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Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
SIVARAMAN RAGHU
1972

SYNTHETIC APPROACHES TO TRUNCATED TETRAHEDRANE AND OTHER $(CH)_{12}$ HYDROCARBONS

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This is to certify that the

thesis entitled

SYNTHETIC APPROACHES TO TRUNCATED TETRAHEDRANE
AND OTHER $(CH)_{12}$ HYDROCARBONS

presented by

Sivaraman Raghu

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Organic Chemistry

Major professor

Date January 24, 1972

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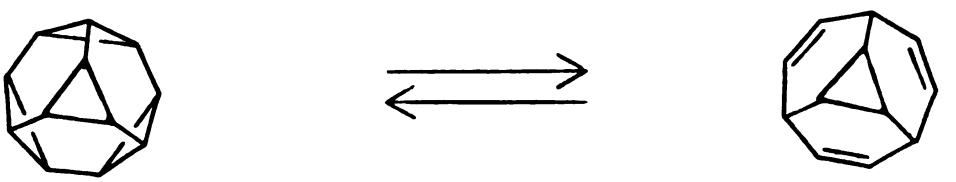
ABSTRACT

SYNTHETIC APPROACHES TO TRUNCATED TETRAHEDRANE
AND OTHER $(CH)_{12}$ HYDROCARBONS

By

Sivaraman Raghu

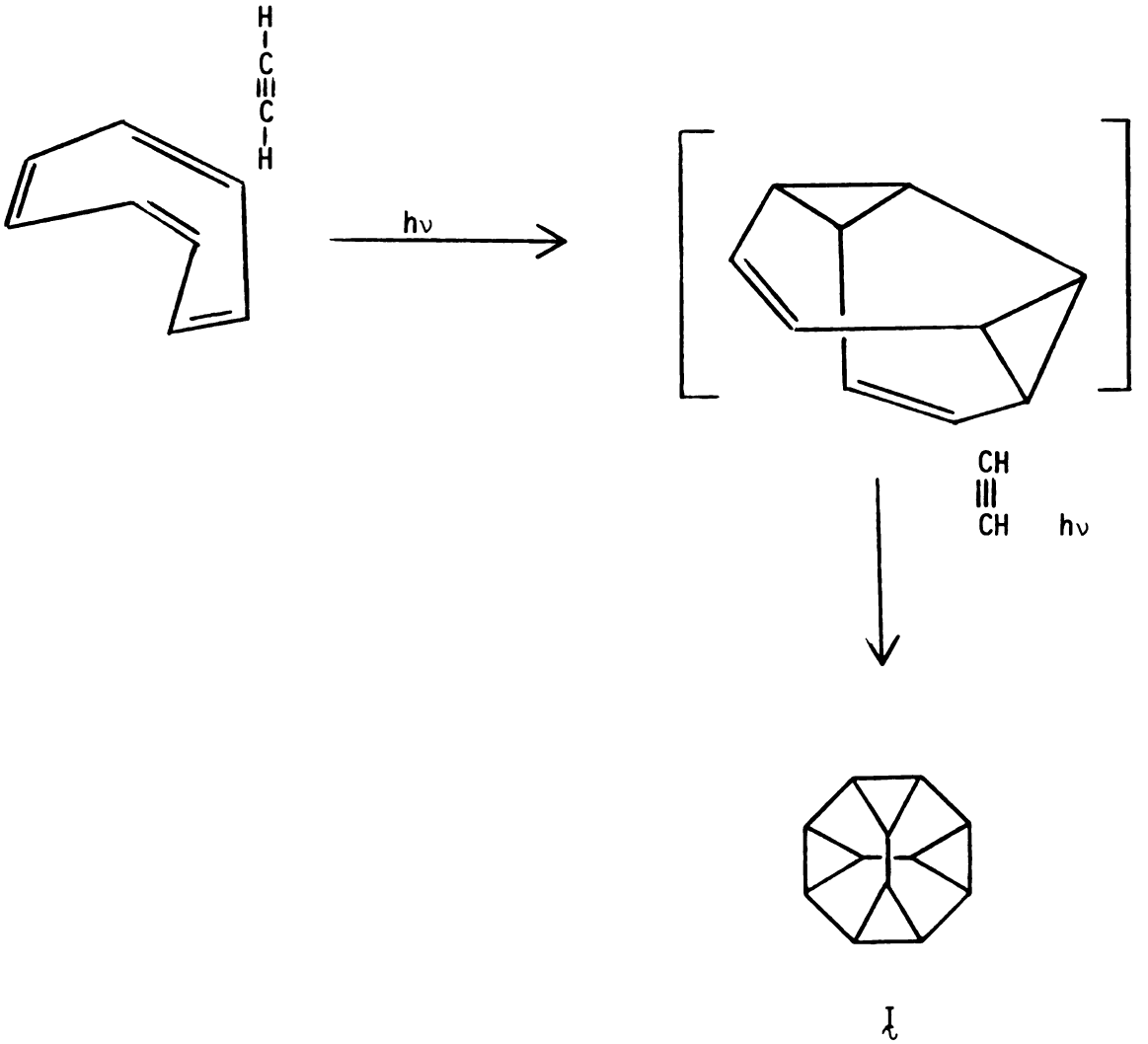
The quadruple trishomobenzene nature of the heptacyclododecane molecule I and the possibility of it being in equilibrium with II through a thermally allowed ($\pi_{2s} + \pi_{2s} + \pi_{2s}$) process, prompted us to embark on its synthesis.



I II

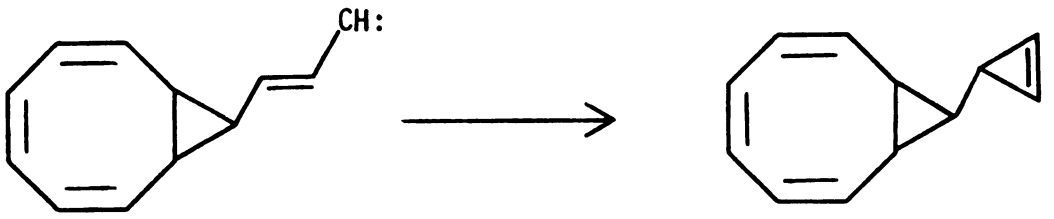
The most direct, simple and elegant approach investigated for the synthesis of I depended on the addition of two acetylenes to cyclooctatetraene in two symmetry allowed photochemical [$\pi_{2s} + \pi_{2s} + \pi_{2s} + \pi_{2s}$] reactions. We were dissappointed,

however, to find that none of the acetylenes studied gave cycloadducts possessing the carbon framework in I.



I

A somewhat less directed approach was the generation of the $(CH)_{12}$ carbene III from its precursor tosylhydrazone by low temperature photolysis. The carbene III isomerized under these conditions to the cyclopropene IV.



III IV

Our initial attempts to isomerize the cyclopropene IV by photolysis and rhodium complex catalysis to the triene II have not been successful. Other conditions such as different transition metal catalysts, and different sensitizers for the photolysis are currently being investigated in our laboratories.

SYNTHETIC APPROACHES TO TRUNCATED TETRAHEDRANE AND OTHER $(CH)_{12}$ HYDROCARBONS

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1972

TO MY PARENTS AND WIFE
WITHOUT WHOSE CONSTANT
ENCOURAGEMENT THIS WORK
WOULD NOT HAVE BEEN
POSSIBLE.

ACKNOWLEDGEMENT

The author would like to thank Professor Donald G. Farnum for his expert professional guidance, his understanding, his encouragement, and his sincere friendship throughout the course of this study. Thanks are also due to other members of the organic faculty for their assistance and advice during the author's graduate studies. Thanks are extended to all the members of "the group" for their technical assistance and friendship. Finally, the author gratefully acknowledges financial assistance by the Department of Chemistry in the form of teaching assistantships from Fall, 1967, to Fall, 1969, by The Petroleum Research Fund, administered by the American Chemical Society, from January, 1970, to March, 1971, and by The National Science Foundation from September, 1971, to February, 1972.

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INTRODUCTION

Investigation of the synthesis, properties and interconversions of $(CH)_n$ hydrocarbons especially for $(CH)_6$,[1] $(CH)_8$[2] and $(CH)_{10}$[3] representatives as illustrated in Figures 1, 2 and 3 have been among the intriguing developments in modern organic chemistry. Though these interconversions could be taking place through the intermediacy of free radicals, nevertheless it is more gratifying to view them

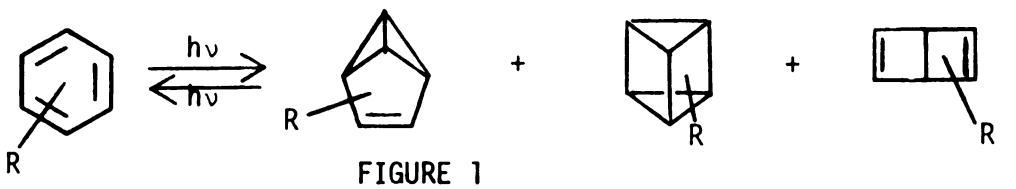


FIGURE 1

Interconversions of $(CH)_6$ hydrocarbons.

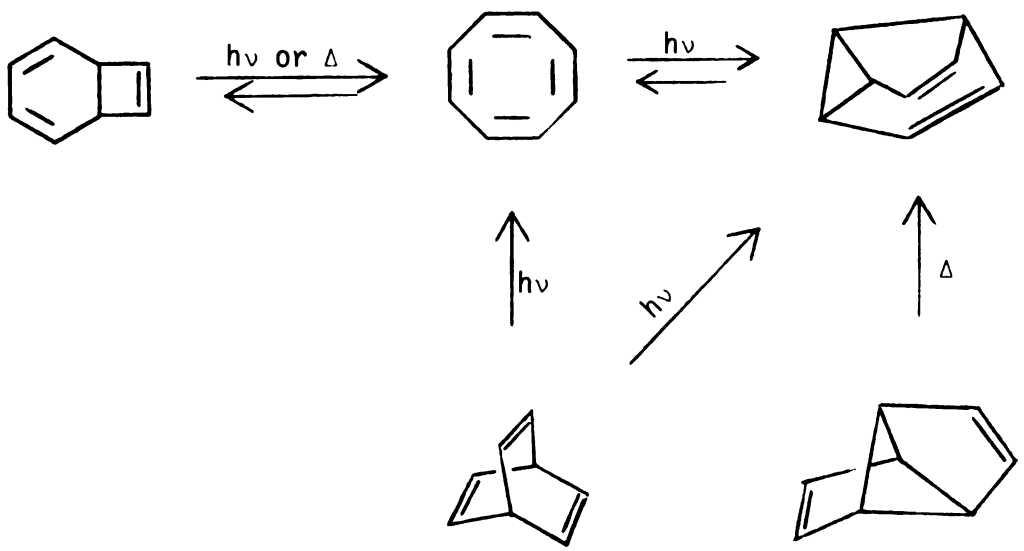


FIGURE 2

Interconversions of $(CH)_8$ hydrocarbons.

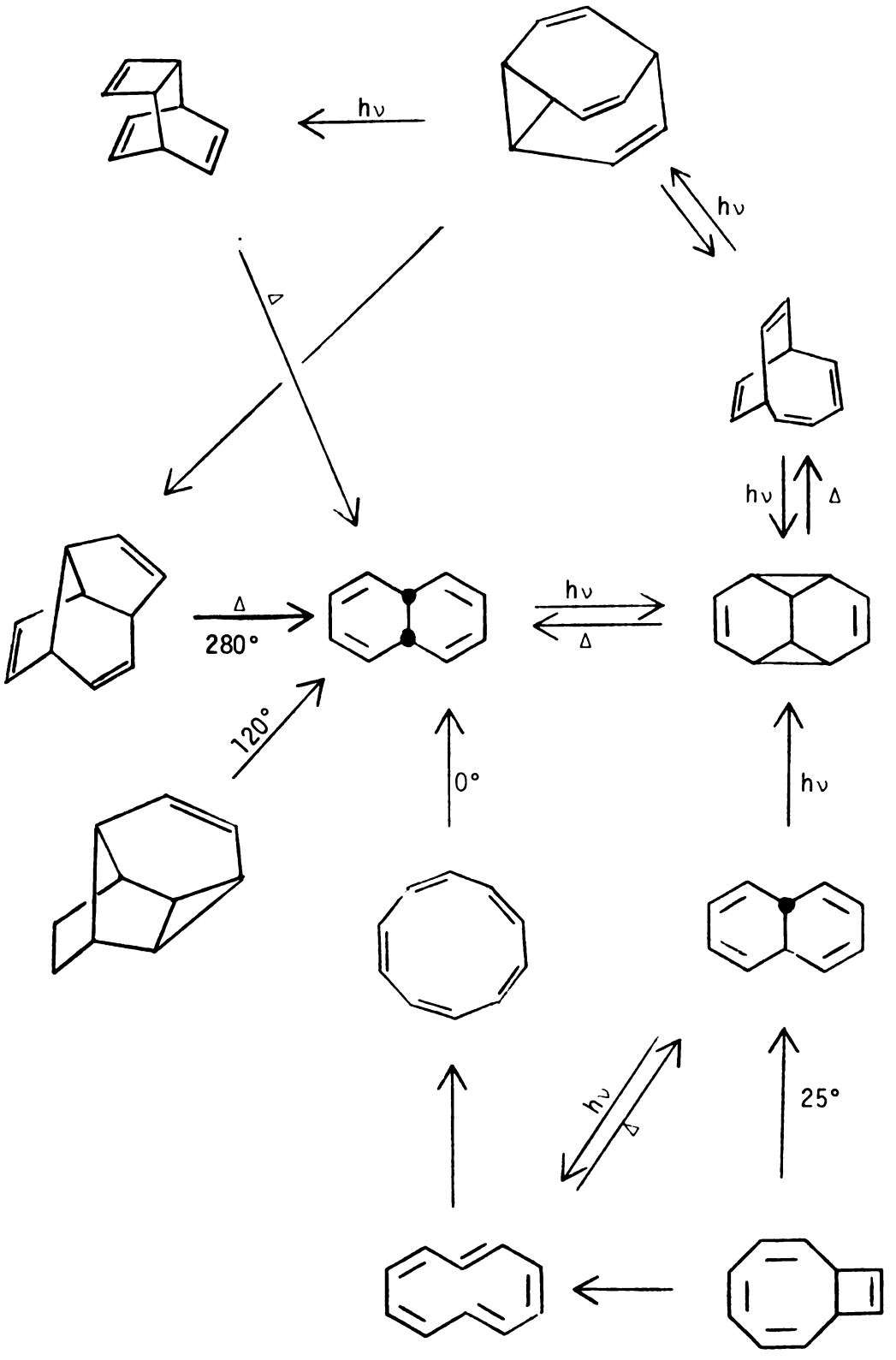


FIGURE 3

Interconversions of $(CH)_{10}$ hydrocarbons.

as proceeding through a series of concerted processes in accordance with the selection rules prescribed by Woodward and Hoffman, based on orbital symmetry considerations.[4] It is particularly interesting to note the suggestion[5] of Doering that the $(CH)_{10}$ hydrocarbons could all be lying on a common potential free energy surface. This is borne out by the fact, that, in any attempt to generate these hydrocarbons by a general synthesis,[3f,h,j] a mixture of these always results.

Some $(CH)_{12}$ hydrocarbons are also found in the literature. Thus Schröder has synthesized[6] two of these by pyrolysing the Diels-Alder adduct of the dimers of cyclooctatetraene and dimethylacetylene dicarboxylate. These have been observed to undergo isomerization under various conditions to other $(CH)_{12}$ hydrocarbons,[7] as illustrated in Figure 4. Pacquette has also observed some of these transformations.[8]

In view of these transformations and observations with $(CH)_{10}$ hydrocarbons, it was thought that a general synthesis, where many of these hydrocarbons are allowed to equilibrate might lead to a mixture of known and yet unknown interesting $(CH)_{12}$ hydrocarbons.

