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$(CH)_{12}$ HYDROCARBONS: THERMAL AND PHOTOCHEMICAL PREPARATION, STRUCTURE DETERMINATION, AND MECHANISTIC INVESTIGATION

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Major professor

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$(CH)_{12}$ HYDROCARBONS: THERMAL AND PHOTOCHEMICAL PREPARATION, STRUCTURE DETERMINATION, AND MECHANISTIC INVESTIGATION

By

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ABSTRACT

$(CH)_{12}$ HYDROCARBONS: THERMAL AND PHOTOCHEMICAL PREPARATION, STRUCTURE DETERMINATION, AND MECHANISTIC INVESTIGATION

By

Mehdi Ghandi

Pyrolysis of the dry _trans_-β-[_anti_-9-bicyclo[6.1.0]-nona-2,4,6-trienyl]acrolein tosylhydrazone lithium salt **I** at 250° resulted in the formation of six products, characterized as: _exo_ and _endo_-tricyclo[$4.4.2.0^{2,5}$]dodeca-3,7,-9,11-tetraenes **II** and **III**, pentacyclo[$6.4.0.0^{2,12}.0^{3,7}$-$0^{4,11}$]dodeca-5,9-diene **IV**, 1,2-benzocycloocta-1,3,7-triene **V**, and 9-_syn_ and _anti_ (5-pyrazola)bicyclo[4.2.1]nona-2,4,-7-trienes **VI** and **VII**. On the other hand, the formation of diene **IV** as the only $(CH)_{12}$ hydrocarbon from either pyrolysis or photolysis of trans-β-[_syn_-9-bicyclo[4.2.1]nona-2,4,7-trienyl]acrolein tosylhydrazone salt **VIII** showed that hydrocarbons **II** and **III** have arisen from a different carbene intermediate than diene **IV** in the pyrolysis of tosylhydrazone salt **I**. Thermolysis of _anti_-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]-nona-2,4,6-triene **IX** resulted in the

formation of a new $(CH)_{12}$ isomer, characterized as pentacyclo[$6.4.0.0^{2,4}.0^{3,10}.0^{5,9}$]dodeca-6,11-diene **X**. This latter result clearly ruled out the hydrocarbon **IX** as the potential thermal precursor of diene **IV** in the pyrolysis of tosylhydrazone salt **I**.

To The Heroic People of Iran

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TABLE OF CONTENTS

Chapter Page

Chapter Page

Chapter Page

LIST OF FIGURES

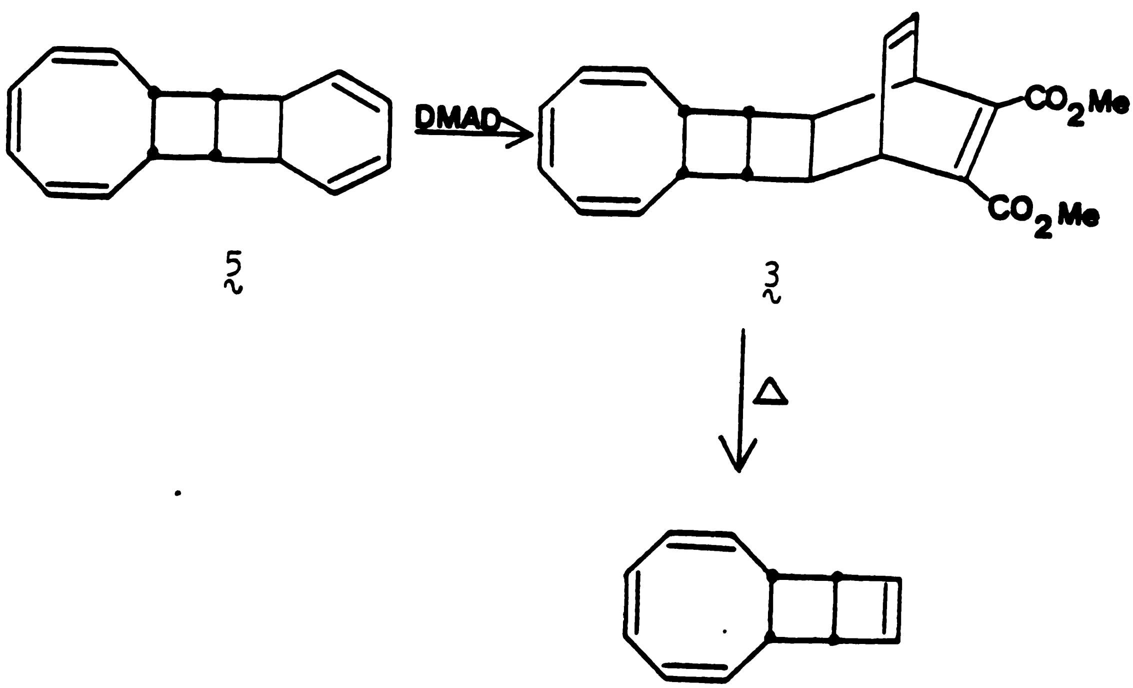
Figure		Page

Figure | Page

INTRODUCTION

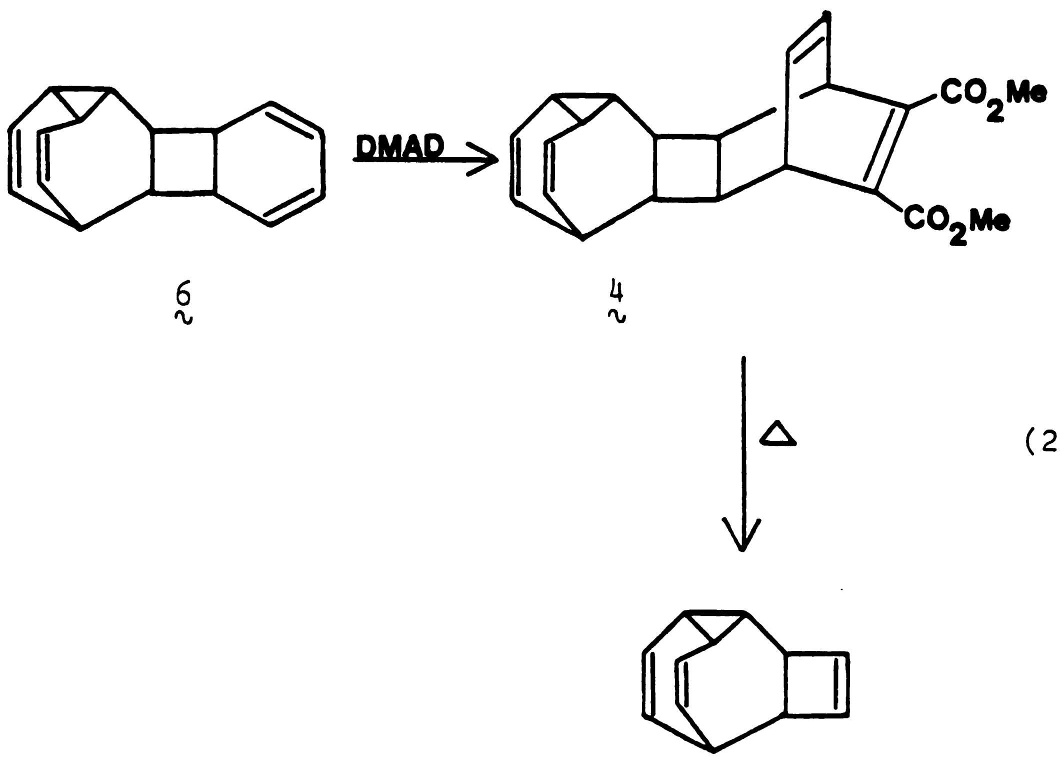
The chemistry of $(CH)_n$ hydrocarbons has been studied intensively over the past two decades. The reasons for this are many but include the discovery of bullvalene by Schröder in 1963[1] and the chemist's surprise and joy at the range of isomers related in both an energetic and conceptual sense. The behavior of the $(CH)_{10}$ hydrocarbons has been mimicked by the other $(CH)_n$'s, and the entire area has become a fertile ground for the discovery of new compounds and reactions. As a result, many of the possible $(CH)_8$[2] and $(CH)_{10}$[3] structures have been synthesized and much is known about the diverse and surprising rearrangements which occur thermally and photochemically. The early review by Balaban[4] which published a series of computer generated valence isomers of $(CH)_n$ hydrocarbons (where n = 2,3,4,5,[4a] and n = 6[4b]) has been very useful and remains the excellent compendium of $(CH)_n$ isomers.

The isomeric $(CH)_{12}$ hydrocarbons present an interesting family of compounds because of the members, and the varied electrocyclic and sigmatropic processes expected of the numerous valence tautomers. Despite these attractive features, chemical investigation in this area has been limited because of the relative unavailability of synthetic entries to these polyenes. For these reasons, various research groups have been interested in the possibility of developing facile and stereochemically controlled syntheses of several $(CH)_{12}$'s. Some of the findings for $(CH)_{12}$ hydrocarbons are mentioned below. **Schröder** has synthesized two $(CH)_{12}$ hydrocarbons **1** and **2** by pyrolyzing the Diels-Alder adducts of the dimers of cyclooctatetraene and dimethyl acetylenedicarboxylate (DMAD) **3** and **4**[5,6] (Equations 1,2).



5 **3** **1**

Low temperature photolysis of hydrocarbon **1** resulted in the formation of several other $(CH)_{12}$ hydrocarbons[7]

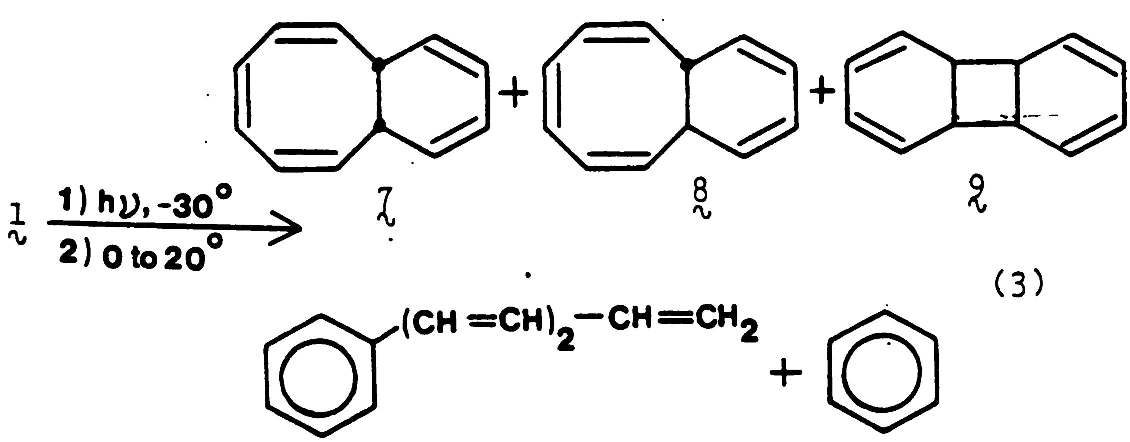


6 4

(2)

2

(Equation 3).



7 8 9

(3)

10 11

The formation of hydrocarbons 7 and 8 was found to have arisen through the unstable [12] annulene 12.[8] This [12] annulene could then rearrange thermally or photochemically into 7 or 8 in accordance with the Woodward-Hoffmann rules.[8] It was also proved that 9 and 11 were formed thermally at the expense of 7 while 10 could result from a photochemically induced suprafacial sigmatropic 1, 7 [H] shift in 7 and/or 8[3] (Figure 1).

