenone 112 and several tri-*tert*-butyltricyclo-$[2.1.0.0^{2,5}]$pentane derivatives have been successfully prepared, and their properties have revealed intriguing features of these systems. Further studies toward the final goal, a synthesis of tetrahedrane, will be continued.

CHAPTER III. EXPERIMENTAL.

General

See page 65.

Mono-methyl 3,3-dimethylglutarate.[84,110]

A solution of 3,3-dimethylglutaric acid[111] (10.09 g, 63.1 mmol) in acetic anhydride (8.0 g) was refluxed for 1 hr. The excess acetic anhydride as well as acetic acid were removed by distillation. To the residue was added at 0° a methanol solution of sodium methoxide, prepared from sodium metal (2.0 g, 87 matom) and methanol (40 ml). The mixture was refluxed for 1 hr. After the addition of water (20 ml), the methanol was removed. The aquous solution was acidified with HCl, and extracted four times with 50 ml portions of ether. The combined ether layers were dried over $MgSO_4$, and the solvent was removed. The residue was distilled, giving the monoester, 9.04 g (82%), bp 92°/0.3 mmHg (lit. 144-146°/10 mmHg).[84]

3,3,6,6-Tetramethylsuberic acid.[84,110]

Mono-methyl 3,3-dimethylglutarate (9.04 g, 52 mmol) was dissolved in methanol (50 ml) and hexane (50 ml). To this solution was added sodium metal (0.3 g). Electrolysis (with *ca.* 30 V and 0.6 A) was allowed to proceed at room temperature for 4 hr. The progress of the reaction was monitored by ir spectroscopy. After the removal of the solvent, the residue was dissolved in a 15% KOH methanol solution (80 ml) and refluxed for 3 hr. The bulk of the solvent was removed, and the residue was dissolved in water (50 ml) and acidified with HCl. The resulting precipitate was collected and recrytallized from methanol to afford the diacid, 3.74 g (63%), mp 161-162° (lit. 166.4-167.4°).[84]

3,3,6,6,-Tetramethylcycloheptanone. (123)

A mixture of 3,3,6,6-tetramethylsuberic acid (5.00 g, 21.7 mmol), manganese carbonate (5 g), sea sand (10 g), and some glass wool was placed in a thick-wall test tube. On top of this mixture was placed a layer of glass wool. A mixture of manganese carbonate (5 g) and sea sand (10 g) was then placed on top of this glass wool layer. Another glass wool layer covered the whole mixture to prevent the direct transfer of any solid particles. This test tube was connected through a trap cooled in a liquid nitrogen bath, to a vacuum pump. The reaction system was evacuated carefully to a pressure of 0.1 mmHg, and the test tube was heated in a pyrolysis oven. As the temperature was increased slowly from 300° to 380° over a 1 hr period, the product distilled out of the reaction mixture. The contents of the trap were dissolved in dichloromethane (50 ml), washed with 0.5 N KOH (30 ml) and dried over $MgSO_4$. After removal of the solvent, the residue was distilled (short-path)(bath temperature 50°/0.1 mmHg) to give the ketone, 3.51 g (96%) (lit. bp 94.7°/14 mmHg).[84]

pmr $\delta(CDCl_3)$; 1.00 (12H,s), 1.55 (4H,s), 2.35 (4H,s).

2,7-Dibromo-3,3,6,6-tetramethylcycloheptanone. (124)

A dichloromethane (65 ml) solution of 123 (6.32 g, 37.6 mmol) and bromine (15 g, 94 mmol) was stirred at room temperature for 20 hr. The mixture was transferred to a separatory funnel with the aid of dichloromethane (140 ml), washed successively with 5% Na_2SO_3 (80 ml), 5% $NaHCO_3$ (2x50 ml), brine (30 ml), and dried over $MgSO_4$. Removal of the solvent gave the crude product (11.1 g), which was recrystallized from hexane, yielding 7.64 g (62%) of the dibromide, mp 70.5-71.0°. An analytical sample was prepared by sublimation.

pmr $\delta(CDCl_3)$; 1.15 (12H,s), 1.60 (4H,s), 4.77 (2H,s).
ir $(CHCl_3)$; 1718 cm^{-1} (s).
elemental analysis; Calcd for $C_{11}H_{18}OBr$: C,40.52; H,5.56
Found: C,40.82; H,5.79.

2,2,5,5-Tetramethylbicyclo[4.1.0]hep-1(6)-en-7-one. (112)

To a suspension of potassium *tert*-butoxide (687.6 mg, 6.13 mmol) in THF (30 ml) was added at -20° a THF (5 ml) solution of dibromoketone 124 (861 mg, 2.62 mmol) over 15 min. After stirring at -20° for 1 hr, the reaction mixture was poured into a stirred ice-cold solution of 5% NaH_2PO_4 (100 ml). The mixture was transferred to a separatory funnel with the aid of pentane (100 ml). The organic layer was separated, washed twice with 30 ml portions of 5% $NaHCO_3$, and with brine (40 ml), and dried over Na_2SO_4. Removal of the solvent at 0° gave a white crystalline product, which was sublimed at room temperature under high vacuum. Pure product was obtained as white crystals, 175.3 mg (41%), mp 89.0-89.5° (pentane).

pmr δ($CDCl_3$); 1.22 (12H,s), 1.73 (4H,s).

ir (CCl_4); 1890 cm^{-1}(w), 1852 (s), 1790 (m), 1617 (s).

uv (cyclohexane); 263 nm (ε 95).

cmr δ($CDCl_3$); 25.9 (CH_3), 32.8 (quart-C), 36.4 (CH_2), 146.7 (C=O), 169.0 (olefinic-C).

elemental analysis; Calcd for $C_{11}H_{16}O$: C,80.44; H,9.83.
Found: C,80.27; H,9.76.

The dibromoketone <u>124</u> (1.149 g, 3.50 mmol) was similarly treated with potassium tert-butoxide (1.281 g, 11.4 mmol). After stirring at -20° for 1 hr, 1.1 M H_2SO_4 (37 ml) was added slowly to the reaction mixture, which was then warmed to 0°. The bulk of the solvent was removed and the residue was diluted with pentane (100 ml), washed with cold water (30 ml), and dried over $MgSO_4$. Removal of the solvent afforded a mixture (601 mg) of oil and solid. Chromatography on silicic acid (15 g) using chloroform as the eluent gave a pure crystalline acid <u>125</u> (309 mg, 48%), which was recrystallized from pentane and sublimed at 60°/0.1 mmHg, mp 115.0-116.0°, for elemental analysis.

pmr δ(CDCl$_3$); 1.05 (6H,s), 1.23 (6H,s), 1.50 (4H,s), 6.71 (1H,s).

ir (CHCl$_3$); 2640 cm^{-1} (b), 1676 (s).

elemental analysis; Calcd for $C_{11}H_{18}O_2$: C,72.49; H,9.96.
Found: C,72.15; H,9.94.