Another $(CH)_{12}$ hydrocarbon of considerable theoretical discussion and interest is the hydrocarbon heptacyclo[5.5.0.$0^{2,12}$-.$0^{3\ 5}$.$0^{4,10}$.$0^{6,8}$.$0^{9,11}$]dodecane], otherwise called "truncated tetrahedrane", because of its tetrahedral symmetry. Besides the aesthetic value of such a molecule, with a cage-like array of

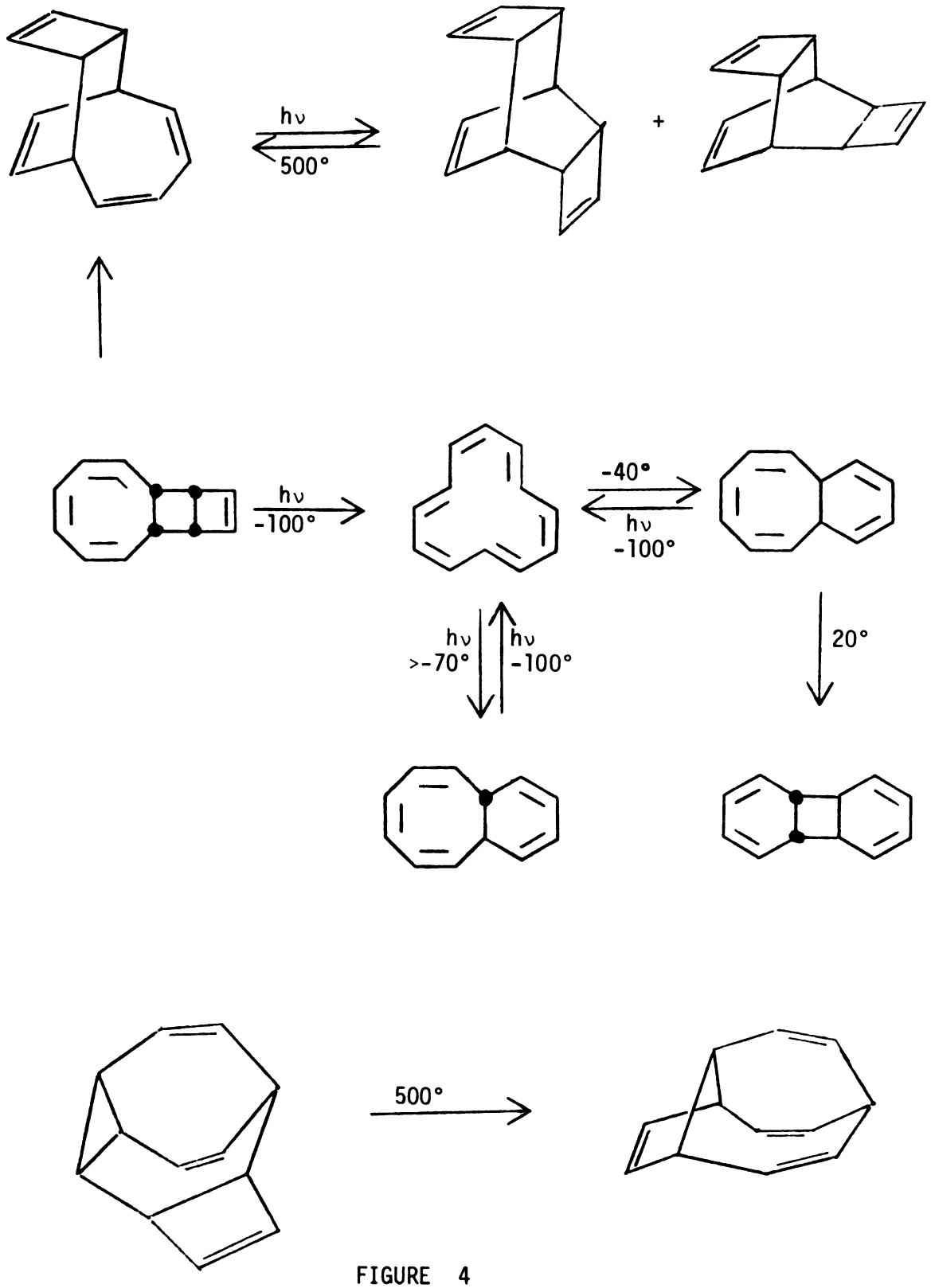
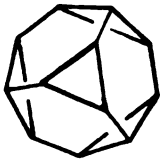


FIGURE 4

Interconversions of $(CH)_{12}$ hydrocarbons.

cyclopropane rings, it may have some unusual properties. Thus it may undergo proton exchange with D_2O in acid,[9] perhaps through an edge protonated cyclopropane in which the proton exchanges rapidly



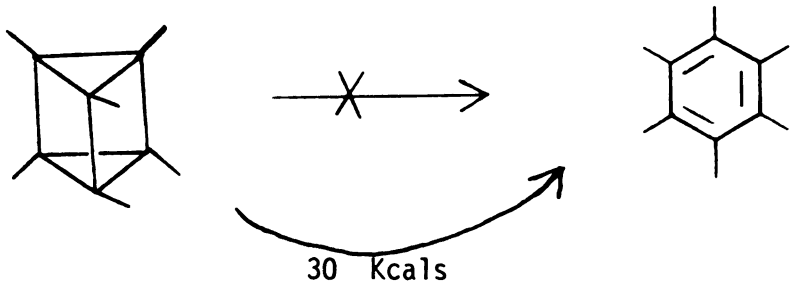
1

with all hydrogens. Determination of the nmr spectrum of 1 in super acid at low temperatures might detect this phenomenon, as in the case of tricyclene.[10]

Since the formation of a radical anion from cyclopropane with sodium-potassium alloy has been claimed,[11] it would be interesting to see the effect of a similar reduction of 1. An esr spectrum might reveal if the odd electron absorbed is localized on one cyclopropane or is dispersed over four.

The quadruple trishomobenzene nature of 1 makes it an ideal molecule for testing the theory of homoaromaticity as applied to neutral systems. Indeed its very existence could be considered as a triumph of the theory. It is interesting to note that whereas the comparably strained hexamethylprismane molecule needs another thirty kilocalories of energy[12] before decomposing to hexamethylbenzene, because of the process being symmetry forbidden[4] in the ground state, 1 has a symmetry allowed mode of thermal decomposition to 2, through a cycloreversion of a $\pi_{2s} + \pi_{2s} + \pi_{2s}$ type.[4] Since

at one time any three of the cyclopropane rings could be involved in this process, there would be four identical tautomers possible for 2. This is illustrated in Figure 5.



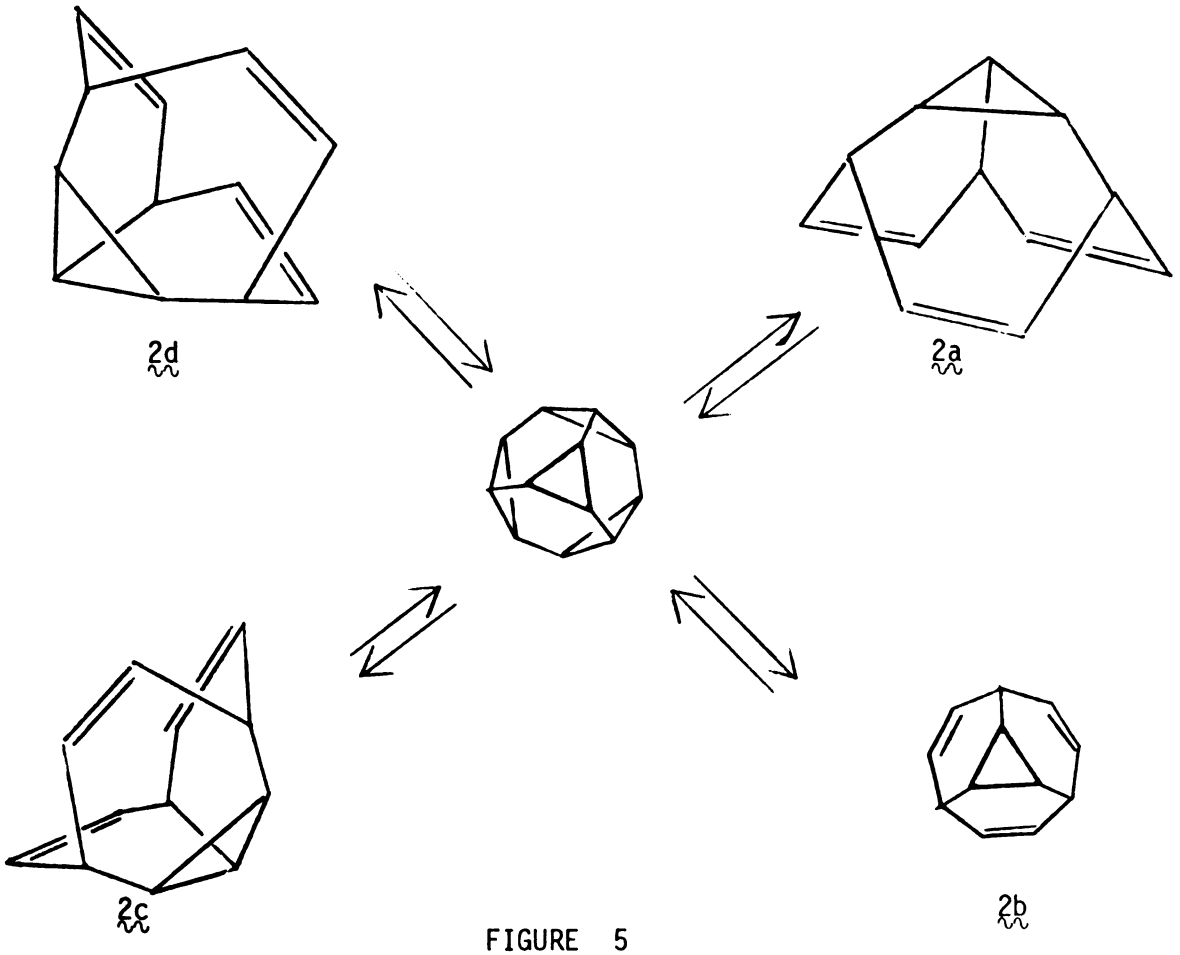
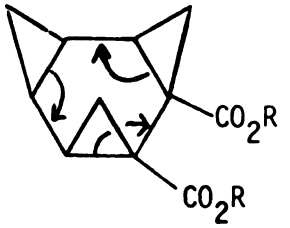


FIGURE 5

Thermally allowed ($\pi_{2s} + \pi_{2s} + \pi_{2s}$) interconversions of 1 and 2.

A similar process for two other trishomobenzenes 3[13] and 4[14] has been reported in the literature.



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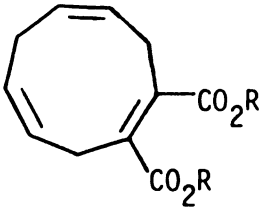

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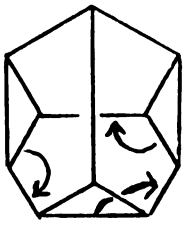

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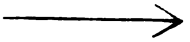
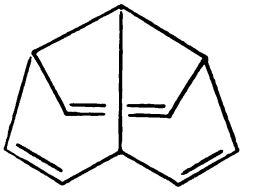
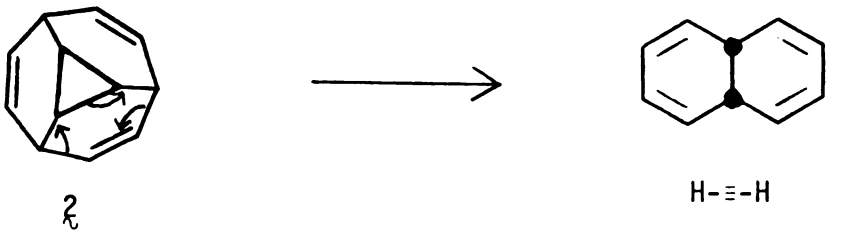




6

Whether the delocalization energy of 1 would be able to overcome the strain energy to prevent its decomposition to 2, is difficult to predict. A lesser stability of 1 might still permit its detection as an intermediate in the degenerate interconversion of 2a, b, c and d. This could be done by a study of the variable temperature nmr spectrum of 2, and hence the relative energy of 1 could be estimated. The spectrum in the limit might simplify to a single peak. A high activation energy for the process 2 to 1 on the other hand might force 2 to decompose to cis-9,10-dihydronaphthalene and acetylene by a

thermally allowed reversal of a $(\pi_{2s} + \pi_{2s} + \pi_{2s})$ process.[15]



2

Figure 6

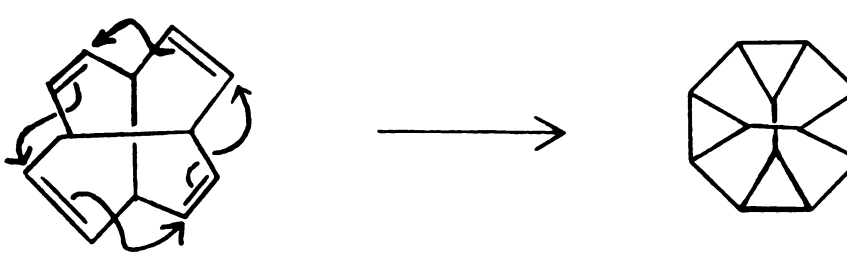
Symmetry allowed mode of decomposition for 2.

Clearly these considerations and the abundance of opportunities to study the interconversions of many $(CH)_{12}$ hydrocarbons led us to embark on their synthesis.

DISCUSSION A

The heptacyclo[5.5.0.$0^{2,12}$.$0^{3,5}$.$0^{4,10}$.$0^{6,8}$.$0^{9,11}$]dodecane molecule 1 (truncated tetrahedrane) contains an array of four cyclopropane rings joined to one another at the three corners of each cyclopropane ring.

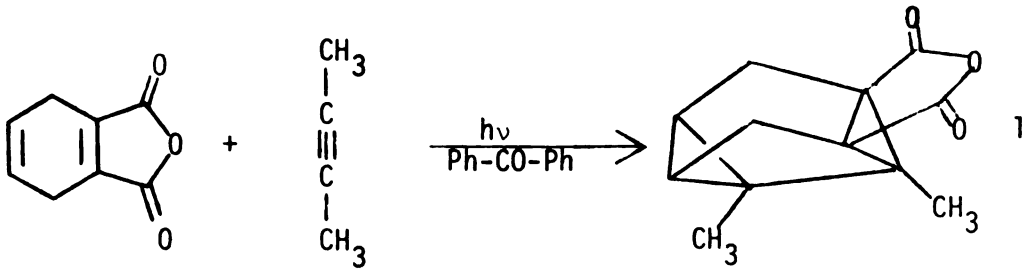
One synthetic approach that has been discussed[15] proposes the formation of the four cyclopropane rings in the last step by a [$\pi_{2a} + \pi_{2a} + \pi_{2a} + \pi_{2a}$] photochemical process. This is illustrated in equation 1. A study of molecular models of 7 reveals that the orbitals involved are very nicely aligned for this all antarafacial photochemical addition.



7 1 (1)

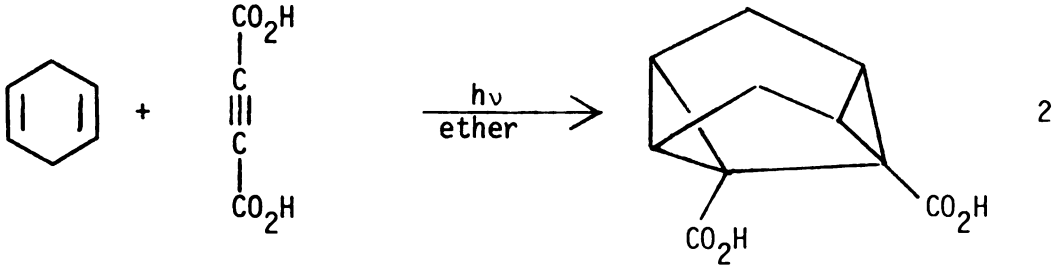
Another approach that one might consider in any synthetic attempt at 1 would be the construction of the cyclopropane rings in a stepwise process.

A look into the literature showed at least three successful attempts at the synthesis of a bis-cyclopropyl moiety in a one step photochemical reaction. These are illustrated below.



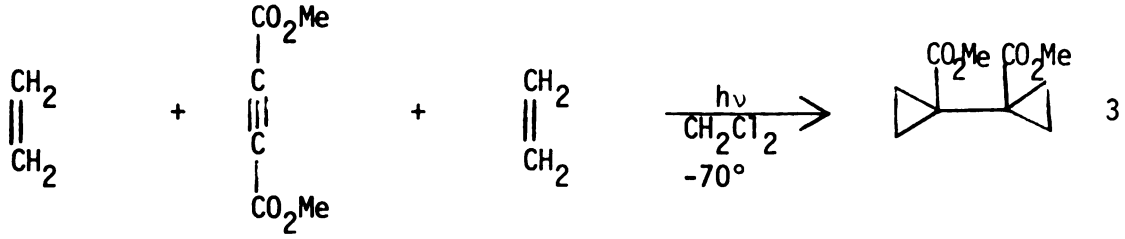
1

Ref. 16



2

Ref. 17

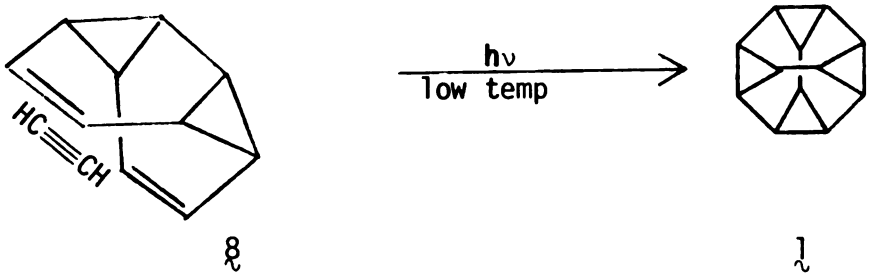


3

Ref. 18

These are symmetry allowed ($\pi_{2s} + \pi_{2s} + \pi_{2s} + \pi_{2s}$) photochemical reactions, where the two acetylenic π-orbitals are acting independently of one another.

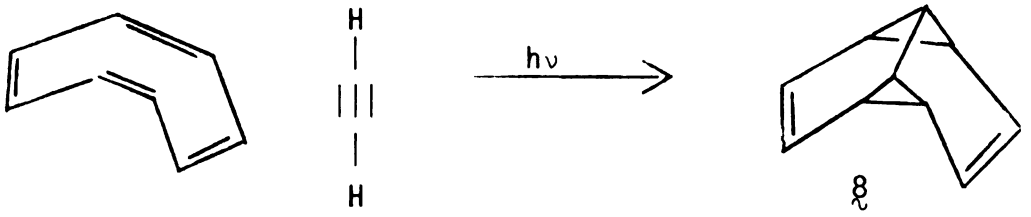
A proper choice of the diene moiety such as 8 might directly lead to truncated tetrahedrane as illustrated in equation 4 by an analogous route.



4

8 1

The diene itself contains two cyclopropane rings joined to one another and could be constructed by the same reaction starting with cyclooctatetraene, as shown in Equation 5.



8

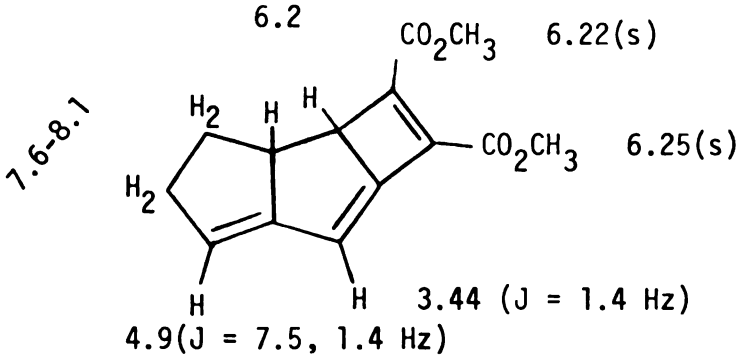
It was this simple and elegant approach to truncated tetrahedrane that we decided to concentrate our efforts on initially. To this end, we embarked on the photolysis of various acetylenes with cyclooctatetraene under a variety of conditions involving

different solvents, temperature and time. The reaction did not seem to work under the conditions employed.

The only photolysis that yielded an isolable adduct was the one in which a 3:1 ratio of dimethylacetylenedicarboxylate to cyclooctatetraene in methylene chloride was photolyzed in the presence of benzophenone as a sensitizer at -60°C. The crude product obtained after removing the solvent and starting materials by distillation, on chromatography on Florisil gave a compound in 10% yield. The compound had infrared absorptions at 1730, 1655 and 1640 cm^{-1} and nmr ($CHCl_3$-d) peaks at τ 3.44 (d, J = 1.4 Hz, 1H), 4.9 (dt, J = 7.5, 1.4 Hz, 1H), 6.2 (m, 2H), 6.22 (s, 3H), 6.25 (s, 3H) and 7.6-8.1 (broad signal, 4H). The u.v. spectrum had absorptions at 210 mμ (ε > 20,000) and 268 mμ (ε = 4,000) and the mass spectrum had fragment peaks at m/e 215, 214, 188, 182 (base peak), 173, 154, 142, 126 and others.