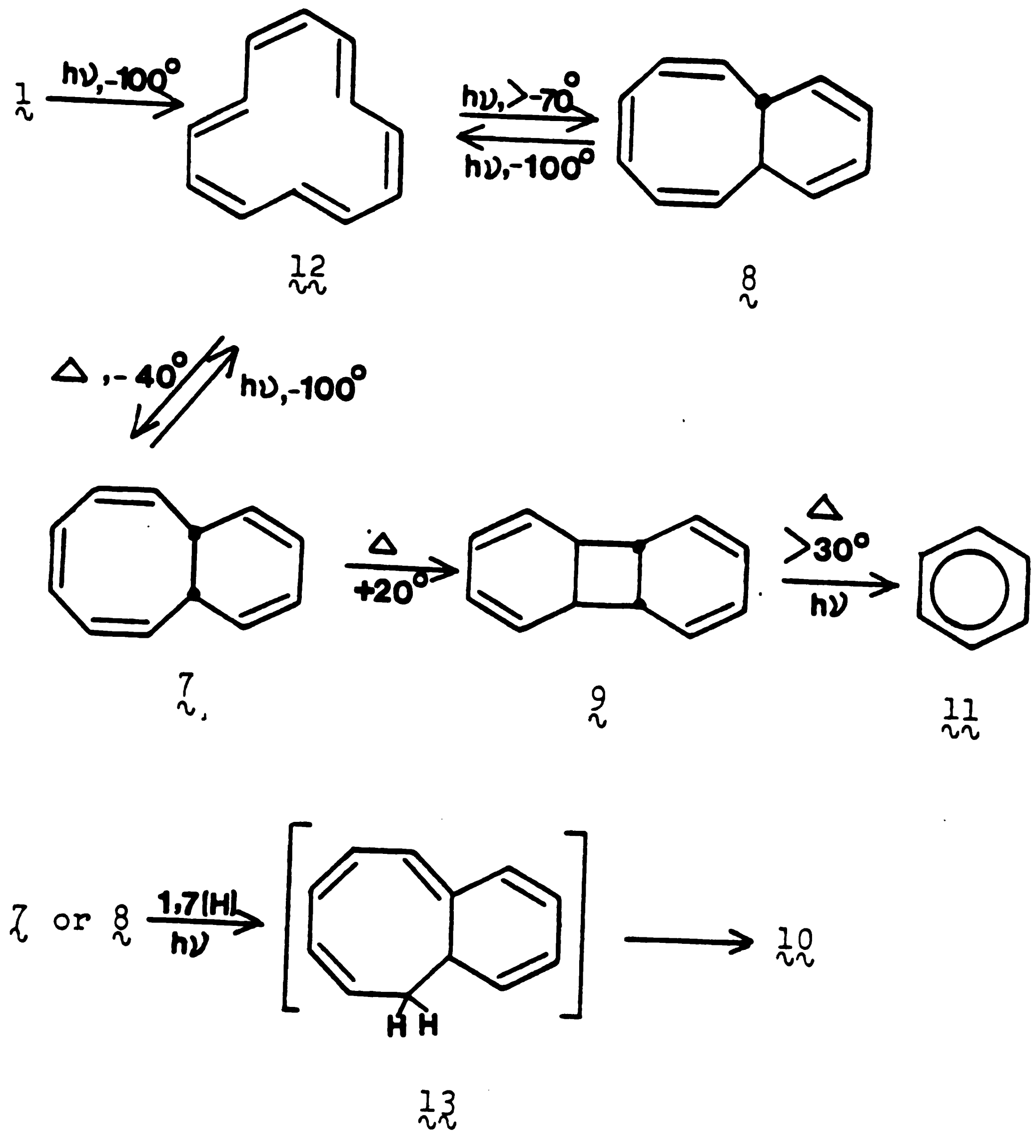
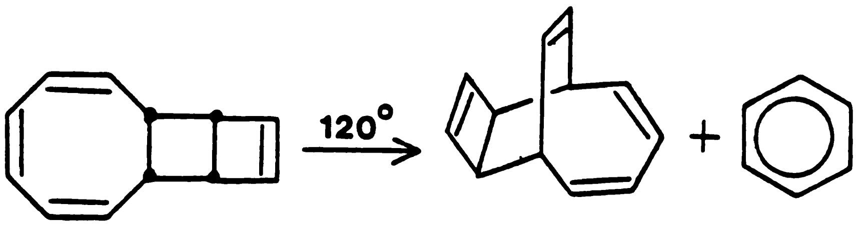


Figure 1. Isomerization mechanism for the photolysis of <u>cis</u>, <u>syn</u>, <u>cis</u>-tricyclo[8.2.0.0^{2,9}]dodeca-3,5,7,11-tetraene 1.

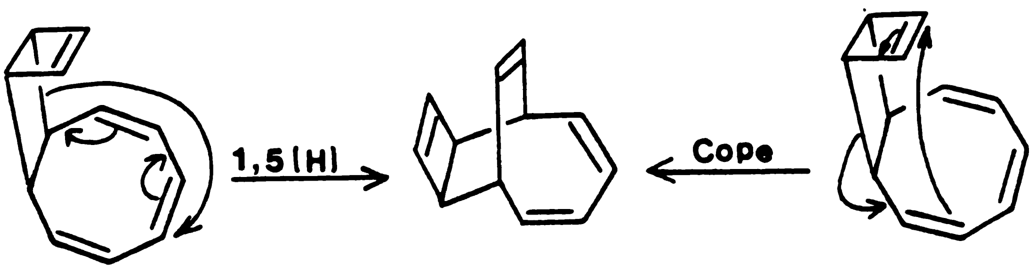
On the other hand, heating of compound 1 at 120° resulted in the formation of equal amounts of exo-tetraene 14 and benzene[5,9] (Equation 4)



(4)

1 14 11

Two possible mechanisms have been suggested for the selectivity of this reaction to the formation of exo-isomer 14. First, a suprafacial [1,5] sigmatropic shift, and second, a Cope rearrangement[9b,10] (Equation 5)

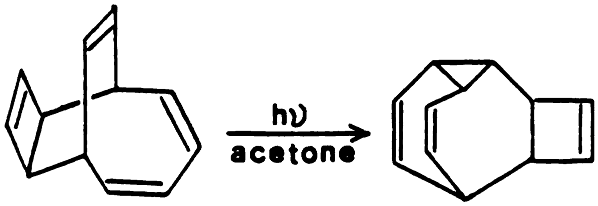


(5)

1 14 1

Deuterium labeling experiments ruled out the Cope rearrangement path in favor of the [1,5] sigmatropic shift.[11]

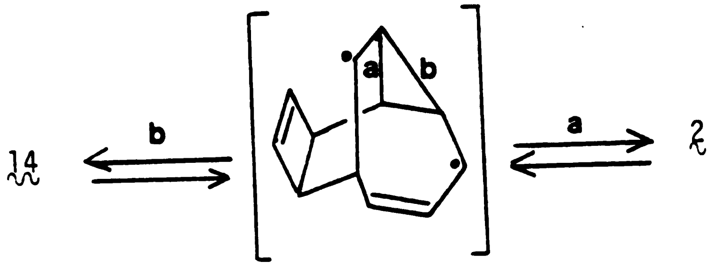
Irradiation of hydrocarbon 14 under triplet conditions (acetone, E_T = ∿82 Kcal/mol) afforded hydrocarbon 2[9b] (Equation 6).



14 2

(6)

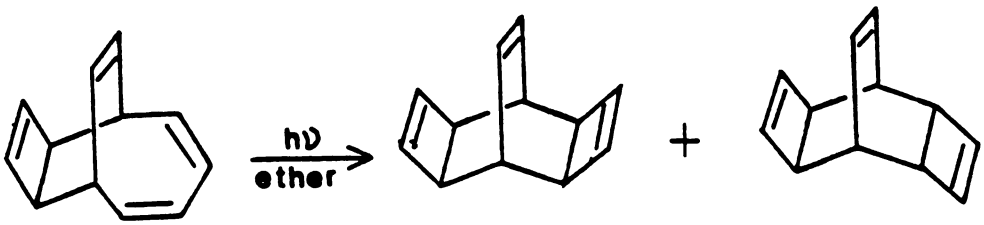
The formation of compound 2 was explained according to the Katz-Cheung mechanism[3k.9b] (Equation 7).



15

(7)

On the other hand, direct photoisomerization of hydrocarbon 14 resulted in two other new $(CH)_{12}$ members, formed in equal amount[9b] (Equation 8).

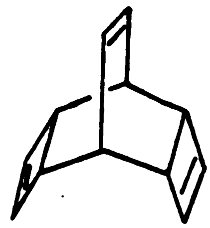


14 16 17

(8)

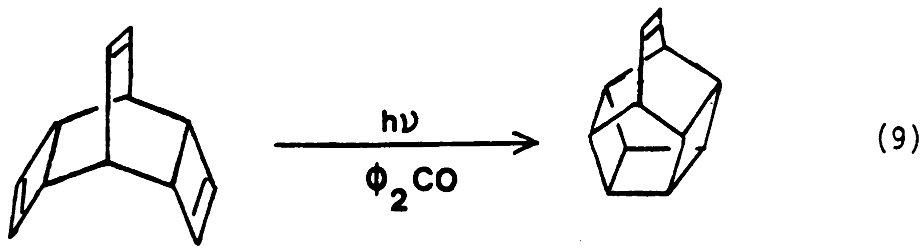
In 1974, Daub completed the set of tetracyclo[$4.4.2.0^{2,5}$.-$0^{7,10}$]dodecatrienes, (16) - (18) by synthesizing the

<u>endo</u>, <u>endo</u> isomer **18**.[12]



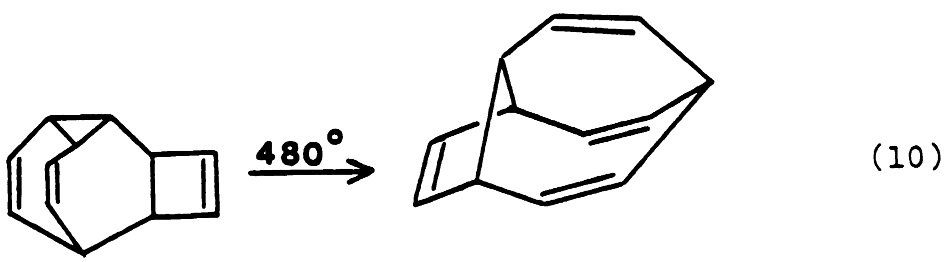
18

He showed that **18** on sensitized irradiation went to the known cage compound **19**[12] (Equation 9).



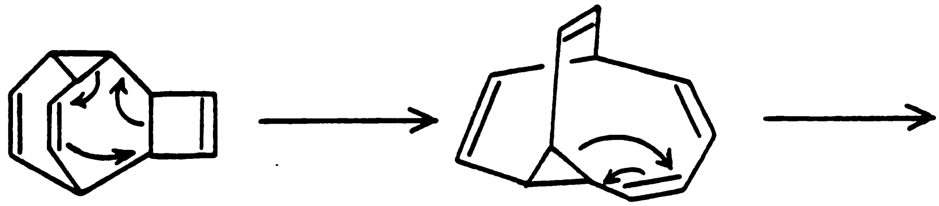
18 **19**

Pyrolysis of hydrocarbon **2** in the gas phase at 480° afforded the new $(CH)_{12}$ isomer **20**[13] (Equation 10).



2 **20**

The conversion of **2** to a hydrocarbon **20** was formulated as follows[13] (Equation 11).