Thermal stability of 112.

Ketone 112 (0.1 g) in dry dichloromethane (0.8 ml) was kept at 100° for 5 hr in a sealed nmr tube and the pmr spectrum showed no change.

Reaction of 112 with acid.

Ketone 112 (10 mg) was dissolved in a mixture of THF (4 ml) and 0.1 N H_2SO_4 (36 ml). The solution was stirred at room temperature for 30 min, after which dichloromethane (20 ml) was added. The organic layer was separated, washed with brine (20 ml), and dried over $MgSO_4$. Glpc analysis (UCW-98) showed a single peak. Removal of the solvent afforded white crystals, the pmr spectrum of which was identical with that of acid 125. After sublimation at 60°/0.1 mmHg, the white crystalline material had a mp of 115.0-116.0°.

Reaction of 112 with base.

Ketone 112 (5 mg) was dissolved in a mixture of THF (10 ml) and 0.1 N NaOH (10 ml) and the mixture was stirred at room temperature for 1 hr. The reaction mixture was acidified with 2% HCl and extracted three times with 10 ml portions of dichloromethane. The combined organic layers were washed with brine (20 ml) and dried over $MgSO_4$. Glpc analysis (UCW-98) showed two major products (ca. 3:2 ratio), one of which (the minor one) corresponded to acid 125.

In order to isolate the major product, ketone 112 (21 mg) was treated similarly. The crude product, which showed ir absorptions at 1710 and 1675 cm^{-1}, was (short-path) distilled at 40°/0.1 mmHg. The major component was then collected by preparative glpc (UCW-98, 130°), and identified as the diketone 126 from the following data.

pmr $\delta(CCl_4)$; 1.04 (6H,s), 1.14 (6H,s), 1.57 (4H,m), 2.25 (2H,s).
ir (CCl_4); 1710 cm^{-1}.
mass spectrum; m/e 182 (M^+, 14%), 154 (3), 139 (5), 110 (100), 83 (56).

Photo-reaction of 112.

Irradiation of a THF-$\underline{d}_8$ solution of ketone 112 at 0° with a high pressure mercury lamp (Pyrex filter) caused no change. Irradiation of the same sample through a Corex filter for 1 hr decomposed the ketone almost completely. The product was assigned as a dimer 131 from its spectroscopic properties.

pmr δ ($CDCl_3$); 1.02 (3H,s), 1.13 (3H,s), 1.20 (3H,s), 1.29 (3H,s), 1.55 (2H,s), 1.69 (2H,m).

ir ($CHCl_3$); 1720 cm^{-1}.

mass spectrum; m/e 328 (M^+, 13%), 313 (20), 285 (18), 272 (11), 259 (28), 165 (100).

Ketone 112 (22.6 mg) was placed in a quartz nmr tube and into this tube was vacuum-transferred 2-methyltetrahydrofuran (dried over LAH). The solution was degassed and the tube sealed. Irradiation with a high pressure mercury lamp (Corex filter) at -198° was continued for 3 hr. The ir and pmr spectra of the photolysate exhibited absorptions ascribed to dimer 131.

Attempted synthesis of 7-tert-butyl-2,2,5,5-tetramethylbicyclo[4.1.0]heptenium fluoroborate(135).

Dibromoketone 124 (991.6 mg, 3.02 mmol) was treated with potassium tert-butoxide (743 mg, 6.62 mmol) as described earlier (page 123). After work-up, the pentane-THF solution (the ir spectrum showed strong absorptions at 1848 and 1619 cm^{-1} indicating the presence of 112) was cooled to -20°. To this was added a small amount of bipyridyl* and then a

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*) Indicator for alkyllithiums.

pentane solution of tert-butyllithium (1.4 M, 2.4 ml, 3.4 mmol) was added dropwise until the brown color remained. After stirring at -20° for 15 min and at 0° for 15 min, the mixture was poured into ice-cold 5% NaH_2PO_4 (100 ml) with vigorous stirring. The pentane layer was separated, washed with ice-cold brine (2x30 ml) and dried over $MgSO_4$. Removal of the solvent at 0° gave an oily residue, which was dissolved in ice-cold ether (15 ml). To this was added at 0° a freshly prepared 10% fluoroboric acid in acetic acid.* No precipitate was formed.

Reaction between tri-tert-butylcyclopropenium fluoroborate (49) and the lithium salt of dithiane.

To a solution of dithiane (409 mg, 3.4 mmol) in THF (25 ml) cooled to -30° in a dry-ice/methanol bath, was added a hexane solution of n-butyllithium (1.5 M, 2.5 ml, 3.75 mmol). Stirring was continued for 30 min at this temperature, and tri-tert-butylcyclopropenium fluoroborate (1.00 g, 3.4 mmol) was added. The reaction mixture was allowed to warm to room temperature and was stirred for 3 hr. Water (2 ml) was added, and the mixture was diluted with penta[illegible] (100 ml), washed with water (2x50 ml) and dried over $MgSO_4$. The solvent

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*) At -40°, 50% HBF_4 (0.6 g) was slowly added into acetic anhydride (2.5 g).

was removed to give a crude product, which was sublimed at 55-60°/0.05 mmHg. Pure dithiane derivative 140 was obtained as a white powder, 856 mg (77%), mp 69-71°.

pmr δ($CDCl_3$); 1.11 (9H,s), 1.32 (18H,s), 1.83-2.00 (2H,m), 2.75-3.06 (4H,m), 4.66 (1H,s).

A mixture of the above dithiane derivative (99 mg, 0.3 mmol), sodium carbonate (106 mg, 1.0 mmol) and methyl iodide (300 mg, 2.1 mmol) in acetone/water (85:15, 2 ml) was sealed in an ample and heated at 70° overnight. The reaction mixture was diluted with chloroform (30 ml) and dried over Na_2SO_4. Removal of the solvent gave a yellow solid, 65 mg (92%). The pmr spectrum showed that the product was almost pure ketone 141.

pmr δ($CDCl_3$); 1.13 (18H,s), 1.22 (9H,s), 2.68 (1H,s).
ir ($CHCl_3$); 1885 cm^{-1} (w), 1678 (s).