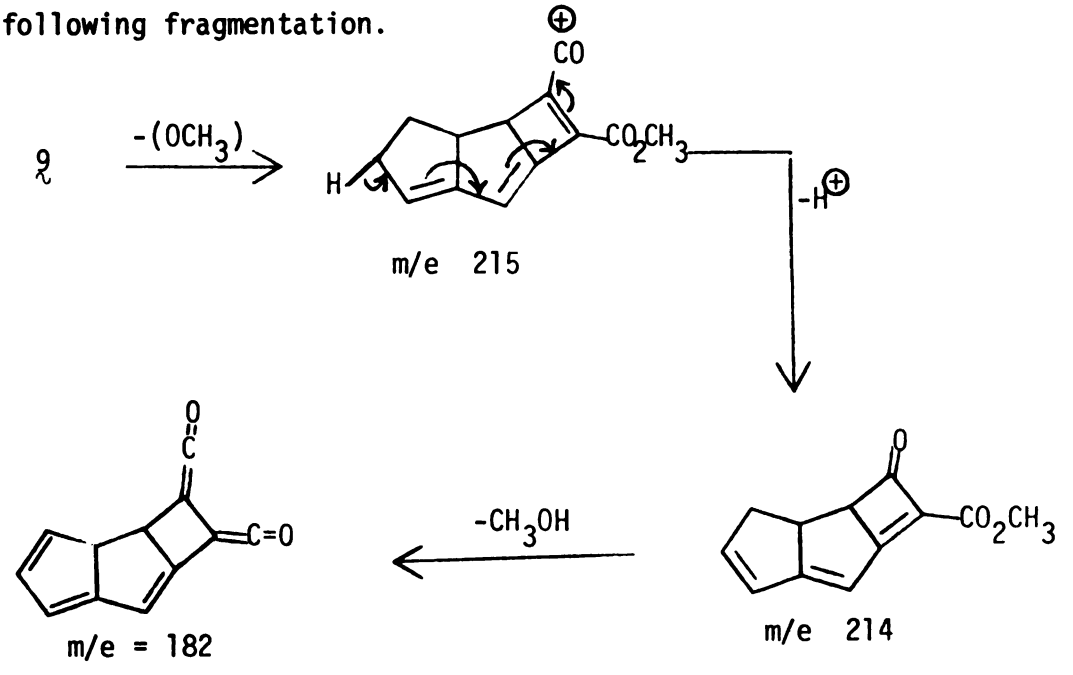
The fact that the base fragment (m/e = 182) loses CO (182 - 28 = 154) and yet another CO (154 - 28 = 126) and that there are two $-OCH_3$ signals in the nmr (τ 6.22 and 6.25) suggests that there are two carbomethoxyl groups. The base peak (m/e = 182) might then arise by the loss of two methanols. However, there was no parent peak at m/e 246 (182 + 64). The highest mass peak was at m/e 215, which corresponds to m/e 246 less a methoxyl group (m/e = 31). Since mass 246 would also correspond to a 1:1 addition product of cyclooctatetraene and dimethyl acetylene dicarboxylate, it was concluded that this probably was the

molecular weight of the compound. Several structures were considered and rejected as incompatible with spectroscopic data, with structure 9 remaining as a working hypothesis for the compound.

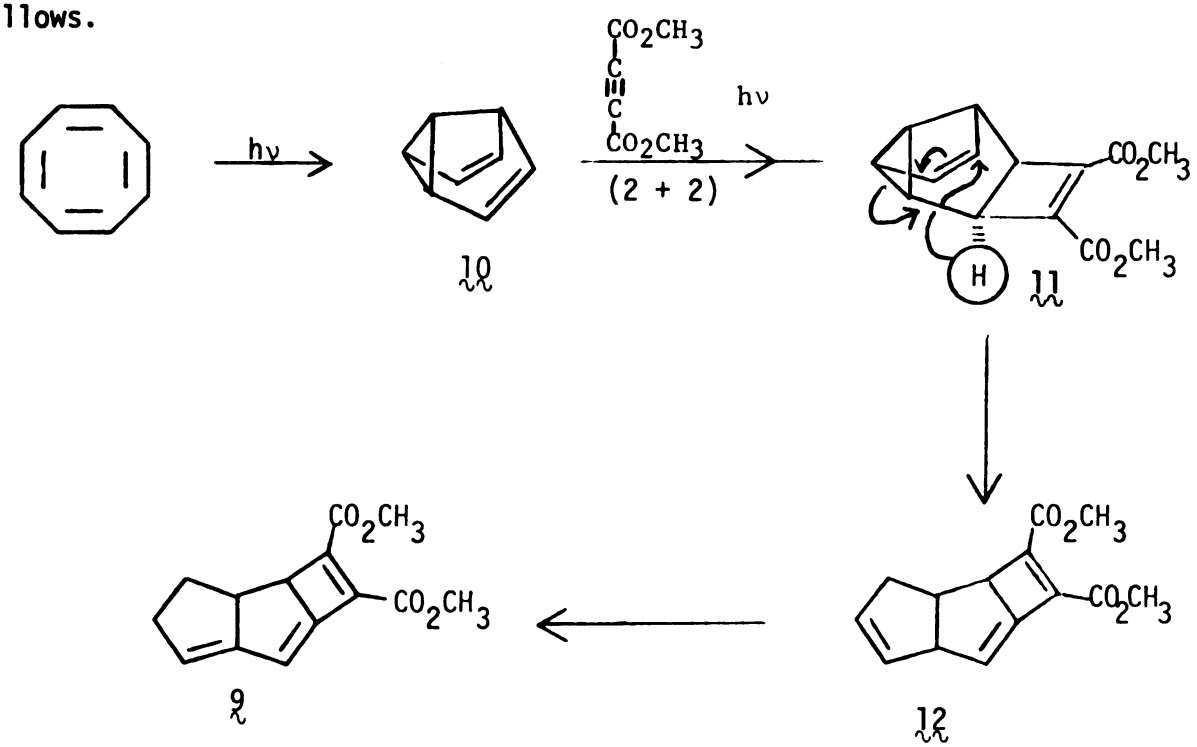


9

The nmr chemical shift values are indicated on a τ scale. The ready loss of a ($-OCH_3$) in the mass spectrum may arise from the following fragmentation.



A plausible mechanism for the formation of 9 could be as follows.



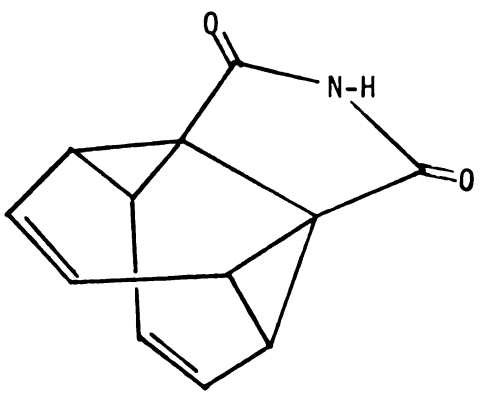
Thus cyclooctatetraene could have rearranged to semibullvalene[19] which in turn might have added a molecule of dimethyl acetylene dicarboxylate to produce the diester 11. 11 could have rearranged to 12 under the workup conditions,[20] followed by rearrangement to the more conjugated 9.

However, attempts to reproduce this reaction thus far have failed, due to some unidentified variable involved in the process.

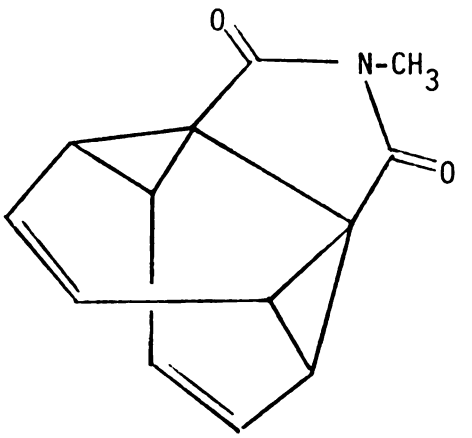
Since the photochemical reaction did not go in the direction desired, we temporarily abandoned the investigation of this interesting side product in order to pursue another approach.

The failure of the acetylene to add to cyclooctatetraene in a ($\pi_{2s} + \pi_{2s} + \pi_{2s} + \pi_{2s}$) process to produce truncated tetrahedrane led us to guess that the intermediate 8, if formed, is not produced in sufficient amounts to add another molecule of acetylene as suggested in Equation 4. This suggestion is plausible since other workers have observed that unsubstituted 8 is unstable at temperatures above -70°C.[21]

A report appeared at this time in the literature[22] that some substituted derivatives of 8 could indeed be isolated at room temperature, especially compounds 13 and 14.



13

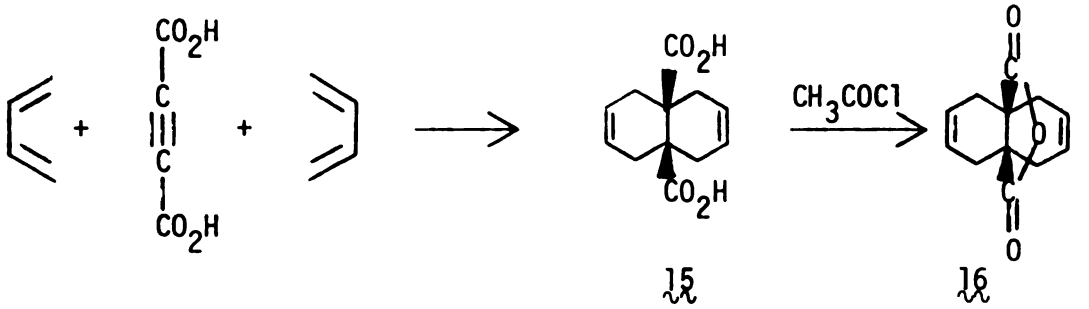


14

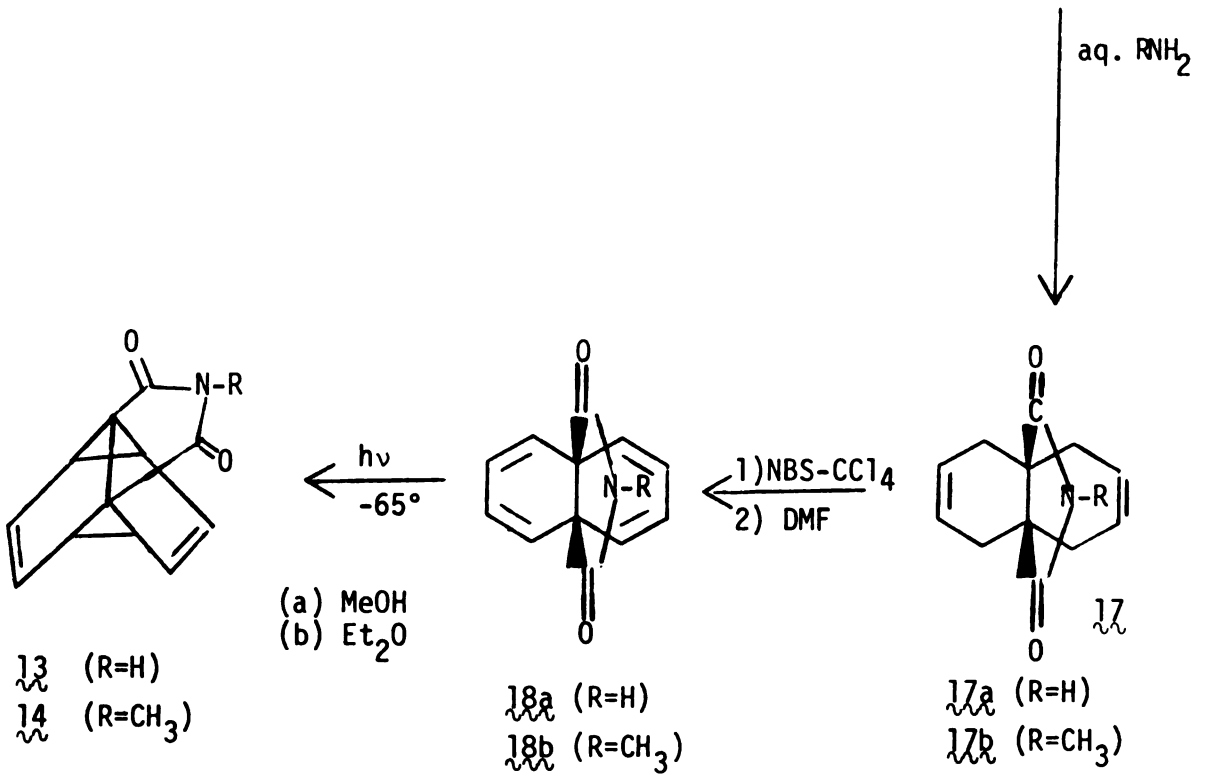
It was therefore decided to investigate the photochemistry of these two compounds, in the presence of various acetylenes. The compounds themselves were prepared in a manner similar to that reported.[22,23]

Thus reaction of acetylene dicarboxylic acid with butadiene in dioxane at 170°C in an autoclave gave the 1,4,5,8-tetrahydronaphthalene cis-9,10-dicarboxylic acid 15 in 39% yield. This

on treatment with acetylchloride gave the corresponding anhydride 16 in 75% yield. The anhydride on reaction with concentrated ammonium hydroxide or aqueous methylamine gave the corresponding dicarboximides 17a or 17b respectively in 60-75% yield. These on allylic bromination with N-bromosuccinimide followed by heating



15 16



13 (R=H)
14 (R=CH_3)

18a (R=H)
18b (R=CH_3)

17

17a (R=H)
17b (R=CH_3)

with N,N-dimethylformamide gave the tetraene dicarboximides 18a and 18b in 50-75% yield. The tetraene dicarboximide 18a in methanol and 18b in anhydrous ether on photolysis at -65 to -70°C gave the tetracyclic dicarboximides 13 and 14 respectively in 80-90% yield.*

Compound 13 was found to be insoluble in organic solvents such as pentane, ether, etc. and was soluble in tetrahydrofuran and methanol. Consequently the photolysis of this compound with various acetylenes under a variety of different conditions was carried out in these two solvents. The photolysis of Compound 13 with acetylenes at lower temperatures did not result in any reaction, whereas photolysis at room temperature simply led to the rearrangement of 13 to bicyclo[4.2.2]deca-2,4,7,9-tetraene-3,4-dicarboximide 19. The structure of 19 was established by comparison of its nmr spectrum with that already reported in the literature.[22] Rearrangement of compound 13 to 19 has been observed[22] thermally and is believed to occur as shown on the next page.

The observation that the rearrangement does not take place in the photolysis at lower temperatures suggests that the reaction probably proceeds by a thermal process.

The N-methyl derivative of 13, compound 14, was chosen for further study because of its ready solubility in most of the organic solvents. Again a variety of acetylenes under different conditions for the photoaddition was tried without any success.

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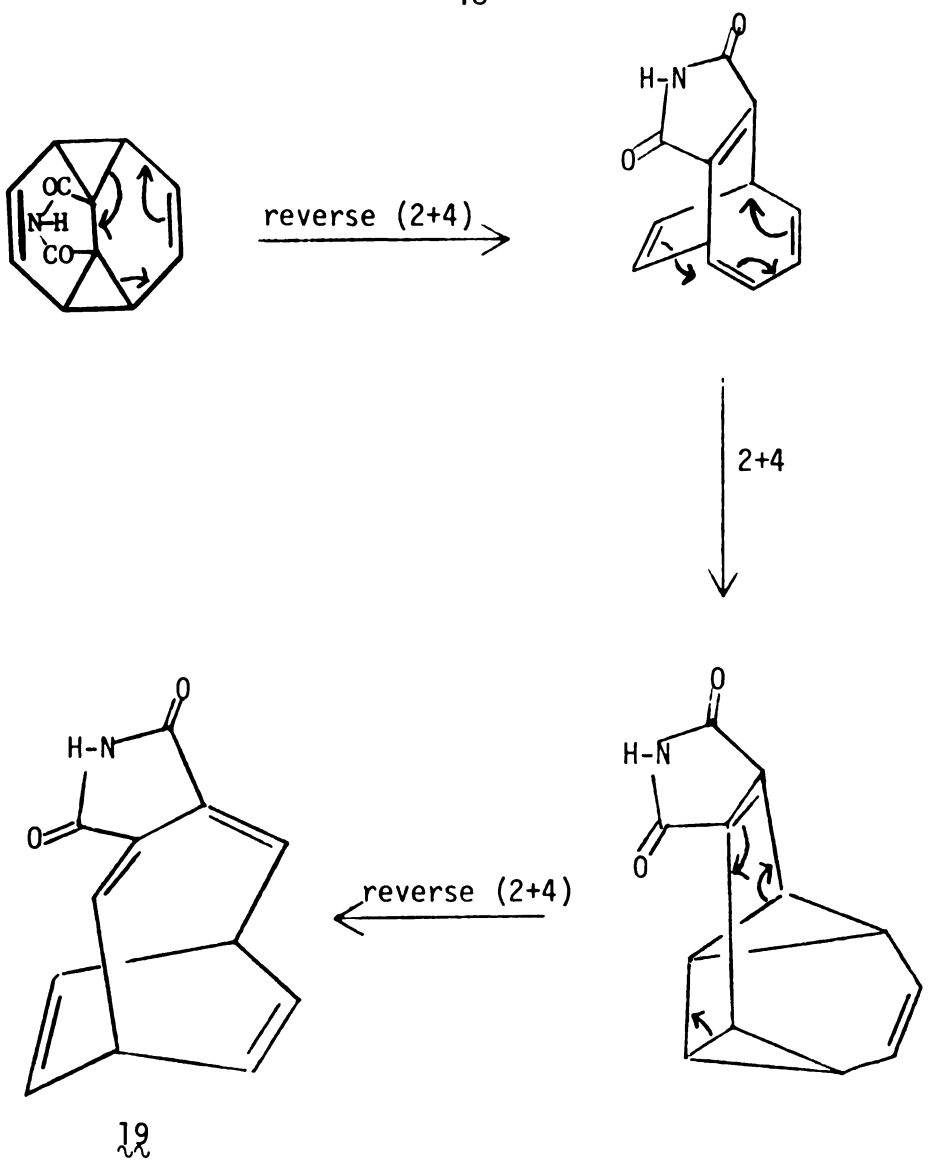
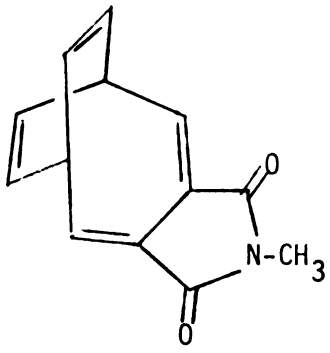
*Obtained by earlier workers in 40% yield.