20 (11)

2 21

Several other new $(CH)_{12}$ isomers have been prepared through a multi-step direct bond reorganization of hydrocarbon 2[3c,14] (Figure 2). Conversion of 23 to 24 is an example of the well precedented[15] $(\sigma_{2a} + \sigma_{2a})$ bond relocation process which simultaneously converts a set of four multiply fused cyclobutane rings to two pairs of cyclopropane and cyclopentane rings. It was thought that diene 25 might serve as an immediate precursor to the desired tetraene 27.[14] Thus thermally activated 25 could experience symmetry-allowed intramolecular $[\pi_{4s} + \pi_{2s}]$ cycloaddition with utilization of one internal cyclopropane bond[14] to provide 30 (Equation 12). The strained nature of this polycyclic hydrocarbon was viewed as adequate to allow subsequent homolysis of the indicated triad of cyclopropyl bonds, perhaps via free radical intermediates, to deliver 27.[14]

Pyrolysis of diene 25 up to 580° did not eventuate in recognizable isomerization to 27 as desired.[14]

In 1975, Farnum reported a new $(CH)_{12}$ isomer 31 which was prepared through a multistep reaction sequence from

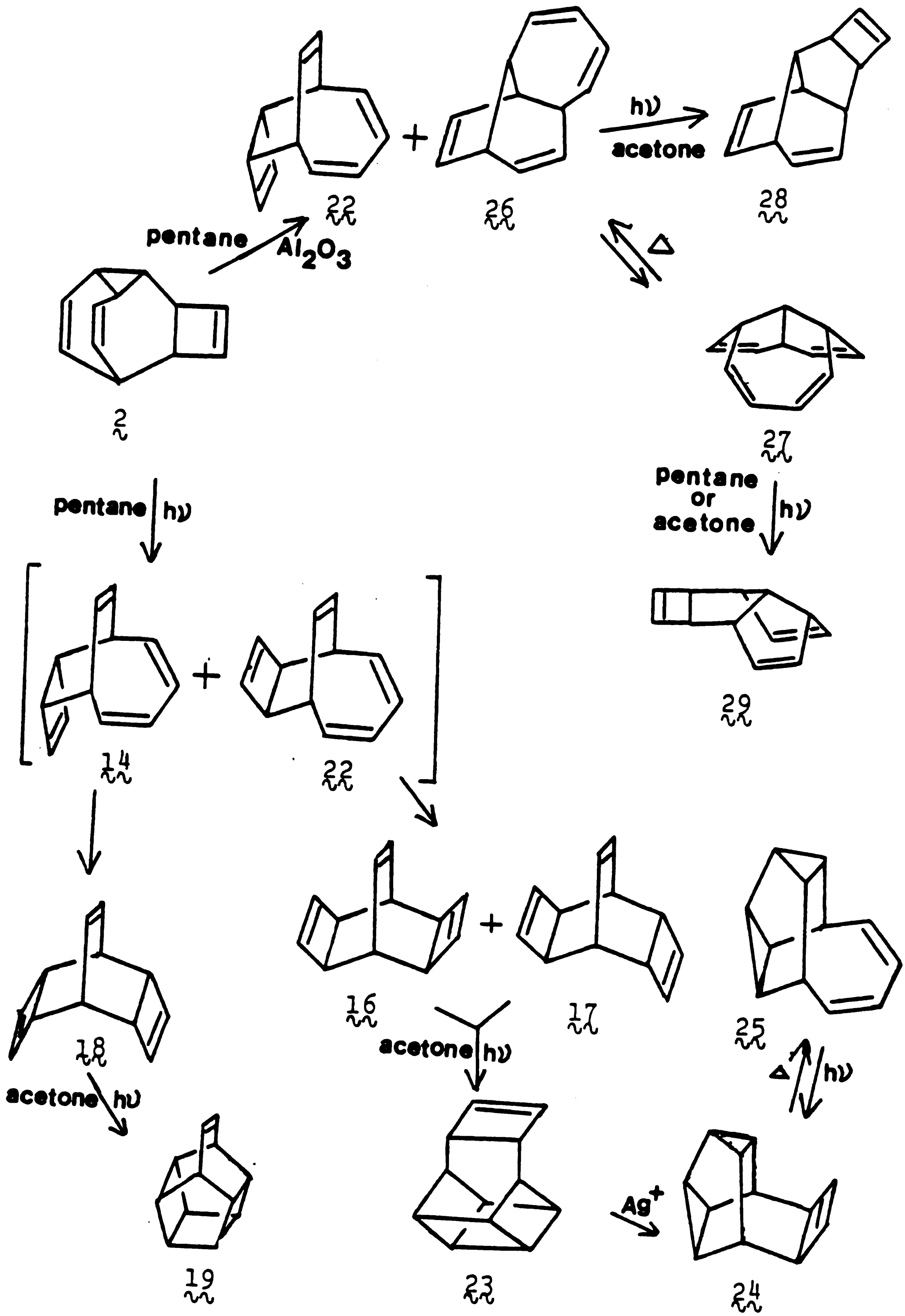
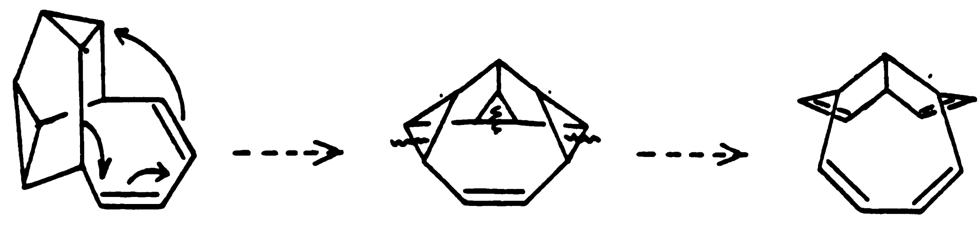


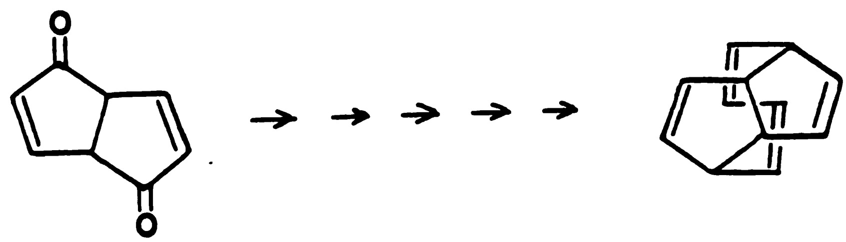
Figure 2. New $(CH)_{12}$ hydrocarbons synthesized from tetracyclo[$5.3.2.0^{2,5}.0^{6,8}$]dodeca-3,9,11-triene 2.



(12)

25 30 27

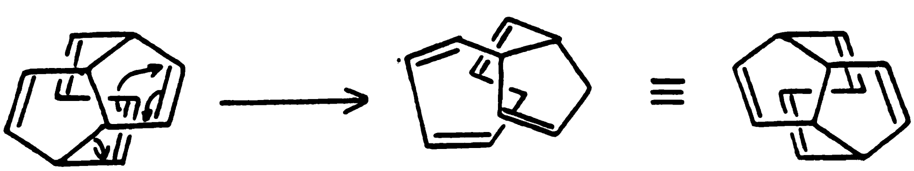
compound 32 as starting material[16] (Equation 13).



(13)

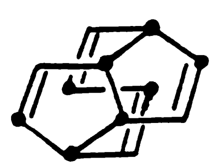
32 31

This hydrocarbon has the potential to undergo a series of structurally degenerate Cope rearrangements, one of which is illustrated below (Equation 14).



(14)

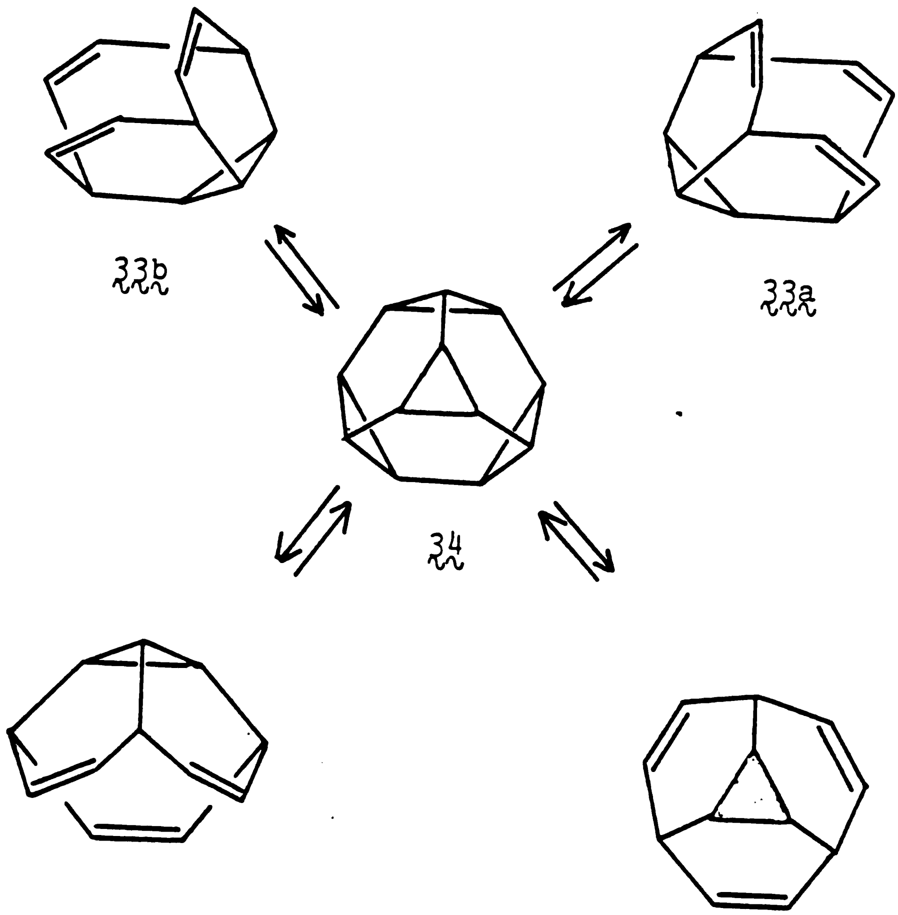
31 32



The complete cycle leads to the scrambling pattern in 31: eight positions (marked ●) form one equivalent set, while the remaining four comprise another.[16] As shown, each Cope rearrangement also interchanges enantiomers.[16] Initial work (up to 140°) showed that the Cope rearrangement, if present, is slow on the nmr time scale. This slow rate, even though the geometry appears ideal, was conjectured to be due to the absence of a small ring and its accompanying strain.[16]

Truncated Tetrahedrane

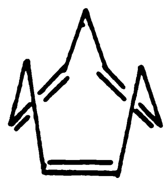
The $(CH)_{12}$ isomer **33** is of interest as a potential photochemical precursor of the hydrocarbon heptacyclo-$[5.5.0.0^{2,12}.0^{3,5}.0^{4,10}.0^{6,8}.0^{9,11}]$dodecane **34**, otherwise called "truncated tetrahedrane", because of its tetrahedral symmetry.[17] Compound **34**, although as yet unknown, is of much theoretical interest, owing to its cage-like array of cyclopropane rings. The quadruple tris-homobenzene nature of **34** makes it and its valence tautomer **33** an ideal system for testing the theory of homoaromaticity in neutral molecules. Since at one time any three of the cyclopropane rings could be involved in this process, there would be four identical tautomers possible for **33**. This is illustrated in Figure 3. Whether the delocalization energy of compound **34** would balance strain energy and prevent its decomposition to **33** is difficult to predict. A



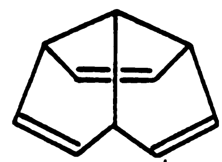
33b **33a** **34** **33c** **33d**

Figure 3. Thermally allowed ($\pi_{2s} + \pi_{2s} + \pi_{2s}$) interconversions.

lesser stability of **34** might still permit its detection as an intermediate in the degenerate interconversion of **33a**, **b**, **c** and **d**. This could be done by a study of the variable temperature nmr spectrum of **33**, and hence the relative energy of **34** can be estimated. On the other hand, the homoconjugative interaction in **33** can be determined by finding the ionization potentials of the interacting double bonds[18] and comparing these with the ionization potentials of isolated, noninteracting systems. There are some examples in the literature which show the application of photoelectron spectroscopy as a tool for determination of homoconjugative interactions in molecules with three properly disposed double bonds, such as compounds 35,[19] and 36.[20]

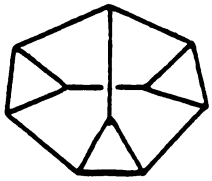


35



36

The photoelectron spectrum of compound 35 has shown a large through space interaction of the π levels and a small through bond interaction.[19] The photoelectron spectrum of 36 suggested a much smaller overall interaction of π levels in 36 relative to compound 35.[20] On the other hand, there is some evidence for homoconjugative stabilization between two adjacent cyclopropane rings in diademane 37, although this stabilization is less than expected.[18e] The observed destabilization was explained as the inductive effect of the central sp^3 carbon atom, which ties the cyclopropane ring together.[18e] Compound 37, on heating to 90° underwent the orbital symmetry allowed $[\sigma_{2s} + \sigma_{2s} + \sigma_{2s}]$cycloreversion,[21] affording triquinacene

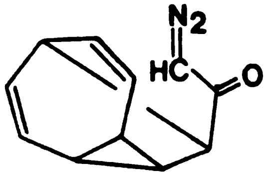


37

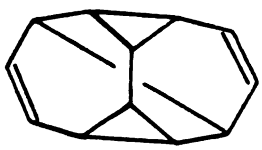
36. This reaction showed the considerable amount of ring strain, which is present in compound 37.[21] The existence of an extra cyclopropane ring in compound 33 might result in a geometric arrangement of π bonds similar to that of cyclononatriene 35. On this basis, some homoconjugative stabilization in compound 33 would be predictable.