Methyl tri-tert-butylcyclopropenyl ketone. (139)

At -10° a hexane solution of n-butyllithium (1.34 M, 4.5 ml, 6.0 mmol) was added to a THF (20 ml) solution of diisopropylamine (607.4 mg, 6.0 mmol). The mixture was warmed to room temperature and then cooled to -78°. To this was added acetaldehyde cyanohydrin ketal 147 (1.1124 g, 7.76 mmol) in THF (3 ml). After 10 min stirring at -78°, tri-tert-butylcyclopropenium fluoroborate (1.799 g, 5.78

mmol) was added in small portions over 15 min. The mixture was stirred at -78° for 20 min and warmed to room temperature. Ether (80 ml) and pentane (20 ml) were added to the reaction mixture, which was then washed with brine (2x50 ml), and dried over $MgSO_4$. The solvents were removed leaving an oily product, which was used directly in the next step.

The oily residue was dissolved in methanol (30 ml) and 3.6 N H_2SO_4 (1 ml). After stirring at room temperature for 3 hr, water (30 ml) was added. The bulk of the methanol was removed, and the concentrate was extracted with ether (3x50 ml), and the combined ether layers were washed with brine (50 ml) and dried over $MgSO_4$. After evaporating the solvent, the product was dissolved in ether (100 ml) and 0.5 N NaOH (50 ml), and the mixture was shaken overnight. The organic layer was separated and the aqueous layer was extracted with a mixture of ether/pentane (1:1, 50 ml). The combined organic layers were washed with brine (50 ml) and pH 7 buffer (50 ml), and dried over $MgSO_4$. Removal of the solvents and chromatography on silicic acid (40 g) using hexane/dichloromethane mixtures as the eluent afforded pure ketone 139, 1.169 g (81%), mp 56.0-58.0°.

pmr $\delta(CDCl_3)$; 1.03 (9H,s), 1.27 (18H,s), 1.86 (3H,s).

ir $(CHCl_3)$; 1850 cm^{-1}(w), 1660 (s).

elemental analysis; Calcd for $C_{17}H_{30}O$: C,81.53; H,12.08.

Found: C,81.65; H,12.08

Diazomethyl tri-tert-butylcyclopropenyl ketone. (150)

A hexane solution of n-butyllithium (1.34 N, 3.6 ml, 4.8 mmol) was diluted with THF (30 ml). To this was added a THF (5 ml) solution of ketone 139 (1.169 g, 4.67 mmol) over 10 min at -78°. After stirring for 1 hr at -78°, a solution of tosyl azide (969.4 mg, 4.92 mmol) in THF (5 ml) was added over 5 min. The reaction mixture was stirred at -78° for 30 min and then warmed to room temperature. The reaction mixture was diluted with ether (100 ml) and pentane (100 ml), washed with brine (2x100 ml) and dried over Na_2SO_4. Removal of the solvent and rapid chromatography on neutral alumina (grade III, 20 g) using hexane as the eluent afforded the diazoketone, 1.153 g (89%), mp 93-100°.

pmr δ ($CDCl_3$); 1.10 (9H,s), 1.30 (18H,s), 5.08 (1H,s).

ir ($CHCl_3$); 2120 cm^{-1} (s), 1615 (s).

1,2,5-Tri-tert-butyltricyclo[2.1.0.0^{2,5}]pentan-3-one. (151)

Diazoketone 150 (1.028 g, 3.72 mmol) in ether (120 ml) was irradiated with a high pressure mercury lamp (Pyrex filter) at 0° for 1 hr. The solvent was removed and chromatography on silicic acid (50 g) using dichloromethane as the eluent afforded the tricyclic ketone, 287 mg (31%), mp 39.0-41.0°.

pmr δ(CCl_4); 1.16 (9H,s), 1.26 (18H,s), 1.80 (1H,s).

J(^{13}C-H for the methine)=184 Hz.

ir (CCl_4); 1765 cm^{-1}.

mass spectrum; m/e 249 (M^++1, 0.4%), 248 (M^+, 0.4), 220 (19), 205 (21), 191 (38), 149 (69), 108 (38), 57 (100).

elemental analysis; Calcd for $C_{17}H_{28}O$: C,82.20; H,11.36.
Found: C,82.28; H,11.19.

Treatment of 151 with base.

Ketone 151 (45.2 mg) was refluxed for 1 hr in a methanol solution of sodium methoxide (1.18 M, 5 ml). After work-up the pmr and ir spectra showed only the starting material to be present.

Treatment of 151 with acid.

Ketone 151 (11 mg) in methanol (5 ml) and 1.24 N HCl (1 ml) was stirred at room temperature for 24 hr. Only starting material was recovered.

Photolysis of 151.

Irradiation of 151 in methylcyclohexane-d_{14} either with a high pressure mercury lamp (Vycor filter) or with a low pressure mercury lamp, caused no change.

Thermolysis of 151.

Heating a methylcyclohexane-d_{14} solution of ketone 151 in a sealed nmr tube at 95° for 31 hr yielded a new compound, which was formulated as ketene 152.

pmr δ(methylcyclohexane-d_{14}); 0.94 (9H,s), 1.24 (18H,s), 2.87 (1H,s).

ir (CCl_4); 2110 cm^{-1}.

4-Bromo-1,2,5-tri-tert-butyltricyclo[2.1.0.$0^{2,5}$]pentan-3-one. (155)

Potassium metal (192 mg, 4.91 matom) was dissolved in dry ethanol (5 ml). To this solution was added a solution of methylmercuric chloride (782 mg, 3.11 mmol) in dry ethanol (25 ml), and the mixture was kept at 60° for 3 hr. The insoluble salt was filtered off, and an ethanol (25 ml) solution of diazoketone 150 (790.3 mg, 2.86 mmol) was added to the filtrate at 0°. After 15 min of stirring at 0°, the solvent was removed and THF (10 ml) and ether (10 ml) were added. The solution was cooled to -110° and to this was added bromine (456.9 mg, 2.86 mmol) in dichloromethane (3 ml). Stirring at -110° for 2 hr was followed by warming to 0°, and removal of the solvent at 0°. Pentane (20 ml) was added to the residue and the insoluble mercuric compound was filtered off. The pentane solution was kept at 40° for 15 min, during which time nitrogen evolution was observed. Removal of the solvent and chromatography on silicic acid (10 g) afforded bromoketone 155, 490 mg (52%).

pmr δ($CDCl_3$); 1.36 (18H,s), 1.23 (9H,s).

ir (CCl_4); 1780 cm^{-1}.

mass spectrum; Calcd for $C_{17}H_{28}O^{79}Br$: m/e=327.1323.
Found: m/e=327.1317.

Thermolysis of 155.

Bromoketone 155 was dissolved in chloroform and heated at 60° for 30 min. The pmr spectrum of the product showed it to be a mixture of starting material and perhaps ketene 157 (ca. 2:1). Even after 2 hr of heating, the pmr spectrum showed no further change. The ir spectrum of this product showed peaks at 2120 (ketene) and 1780 cm^{-1} (starting material).

Reaction of 155 with base.