19

Whereas the compound 13 rearranged to 19 in the photolysis at room temperature, compound 14 rearranged even at lower temperatures to 20. Some other derivatives of 8 have also been reported[22] to rearrange to bicyclodecatetraene derivatives at lower temperatures during photolysis.

Although these attempts have thus far failed to achieve the primary goal of synthesizing truncated tetrahedrane, nevertheless they have led to an interesting compound 9.

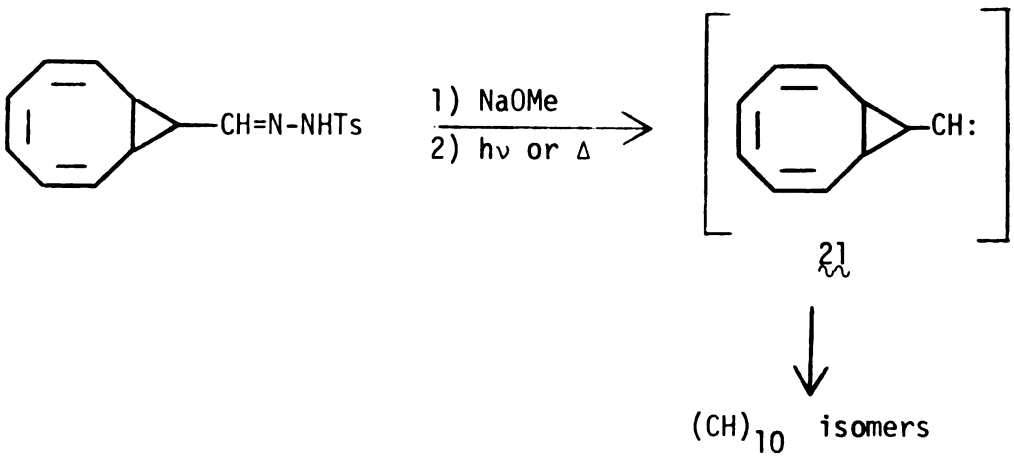


20

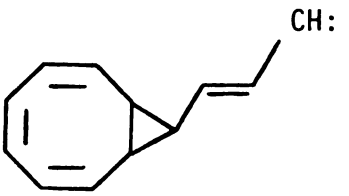
Several other conditions not attempted are yet to be explored. However, at this stage of the work another approach which we had been exploring for the synthesis of the $(CH)_{12}$ hydrocarbons was beginning to look more promising. We therefore turned our full attention to it as discussed in the next chapter.

DISCUSSION B

A number of successful synthetic approaches[3c,f,h,i] to the $(CH)_{10}$ hydrocarbons used the carbenoid intermediate 21 generated either thermally or photochemically from the sodium or lithium salt of the corresponding p-toluenesulfonylhydrazone 22. This is shown below.



Based on this, we felt that if we were to construct a $(CH)_{12}$ carbene with similar reactive centers such as cyclopropane bonds and double bonds within the molecule in conjugation with one another, then we might successfully synthesize several $(CH)_{12}$ isomers. To this end we decided to look for precursors to the carbenoid species 23.



23

Some of the rearrangements that this carbene might undergo are listed in Figure 7.

Thus the carbene 23 might rearrange to either 23a or 23b and thereby go to compounds 24, 25 or 26. Rearrangement of 23a to 23d might lead to either 27 or 28.

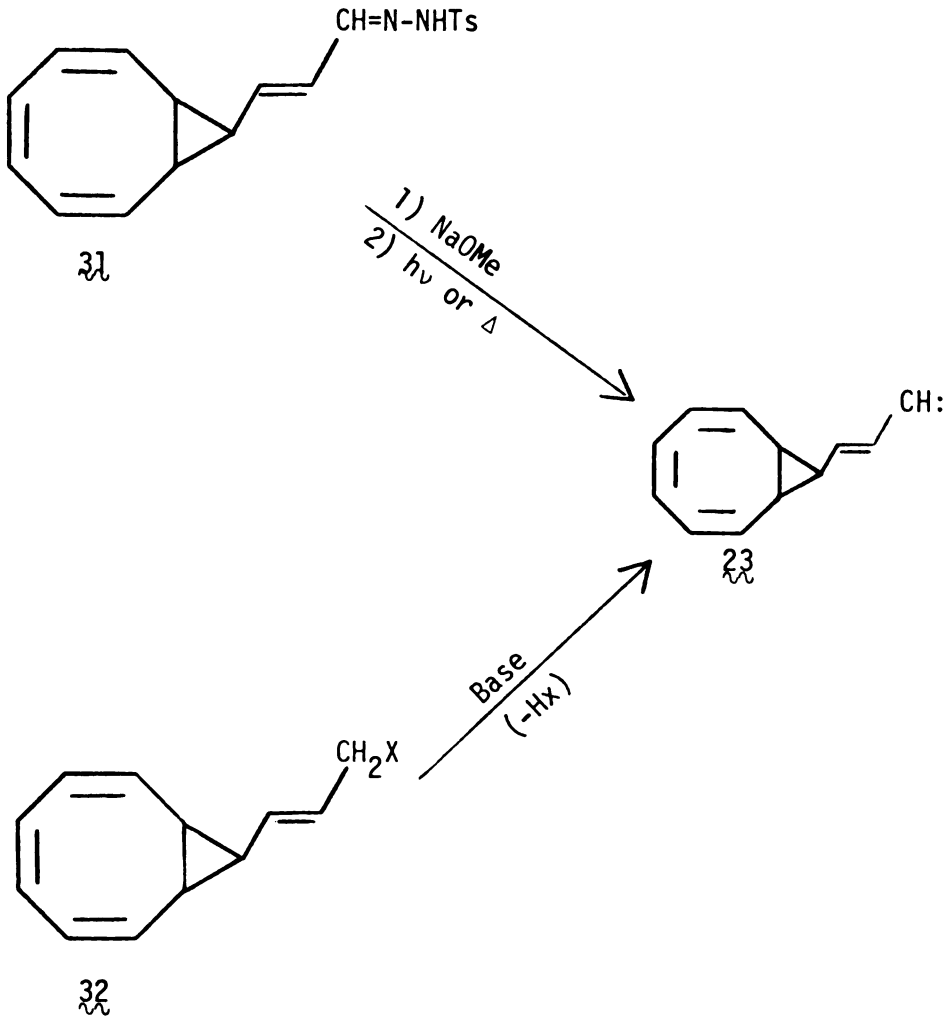
On the other hand the carbene might cyclize to give the cyclopropene 29, which on photolysis might undergo ring opening followed by a (4 + 2) reaction to give 30.

Except for compound 24, all others are yet unknown, though several groups are working on synthetic approaches to each one of them. Thus realizing the importance of the carbene 23, we decided to focus our attention on the synthesis of its precursors.

The carbene 23 might be generated by either of the two following methods:

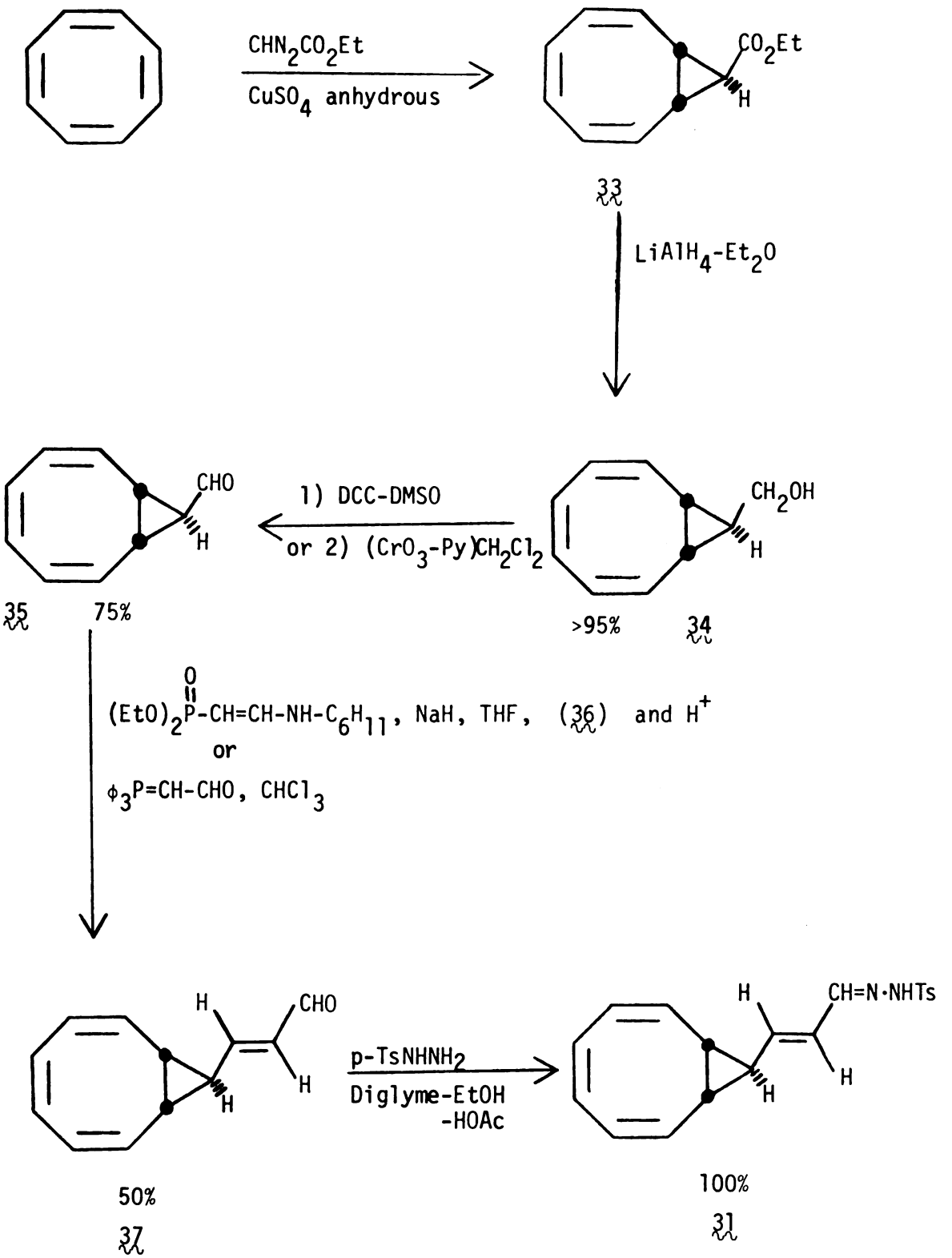
(i) by the pyrolysis or photolysis of the sodium salt of the corresponding p-toluene sulfonyl hydrazone 31 or

(ii) by the action of strong base on the corresponding allylic halide 32.



It was the first method that we decided to concentrate on, although work is currently being pursued on the second method in our laboratories.

The synthesis of the p-toluenesulfonylhydrazone 31 as worked out starting from cyclooctatetraene was as follows.


CHN2CO2Et
CuSO4 anhydrous
CO2Et
H
33
LiAlH4-Et2O
CHO
H
1) DCC-DMSO
or 2) (CrO3-Py)CH2Cl2
CH2OH
H
35
75%
>95%
34
(EtO)2P-CH=CH-NH-C6H11, NaH, THF, (36) and H+
or
φ3P=CH-CHO, CHCl3
H
CHO
H
H
50%
37
p-TsNHNH2
Diglyme-EtOH
-HOAc
H
CH=N·NHTs
H
H
100%
31

Thus reaction of cyclooctatetraene with ethyl diazoacetate in the presence of anhydrous copper sulfate at 100-110° has been known[24] to produce the bicyclic ester 33 in about 50% yield. The major component of the ester (95%) has the anti-configuration at the cyclopropane ring as is known from the coupling constants of the trans-cyclopropane hydrogens in the nmr (J = 5 Hz). This has also been shown by other workers chemically by oxidation to the corresponding cyclopropane trans-tricarboxylic acid.

The ester 33 on reduction with lithium aluminum hydride in anhydrous ether gave the alcohol 34 in greater than 95% yield. The alcohol on oxidation with either chromium trioxide and pyridine in methylene chloride,or dicyclohexyl carbodiimide and dimethyl sulfoxide gave the aldehyde 35 in 60-75% yield. The aldehyde on treatment with the anion of the enamine reagent[26] 36 or formyl methylene triphenyl phosphorane[27] in refluxing chloroform gave the unsaturated aldehyde 37 in 50% yield.

The unsaturated aldehyde 37, besides having the already mentioned anti-configuration at the cyclopropane ring, has a trans-geometry at the double bond, as shown by the coupling constant between the trans olefinic hydrogens in the nmr (J_{AB} = 16 Hz).

The compound had infrared absorptions at 2980, 2890, 2800, 1690, 1625 cm^{-1} and others, u.v. absorptions at 254 mμ (ϵ = 28,500), nmr ($CHCl_3$-d) peaks at, τ values, 0.60 (d, J = 7.5 Hz, 1H) 3.57-3.75

(complex AB pattern, J = 7.5 Hz, J_{AB} = 16 Hz, 2H) 4.0 (s, 4H), 4.1 (s, 2H), 8.1 (d, J = 5 Hz), 8.6 (m, 1H) and a parent peak in the mass spectrum at m/e = 172, with fragment peaks at 149, 143, 141 128 and others.

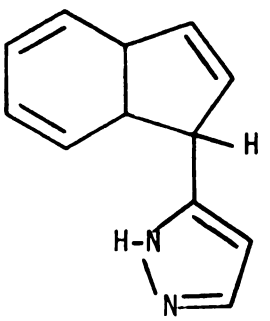
The unsaturated aldehyde 37, dissolved in ethanol on reaction with p-toluenesulfonylhydrazine dissolved in diglyme in the presence of a trace of acetic acid gave the corresponding p-toluenesulfonylhydrazone 31 in quantitative yield.

The tosylhydrazone had peaks in the ir at 3200, 1750, 1670, 1585, 1460 and 1440 cm^{-1}, nmr ($CHCl_3$-d) τ values, 1.9 to 2.7 (m, 6H becomes 5H in D_2O or CH_3-CO-CH_3d_6), 4-4.1 (d, 6H), 3.5-4.5 (AB pattern 2H), 7.6 (s, 3H), 8.35 (d, 2H), 8.8 (m, 1H). The parent peak in the mass spectrum was at m/e = 340 corresponding to $C_{12}H_{12}$ = N-NH-$SO_2C_7H_7$ ($C_{19}H_{20}N_2SO_2$).

The tosylhydrazone, on pyrolysis with an equivalent amount of sodium methoxide under a variety of conditions, yielded a pyrazole by rearrangement, rather than any $(CH)_{12}$ hydrocarbon. Even though this was contrary to our hopes, the rearrangement is well precedented[28] in the case of α:β unsaturated diazo compounds.

The pyrazole had the parent peak in the mass spectrum at m/e = 184 in conformity with the molecular formula $C_{12}H_{12}N_2$. It had peaks in ir at 3250, 1650 cm^{-1} and others, nmr at τ values 0.14 (bd s, 1H), 2.3-2.9 (m, 2H), 3.6-4.5 (m, 5H), 4.65 (d, J = 5 Hz, 1H), 6.4-7.0 (m, 3H).

Based on the number of vinylic and saturated hydrogens in the nmr, structure 38, shown below was considered as a possibility.

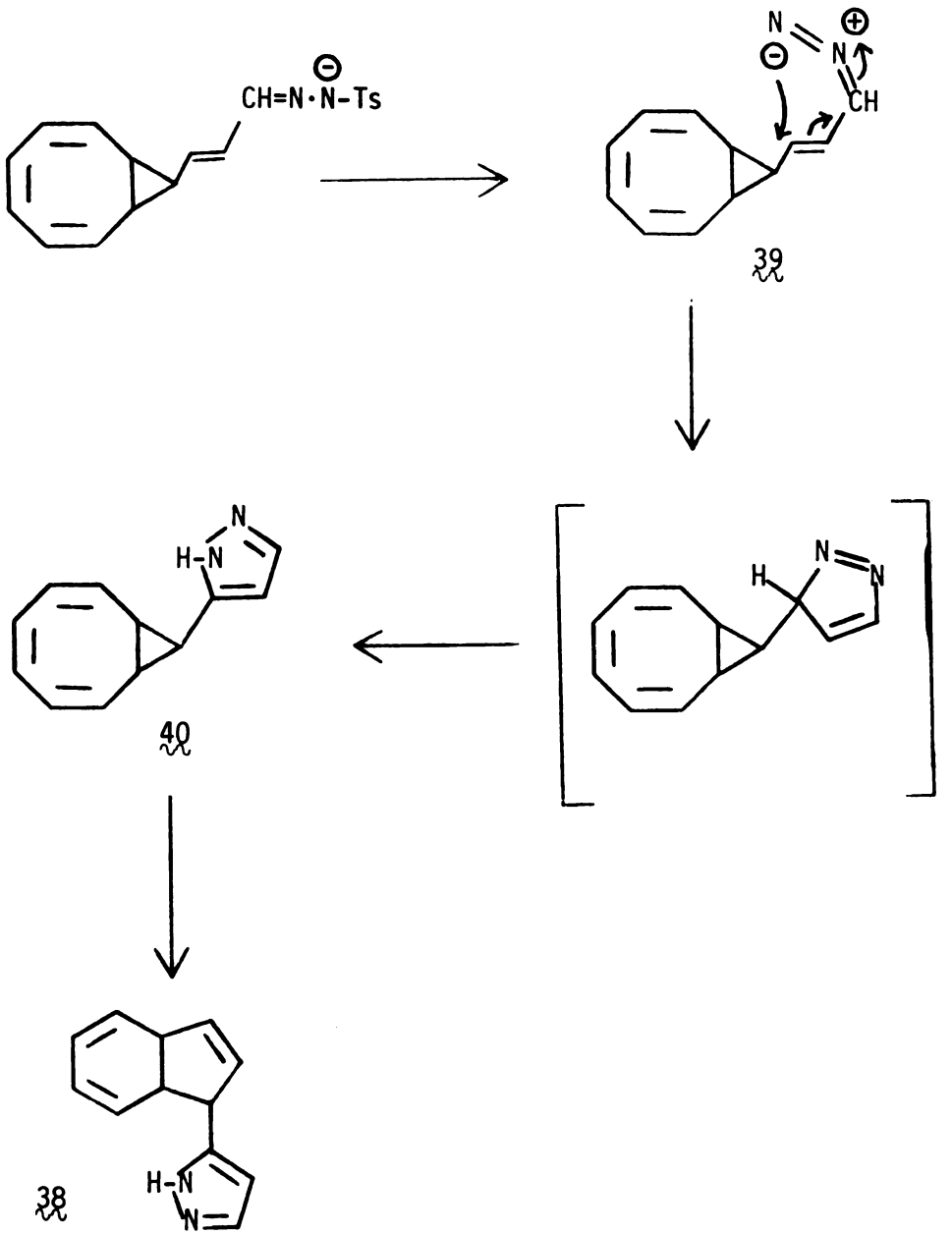


38

A plausible reaction path for its formation would be a cyclization of the initial diazo compound 39 formed, followed by a thermally allowed 1,5 hydrogen migration and hence the aromatization to the substituted pyrazole, 9-pyrazolino bicyclo[6.1.0]nonatriene 40. This might have undergone the well known[29] bicyclo[6.1.0]nonatriene-dihydroindene rearrangement under the pyrolytic conditions. This is illustrated on next page.