Synthetic Approach to Truncated Tetrahedrane 34

Vedejs has reported an elegant synthesis of pentacyclo-[5.5.0.0^{2,12}.0^{6,8}.0^{3,9}]dodeca-4,11-diene 39 using the diazo compound 38.[22]

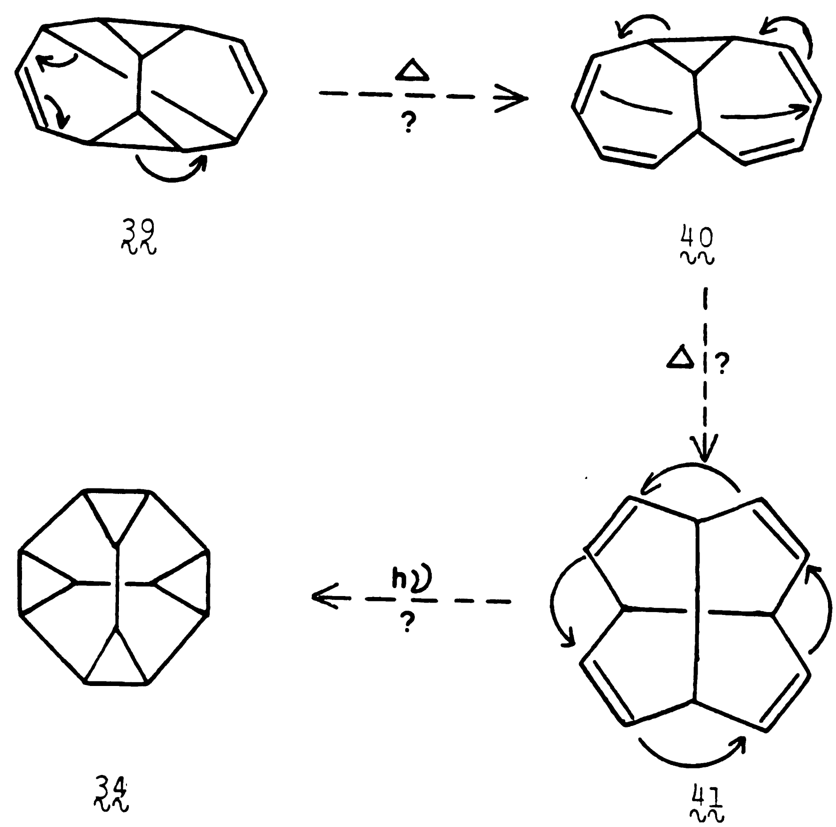


38



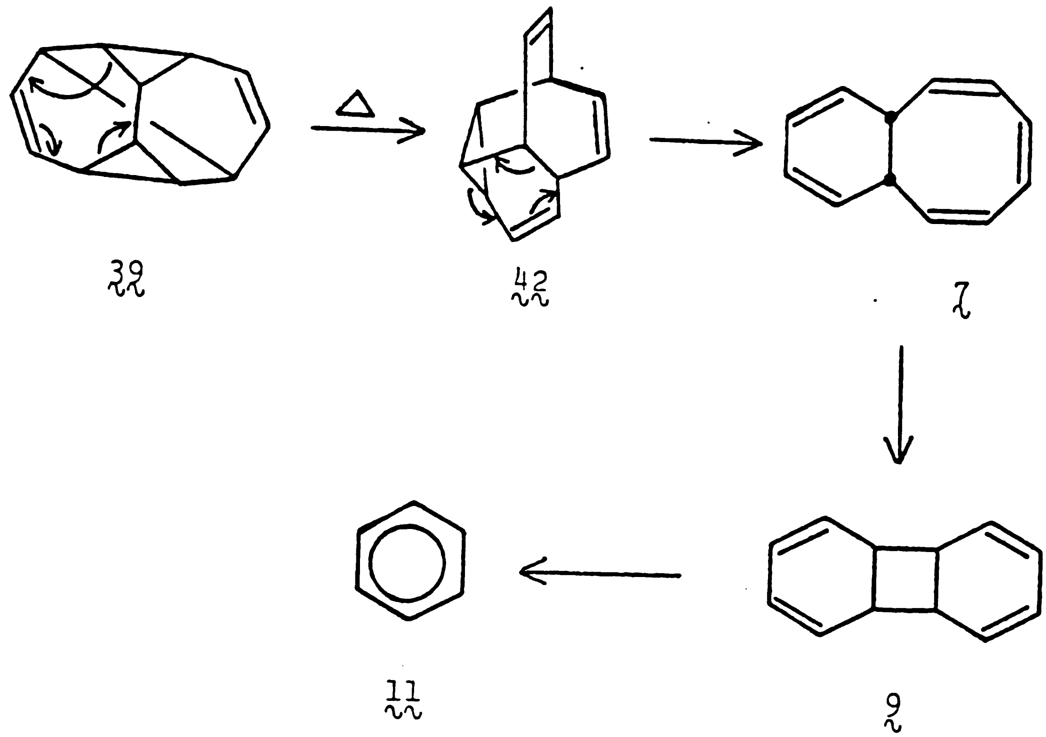
39

A possible approach to 41, as a potential photochemical precursor of truncated tetrahedrane 34 involved the Cope rearrangement of a divinylcyclopropane 40 which in turn was expected to be available[22a] by retro Diels-Alder cleavage of 39 (Equation 15).



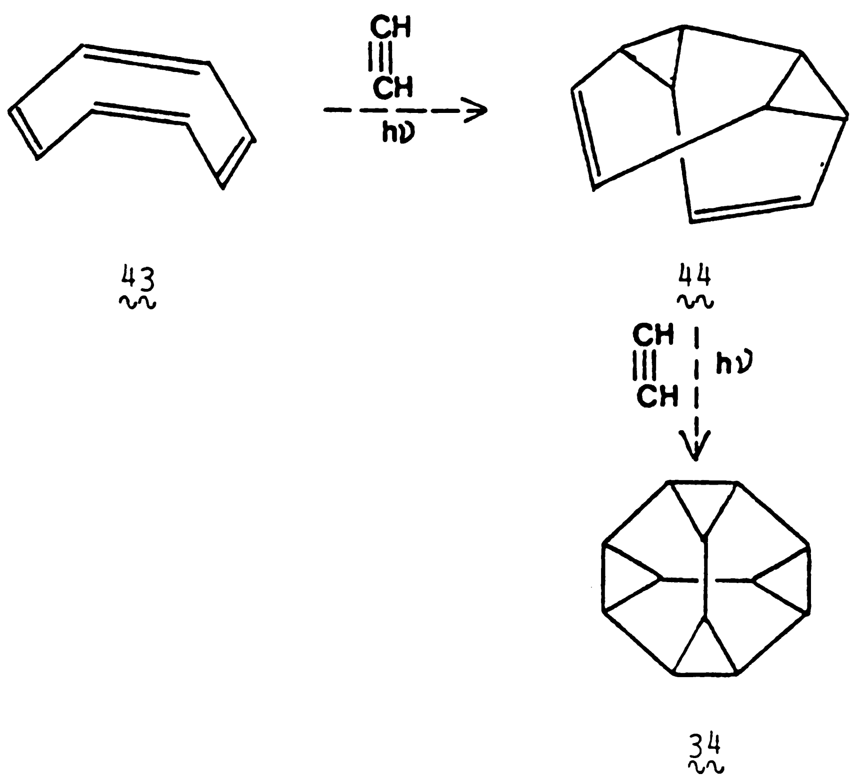
(15)

Thermolysis of 39 above 160° gave benzene, and not hydrocarbon 40.[22a] The formation of benzene from compound 39 was explained[22b] according to the following mechanism (Equation 16). The most direct, simple and elegant proposal investigated for the synthesis of 34 depended on the addition of two acetylenes to cyclooctatetraene in two



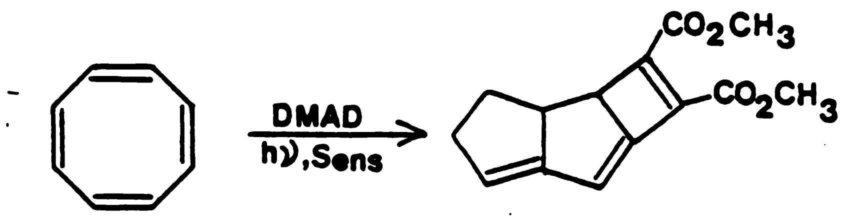
(16)

symmetry allowed photochemical $[\pi_{2s} + \pi_{2s} + \pi_{2s} + \pi_{2s}]$ reaction[23] (Equation 17).



(17)

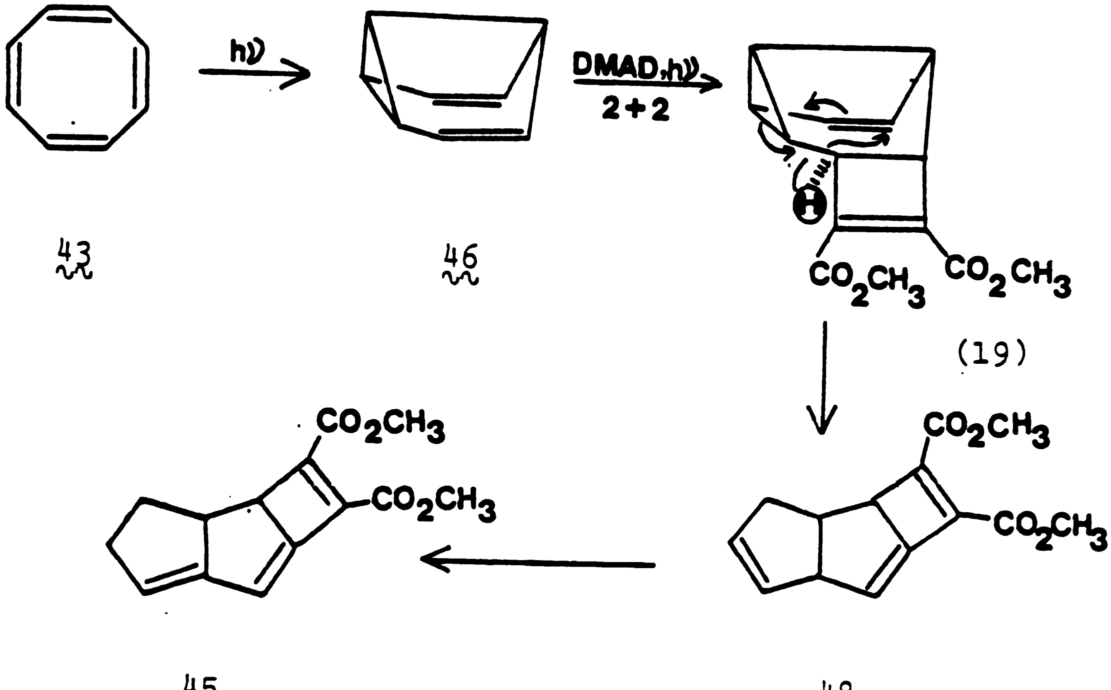
This reaction has been tried under a variety of conditions involving different solvents, temperature, and time.[23] The only photolysis that yielded an insolable adduct[23] was the one in which dimethylacetylenedicarboxylate (DMAD) and cyclooctatetraene in methylene chloride were photolyzed in the presence of benzophenone as a sensitizer at -60° (Equation 18).