Bromoketone 155 (30 mg) and sodium methoxide (20 mg) in CD_3OD (0.5 ml) were sealed in an nmr tube. The reaction was followed by pmr spectroscopy. The half life of the bromoketone at 40° (pmr probe temperature) was about 15 min. The product showed three *tert*-butyl peaks of equal intensity in the pmr spectrum, and the ir spectrum exhibited a carbonyl band at 1710 cm^{-1}. The structure of the product is likely to be α-bromoester 158.

Photolysis of 155.

A methylcyclohexane-d_{14} solution of bromoketone 155 was irradiated with a low pressure mercury lamp at -78°

for 3 hr. The pmr spectrum showed no change.

Reaction of 155 with methyllithium.

To a THF (5 ml) solution of bromoketone 155 (35.4 mg, 0.11 mmol) was added an ether solution of methyllithium (1.7 M, 0.1 ml, 0.17 mmol) at -78°. After stirring at -78° for 10 min, the mixture was quenched with wet ether. Pentane (10 ml) and Na_2SO_4 were added to the reaction mixture. Filtration and removal of the solvent gave an oil (56.4 mg), whose pmr spectrum was complex, and whose ir spectrum showed peaks at 2100 (ketene ?), 1760 (ketone ?), and 1690 cm^{-1}.

Reduction of 155 with LAH.

Bromoketone 155 (285.3 mg, 0.87 mmol), dissolved in THF (15 ml), was cooled to -78°. To this was added a THF solution of LAH (1.11 M, 0.4 ml, 1.78 mmol). After 15 min stirring at -78°, wet ether (10 ml) was carefully added and the mixture was warmed to room temperature. Pentane (15 ml) and Na_2SO_4 were added. Filtration through a Celite pad, removal of the solvent and sublimation at 50°/0.05 mmHg afforded bromohydrin 159, 153.6 mg (54%), mp 96.0-98.0°. pmr $\delta(CDCl_3)$; 1.08 (9H,s), 1.31 (18H,s), 4.23 (1H,s). (In benzene-pyridine, three *tert*-butyl peaks are observed.) ir (CCl_4); 3580 cm^{-1} (b).

Isomerization of 159 to ketone 151.

Purified bromohydrin 159, upon standing at room temperature, produced ketone 151 with the liberation of HBr. The product was identified by pmr, ir, and glpc comparisons with authentic material.

Thermal stability of 159 under basic conditions.

Bromohydrin 159 was dissolved in benzene/pyridine and heated to 80° for 30 min. The pmr spectrum showed no change.

Reaction of 159 with base.

To a suspension of NaH (56 mg, 2.3 mmol) in THF (5 ml) at -78° was added bromohydrin 159 (81.9 mg, 0.25 mmol) in THF (3 ml). After 5 min, the reaction mixture was warmed to room temperature. Filtration and removal of the solvent afforded an oil (79.5 mg). The ir and pmr spectra showed the oil to be the starting material.

The same sample was then dissolved in THF (10 ml) and to this was added NaH (62.3 mg), and the mixture was kept at 60° for 30 min. Work-up as above gave an oil (66.9 mg). The pmr spectrum was complex and no product was identified.

Adduct of 11 and N-phenyltriazolinedione. (165)

Diazoester 46 (133.2 mg, 0.435 mmol), dissolved in ether (3 ml), was irradiated as described above. N-Phenyltriazolinedione (68.8 mg, 0.46 mmol), dissolved in ether (3 ml), was added at -78°, and the mixture was warmed to room temperature. Chromatography on silicic acid (12 g) using dichloromethane/hexane (1:1,v/v) as the eluent gave a white crystalline adduct, 22.5 mg (12%).

pmr δ(CDCl$_3$); 1.24 (9H,s), 1.26 (9H,s), 1.33 (9H,s), 3.78 (3H,s), 7.41 (5H,b).

Adduct of 11 and diethyl azodicarboxyalte.

An ether (3 ml) solution of 46 (168.4 mg, 0.55 mmol) and diethyl azodicarboxylate (99.2 mg, 0.57 mmol) was irradiated at 0° for 3 hr. Chromatography on silicic acid (10 g) using dichloromethane as the eluent afforded the adduct, 123.4 mg (50%).

pmr δ(CDCl$_3$); 1.21 (9H,s), 1.28 (9H,s), 1.36 (overlapped with a triplet), 3.73 (3H,s), 4.15 (4H,bq).

Diethyl 2,3-diazabicyclo[2.2.0]hex-5-ene-2,3-dicarboxylate. (170)

To a stirred mixture of lead tetraacetate (8.37 g, 18.9 mmol) and ethyl azodicarboxylate (556 mg, 3.2 mmol) in pyridine (20 ml) was added a solution of cyclobutadiene-iron tricarbonyl 3 (998 mg, 5.2 mmol) in pyridine (10 ml) over 40 min at 15°. The reaction mixture was stirred for further 2 hr. The resulting precipitate was removed by filtration and washed with a pyridine/dichloromethane (1:1, v/v, 60 ml). The combined filtrate was diluted with dichloromethane (200 ml), washed with water (2x100 ml), ice-cold 1% HCl (5x100 ml), 10% $NaHCO_3$ (2x100 ml), and water (3x100 ml). After dring over $MgSO_4$, the solvent was removed to give the crude product (540 mg). Chromatography on silicic acid (10 g) using chloroform as the eluent gave the pure adduct, 470 mg (65%).

pmr δ ($CDCl_3$); 1.29 (6H,t,J=7), 4.22 (4H,q,J=7), 5.15 (2H, d,J=3.5), 6.70 (2H,d,J=3.5).

Reaction of 170 with silver perchlorate.

To a solution of 170 (200 mg, 0.88 mmol) in benzene (2 ml) was added silver perchlorate (7 mg, 0.03 mmol) at room temperature and the mixture was stirred for 14 hr. The solvent was removed to leave an oil, which was dissolved in ether (4 ml) and filtered. The filtrate was evaporated to give a clear oil. The pmr spectrum showed peaks, besides those of the starting material, at δ ($CDCl_3$); 5.50 (m) and 6.35 (m). The conv[illegible] was ca.40%.

Photolysis of 11.

Diazoester 46 (16 mg) was dissolved in methylcyclohexane-d_{14} (0.5 ml). The solution was placed in a quartz nmr tube, degassed and sealed. Irradiation with a high pressure mercury lamp (Pyrex filter) at -78° for 4 hr changed

46 completely to 11. Then irradiation using a low pressure mercury lamp at -198° was continued for 14 hr, but no further change was observed in the pmr spectrum.