However, at this stage, we have not made any attempt either to ascertain the stereochemistry of the ring fusion or the gross structure of the pyrazole, because of our interest in another approach to the problem.

Because of our failure to effect the decomposition of the sodium salt of the p-toluenesulfonylhydrazone to the $(CH)_{12}$ hydrocarbons pyrolytically, we decided to turn our attention to the photochemical decomposition.

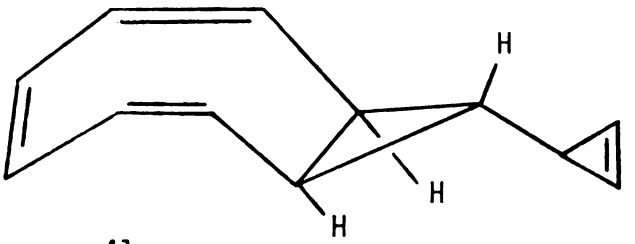


39

40

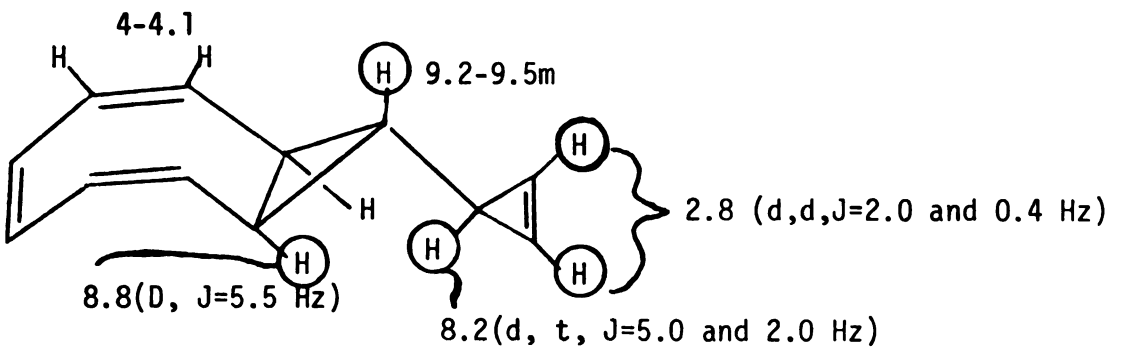
38

Our initial attempts to photolyze the tosylhydrazone in the presence of an equivalent amount of sodium methoxide led to little success using quartz or a Pyrex filter. Nevertheless, photolysis at -78°C in dry tetrahedrofuran using an acetone filter, did indeed give decomposition to the carbene, as evidenced by formation of compound 41 (= 29), obtained in 30-50% yield.

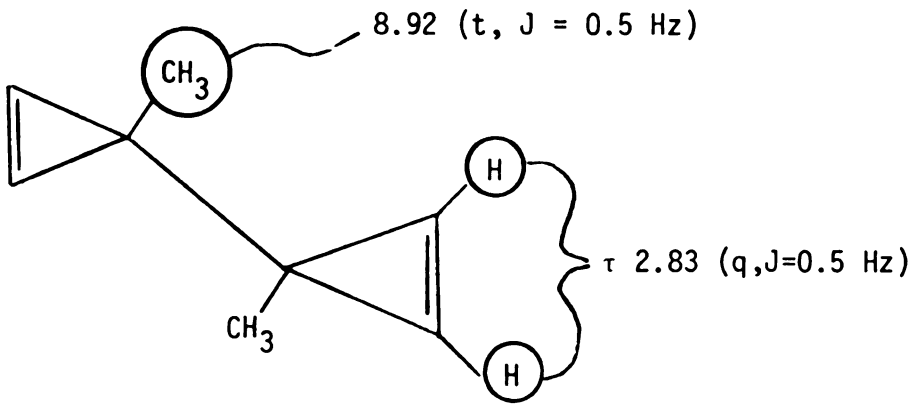


41

The structure 41 was assigned on the basis of its nmr, ir, and mass spectral data. Thus the nmr spectrum consists of peaks at τ 2.8 (d, d, J = 2 Hz and 0.4 Hz, 2H), 4-4.1 (d, 6H), 8.2 (d, t, J = 5.0 and 2.0 Hz, 1H), 8.8 (d, J = 5.5 Hz), 9.2-9.5 (m, 1H). The chemical shift assignments were made as follows by decoupling experiments and by analogy with the literature.



Thus the cyclooctatrienyl unit had the characteristic doublet at τ 4-4.1, and a doublet with a coupling constant of 5.5 Hz for the bridgehead cyclopropyl hydrogens. The cyclopropene hydrogen chemical shift values and coupling constants were assigned by comparison with the following reported nmr data for the compound 42.[30]

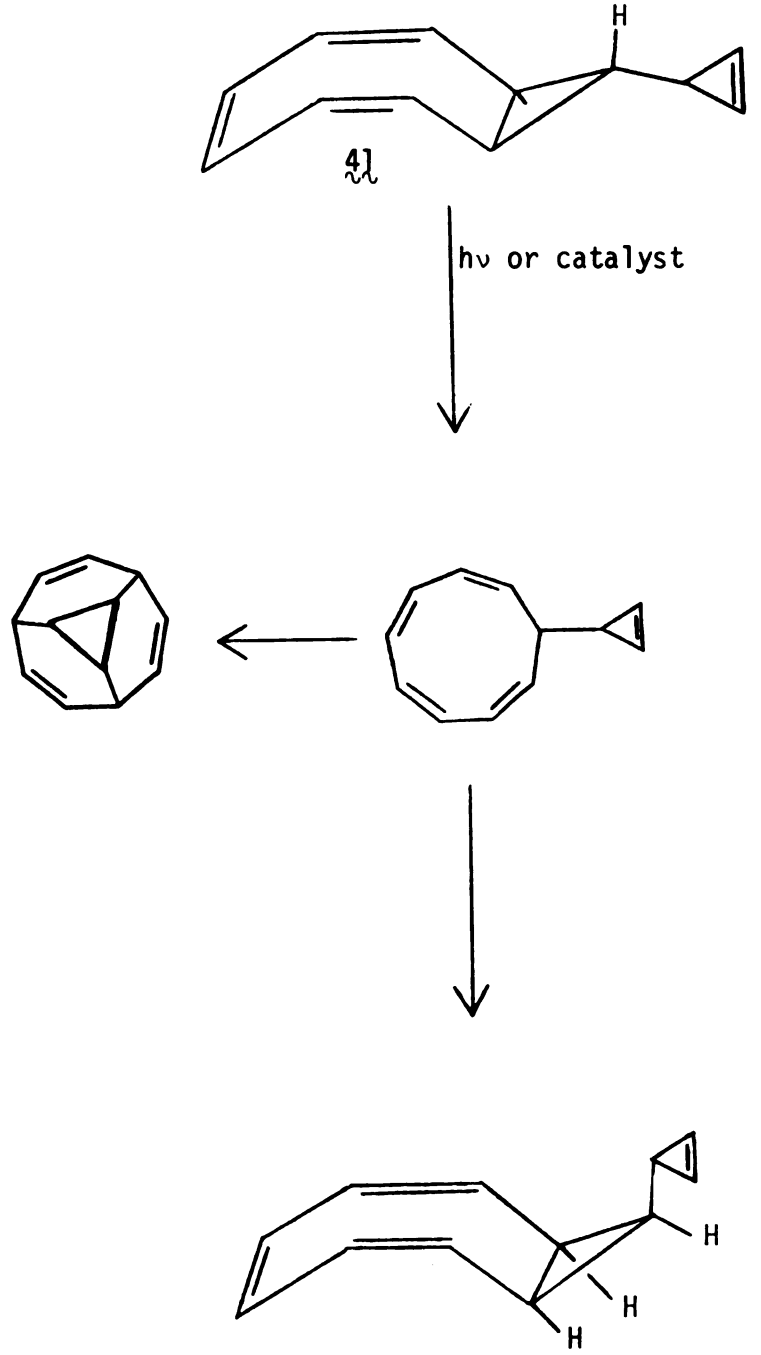


42

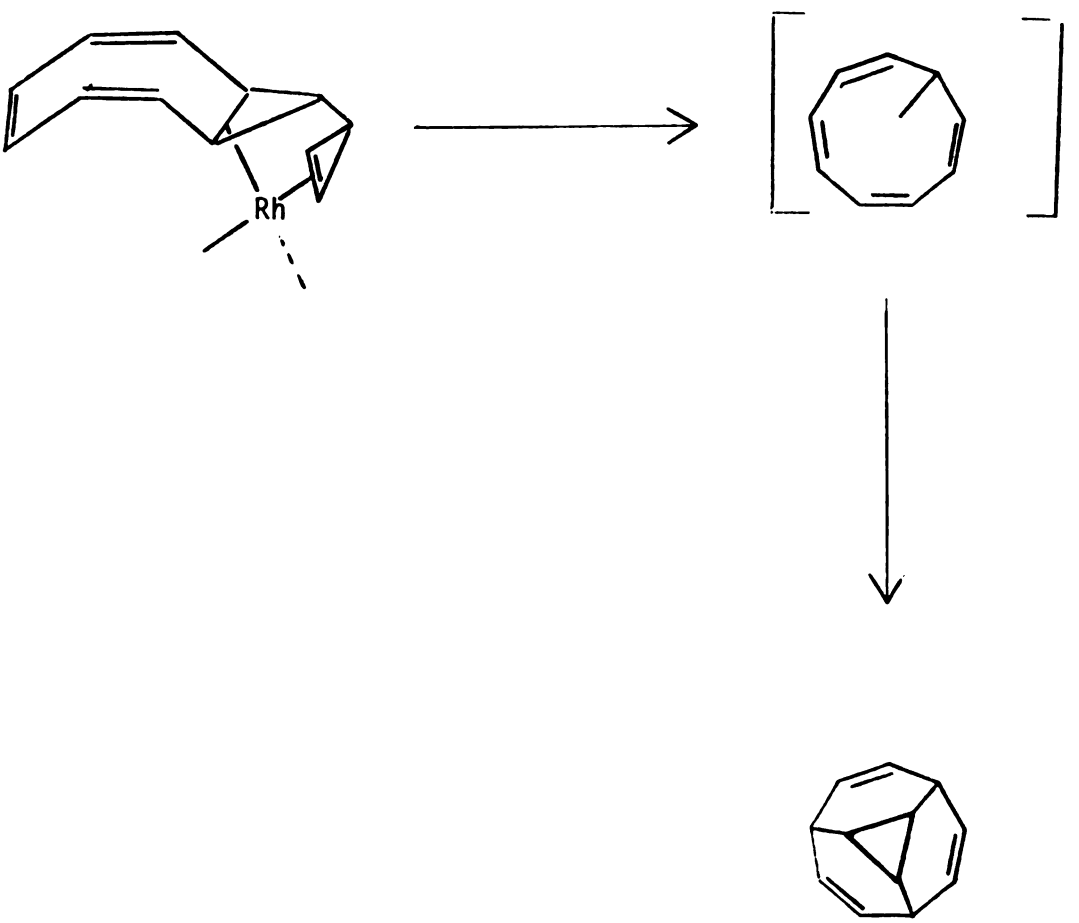
In the mass spectrum of the cyclopropene compound 41, the parent molecular ion peak was at m/e 156 corresponding to $C_{12}H_{12}$ and fragment ion peaks appeared at m/e 155, 141, 129, 128, 115, 91 (base peak), 78 and 39. These probably could be explained by the fragmentation pattern indicated on next page.

The cyclopropene 41 was extremely reactive and rapidly polymerized neat at room temperature, although a dilute pentane solution of it remained unchanged at Dry-Ice temperatures for several days. Because of the extreme reactivity of the compound, attempts to purify the material were not successful. Consequently the chemical shift assignments had to be made by spin decoupling experiments and by anology with similar compounds. The remaining components of the crude product mixture are not yet identified.

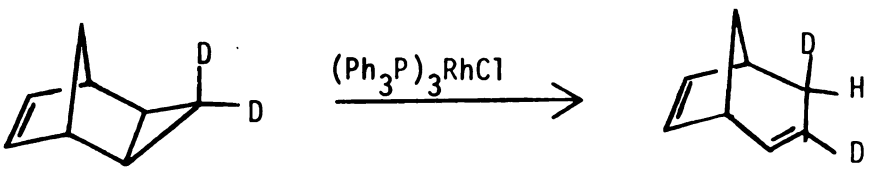
Once having obtained the cyclopropene 41 we concentrated our efforts on isomerizing it to other $(CH)_{12}$ hydrocarbons. Some of the possibilities are indicated below.



In order to try out these possibilities we first reacted the cyclopropene compound in pentane with a catalytic amount of diethylene rhodium-chloride-dimer complex, in the hope that the complex might cling to the cyclopropene double bond first and then open the other cyclopropane bond as shown.



A similar reaction has been reported[31] by Katz for compound 43.



43 43a

However, we did not succeed in effecting a similar reaction in 41. When compound 41 was stirred in pentane with a catalytic amount of diethylene rhodium chloride dimer overnight, the mixture filtered, the solvent removed, and the residue analyzed on tlc, there was a spot with an R_f of 0.8, with hexane. When this was separated by preparative tlc and an nmr taken, there was a sharp singlet at τ 8.60 and a small broad signal at τ 8.8-8.9. The mass spectrum of this compound indicated it to be a long straight chain hydrocarbon. In this run we had used the nmr sample of the compound 41 in carbon tetrachloride, to avoid polymerization of 41 in attempting to remove the carbon tetrachloride. However, when the reaction was run without any carbon tetrachloride but with or without compound 41, none of the above straight chain hydrocarbon was obtained. The pentane used had been purified before use and in itself did not contain any component with an R_f = 0.8 in hexane. Consequently the long chain hydrocarbon could have come only by the polymerization of pentane by the rhodium complex catalyst, in the presence of carbontetrachloride. When

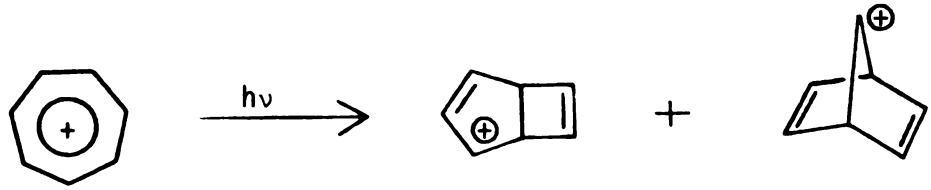
this was checked by treating purified pentane containing a little carbon tetrachloride with the rhodium complex, the long chain hydrocarbon was indeed obtained.

Having failed to isomerize 41 catalytically we decided to photolyze it at low temperatures. We attempted the photolyses in acetone, in pentane and in pentane with pyrene without any success.

Although this approach has thus far failed to achieve the synthetic goal of truncated tetrahedrane, nevertheless, it has proved to be a valuable entry to the $(CH)_{12}$ hydrocarbons, and the carbene generation from the allylic halide 32 might yet lead to some other interesting $(CH)_{12}$ hydrocarbons. This work is by no means complete and hence other innumerable efforts are being made to achieve the isomerization of compound 41 and relate it to other $(CH)_{12}$ hydrocarbons, known and unknown.

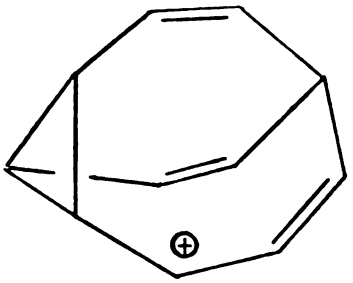
ANCILLARY PROJECT

The interconvertibility of the $(CH)_n$ hydrocarbons and the possibility of a common potential free energy surface for them could be extended to the $(CH)_n^+$ cations also. One such relationship has been shown by Childs,[32] and independently in our laboratories for the $(CH)_7^+$ cation. Thus when tropylium ion 44, is photolyzed it rearranges to 4-bicyclo[3.2.0]hepta-2,6-dienyl cation 45, and 7-norbornadienyl cation 46.



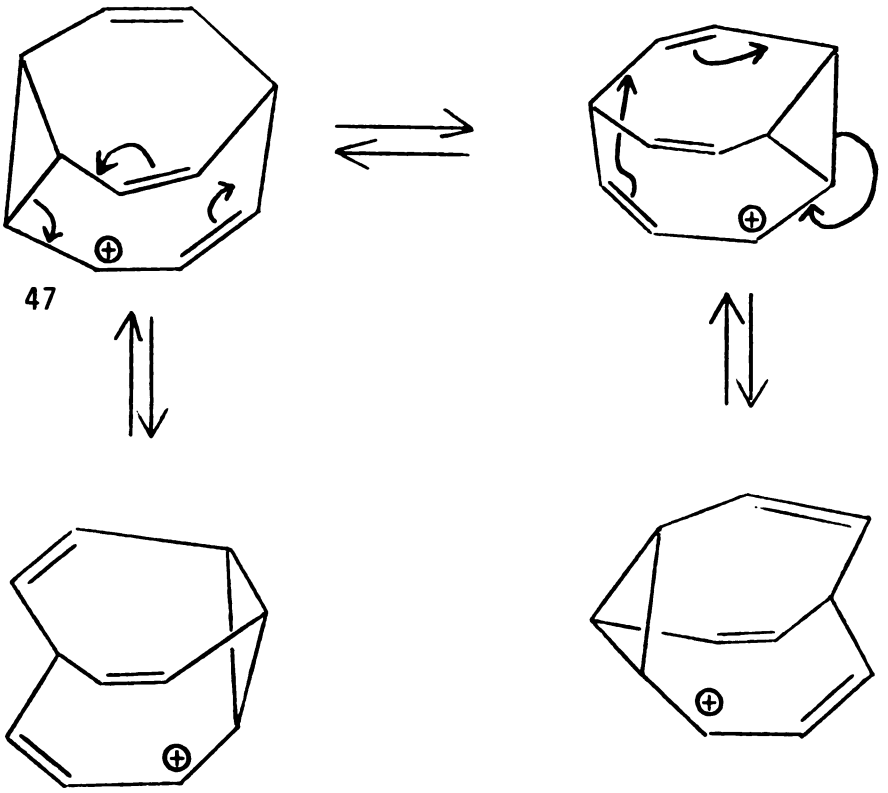
44 45 46

It was our opinion that there might exist such a relationship in $(CH)_{11}^+$ cations also. We were particularly interested in the cation 47, both because we had the synthetic precursor to it, bullvalene, available in our laboratories from other work, and because of some interesting characteristics it might have.