(18)

43 45

A plausible mechanism for the formation of 45 was explained[23] as follows (Equation 19).

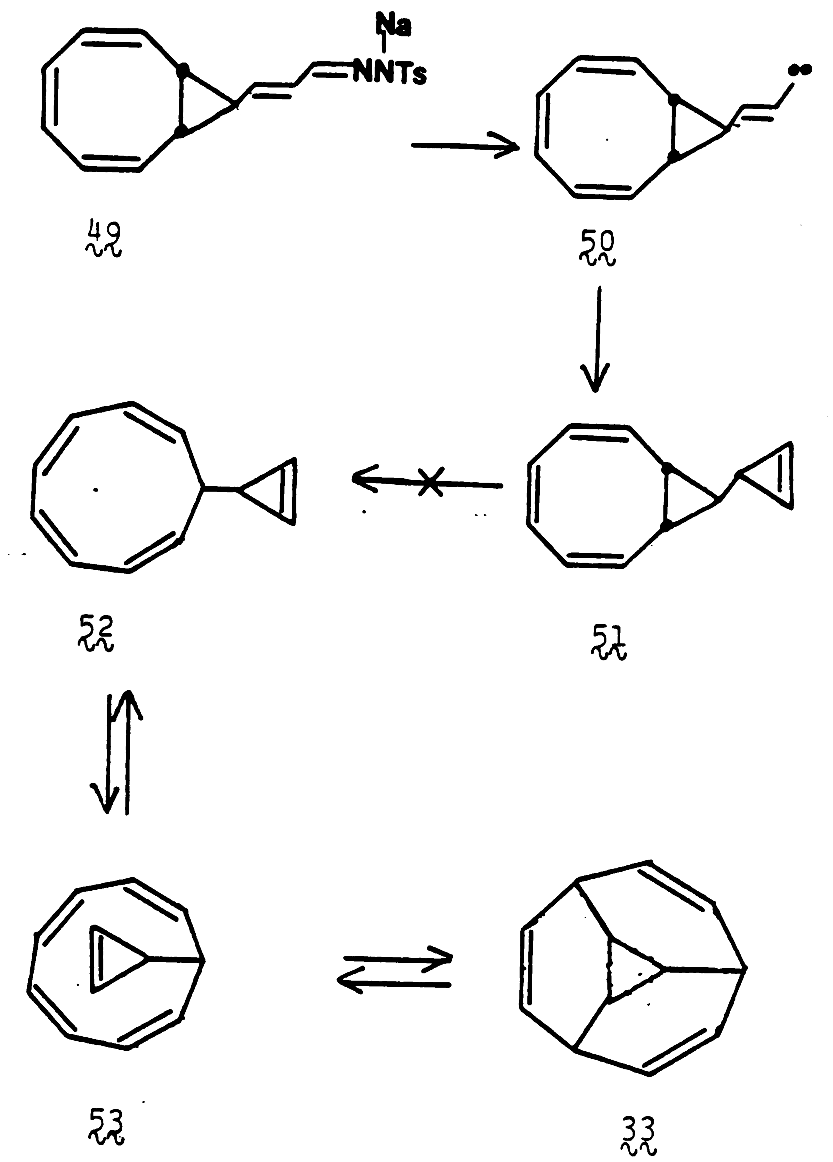


43 46

(19)

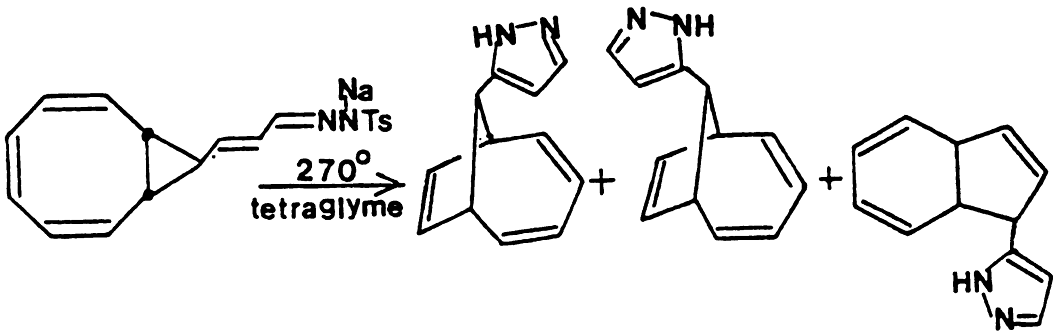
45 48

A somewhat less direct proposed method[23] for the synthesis of 33, was the generation of the $(CH)_{12}$ isomer 52. This compound was expected to be prepared from hydrocarbon 51, which in turn could be generated from decomposition of tosylhydrazone salt 49[23] (Equation 20).



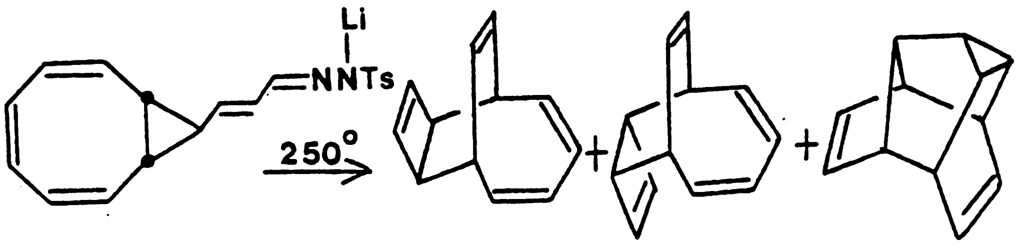
(20)

Tosylhydrazone salt 49 was prepared, and its photolysis in dry tetrahydrofuran, led to the new $(CH)_{12}$ isomer 51.[23] Attempts to produce 52 from 51, both photochemically and catalytically failed.[11,23] Thermal decomposition of tosylhydrazone sodium salt 49 in tetraglyme at 270° led to a mixture of pyrazoles (54) - (56)[11,23] (Equation 21).



49 54 55 56

On the other hand, thermal decomposition of the dry tosyl= hydrazone lithium salt 57 at 250° led to the formation of the two known epimeric tetraenes 14 and 22, and a new $(CH)_{12}$ isomer[9,11,14] (Equation 22).



(22)

57 14 22 58

According to the spectroscopic data and using Balaban's planar trivalent multigraph of order 12,[4b] the structure of 58 was assigned to this new isomer.[11] Unfortunately, the spectroscopic information did not allow rigorous assignment of the structure of this new $(CH)_{12}$ member as 58.

The original purpose of this project was to reinvestigate the pyrolysis of tosylhydrazone lithium salt 57 in order to permit:

(a) careful analysis of the product mixture to find out any other known or unknown $(CH)_{12}$ isomers,

(b) Generation of this new isomer, and studying its spectrosopic data to find out the exact structure,

(c) Mechanistic investigation of the formation of hydrocarbons 14, 22 and 58,

(d) Development of another method for the production of diene 58 with higher yield (because under the mentioned conditions, it was isolated in 1.0% yield).

We were also interested in studying the thermal isomerization of cyclopropene hydrocarbon 51. Hydrocarbon 51 was expected to be a potential precursor for the pyrolytic formation of diene 58.

RESULTS AND DISCUSSION

Part A

Synthesis of Trans-β-[anti-9-bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein Tosylhydrazone 63

The general procedure for the synthesis of a large quantity of tosylhydrazone 63 was adapted from S. Raghu[23] and T. Reitz's[11] theses. This is illustrated in Figure 4.

Thermal Decomposition of Trans-β-[anti-9-bicyclo[6.1.0]nona-2,4,6-trienyl]Acrolein Tosylhydrazone Lithium Salt 57. Preparation of Exo-tricyclo[$4.4.0.0^{2,5}$]dodeca-3,7,9,11-tetraene 14, Endo-tricyclo[$4.4.0.0^{2,5}$]dodeca 3,7,9,11-tetraene 22, Pentacyclo[$6.4.0.0^{2,12}.0^{3,7}.0^{4,11}$]dodeca-5,9-diene 58, 1,2-Benzocycloocta-1,3,7-triene 64, 9 syn and Anti(5-pyrazola)bicyclo[4.2.1]nona-2,4,7-triene 54, 55

The best method that we found to pyrolyze the tosylhydrazone lithium salt 57 was to add it in small portions to a hot flask maintained at 250° in a sand bath. After each addition, about 10-15 glass beads were added to provide a fresh surface for the pyrolysis of salt. The volatiles were then pumped into a trap kept in liquid

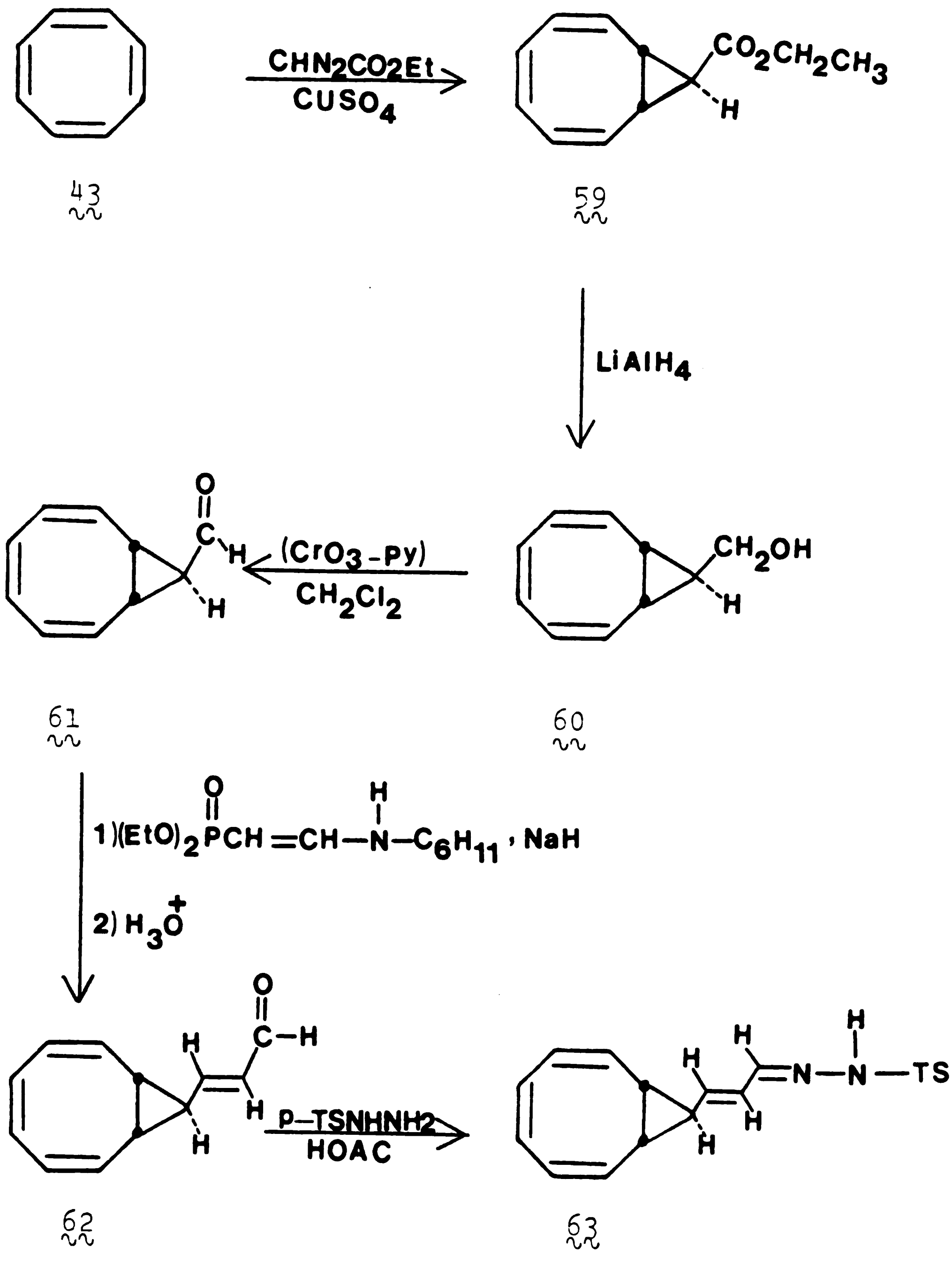
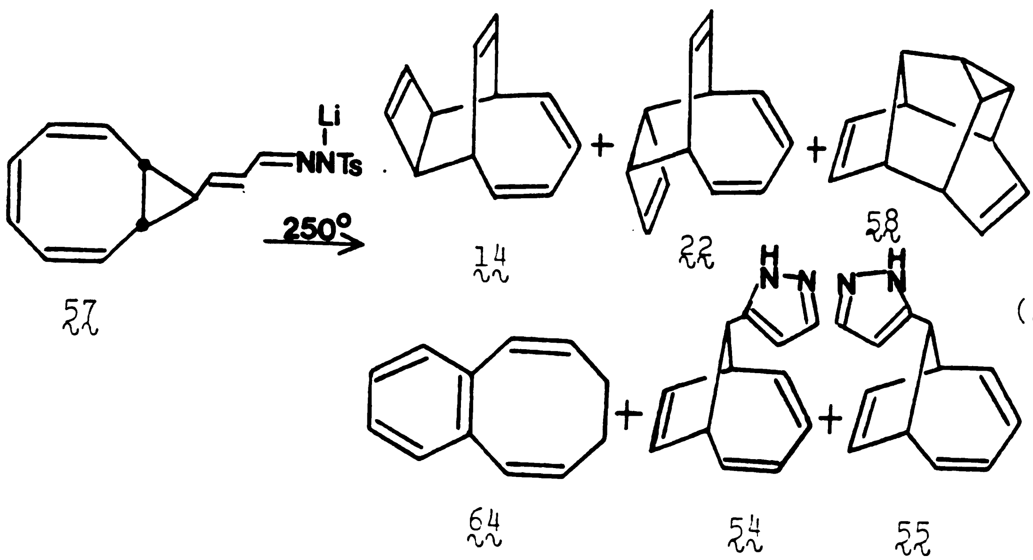