Diazo(tri-tert-butylcyclopropenyl)methyl neopentyl ketone. (173)

To a solution of diisopropylamine (225.2 mg, 2.23 mmol) in ether (15 ml) and THF (13 ml) was added an n-butyllithium (hexane solution, 1.45 M, 1.4 ml, 2.03 mmol) at -10°. The solution was cooled to -110° and to this was added a THF (2 ml) solution of diazomethyl neopentyl ketone (255.7 mg, 1.82 mmol). After 10 min stirring at -110°, tri-tert-butylcyclopropenium fluoroborate 49 (595.8 mg, 2.02 mmol) was added in small portions. After stirring at -110° for 1.25 hr, the reaction mixture was warmed to room temperature, diluted with ether (10 ml) and pentane (40 ml), washed with brine (3x40 ml), and dried over Na_2SO_4. Evaporation of the solvent and chromatography on alumina (neutral, grade IV, 20 g) using hexane/ether (10:1,v/v) as the eluent afforded a yellow oil, 572.8 mg (91%).

pmr δ($CDCl_3$); 0.93 (9H,s), 1.03 (9H,s), 1.28 (18H,s), 2.33 (2H,s).

ir (CCl_4); 2050 cm^{-1} (s), 1615 (s).

(3,3-dimethyl-1-oxo-butyl)-tri-*tert*-butyl[4]annulene. (176)

A solution of diazoketone 173 (11.8 mg, 0.0[illegible]4 mmol) in methylcyclohexane-$\underline{d}_{14}$ (0.4 ml) was placed in a quartz nmr tube, which was degassed and sealed. Irradiation at liquid nitrogen temperature by a high pressure mercury lamp (Pyrex filter) for 4.5 hr produced [4]annulene derivative 176. The photolysate was dark purple at -198°. The color disappeared instantly upon warming to -78°.

pmr δ(methylcyclohexane-$\underline{d}_{14}$); 1.03 (9H,s), 1.12 (18H,s), 1.20 (9H,s), 2.57 (2H,s).

Photolysis of 176.

The photolysate in the quartz nmr tube was subsequently irradiated with a low pressure mercury lamp at -198° for 6 hr. No change was observed in the pmr spectrum. Irradiation with a high pressure mercury lamp (Vycor filter) for 2.5 hr also caused no change in the pmr spectrum.

A solution of diazoketone 173 (5.5 mg) in 2-methyltetrahydrofuran (10 ml) was placed in an quartz uv cell and degassed. Irradiation with a high pressure mercury lamp (Pyrex filter) at -78° was continued for 1 hr. The uv spectrum was recorded at -130°. Irradiation with a low pressure mercury lamp at -140° was continued for 1 hr and the uv spectrum was recorded at -140°. No change in the uv spectrum was observed.

3,4,5-Trimethylpyrazole.[112]

To a solution of 3-methyl-2,4-pentandione (1.14 g, 10 mmol) in methanol (1.5 ml) was added hydrazine hydrate (85% solution, 0.565 ml, 10 mmol) at 0°. The mixture was stirred at 30° for 5 hr. The methanol was evaporated and the residue was dissolved in ether (20 ml) and dried over BaO. Evaporation of the solvent afforded white crystals, 1.02 g (91%), which were used directly in the next step.

3-Methoxy-3,4,5-trimethyl-3H-pyrazole.[112a,113]

To an ice-cold solution of 3,4,5-trimethylpyrazole (13.9 g, 0.126 mol) in methanol (160 ml) was added N-bromosuccinimide (25 g, 0.14 mol) in small portions. After stirring at 0° for 20 min, a KOH methanol solution (1.125 N, 122.5 ml, 0.138 mol) was slowly added. Stirring was continued for 1 hr at 0°. The bulk of the solvent was removed, and distillation afforded the product, 10.8 g (63%), bp ca. 45°/3 mmHg (lit. 52-53°/2.8 mmHg).[112a]

Trimethylcyclopropenium fluoroborate.[112a]

3-Methoxy-3,4,5-trimethyl-3H-pyrazole (2.0 g, 14.7 mmol) dissolved in pentane (200 ml) was irradiated with a high pressure mercury lamp (Pyrex filter) for 1 hr, while the photolysis vessel was cooled at ca. -40°. The photolysate was transferred to a flask at -30° and a 54% HBF_4

ether solution (3.45 ml) was added. After stirring at -30° for 1 hr, ice-cold ether (200 ml) was added to the reaction mixture. The fluoroborate was collected and recrystallized from acetone/ether. Yield was 2.0 g (81%), and mp was 130-131° (lit. 130-131°).[112a]

Trimethylcyclopropenyldiazoacetate. (174)

This diazoester was prepared in a similar manner to that for tri-*tert*-butylcyclopropenyldiazoacetate 46, except that the chromatography on alumina was carried out at -10°. pmr δ($CDCl_3$); 1.31 (3H,s), 2.05 (6H,s), 3.75 (3H,s). ir (neat); 2070 cm^{-1} (s), 1690 (s).

This diazoester slowly isomerized at 0° to methyl 4,5,6-trimethylpyridazinecarboxylate 173. pmr δ($CDCl_3$); 2.32 (3H,s), 2.48 (3H,s), 2.75 (3H,s), 4.06 (3H,s).

Photolysis of 174.

Diazoester (174), frozen in methylcyclohexane, was irradiated at -198° and the matrix turned black. The color disappeared instantly upon warming. 2-Butyne, methyl 2-butyrate, and dimers of trimethyl[4]annulenecarboxylate were identified (in *ca*. a 1:2:2 ratio, respectively) in the product mixture by glpc (UCW-98) analysis.

The photolysis was then carried out in either cyclopentene or in butadiene at -78°. The products in both cases were identical with those from the above reaction. No adduct with the solvent was formed.

The esr spectrum of the black photolysate was recorded at -170°, but no signal that may be ascribed to a triplet species was observed.

Dipenylcyclopropenium fluoroborate.[114]

Acetic anhydride (3 ml) was added to a mixture of diphenylcyclopropenylcarboxylic acid (1.0 g, 4.23 mmol) and 54% HBF_4-ether solution (4 ml) at room temperature. After 1 hr stirring, ether (400 ml) was added and the precipitated product was collected and recrystallized from acetone/ether, yielding 434 mg (37%) of the fluoroborate.

Methyl diphenylcylcopropenyldiazoacetate. (176)

Diphenyl derivative 176 was prepared in a similar manner to the other diazoesters, (purity was *ca.* 30%).
pmr $\delta(CDCl_3)$; 3.00 (1H,s), 3.81 (3H,s), 6.9-7.3 (10H,m).

This diazoester isomerized to diphenylpyridazinecarboxylate at room temperature.
pmr $\delta(CDCl_3)$; 4.08 (3H,s), 8.18 (1H,s).

Photolysis of 176.