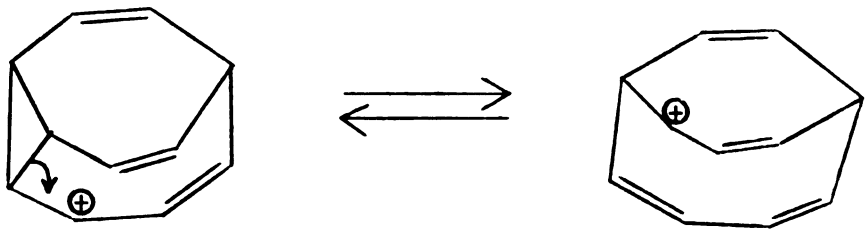
47

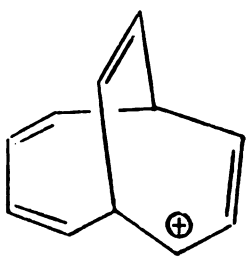
The cation 47 itself is cyclopropyl carbinyl and allylic in character and might therefore be reasonably stable. It is also capable of rearranging to itself, as indicated below, by a thermally allowed process.



Such a degenerate rearrangement would lend itself to detection by the determination of the variable temperature nmr spectrum of the cation in super acid medium.

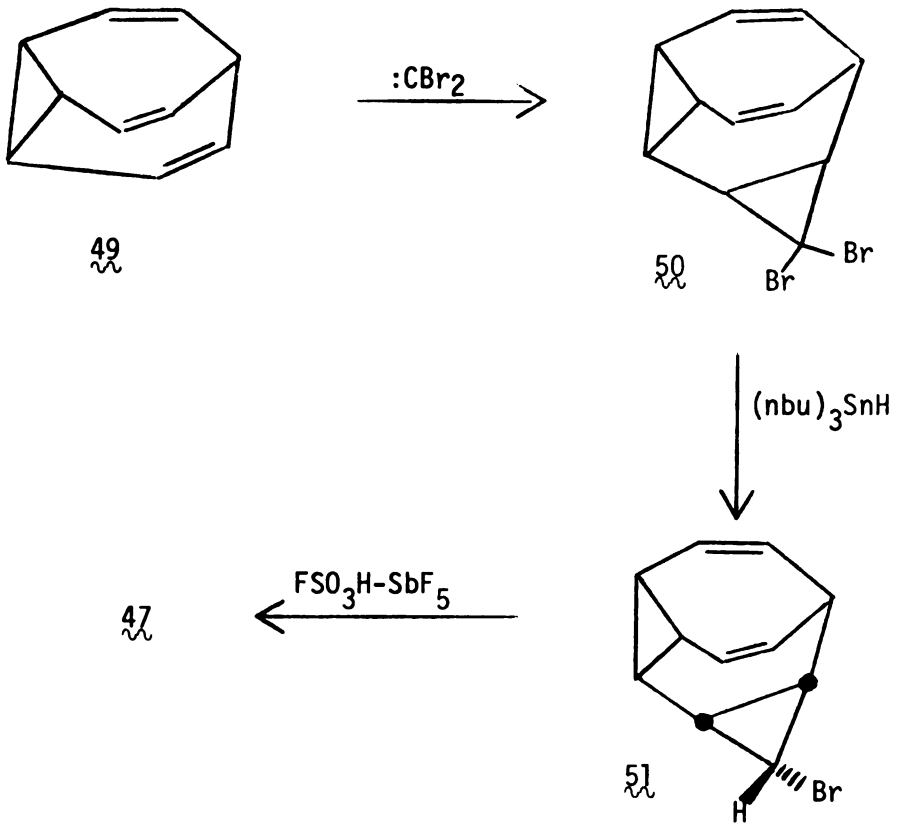
On the other hand, the cation might rearrange to 9-bicyclo-[4.3.2]undeca-2,4,7,10-tetraenyl cation 48, which is predicted to be bicycloaromatic.[33]





48

Soon after we realized the importance of this cation we turned our attention to the obvious synthetic route shown below for its synthesis.

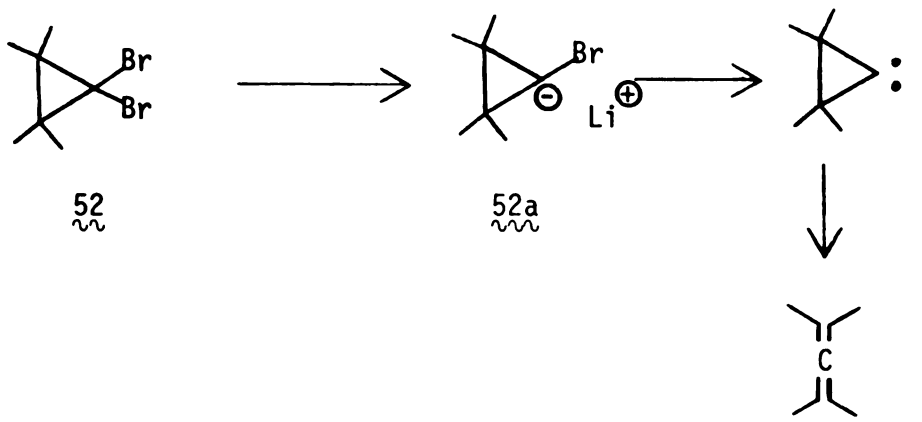


49 50 51 47

Thus, bullvalene, on reaction with tribromomethylphenyl mercury in refluxing benzene, gave the dibromohomobullvalene 50 in about 60% yield.

When we attempted to reduce the dibromide with tri-n-butyl tin hydride at lower temperatures, there was no reaction, and at higher temperatures, a complex mixture of products resulted which was not easily separable.

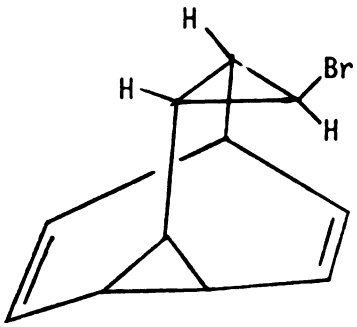
We therefore were interested in finding some other stereoselective stepwise reduction of the dibromide. We turned our attention to the organolithium reagents, which are known[34] to convert gem-dibromocyclopropanes to allenes by the following route.



52 52a

It was our opinion that if we were able to trap the halocyclopropyl carbanion 52a, by a proton source before it could lose bromide ion to go to the cyclopropyl carbene, we would have a nice method for the reduction of dibromocyclopropane to monobromocyclopropane. Further if the bromine atom initially removed by the organolithium were the less hindered one (exo in the case of bicyclics) and the quenching were to take place from the same side (this is possible because cyclopropyl carbanions are known to invert very slowly), then the reduction would be stereospecific (endo-bromocyclopropyl compounds are hard to obtain by the addition of bromocarbenes to olefins).

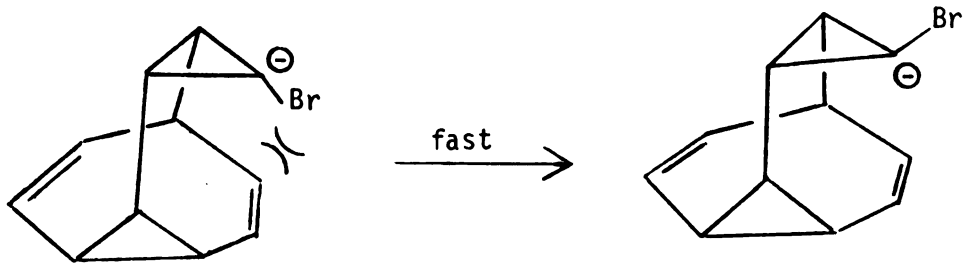
When we reacted the dibromide 50 with n-butyllithium at -78°C in anhydrous ether, immediately quenched with ethanol, allowed the mixture to warm up to room temperature and worked it up with water, we obtained a compound in 88% yield which had a triplet (J = 3.5) at τ 6.7 for one hydrogen in the nmr besides all the other peaks in common with the dibromide. Based on the coupling constant and comparison with an authentic spectrum supplied by Professor Goldstein of Cornell University this was determined to be the exo-bromide 53.



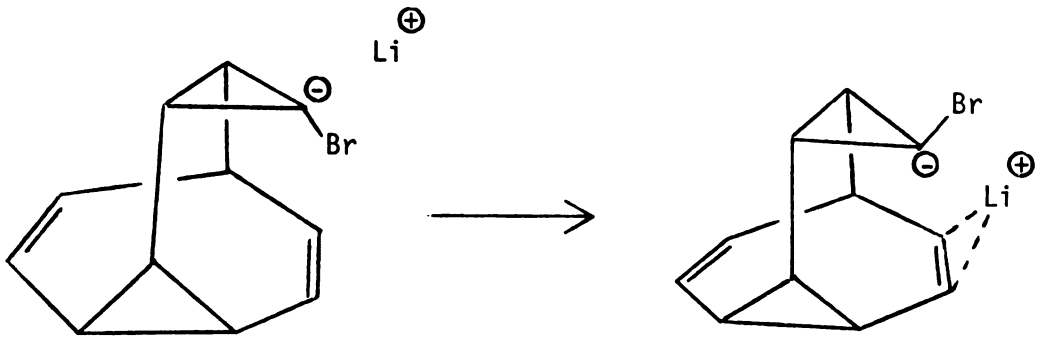
53

We were surprised at this result initially, since it would mean that the endo bromide (syn) was reduced. This might be because of either of the following:

(i) The halocarbanion intermediate might invert because of strong steric effects between the bromine and the vinyl bridge before getting quenched.



(ii) The counter ion Li^+ may be strongly bound to the vinyl brdige in the transition state, furnishing the proton for quenching from the endo-side.



In order to see if the reduction would be stereospecific in less rigid systems we attempted the reduction in an analogous manner with 7,7-dibromonorcarane and 9,9-dibromo bicyclo[6.1.0]-non-4-ene.

In the case of the dibromonorcarane, the reduction was effected in 85% yield with the ratio of endo to exo bromide in the product being 65:35, a result comparable to that obtained by tri-n-butyl tin hydride.[35]

In the case of the dibromobicyclo[6.1.0]nonene the reduction was effected in 75% yield with the ratio of syn to anti bromine being 85:15.

Thus the reactions was found to be generally stereoselective (although in certain special cases like the homobullvalene it was stereospecific in the opposite sense), extremely clean, easily workable and very easily applicable to thermally unstable compounds (in the case of tributyl tin hydride, the tributyl tin halide formed is usually separated by distillation).

At this stage of the homobullvalene cation problem, while we were looking for other alternatives for obtaining the endo-bromide, we were informed by Professor Goldstein of Cornell University and Professor Groves of the University of Michigan, that they were working on the same problem. We therefore, decided to abandon our efforts, satisfying ourselves with the new synthetic method developed for the reduction of gem-dibromocyclopropanes.

EXPERIMETTAL

General

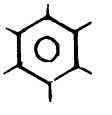
Melting points were taken on a Thomas Hoover melting point apparatus and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 137B infracord spectrophotometer. The mass spectra were taken by Mrs. Lorraine Guile of the Chemistry Department on a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. The nmr spectra were taken on a Varian T-60 nmr spectrometer. The ultraviolet spectra were recorded on a Unicam SP 800 or a Beckman DB spectrometer. The gas chromatographs were run on an F&M model 700 laboratory chromatograph and the peak ratios reported were not corrected for the thermal conductivity detector response for the compounds.

Attempted Photoaddition of Cyclooctatetraene to Various Acetylenes.

The photolyses were varried out in a regular photolysis vessel, with a nitorgen inlet at the bottom to stir the solution. Unless otherwise noted a 550 watt Hanovia Hg vapor lamp in a quartz immersion well was used. All the low temperature photolyses were carried out using precooled ethanol as coolant for the immersion well, the photolysis vessel itself being immersed in Dry-Ice and acetone. The U.V. spectrum of the ethanol was frequently checked to make sure that it had no absorption. The reactions were monitored by VPC or by TLC on silica gel, looking for the appearance of any new peaks

TABLE 1

Photolysis of Cyclooctatetraene with Various Acetylenes
Using a 550 Watt Medium Pressure Hg Vapor Lamp

	Acetylene	Solvent	Sensitizer	Temp	Time	Product Isolated
1	2-Butyne	Ether	Nil	25°	1 week	Nil
2	2-Butyne	Ether	Ph-CO-PH	25°	1 week	Trace of 
3	Acetylene-dicarboxylic acid	Ether	Nil	25°	3 days	Nil
4	Dimethyl-acetylene-dicarboxylate	Ether	Nil	-60°	1 week	Nil
5	Dimethyl-acetylene-dicarboxylate	Ether	Ph-CO-Ph	25°	1 week	Some polymeric material
6	Dimethyl-acetylene-dicarboxylate	Ether	Nil	25°	1 week	Nil
7	Dimethyl-acetylene-dicarboxylate	CH_2Cl_2	Ph-CO-Ph	-60°	8 hrs	9%
8	2-Butyne	CH_2Cl_2	Nil	-60°	8 hrs	Nil
9	2-Butyne	CH_2Cl_2	Ph-CO-Ph	-60°	8 hrs	Nil
10	Dimethyl-acetylene-dicarboxylate	CH_2Cl_2	Nil	-60°	8 hrs	Nil

or spots respectively. The photolyses were carried out at different concentrations of reactants. Various acetylenes attempted are listed in the Table on the previous page.

Photoaddition of Dimethylacetylenedicarboxylate to Cyclooctatetraene.

A solution of cyclooctatetraene (10.4 g, 0.1 mole), dimethylacetylenedicarboxylate (42.6 g, 0.3 moles) and benzophenone (0.5 g) in methylene chloride (250 ml) was photolyzed at -60°C with a 550 watt mercury vapor lamp. Nitrogen was bubbled through the solution throughout the photolysis. The reaction was monitored by TLC on silica gel, using 20-80 benzene-hexane. A new spot with an R_f less than either of the reactants appeared after photolyzing for 6 hours. The solution was further photolyzed for 2 hours, methylene chloride was removed on a rotary evaporater and the residue was distilled. Cyclooctatetraene (8 g) distilled over at 25° at 1 mm, an intermediate fraction (5 g) distilled at 30-35° at 1 mm and then dimethylacetylenedicarboxylete (32 g) at 38-40° (0.5 mm). The residue, which contained some dimethylacetylenedicarboxylate, was then chromatographed on Florisil. Benzophenone and dimethylacetylenedicarboxylate were eluted with petroleum ether and a new compound 9 (500 mg) was obtained on elution with petroleum ether-benzene (60-40) mixture. The compound, a light yellow oil, gave >95% in a single peak on PVC and had the following spectral characteristics: ir: 1730, 1655, 1640, 1260, 1125, 1060, 1040 and 930 cm^{-1}; nmr ($CHCl_3$-d): τ values 3.44 (d, J = 1.4 Hz, 1H), 4.9 (dt, J = 7.5 Hz, 1.4 Hz, 1H), 6.2 (m, 2H), 6.22 (s, 3H), 6.25 (s, 3H), 7.6-8.1 (bd m, 4H); uv (MeOH): 210 mμ (ε > 20,000), 268 mμ (ε = 4,000); mass spectra: (m/e) 215, 214, 188, 182, 173, 154, 142, 126, 113, 95, 70 and 53.

1,4,5,8-Tetrahydronaphthalene-cis-4a,8a-dicarboxylic Acid (15).

Acetylenedicarboxylic acid (228 g, 2 moles), butadiene (500 ml) and dry dioxane (700 ml) were heated in a stainless steel bomb at 170°C for 20 hours. The dioxane was removed on a rotary evaporator and 2 l. of carbon tetrachloride was added to the semisolid residue. The precipitated dicarboxylic acid (70 g) was filtered and the filtrate was concentrated to dryness on a rotary evaporator. The residue was then heated with 20% sodium hydroxide solution (600 ml) on a steam bath for 2 hours, to hydrolyze any anhydride that might have been formed during the reaction. The solution was then cooled and acidified with cold dilute sulfuric acid. The precipitated dicarboxylic acid was filtered and washed with cold water to give 100 g of crude product. The combined products were recrystallized from acetone. mp 217-220° (lit. mp 220-226°).

1,4,5,8-Tetrahydronaphthalene-cis-4a,8a-dicarboxylic Acid Anhydride (16).

The dicarboxylic acid 15 (55 g, 0.25 mole) was stirred with acetyl chloride (200 ml) for 5 hours. Most of the acetyl chloride was then distilled off and the residue poured into hexane (300 ml). The off-white solid was filtered and recrystallized from 600 ml of hexane to yield colorless crystals of the anhydride. Yield 39 g (76%), mp 99-100° (lit. mp 102-103°). i.r. (Nujol mull) 3030, 1850, 1780, 1625 cm^{-1}.

1,4,5,8-Tetrahydronaphthalene-cis-4a,8a-dicarboximide (17a).

The anhydride 16 (8 g, .04 mole) and concentrated ammonium hydroxide (500 ml of 25-28% solution of NH_3) were refluxed in a 1 l. round-bottom flask for 6 hours. The mixture was cooled and stirred overnight. The precipitated solid (3 g) was filtered and filtrate was extracted with ethyl acetate (2 x 100 ml). The organic layer was dried over anhydrous sodium sulfate and the solvent was removed on a rotary evaporator. The residual solid (3 g) was combined with the precipitate obtained and recrystallized from 95% ethanol to give the product (5 g, 62%), mp 215-216° (lit. mp 217-219°), ir (Nujol mull) 3150, 1770 and 1710 cm^{-1}, nmr $CHCl_3$-d τ values 4.15 (t, J = 4 Hz, 4H), 7.15-8.15 (4 broad signals, 8H).

N-Methyl-1,4,5,8-tetrahydronaphthalene-cis-4a,8a-dicarboximide (17b).

The anhydride 16 (8 g, .04 mole) and 40% aqueous methylamine (200 ml) were refluxed in a 500 ml round-bottom flask for 4 hours. The solution was then cooled and stirred overnight. The solid precipitate was filtered, washed with water and recrystallized from ethanol to give the product (7.2 g, ~85%), mp 158-170° (lit. mp 161-162°), ir (Nujol Mull) 1770 and 1700 cm^{-1}, nmr ($CHCl_3$-d) τ 4.15 (t, J = 4 Hz, 4H), 7.0 (s, 3H), 7.15-8.15 (4 bd signals, 8H).