Figure 4. Preparation of Tosylhydrazone 63.

nitrogen. There were some less volatile products which were deposited on the extension tube wall between the flask and trap. GC/MS analysis of the volatiles showed the presence of five products. Mass spectra taken showed all these compounds to have molecular ion peaks at 156 corresponding to $(CH)_{12}$ hydrocarbons. Gas chromatographic separation of this mixture gave four major products 22, 14, 58 and 64 in a ratio of 4.0:2.2:2.0:1.0, respectively (one of the compounds was not enough to be identified). On the other hand, by flash chromatography of the less volatiles, two pyrazoles 54 and 55 were obtained in a ratio of 2.7:1.0, respectively (Equation 23).



(23)

Compounds 14, 22 and 64 were identified by comparison of their proton nmr chemical shifts with the literature values.[9b,14,24]

Pentacyclo[$6.4.0.0^{2,12}.0^{3,7}.0^{4,11}$]dodeca-5,9-diene **58**

The mass spectrum of diene **58** showed a molecular ion peak at 156 corresponding to $C_{12}H_{12}$ hydrocarbons. The 250 MHz proton nmr (δ, $CDCl_3$) (Figure 4) showed peaks at: 1.75 (dt,J=4.7 and 7.0 Hz, 1H), 1.91 (ddt, J=7.0, 5.5 and 1.5 Hz, 2H), 2.90 (m,2H), 3.15 (ddd, J=9.3, 5.5 and 1.5 Hz, 2H), 3.35 (dt, J=4.7 and 5.5 Hz, 1H), 5.45 (t, J=1.2 Hz, 2H), and 6.05 (dd, J=5.8 and 2.8 Hz, 2H). The proton decoupled ^{13}C nmr (δ, $CDCl_3$) (Figure 5) showed lines at: 134.8 (2c), 131.3 (2c), 66.3 (1c), 62.6 (2c), 41.8 (2c), 36.1 (2c), and 26.6 (1c). The proton coupled ^{13}C nmr (δ, $CDCl_3$) (Figure 6) consisted of peaks at: 134.6 (d, J=160.9 Hz, 2c), 131.1 (d, J=156.4 Hz, 2c), 66.2 (d, J=137.8 Hz, 1c), 62.3 (d, J=137.8 Hz, 2c), 41.6 (d, J=135.9 Hz, 2c), 36.0 (d, J=166.5 Hz, 2c), and 26.4 (d, J=171.1 Hz, 1c). According to the proton decoupled ^{13}C nmr, the molecule has a plane of symmetry reflecting five pairs of carbons and containing the two others. On the basis of the proton coupled ^{13}C nmr, the three carbons located at 36.0 and 26.4 ppm with C-H coupling of 166.5 and 171.1 Hz belong to a three membered ring.[25] With these data in hand and Balaban's graph,[4b] the structure of the diene can be one of the possibilities, 2-1-2-5, 2-1-2-9, 2-1-0-3, and 2-1-2-1 (named using Balaban's nomenclature, β, t, g, S; where β is the number of double bonds, t is the number of three membered rings, g is the number of four membered rings

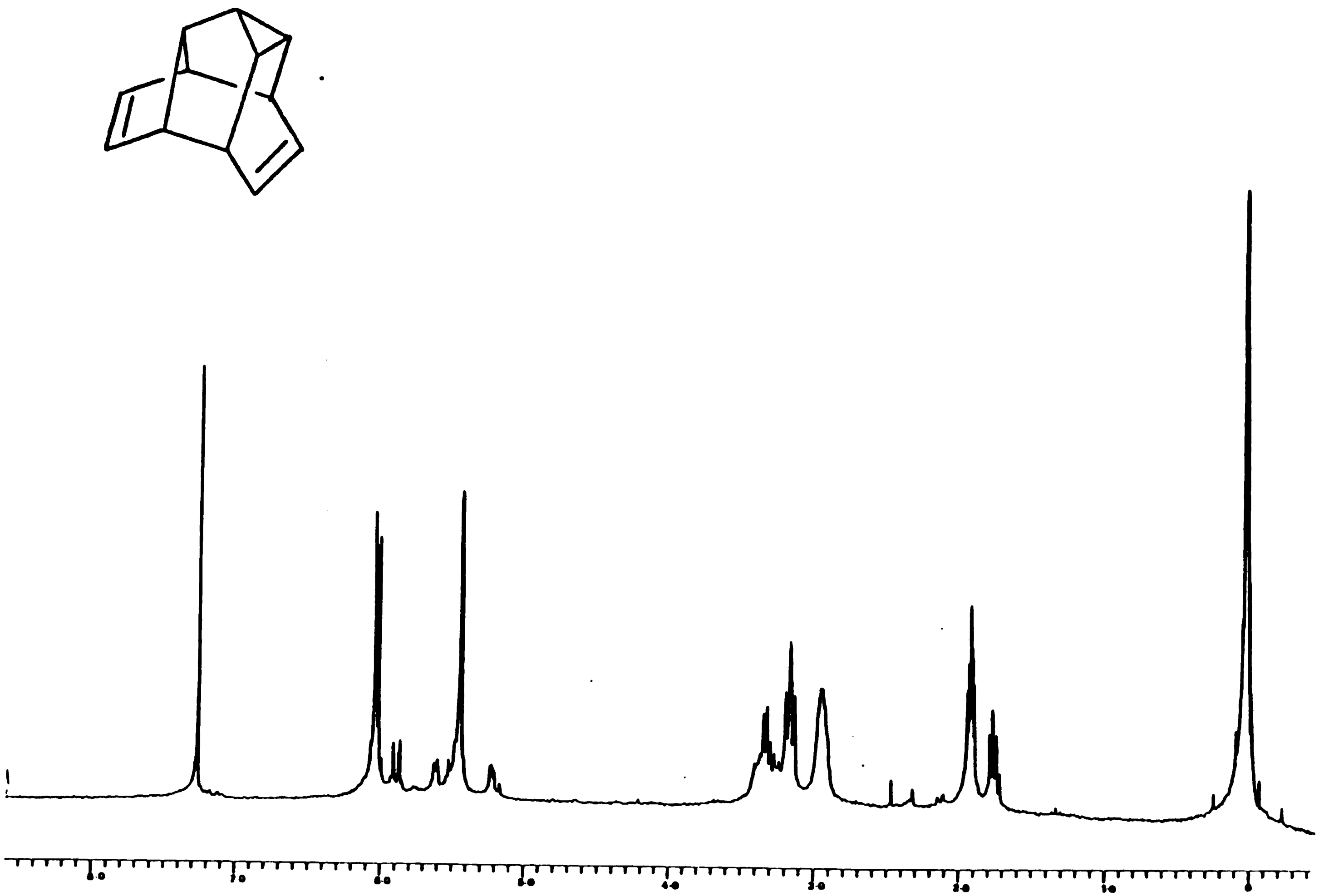


Figure 5. 250 MHz proton nmr spectra of diene 58.

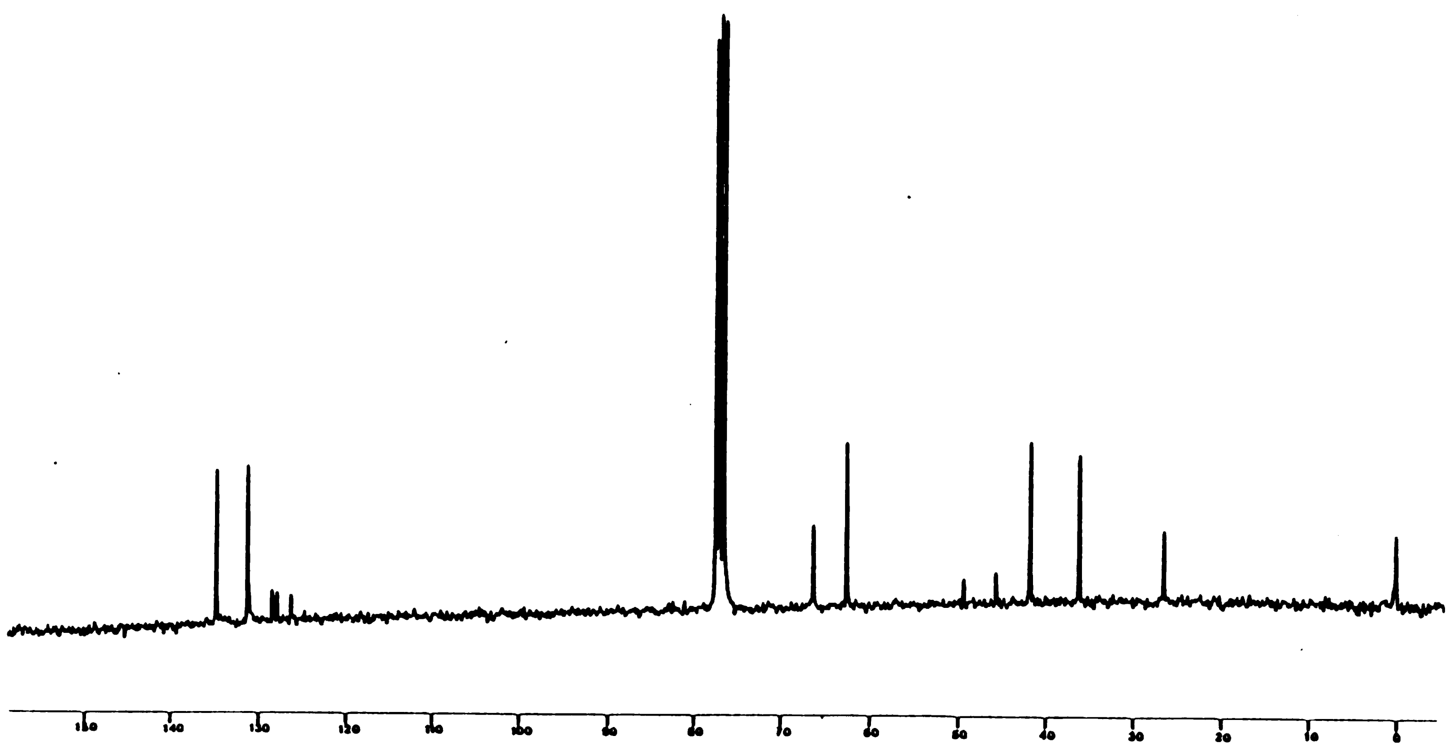


Figure 6. Proton decoupled ^{13}C nmr spectra of diene 58.