Diazoester 176 (20 mg) in methylcyclohexane-d_{14} (0.5 ml) and THF-d_8 (0.1 ml) was irradiated with a high pressure mercury lamp (Pyrex filter) for 2 hr. No starting material remained and glpc analysis (UCW-98) showed the presence of diphenylacetylene (*ca.* 50% yield) but no phenylacetylene.

Photolysis of dipropylcyclopropenyldiazoacetate 177.

Diazoester 177 was similarly prepared,[115] but in *ca.* 50% purity. Because of its instability, further purification was not attempted. Even at room temperature, 177 isomerized to the pyridazine derivative. The crude diazoester 177 was dissolved in methylcyclohexane and irradiated with a high pressure mercury lamp (Pyrex filter) at -78° for 2.5 hr. Glpc analysis (UCW-98) of the photolysate showed the presence of 4-octyne but no other volatile material was observed.

Photlysis of azide 45.

A solution of azide 45[39] (55 mg) in methylcyclohexane-d_{14} (0.3 ml) was placed in a quartz nmr tube, degassed and sealed. Irradiation using a high pressure mercury lamp (Corex filter) at -110° caused nitrogen evolution. After the cessation of gas evolution (*ca.* 5 hr) the reaction mixture was checked by pmr spectroscopy and glpc analysis. Both the pmr spectrum (two singlets at δ 1.14 and 1.28 with an intensity ratio of 2:1, at -50°) and the glcp analysis (UCW-98) showed that the only products were di-*tert*-butylacetylene and pivalonitrile. Irradiation at -198° produced the identical products.

Reaction of tri-*tert*-butylcyclopropene *181* with dichlorocarbene.

A solution of chloroform (180 mg, 1.51 mmol) in THF (9 ml) and pentane (1 ml) was cooled to −110°. A hexane solution of *n*-butyllithium (1.49 *M*, 0.83 ml, 1.34 mmol) was then added. After stirring for 15 min, tri-*tert*-butylcyclopropene (193 mg, 0.926 mmol) in THF (3 ml) was added over a period of 5 min. After stirring at −110° for 15 min, the mixture was warmed to −78° over 30 min. Stirring at −78° for 1 hr was followed by warming to 0° over 30 min. Wet ether (20 ml) was added to the reaction mixture, which was then diluted with ether (30 ml), washed with pH 7 buffer (20 ml) and dried over $MgSO_4$. The pmr spectrum of this product (274.7 mg) showed that it was a mixture of the starting material and dichloride *24*.

REFERENCES

(1) F.Sondheimer and R.Wolovsky, *J. Amer. Chem. Soc.*, *84*, 260 (1962).

(2) A.Kekulé, *Ann.*, *137*, 129 (1866).

(3) R.Willstätter and E.Wase, *Chem. Ber.*, *44*, 3423 (1911).

(4) E.Hückel, *Z. Phyzik*, *70*, 204 (1931).

(5) a) F.Sondheimer and R.Wolovsky, *Tetrahedron Letters*, 3, (1959).

b) F.Sondheimer, R.Wolovsky and Y.Amiel, *J. Amer. Chem. Soc.*, *84*, 274 (1962).

(6) For a rewiew; F.Sondheimer, I.C.Calder, J.A.Elix, U.Gaoni and R.Wolovsky, *Chem. Soc.*, *Spec.Publ.*,No. 21, 75 (1967).

(7) a) J.F.M.Oth, H.Röttele and G.Schröder, *Tetrahedron Letters*, 61 (1970).

b) J.F.M.Oth, J.M.Gilles and G.Schröder, *Tetrahedron Letters*, 67 (1970).

(8) a) F.Sondheimer and Y.Gaoni, *J. Amer. Chem. Soc.*, *83*, 4863 (1961).

b) G.Schröder and J.F.M.Oth, *Tetrahedron Letters*, 4083 (1966).

c) S.M.Johnson, I.C.Paul and G.S.D.King, *J. Chem. Soc.* (B), 643 (1970).

(9) F.Sondheimer and Y.Gaoni, *J. Amer. Chem. Soc.*, *83*, 1259 (1961).

(10) H.C.Longuett-Higgins and L.E.Orgel, J. Chem. Soc., 1969 (1956).

(11) R.Criegee and G.Schröder, Ann, 623, 1 (1959).

(12) G.F.Emerson, L.Watts and R.Pettit, J. Amer. Chem. Soc., 87, 131 (1965).

(13) J.D.Roberts, Speç. Publ. (Chem. Soc. London), No.12, 111 (1958).

(14) R.Hoffmann, Chem. Commun., 240 (1969).

(15) a) R.Gompper and G.Seybold, Angew. Chem., Internat. Edit., 7, 824 (1968).

b) M.Neuenschwander and A.Niederhauser, Chimia, 22, 491 (1968).

(16) a) L.Watts, J.D.Fitzpatrick and R.Pettit, J. Amer. Chem. Soc., 87, 3253 (1965).

b) G.F.Emerson, L.Watts and R.Pettit, J. Amer. Chem. Soc., 88, 623 (1966).

(17) a) W.J.R.Tyerman, M.Kato, P.Kebarle, S.Masamune, O.P.Strausz and H.E.Gunning, Chem. Commun., 497 (1967).

b) J.Front, S.C.Barton and O.P.Strausz, Chem. Commun., 499 (1970).

(18) E.Hedaya, R.D.Miller, D.W.McNeil, P.F.D'Angelo and P.Schissel, J. Amer. Chem. Soc., 91, 1875 (1969).

(19) a) E.K.G.Schmidt, Angew. Chem., Internat. Edit., 12, 777 (1973).

b) R.H.Grubbs and R.A.Grey, J. Amer. Chem. Soc., 95, 5765 (1973).

c) See also; J.Rebek and F.Gavina, *J. Amer. Chem. Soc.*, *97*, 3453 (1975).

(20) M.P.Cava and M.J.Mitchell, "Cyclobutadiene and related compounds", Academic Press, New York, 1967.

(21) A.Streitweiser,Jr., "Molecular Orbital Theory for Organic Chemists", Wiley and Sons, Inc., 1961.Part I,2

(22) a) L.Pauling, *J. Chem. Phys.*, *4*, 673 (1936).

b) F.London, *J. Phys. Radium*, *8*, 397 (1937).

c) J.A.Pople, *J. Chem. Phys.*, *24*, 1111 (1956).

d) L.M.Jackman, F.Sondheimer, Y.Amiel, D.A.Ben-Efraim, Y.Gaoni, R.Wolovsky and A.A.Bothner-By, *J. Amer. Chem. Soc.*, *84*, 4307 (1962).

(23) J.A.Pople and K.G.Untch, *J. Amer. Chem. Soc.*, *88*, 4811 (1966).