Naphthalene-4a,8a-dicarboximide (18a).

The diene dicarboximide 17a (5 g, 0.025 moles), benzoyl peroxide (50 mg), N-bromosuccinimide (9.6 g, 0.054 moles) and carbon tetrachloride (500 ml) were taken in a 1 l. flask fitted with a reflux condenser. The magnetically stirred solution was kept under gentle reflux with an ir lamp until all the NBS had reacted. It was then filtered and the filtrate was concentrated on a rotary evaporator to dryness. The residue was diluted with 400 ml of N,N-dimethyl formamide and heated in an oil bath to 100°C. It was kept at 100° overnight and then cooled and poured into 1.5 l. of water and extracted with ether (3 x 200 ml). The ether extracts were washed with water, dried over anhydrous magnesium sulfate and concentrated. The residual semi-solid weighed 3 g and on recrystallization from 95% ethanol gave the product (2.5 g, 51%), mp 162-164 (lit. mp 164-165°), ir (Nujol mull) 3180, 1780, 1700, 1590 cm^{-1}, nmr ($CHCl_3$-d) τ symmetrical-multiplet at 4.2.

N-methylnaphthalene-4a,8a-dicarboximide (18b).

N-methyldieneimide 17b (5.4 g, 0.025 mole), N-bromo succinimide (10 g, 0.056 mole), benzoyl peroxide (50 mg) and carbon tetrachloride (500 ml) were taken in a 1 l. round-bottom flask fitted with a reflux condenser. The magnetically stirred solution was kept under gentle reflux until all the NBS had reacted. The solution was then filtered and the filtrate concentrated to dryness. The residue was diluted with 400 ml of N,N-dimethyl

formamide and heated at 100° in an oil bath overnight with magnetic stirring. The solution was then poured into 1-5 l. of ice-cold water and extracted with ether (3 x 200 ml). The extracts were washed with water, dried over anhydrous magnesium sulfate and concentrated. The residue on recrystallization from methanol gave the product (3 g, 61%), mp 151-152°C (lit. mp. 151-152°), ir (Nujol mull) 1780, 1710, 1590 cm^{-1}, nmr ($CHCl_3$-d) τ 4.1 (sym. mult., 8H), 6.87 (s, 3H).

Tetracyclo[4.4.0.$0^{2,10}$.$0^{5,7}$]deca-3,8-diene-1,6-dicarboximide (13).

A methanolic (300 ml) solution of the tetraene dicarboximide 18a (3 g) was irradiated using a 200 W Hg vapor lamp in a quartz immersion well, in a regular photolysis vessel cooled externally by a Dry-Ice-acetone bath. Precooled ethanol was circulated for cooling the immersion well. The effective temperature in such a set-up was found to be about -60°C. After 4 hours of irradiation the precipitated solid was filtered and the filtrate concentrated to dryness. The residue was triturated with 10 ml of methanol and filtered to give another 0.75 g of solid. The nmr spectrum of the two portions was identical to that reported[22] for the tetracyclic imide 13 (combined 2.35 g, 78.3%), nmr ($CHCl_3$-d) τ 4.0 (bd s, 4H), 7.8 (bd s, 4H), ir (Nujol mull) 3200, 1780, 1700, 1640 cm^{-1}, mp 246-255° (rearranged).

N-methyl Tetracyclo[4.4.0.$0^{2,10}$.$0^{5,7}$]deca-3,8-diene-1,6-dicarboximide (14).

An ethereal (200 ml) solution of N-methyl tetraeneimide 18b (2 g) was photolyzed in the set-up described above for 4 hours. The precipitated solid (0.5 g) was filtered and the filtrate was concentrated to dryness and the residue triturated with 10 ml of methanol, and filtered to give another 1.2 g of solid. The two portions of the solid had nmr spectra consistent with the expected product (combined 1.7 g, 85%), mp 204-208°C (rearranged), nmr ($CHCl_3$-d) τ 4.1 (bd s, 4H), 7.8 (bd s, 4H), 6.82 (s, 3H), mass spec M^+ 213, fragment ions at 156, 155, 128, 127, 102, 78, 77, 64 and 63.

Attempted Photoaddition of the Tetracyclic Imides 13 and 14 with Various Acetylenes.

The photolyses of the two compounds with different acetylenes were carried out in a regular photolysis vessel in dilute solution, with a 200 watt medium pressure Hanovia Hg vapor lamp using a quartz immersion well. The low temperature photolyses were carried out similar to that described above, using precooled ethanol for cooling the immersion well. The various acetylenes attempted with the two compounds, the solvents used and the conditions employed are listed in the following Table.

TABLE 2

Photolysis of 13 and 14 with Various Acetylenes

Comp	Acetylene	Solvent	Sentisizer	Temp	Time	Product Isolated
13	Dimethyl-acetylene-dicarboxylate	THF	Nil	-60°	3 hrs	Nil
13	Dimethyl-acetylene-dicarboxylate	Methanol	Nil	25°	3 hrs	19
13	Dimethyl-acetylene-dicarboxylate	THF	Nil	25°	4 hrs	19
13	Acetylene-dicarboxylic acid	Methanol	Nil	-60°	4 hrs	Nil
13	Acetylene-dicarboxylic acid	Methanol	Nil	25°	24 hrs	19
13	2-Butyne	Methanol	Nil	-60°	4 hrs	Nil
14	2-Butyne	Nil	Ph-CO-Ph	0°	24 hrs	20
14	2-Butyne	Et_2O	Nil	-60°	53 hrs	20
14	2-Butyne	CH_2Cl_2	Ph-CO-Ph	-40°	6 hrs	20
14	1,4-Dimethoxy-2-butyne	Et_2O	Nil	-60°	12 hrs	Nil
14	Dimethyl-acetylene-dicarboxylate	CH_2Cl_2	Nil	-60°	8 hrs	Nil
14	Dimethyl-acetylene-dicarboxylate	CH_2Cl_2	Ph-CO-Ph	-60°	8 hrs	Nil

The progress of the reaction was monitored by TLC on silica gel. The rearranged dicarboximides 19 and 20 were identified by their melting points and nmr spectra, already reported in the literature.[22]

9-Carbethoxybicyclo[6.1.0]nona-2,4,6-triene 33.

A mixture of cyclooctatetraene (150 ml) and anhydrous copper sulfate (10 g) was taken in a 500 ml three-neck round-bottom flask fitted with a N_2 inlet, reflux condenser and an addition funnel. The flask was heated in an oil bath to 110° and magnetically stirred. The flask was flushed with nitrogen several times and ethyldiazoacetate (80 g, 0.7 moles) was then added dropwise. Nitrogen evolution was vigorous in the beginning and gradually subsided. The temperature of the oil bath was maintained at 105-110°C throughout the addition, which took 3 hours. After the addition was complete, the flask was heated at 110° for another 30 min, cooled to room temperature, the contents diluted with 300 ml of ether and filtered. The filtrate was concentrated on a rotary evaporator and the residue was distilled to give cyclooctatetraene (bp 60° at ν 20 mm, 80 ml) and 9-carbethoxybicyclo[6.1.0]nona-triene (63 g, 0.33 mole, 47%) as a pale yellow liquid (bp 88-90° at 0.8 mm) (lit 89-90°, 0.8 mm), ir λ_{max} (neat film) 2960, 1750, 1650 and 1625 cm^{-1}, nmr (CCl_4) τ 4.0 (s, 4H), 4.1 (s, 2H), 5.9 (q, J = 7 Hz, 2H), 7.95 (d, J = 5 Hz, 2H), 8.7 (t, J = 5 Hz, 1H), 8.75 (t, J = 7 Hz, 3H). Literature nmr (solvent not reported), Ester peaks + τ 4.25 (s, 4H), 4.30 (s, 2H), 7.88 (d, J = 4.7 Hz), 8.68 (t, J = 4.7 Hz).

9-Hydroxymethylbicyclo[6.1.0]nona-2,4,6-triene (34).

Lithium aluminum hydride (8 g) and anhydrous ether (300 ml) were taken in a 500 ml three-neck round-bottom flask fitted with a reflux condenser and an addition funnel. 9-Carbethoxybicyclo-[6.1.0]nonatriene 33 (30 g, 0.158 mole) dissolved in ether (50 ml) was added dropwise, with magnetic stirring. The addition was controlled to have a gentle reflux. After the addition was complete, the mixture was stirred overnight, then sodium hydrogen tartrate (30 g) was added followed by water (10 ml) dropwise. The white precipitate formed was filtered and washed with methylene chloride. The filtrate was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator to give a pale yellow liquid (22 g, 94%). Recrystallization from methanol-water (4:1) gave the alcohol as white needles (15 g). On concentration the mother liquor afforded another crop (5 g) (20g 85.6%) mp 60-61°C, ir (KBr) 3260, 2980, 1650, 1620, 1100 and 1080 cm^{-1}, nmr (CCl_4) τ 4.0 (s, 4H), 4.1 (s, 2H), 5.45 (bd s, 1H washed by D_2O), 6.4 (d, J = 6.0 Hz, 2H), 8.6 (d, J = 5.0 Hz 2H), 9.22 (t, J = 5.0 and 6.0 Hz, 1H).

Anal, Calc: C, 81.08; H, 8.11.

Found: C, 80.67; H, 8.17.

Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde (35).

A) Oxidation of Alcohol 34 with Chromium Trioxide and Pyridine in Methylene Chloride.

To a solution of pyridine (200 ml) in dry methylene chloride (1.6 l.) chromic anhydride (64 g) was added in small amounts with vigorous stirring. After all the chromium trioxide had been added, the mixture was further stirred for 15 min. A solution of the alcohol (14.8 g, 0.1 mole) in methylene chloride (100 ml) was added to the solution of the complex. The flask was stoppered and shaken well for 15 min. Black polymeric chromium oxides were deposited on the sides of the flask. The solution was then filtered and the residue was washed with 300 ml of methylene chloride. The filtrate was transferred to a 4 l. separatory funnel and washed twice with ice cold dilute hydrochloric acid (3N, 500 ml). The organic layer was then washed with sodium bicarbonate solution, with water and then dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator and the residue was distilled to give the aldehyde as a pale yellow liquid bp 58-62° at 0.25 mm (lit. 79-83° at 0.8 mm) (11g, 75.3%), ir (neat) 2970, 2810, 2710, 1700, 1640 and 1610 cm^{-1}, nmr ($CHCl_3$-d) τ 0.74 (d, J = 6 Hz, 1H), 4.0 (s, 4H), 4.1 (s, 2H), 7.76 (d, J = 5 Hz, 2H), 8.3 (d t, J = 6.0 and 5.0 Hz), mass spec M^+ 146, fragment ions at 145, 117, 115, 91 and 39.

B) Oxidation of Alcohol 34 with Dimethylsulfoxide and Dicyclohexylcarbodiimide.

The alcohol 34 (11.1 g, 0.075 mole) was taken in freshly distilled dry dimethylsulfoxide (30 ml). To this was added a solution of dicyclohexylcarbodiimide (51.5 g, 0.25 mole) in dry dimethylsulfoxide (50 ml) and phosphoric acid (1 g). The mixture was stirred at room temperature for two hours. Ethylacetate (20 ml) was then added followed by a solution of oxalic acid (30 g) in methanol (50 ml). The mixture was further stirred for 30 min and then the precipitated dicyclohexylurea oxalate was filtered. The residue was washed with methanol (20 ml). The filtrate was poured into 1 l. of ice cold water and extracted with ether (3 x 200 ml). The combined ether extracts were washed successively with sodium bicarbonate solution and water and then dried over anhydrous sodium sulfate. Removal of ether on a rotary evaporator and distillation gave the aldehyde, bp 58-62° (0.25 mm) (7.5 g, 68%). The spectral characteristics were identical with those described above.

Trans-β-[anti-9-bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein 37.

A) By Using Formylmethylenetriphenylphosphorane.

The ylid reagent, formylmethylenetriphenylphosphorane, was prepared according to the procedure[27] of Trippett and Walker.

The aldehyde 35 (2.92 g, 0.02 moles), formylmethylenetriphenyl phosphorane (6.7 g, 0.022 moles) and chloroform (50 ml) were refluxed together in an oil bath for 18 hours under nitrogen. The chloroform was then distilled off on a rotary evaporator and cold anhydrous ether (200 ml) was added, to precipitate the triphenylphosphine-oxide formed. The mixture was filtered and the filtrate was concentrated on a rotary evaporator. The residue was then chromatographed on Florisil. After eluting the starting material with petroleum ether, elution with a benzene: petroleum ether (30:70) mixture gave a solid (1.4 g) which on recrystallization from hexane gave the α:β-unsaturated aldehyde as pale yellow crystals (1.3 g, 42%) mp 88-90°C, ir (Nujol mull) 2980, 2890, 2800, 1690, 1625 cm^{-1}, uv (hexane) 254 mμ (ε = 28,500), nmr ($CHCl_3$-d) τ 0.60 (d, J = 7.5 Hz, 1H), 3.57-3.75 (AB pattern, J = 7.5, J_{AB} = 16 Hz, 2H), 4.0 (s, 4H), 4.1 (s, 4H), 8.1 (d, J = 5 Hz), 8.6 (m, 1H), mass spectrum m/e 172, 149, 143, 141, 128 and others.

Anal, Calc.: C, 83.72; H, 6.98.

Found: C, 83.77, H, 6.94.

B) Using the Enamine Reagent 36.

The reagent was made according to the procedure described[26] by Nagata and Hayase.

The reagent (50 g) was taken in 200 ml of dry tetrahydrofuran in a 500 ml three-neck round-bottom flask fitted with a N_2 inlet, a reflux condenser and a rubber septum. Sodium hydride (4.8 g) was added, and the mixture was stirred under nitrogen for 30 min. The aldehyde 35 (4.38 g 0.03 mole) dissolved in 20 ml of dry tetrahydrofuran was injected through the rubber septum. The mixture was stirred for another 3 hours, then poured into ice cold 1% oxalic acid solution. After 1 hour the mixture was extracted with ether (3 x 200 ml). The ether extracts were washed with sodium bicarbonate solution and then with water. The organic layer was then dried over anhydrous magnesium sulfate, the ether was removed on a rotary evaporator, and the residue was chromatographed on Florisil. Elution with a benzene-petroleum ether (30:70) mixture and then subsequent recrystallization from hexane gave the unsaturated aldehyde, (2.6 g, 46.5%). The melting point and spectral characteristics were identical with those described above.

p-Toluenesulfonylhydrazone (31) of the Unsaturated Aldehyde 37.

The unsaturated aldehyde 37 (1 g) was dissolved in ethanol (10 ml). p-Toluenesulfonylhydrazone (1.1 g) was dissolved in diglyme (6 ml). The two solutions were mixed and 2 ml of glacial acetic acid was added. The mixture was shaken for 2 min and allowed to stand for 15 min. The white precipitate of the p-toluene-sulfonylhydrazone (1.6 g) was filtered and washed with a little ethanol. Addition of 2 ml of water to the filtrate gave another

0.4 g of product. The combined solids were recrystallized from 95% ethanol to give the tosylhydrazone as a white solid (1.9 g, 94%), mp 148-150°, ir (Nujol) 3200, 1750, 1670, 1585, 1460 and 1440 cm^{-1}, nmr ($CHCl_3$-d) τ 1.9-2.7 (m, 6H becomes 5H in D_2O or acetone-d_6), 4-4.1 (d, 6H), 3.5-4.5 (AB pattern, 2H), 7.6 (s, 3H), 8.35 (d, J = 5 Hz), 8.8 (m, 1H), mass spectrum m/e M^+ 340, fragment ions at 246, 185, 184, 156, 155, 141, 129, 128, 124, 115, 91, 78, 65, 51, 39 and 28.

Anal. Calc.: C, 67.06; H, 5.88; S, 9.41; N, 8.24.

Found: C, 66.64; H, 5.96; S, 9.21; N, 8.75.

Pyrolysis of the Tosylhydrazone 31. Preparation of Pyrazole 38.

The tosylhydrazone was pyrolyzed with an equivalent of sodium methoxide under a variety of conditions listed below in a 100 ml three-neck round-bottom flask. The flask was fitted with a nitrogen inlet and was attached to a vacuum line through a trap cooled in liquid nitrogen. The flask was heated to the appropriate temperatures under vaccum with a small stream of nitrogen flowing through. After the pyrolysis, analysis of the contents of the trap gave no indication of the presence of any product. The residue in the flask was worked up with water and extracted with ether. The ether extracts were dried over anhydrous sodium sulfate, the ether was removed on a rotary evaporator and the residue was analysed. The residue in each case was found to be the pyrazole 38.

The conditions tried for the pyrolysis follow.

Solvent or Adsorbent	Temp	Prod
Tetraglyme	120°	38
Tetraglyme	170°	38
Tetraglyme	250°	38
Tetraglyme	310°	38
Tetraglyme + $CuSO_4$	150°	38
Anakrom	220°	38

The pyrazole, which was not purified, had the following spectral characteristics.

IR (neat) 3250, 1650 cm^{-1}, nmr ($CHCl_3$-d) τ 0.14 (bd s, 1H), 2.3-2.9 (m, 2H), 3.6-4.5 (m, 5H), 4.65 (d, J = 5 Hz, 1H), 6.4-7.0 (m, 3H), mass spec m/e M^+ 184 and fragment ions at 169, 156, 141, 115, 104, 91, 85, 83, 76 and 59.

Anti-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]nona-2,4,6-triene 41.

The tetrahydrofuran used was distilled over lithium aluminum hydride. The pentane used was purified by stirring it with concentrated sulfuric acid for 2 hours, treating it with sodium carbonate and then distilling it through a 2 foot column.

The tosylhydrazone (510 mg, 15 mmoles) was taken in dry tetrahydrofuran (60 ml) in a test tube with a narrow neck. Sodium methoxide (81 mg, 15 mmoles) was added to this and the mixture shaken for 2 min. This was then placed close to a Pyrex immersion

well in a Dry Ice-acetone bath. Nitrogen was constantly bubbled through the solution of the sodium salt of the tosylhydrazone while it was photolyzed externally using a 200 W Hg vapor lamp. After 4 hours of photolysis the solution was transferred to a 100 ml round-bottom flask and concentrated to 20 ml at -30 to -40° using a high vacuum. The solution was then poured into 300 ml of ice water and 200 ml of pentane. The pentane layer was separated, and the aqueous layer was extracted with another 100 ml of pentane. The pentane extracts were combined, washed with ice cold water and dried over anhydrous sodium sulfate. The solution was then rapidly filtered through silica gel (20 g), the pentane was removed at 0° and an nmr and mass spectrum were taken. NMR (CS_2) τ 2.8 (d d, J = 2.0 and 0.4 Hz, 2H), 4-4.1 (d, 6H), 8.2 (dt, J = 5.0 and 2.0 Hz, 1H), 8.8 (d, J = 5.5 Hz, 2H), 9.2-9.5 (m, 1H), mass spec m/e M^+ 156 and fragment ions at 155, 141, 129, 128, 115, 91 (base peak), 78 and 39.