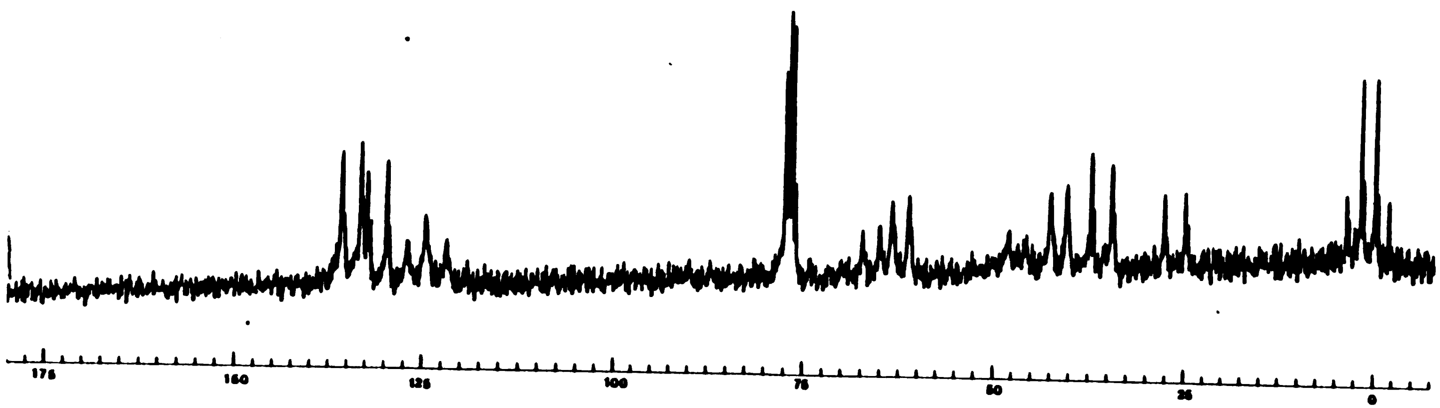


Figure 7. Proton coupled ^{13}C nmr spectra of diene 58.

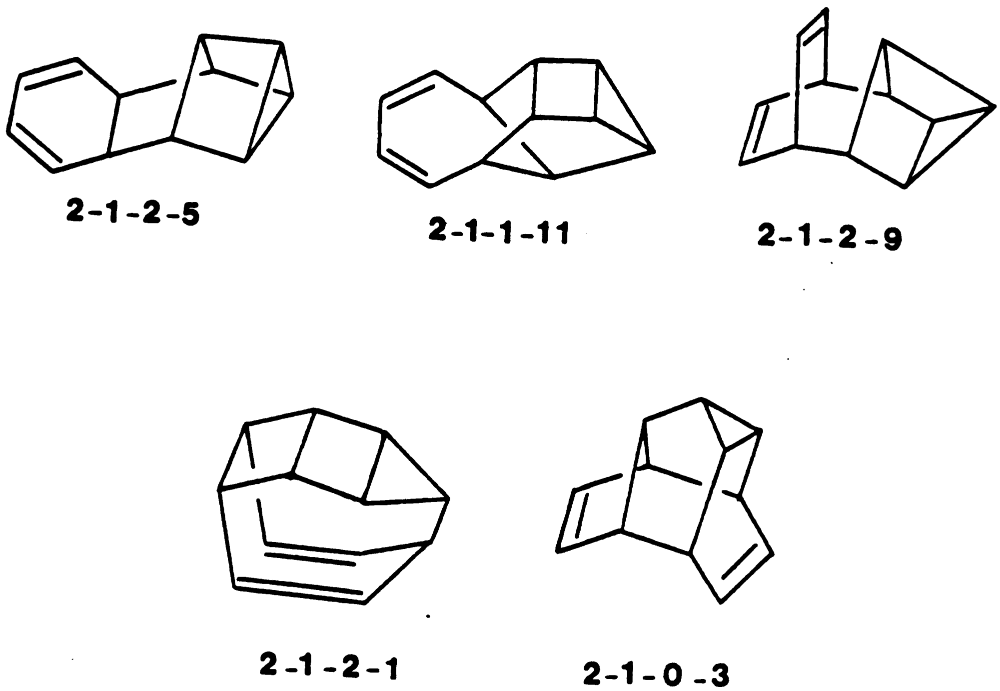
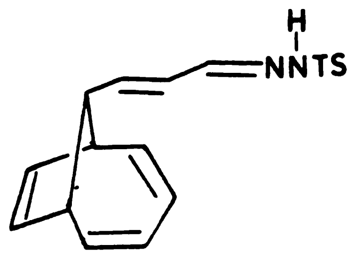


Figure 8. Cyclopropane containing symmetric structures possible for diene **58**.

and S is a serial number) (Figure 8).[4b] Since the ultraviolet spectrum of **58** showed no absorption above 250 nm[11] and since proton nmr decoupling experiments (see the spin decoupling results) showed the olefinic protons were not coupled to each other, we can say that the diene **58** is not a conjugated diene[26] and that the plane of symmetry must bisect each double bond. These two criteria eliminate the 2-1-2-5, 2-1-1-11, and 2-1-2-1. Isomer 2-1-2-9 cannot be the diene **58**, because the two olefinic pairs should be coupled with the same bridgehead protons. As a matter of fact, the spin decoupling studies showed that the olefinic pairs in diene **58** were coupled with different bridgehead protons. These considerations, and also the direct generation of diene **58** from decomposition of lithium and sodium salts of tosylhydrazone **65** both thermally and photochemically (see next parts) convinced us that the structure of diene **58** was that of 2-1-0-3.



65

Proton chemical shift and coupling constant assignments in diene **58** were made on the basis of spin-decoupling experiments. The results are illustrated in Figures 9 and 10. The multiplet signal at 2.90 ppm (2H) was coupled to signals at 6.05 (2H), 3.15 (2H), and 1.91 ppm (2H). Thus, this was assigned to the bridgehead protons $H_{8,11}$ which are adjacent to the olefinic protons $H_{9,10}$, the bridgehead protons $H_{4,7}$, and the **two bridge protons** $H_{1,12}$. This assignment was confirmed since the signal at 3.15 ppm (2H) was coupled to the signals at 5.45 (2H), 3.35 (1H),

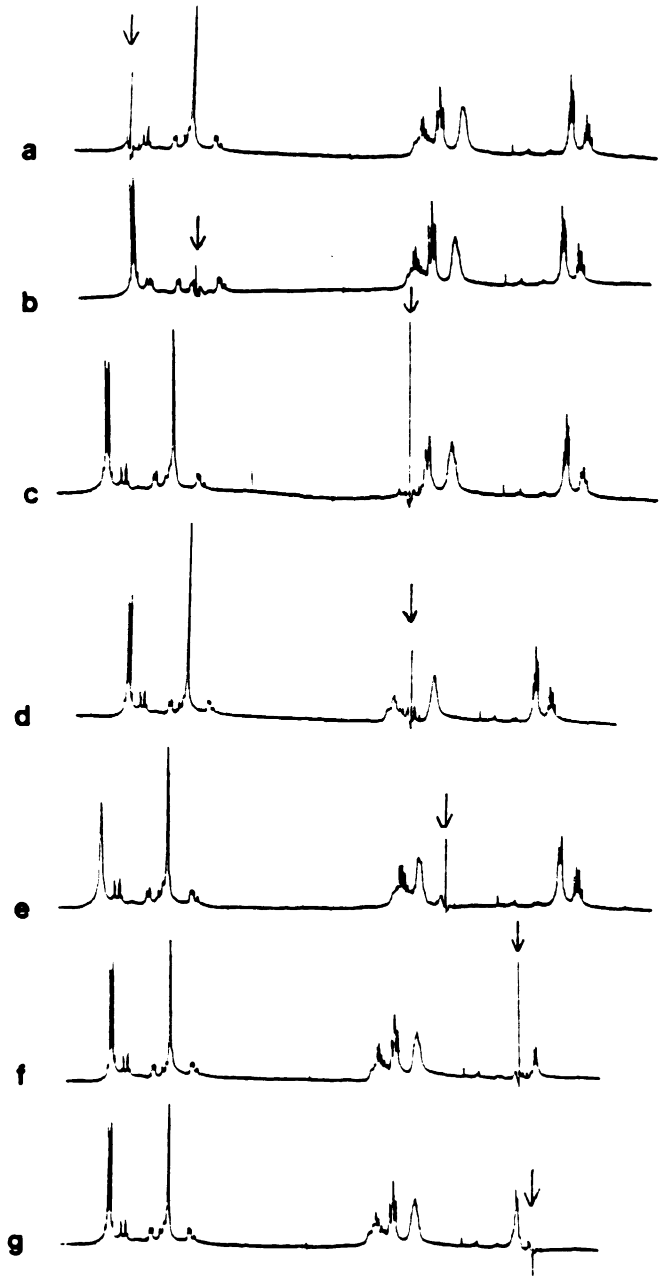


Figure 9. Decoupled proton nmr spectra of diene 58. Irradiation at (a) 6.05, (b) 5.45, (c) 3.35, (d) 3.15, (e) 2.9, (f) 1.91, and (g) 1.75 ppm.