(24) a) M.J.S.Dewar and G.J.Gleicher, *J. Amer. Chem. Soc.*, *87*, 3255 (1965).

b) N.L.Allinger, C.Gilardeau and L.W.Chow, *Tetrahedron*, *24*, 2401 (1968).

c) N.L.Allinger and J.C.Tai, *Theoret. Chim. Acta*, *12*, 29 (1968).

d) R.J.Buenker and S.D.Peyerimhoff, *J. Chem. Phys.*, *48*, 354 (1968).

e) M.J.S.Dewar, M.C.Kohn and N.Trinajstic, *J. Amer. Chem. Soc.*, *93*, 3437 (1971).

f) A.Krantz, C.Y.Lin and M.D.Newton, *J. Amer. Chem. Soc.*, *95*, 2744 (1973).

g) M.J.S.Dewar and H.W.Kollman, *J, Amer. Chem. Soc.*, *97*, 2933 (1975).

(25) H.Kimling and A.Krebs, *Angew. Chem., Internat. Edi*[illegible] *11*, 932 (1972).

(26) G.Lauer, C.Müller, K.W.Schule, A.Schweig and A.Krebs, *Angew. Chem., Internat. Edit.*, *13*, 544 (1974).

(27) a) A.V.Kemp-Jones, A.J.Jones, M.Sakai, C.P.Beeman and S.Masamune, *Can. J. Chem.*, *51*, 767 (1973).

b) H.Günther, H.Schmickler, H.Konigshoten, K.Recker and E.Vogel, *Angew. Chem., Internat. Edit.*, *12*, 243 (1973).

(28) M.Avram, I.G.Dinulescu, E.Marica, G.Mateescu, E.Sliam and C.D.Nenitzescu, *Chem. Ber.*, *97*, 382 (1964).

(29) G.D.Burt and R.Pettit, *Chem. Commun.*, 517 (1965).

(30) a) J.Ciabattoni and A.E.Feiring, *J. Amer. Chem. Soc.*, *94*, 5113 (1972).

b) J.Ciabattoni and A.E.Feiring, *J. Amer. Chem. Soc.*, *95*, 5266 (1973).

(31) S.Yankelevich and B.Fucks, *Tetrahedron Letters*, 4945 (1967), and references cited therein.

(32) G.L.Closs and V.N.Rao, *J. Amer. Chem. Soc.*, *88*, 4116 (1966).

(33) G.Maier and F.Bosslet, *Tetrahedron Letters*, 4483 (1972).

(34) a) N.C.Baird and M.J.S.Dewar, *J, Amer, Chem. Soc.*, *89*, 3966 (1967).

b) R.C.Buenker and S.D.Peyerimhoff, *J. Amer. Chem. Soc.*, *91*, 4342 (1969).

(35) L.B.Rodewald and H.K.Lee, J. Amer. Chem. Soc., 95, 623 (1973); correction, 95, 3084 (1973).

(36) E.H.White, G.E.Maier, R.Graeve, U.Zirngibl and E.W. Friend, J. Amer. Chem. Soc., 88, 611 (1966).

(37) A.E.Feiring and J.Ciabattoni, J. Org. Chem., 37, 3784 (1972).

(38) G.L.Closs and A.M.Harrison, J. Org. Chem., 37, 1051 (1972).

(39) R.Curci, V.Lucchini, P.J.Kocienski, G,T,Evans and J.Ciabattoni, Tetrahedron Letters, 3293 (1972).

(40) See for instance, "Org. Syntheses", Coll. Vol. 4, 424 (1963).

(41) S.Masamune, N.Nakamura, M.Suda and H.Ona, J. Amer. Chem. Soc., 95, 8481 (1973).

(42) a) J.Ciabattoni and E.C.Nathan, III., J. Amer. Chem. Soc., 91, 4766 (1969).

b) J.Ciabattoni, E.C.Nathan, III., A.E.Feiring and P.J.Kocienski, "Org. Syntheses", in press.

(43) a) U.Schöllkopf and H.Fransnelli, Angew. Chem., Internat. Edit., 9, 301 (1970).

b) See also, E.Wenkert and C.A.McPherson, J. Amer. Chem. Soc., 94, 8084 (1972).

(44) a) G.C.Levy, G.L.Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972, Chap. 3.

b) J.B.Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, Chap. 3.

(45) P.Reeves, J.Henry and R.Pettit, J. Amer. Chem. Soc., 91, 5888 (1969).

(46) J.P.N.Brewer, H.Heaney and B.A.Marples, Chem. Commun., 27 (1967).

(47) H.Kessler, Angew. Chem., Internat. Edit., 9, 219 (1970).

(48) M.Ōki and G.Yamamoto, Chem. Letters, 45 (1972).

(49) L.T.J.Delbaere, M.N.G.James, N.Nakamura and S.Masamune, J. Amer. Chem. Soc.,97, 1973 (1975).

(50) L.E.Sutton, Chem. Soc., Spec. Publ.,No.18 1965

(51) R.S.Brown and S.Masamune, Can. J.Chem., 53, 972 (1975).

(52) G.Lauer, C.Müller, K.W.Schulte, A.Schweig and A.Krebs, Angew. Chem., Internat. Edit., 13, 544 (1974).

(53) G.Lauer, C.Müller, K.W.Schulte, A.Schweig, G.Maier and A.Alzérreca, Angew. Chem., Internat. Edit., 14, 172 (1975).

(54) D.A.Sweigart and D.W.Turner, J. Amer. Chem. Soc., 94, 5592 (1972).

(55) J.W.Robinson, Ed., "Handbook of Spectroscopy", Vol. 1, CRC press, Cleveland, 1974.

(56) See for instance, R.A.Moss, J. Org. Chem., 31, 1082 (1966).

(57) C.A.Coulson and A.Golebiewski, Proc. Phys. Soc., (London), 78, 1310 (1961).

(58) G.Maier and A.Alzérreca, Angew. Chem., Internat. Edit., 12, 1015 (1973).

(59) S.Masamune, M.Suda, H.Ona and L.M.Leichter, Chem.

Commun., 1268 (1972).

(60) S.Masamune and N.Darby, unpublished work.

(61) A.Numata, K.Ono, H.Irie and S.Ueno, *Yakugaku Zasshi*, *88*, 1151 (1968); *C.A.*, *70*, 47193a.

(62) N.M.Hasty and D.R.Kearns, *J. Amer. Chem. Soc.*, *95*, 3380 (1973) and references cited therein.

(63) W.G.Dauben, M.E.Lorber, N.D.Vietmeyer, R.H.Shapiro, J.H.Duncan and K.Yomer, *J. Amer. Chem. Soc.*, *90*, 4762 (1968).

(64) K.B.Sharpless, M.A.Umbreit, M.T.Nieh and T.C.Flood, *J. Amer. Chem. Soc.*, *94*, 6538 (1972).