Attempts to Isomerize Cyclopropene 41 by Diethylene Rhodium Chloride Dimer.

a) The cyclopropene 41 (~100 mg) in CCl_4 (1 ml) was taken in prepurified pentane (100 ml) and to this, rhodium complex catalyst (10 mg) was added. The mixture was stirred overnight and then filtered. The filtrate was concentrated and the residue analyzed by TLC on silica gel. There was a spot with an R_f = 0.8 in hexane. This compound was separated by TLC using purified pentane for elution and an nmr and mass spectrum taken:

nmr sharp singlet at τ 8.60, broad peak (small) τ 8.8-8.9, mass spec high molecular weight straight chain hydrocarbon.

The residual material from the TLC plate was found to contain no monomeric material (by mass spectrum).

b) The reaction was carried out as described above but with no carbon tetrachloride. The product on analysis by TLC indicated the absence of the long straight chain hydrocarbon. The rest of the material did not move with hexane. The crude product had olefinic peaks in the nmr. Attempts to isolate pure compounds by TLC using a pentane-ether (80-20) mixture did not lead to any significant amount of material for characterization.

c) Prepurified pentane (100 ml) was stirred overnight with rhodium complex catalyst (10 mg). The solution was filtered and the filtrate was concentrated to dryness. There was no residue left and there were no peaks in the nmr.

d) Prepurified pentane (100 ml), and carbon tetrachloride (1 ml) were stirred together overnight with rhodium complex catalyst (10 mg). The solution was filtered and the filtrate was concentrated to dryness. The residue had the peaks corresponding to long chain hydrocarbon in nmr.

Attempts to Photolyze the Cyclopropene 41 at Low Temperatures.

The cyclopropene 41 was photolyzed at low temperatures in acetone-d_6 in a quartz nmr tube, in pentane in a quartz test tube, and in pentane with a trace of pyrene. The photolyses were followed by TLC on silica gel using hexane as the solvent. No new spot was observed in the TLC during the photolyses, which were continued for

24 hours. The solvents were then removed and the residues were analyzed by nmr. The nmr in each case was found to be identical with that of the starting material.

3,3-Dibromotetracyclo[4.3.2.$0^{2,4}$.$0^{5,7}$]undeca-8,10-diene 50.

Bullvalene (1 g, 7.7 mmoles), tribromomethylphenylmercury (4 g, 7.6 mmoles) and benzene (20 ml) were refluxed together for 14 hours. The mixture was then cooled and the precipitated phenyl mercury bromide (2.7 g) was filtered. The filtrate was concentrated on a rotary evaporator. The residue was sublimed at 40° (1 mm) and 0.2 g of bullvalene recovered. The residue was then taken in hexane and filtered through alumina (10 g). The filtrate was concentrated to dryness and residual solid was recrystallized from ethanol to give the product, mp 110-112°C (lit. 116°) (1.3 g, 54%). The spectral characteristics were identical with those reported.[36]

NMR ($CHCl_3$-d) τ 4.2 (m, 2H), 6.1 (m, 4H), 7.4 (m, 2H), 8.0 (t, J = 2.5 Hz).

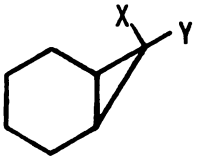
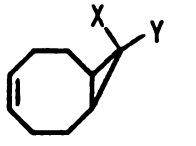
Reduction of gem-dibromocyclopropanes to Monobromocyclopropanes with Butyllithium.

The procedure is similar to that described for the dibromohomobullvalene (50) below.

Dibromohomobullvalene 50 (200 mg, 0.66 mmoles) and ether (15 ml) were taken in a three-neck 100 ml flask fitted with a condenser, nitrogen inlet and rubber septum. The solution was cooled to -78°C with a Dry Ice-acetone bath and n-butyllithium

(0.5 ml of 1.6M in hexane, 0.8 mmoles) was injected through the rubber septum followed by the addition of ethanol (2 ml). The solution was allowed to warm up to room temperature and then poured into 100 ml of water. The organic layer was separated, dried and concentrated. The residue was purified by TLC to give the monobromide 53 (130 mg, 88%), mp 57-58° (lit 59°). Spectral characteristics were identical with those reported.[36] NMR ($CHCl_3$-d) τ 4.2 (m, 2H), 6.2 (m, 4H), 6.7 (t, J = 3.5 Hz), 7.6 (m, 2H), 8.45 (m, 2H).

7,7-Dibromonorcarane and 9,9-dibromobicyclo[6.1.0]non-4-ene were reduced in an identical fashion and the crude products were analyzed by nmr and vpc. The product mixtures contained small amounts of the starting materials as evidenced by comparison of the retention times of the starting materials with the product mixtures.

	Compd.	% Conversion	PROD RATIO by VPC and NMR	J_{syn} (Hz)	J_{anti} (Hz)
	X=Y=Br	85	SYN $^{x=Br}_{y=H}$; ANTI $^{x=H}_{y=Br}$ VPC 65 : 35 NMR 60 40	8.0	3.7
	X=Y=Br	75	VPC 85 : 15 NMR 80 20	7.5	4.0

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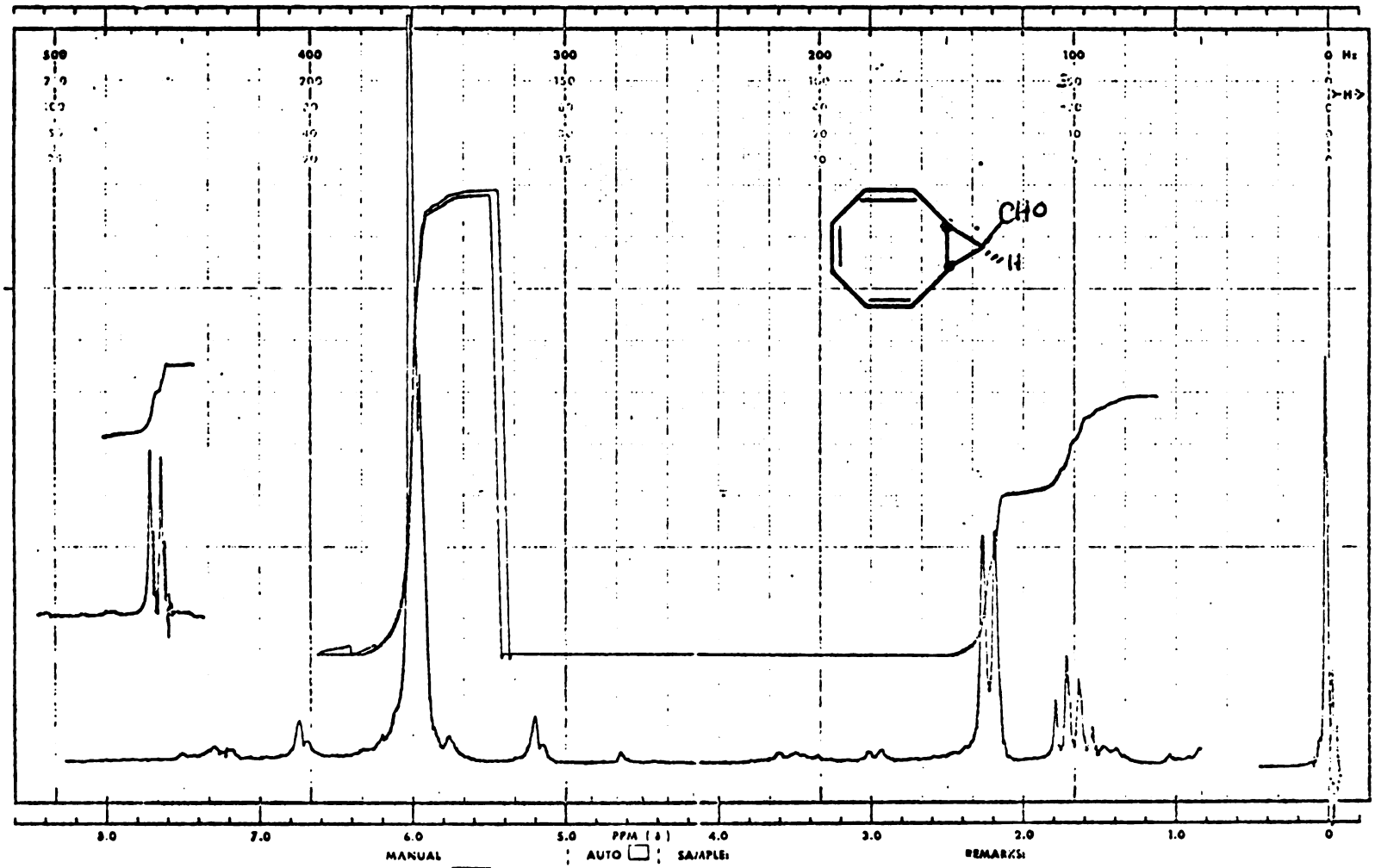

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FILTER: (2)
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SOLVENT: CCl_4

varian
analytical instrument division

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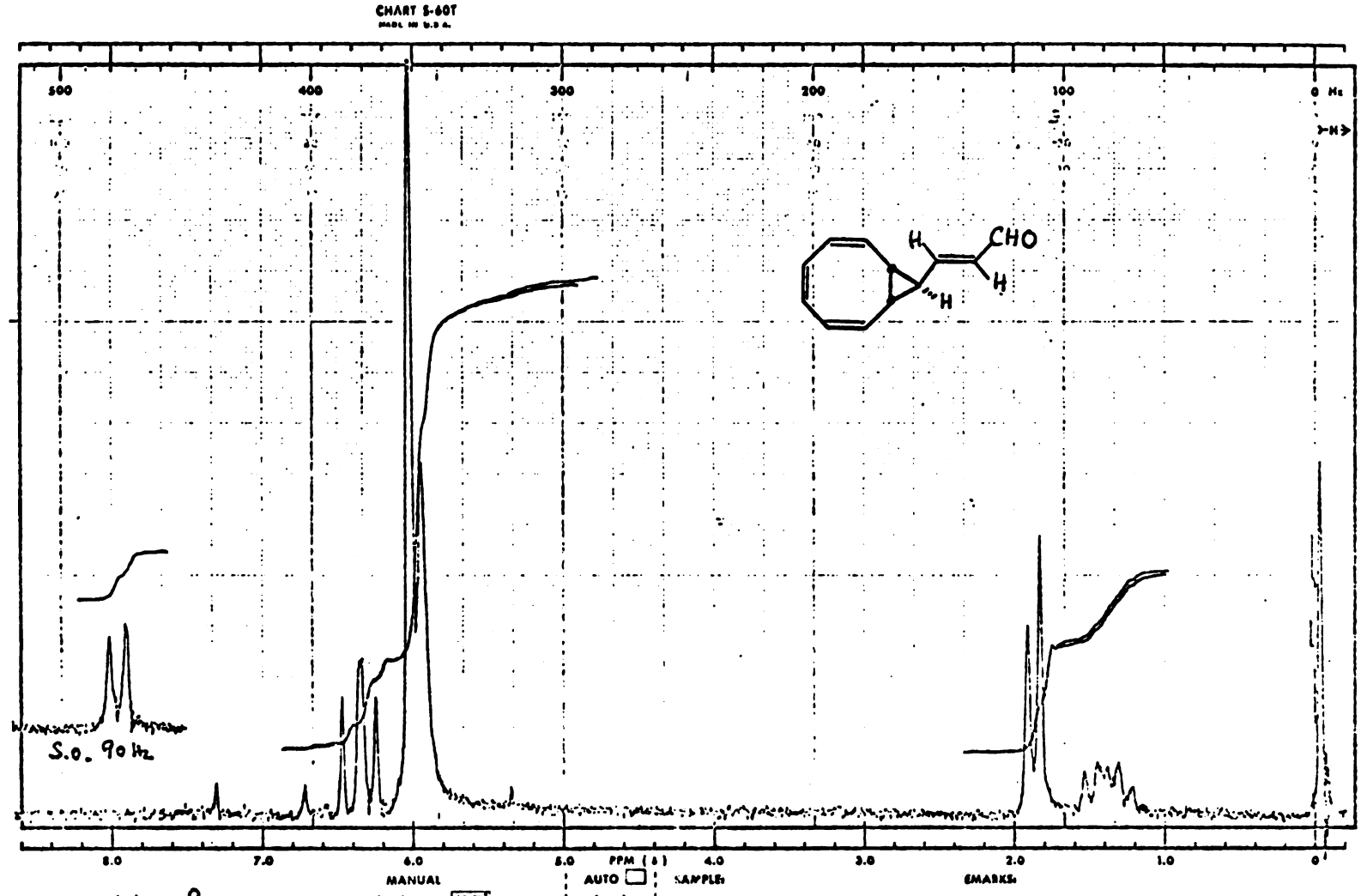

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FILTER: (3)
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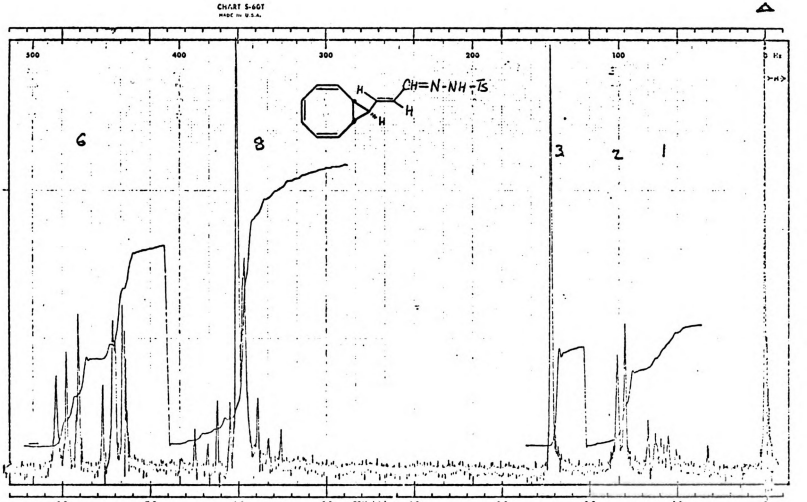
varian analytical instrument division

DATE: 12-23-1971

OPERATOR: Raghu

60 MHz NMR SPECTRUM NO.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H
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2.0
1.0
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AUTO
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varian
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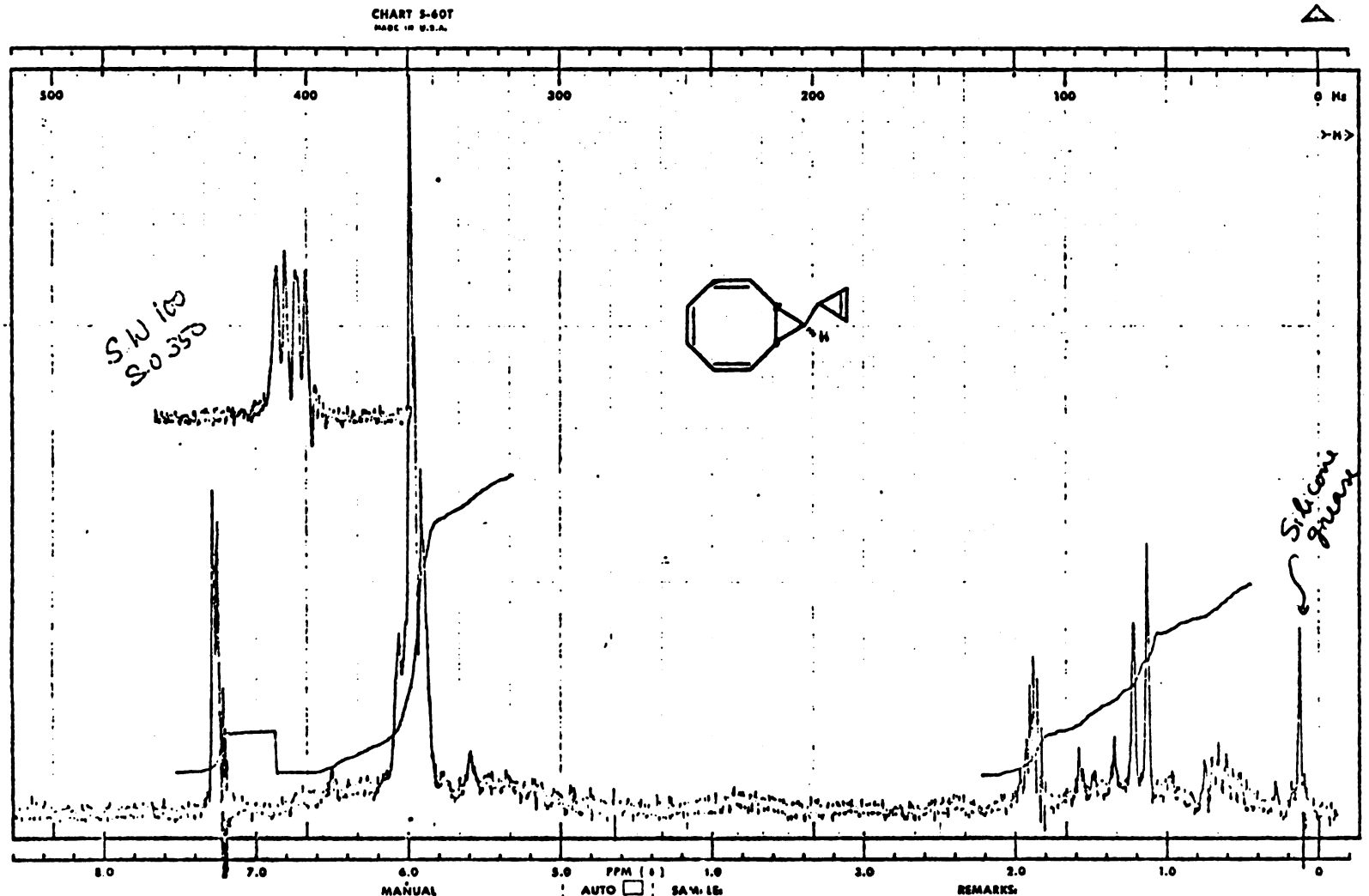
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6.0
5.0
PPM (δ)
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AUTO
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analytical instrument division
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