(65) H.D.Martin and M.Hekman, *Synth.*, 667 (1973).

(66) a) G.Maier and F.Bosslet, *Tetrahedron Letters*, 1025 (1972).

b) See also, G.Maier, *Angew. Chem.*, *Internat. Edit.*, *13*, 425 (1974).

(67) G.Maier and B.Hoppe, *Tetrahedron Letters*, 861 (1973).

(68) G.Maier, W.Maier, C.Haacke and R.Askani, *Angew. Chem.*, *Internat. Edit.*, *12*, 1016 (1973).

(69) a) C.Y.Lin and A.Krantz, *Chem. Commun.*, 1111 (1972).

b) O.L.Chapman, C.L.McIntosh and J.Pacansky, *J. Amer. Chem. Soc.*, *95*, 614 (1973).

c) O.L.Chapman, D.D.L.Cruz and R.Roth, *J. Amer. Chem. Soc.*, *95*, 1337 (1973).

(70) M.J.S.Dewar and H.W.Kollman, *J. Amer. Chem. Soc.*, *97*, 2933 (1975).

(71) P.E.Eaton and T.W.Coley,Jr., J. Amer. Chem. Soc., 86, 3157 (1964).

(72) C.G.Chin, H.W.Cuts and S.Masamune, Chem. Commun., 880 (1966).

(73) J.C.Barbarak, L.Watts and R.Pettit, J. Amer. Chem. Soc., 88, 1328 (1966).

(74) R.B.Woodward, T.Fukunaga and R.C.Kelly,Jr., J. Amer. Chem. Soc., 86, 3162 (1964).

(75) J.M.Schulman and T.J.Venanzi, J. Amer. Chem. Soc., 96, 4739 (1974) and references cited therein.

(76) P.B.Shevlin and A.P.Wolf, J. Amer. Chem. Soc., 92, 406 (1970); correction 92, 5291 (1970).

(77) R.F.Peterson,Jr., R.T.K.Baker and R.L.Wolfgang, Tetrahedron Letters, 4749 (1969).

(78) R.Breslow, L.J.Altman, A.Krebs, E.Mohacsi, I.Murata, R.A.Peterson and J.Posner, J. Amer. Chem. Soc., 87, 1326 (1965).

(79) R.Breslow, J.Posner and A.Krebs, J. Amer. Chem. Soc., 85, 234 (1963).

(80) G.L.Closs and W.A.Böll, J. Amer Chem. Soc., 85, 3904 (1963).

(81) D.E.Applequist, P.A.Gebauer, D.E.Gwynn and L.H.O'Cornor, J. Amer. Chem. Soc., 94, 4272 (1972).

(82) A.Favorskii and W.Boshovskii, Ann, 390, 122 (1912).

(83) M.Suda and S.Masamune, Chem. Commun., 504 (1974).

(84) A.L.Liberman and J.V.Vasina, Zhur. Org. Khim. 3, 690 (1967).

(85) R.Breslow, G.Ryan and J.T.Groves, *J. Amer. Chem. Soc.*, *92*, 988 (1970).

(86) R.Breslow and M.Oda, *J, Amer. Chem. Soc.*, *94*, 4787 (1972)

(87) R.C.Benson, W.H.Flygare, H.Oda and R.Breslow, *J. Amer. Chem. Soc.*, *95*, 2772 (1973).

(88) R.Breslow and L.J.Altman, *J. Amer. Chem. Soc.*, *88*, 504 (1966).

(89) A.Krebs and B.Schrader, *Ann*, *70*[illegible] (1967).

(90) A.Krebs and B.Schrader, *Tetrahedron Letters*, 5935 (1968).

(91) K.T.Potts and J.S.Baum, *Chem. Rev.*, *74*, 189 (1974).

(92) N.J.McCorkindale, R.A.Raphael, W.T.Scott and B.Zwanenburg *Chem. Commun.*, 133 (1966).

(93) R.Breslow, T.Eicher, A.Krebs, R.Peterson and J.Posner, *J, Amer. Chem. Soc.*, *87*, 1320 (1965).

(94) H.Ona, H.Yamaguchi and S.Masamune, *J. Amer. Chem. Soc.*, *92*, 7495 (1970).

(95) S.Masamune, *Tetrahedron Letters*, 945 (1965).

(96) M.Fetizon and M.Jurion, *Chem. Commun.*, 382 (1972) and references cited therein.

(97) G.Stork and L.Maldonado, *J. Amer. Chem. Soc.*, *93*, 5286 (1971).

(98) H.J.Sims, H.B.Parseghian and P.L.DeBenneville, *J. Org. Chem.*, *23*, 724 (1958).

(99) a) M.Regitz, *Synth.*, 351 (1972).
b) M.Regitz and F.Menz, *Chem. Ber.*, *101*, 2622 (1968).

(100) S.Masamune, *J. Amer. Chem. Soc.*, *86*, 735 (1964).

(101) S.J.Valenty andP.S.Skell, J. Org. Chem., 38, 3937 (1073).

(102) U.Schöllkopf, F.Gerhart, M.Reetz, H.Fransnelli and H.Schumacker, Ann., 716, 204 (1968).

(103) a) S.Masamune and H.Ona, J. Amer. Chem. Soc., 94, 8955 (1972).

b) S.Masamune, H.Ona and A.J.Jones, J. Amer. Chem. Soc., 94, 8956 (1972).

(104) T.J.Katz and N.Acton, J. Amer. Chem. Soc., 95, 2738 (1973).

(105) E.J.Corey and W.H.Pirkle, Tetrahedron Letters, 5255 (1967).

(106) G.Maier and M.Schneider, Angew. Chem., Internat. Edit., 12, 162 (1973).

(107) S.Masamune, N.Nakamura and J.Spadaro, J, Amer. Chem. Soc., 97, 918 (1975).

(108) G.Seybold, U.Jersak and R.Gompper, Angew. Chem., Internat. Edit., 12, 847 (1973).

(109) B.M.Trost and R.C.Atkins, Chem. Commun., 1254 (1971).

(110) S.F.Birch, U.E.Gripp, D.F.McAllan and W.S.Nathan, J. Chem. Soc., 1363 (1952).

(111) Org. Synth., Coll. Vol. IV, 345.

(112) a) B.M.Trost, R.C.Atkins and L.Hoffman, J. Amer. Chem. Soc., 95, 1285 (1973).

b) V.Rothenberg, J. Prakt. Chem., 160, 51 (1895).

(113) G.L.Closs and H.Heyn, Tetrahedron, 22, 463 (1966).

(114) D.G.Farnum and M.Burr, J. Amer. Chem. Soc., 82, 2651 (1960).

(115) R.Breslow, H.Höver and H.W.Chang, J. Amer. Chem. Soc., 84, 3168 (1962).