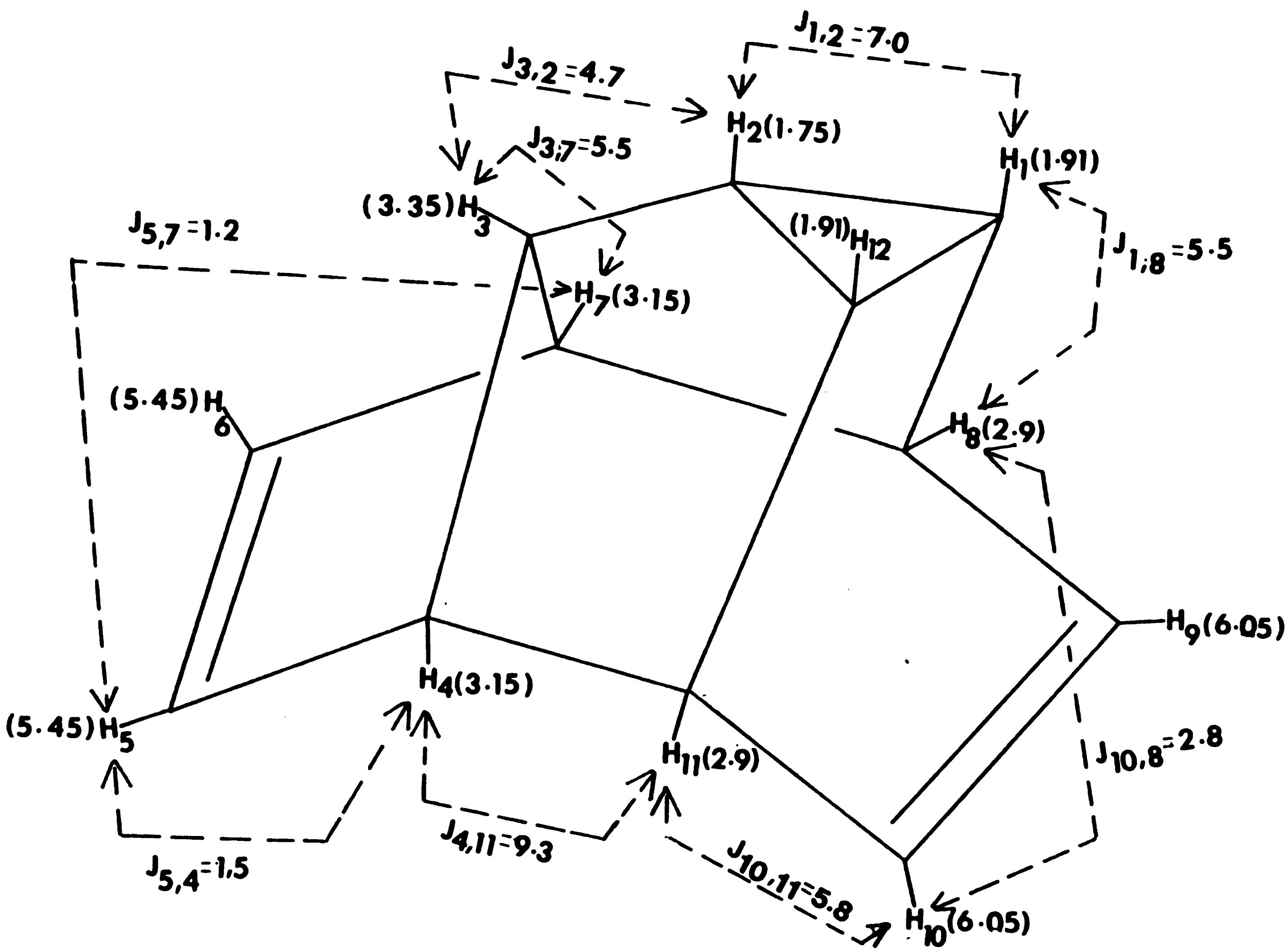


Figure 10. Proton chemical shift and coupling constant assignments in diene **58**.

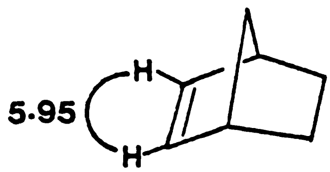
and 2.9 ppm (2H). As a result, the signal at 3.15 ppm was assigned to the bridgehead protons $H_{4,7}$ which are vicinally related to the olefinic protons $H_{5,6}$, the single bridge proton H_3, and the bridgehead protons H_8 and H_{11}.

The assignment for olefinic protons of diene **58** is in agreement with some similar reported compounds in the literature. Two olefinic protons H_5 and H_6 belong to a [4.2.1] bicyclic system, while the other two H_9 and H_{10} are located in a [4.2.2] bicyclic system. Figure 11 lists the reported olefinic chemical shifts for several similar bicyclic compounds.

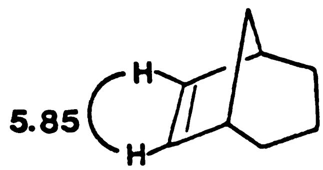
9-syn and anti (5-pyrazola)bicyclo[4.2.1]nona-2,4,7-trienes **54** and **55**

The mass spectrum of pyrazole **54**, the major product, showed a molecular ion peak at 184. The 60 MHz proton nmr spectrum (δ,$CDCl_3$) showed peaks at: 3.1-3.4 (m,3H), 5.12 (s,2H), 5.8 (bs,5H), 7.1 (m,1H), and 11.0 (bs,1H). Proton decoupled ^{13}C nmr (δ,$CDCl_3$) consisted of peaks at: 135.44 (2C), 126.09 (2C), 122.87 (2C), 46.37 (2C), and 36.07 (1C). The spectrum also included three small peaks at 145.69, 134.48, and 104.20 ppm belonging to the pyrazole ring.[31]

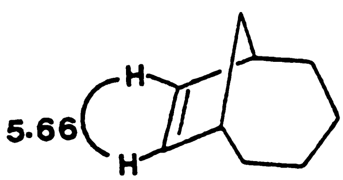
The molecular ion peak of pyrazole **55** similarly appeared at 184. The 60 MHz proton nmr spectrum (δ,$CDCl_3$)



Ref. 27



Ref. 28



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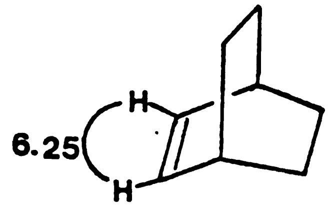

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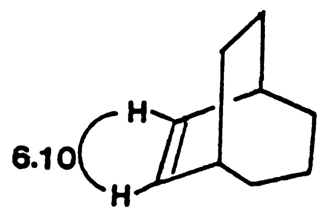
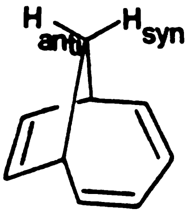


Ref. 30

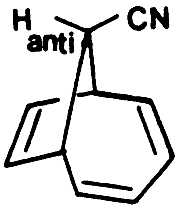
Figure 11. Olefinic chemical shifts (ppm) for bicyclo-[n.2.1] and [n.2.2] systems.

showed peaks at: 2.95 (s,1H), 3.12 (d,J=6.0 Hz,2H), 5.08 (s,2H), 5.6-6.1 (m,5H), and 6.98-7.1 (m,2H). Proton decoupled ^{13}C nmr (δ,$CDCl_3$) consisted of peaks at: 135.75 (2C), 124.26 (2C), 121.21 (2C), 50.08 (2C), and 40.22 (1C). Because of a noisy baseline, it was not possible to distinguish the peaks belonging to the pyrazole ring.

The stereochemistry of pyrazoles 54 and 55 were assigned unambiguously upon comparison of their nmr spectra with that of bicyclo[4.2.1]nona-2,4,7-triene 66[32] and its 9-substituted derivatives.[33]



66



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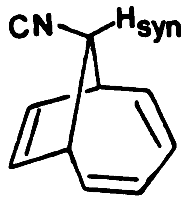

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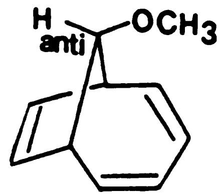
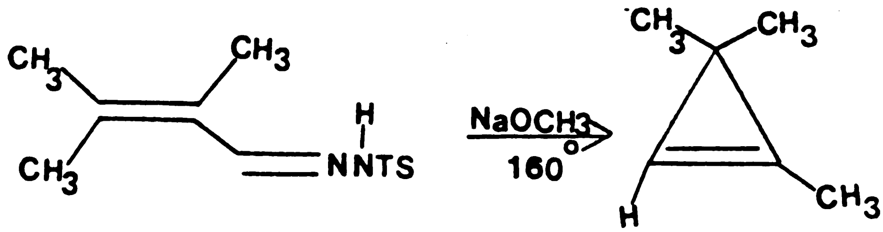


68

In compound 66, the dihedral angle of H_{syn} and bridgehead protons is 90° while the dihedral angle of H_{anti} with the bridgehead protons is close to 0°.[33] Hence, the nmr of H_{syn}, split only by H_{anti}, appears as a doublet, whereas that of H_{anti}, split by H_{syn} and bridgehead protons $H_{1,6}$, occurs as a triplet of doublets.[33] In case of compounds 67[34] and 68[33], the peaks belonging to H_{anti} appeared as a triplet at 3.13 ppm (J=6.0 Hz) and 3.85 ppm (J=6.2 Hz), respectively. On the other hand, the H_{syn} in compound 69[34] appeared as a singlet at 3.50 ppm.[34] So, the appearance of a multiplet at 3.1-3.4 ppm in the spectrum of pyrazole 54 should be an overlap of peaks belonging to the bridge and bridgehead protons characteristic of <u>syn</u> epimer, while the appearance of a singlet at 2.95 ppm in the spectrum of pyrazole 55 characterizes the <u>anti</u>-epimer.

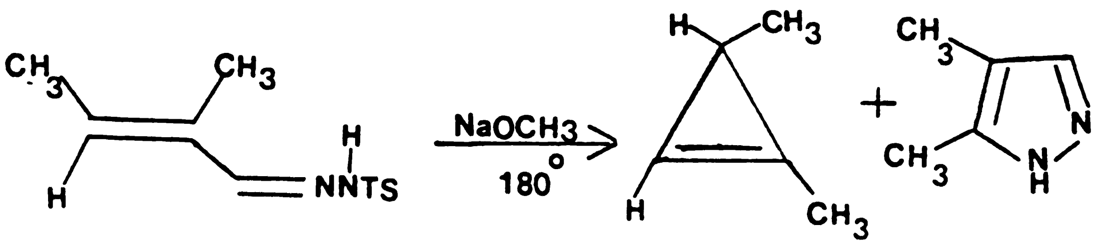
Mechanistic Investigation of the Tosylhydrazone Lithium Salt 57 Decomposition

As is known, decomposition of the tosylhydrazone salts of aldehyde and ketones both thermally and photochemically leads to the formation of carbenes.[35] However, in the case of tosylhydrazone salts of α,β-unsaturated aldehydes and ketones, the amount of carbene and its subsequent reactions strongly depends on the number of substituents at the β-position.[36] Thermal decomposition of the sodium salt of α, β-dimethylcrotonaldehyde tosylhydrazone 70 has been reported to give trimethylcyclopropene 71 in 72% yield[36b] (Equation 24). The presence of one hydrogen at the β-position diminished the yield of cyclopropene 73 substantially to 4% and led to the formation of 3,4-dimethyl pyrazole 74 in 60% yield[36b] (Equation 25).



(24)

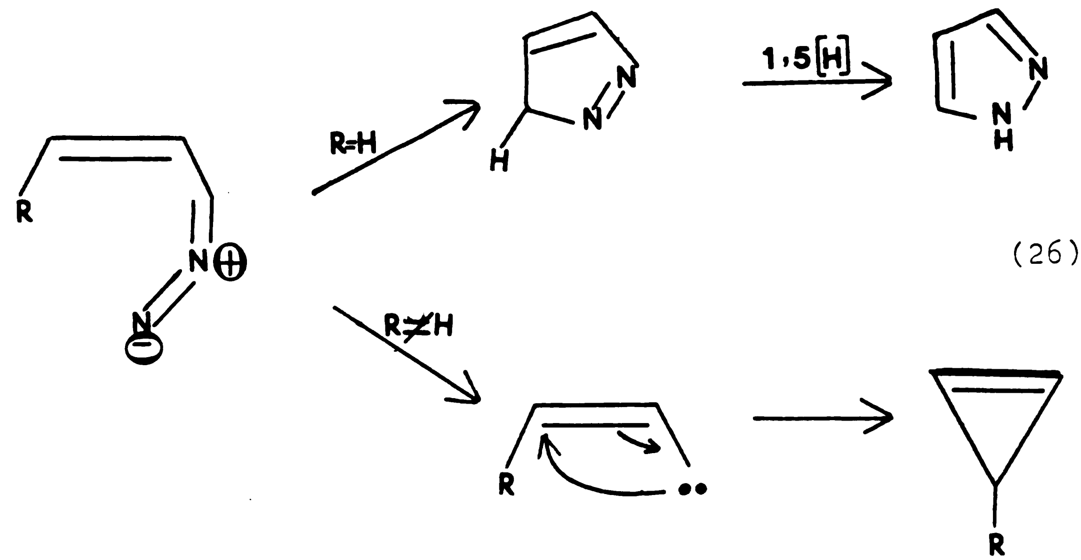
70 71



(25)

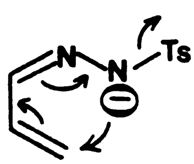
72 73 74

On the other hand, no cyclopropene has been observed from the decomposition of tosylhydrazone salts having two hydrogens at the β-position.[36b] Formation of pyrazole could result from cyclization of the diazo intermediate and subsequent [1,5] hydride shift[36] (Equation 26).



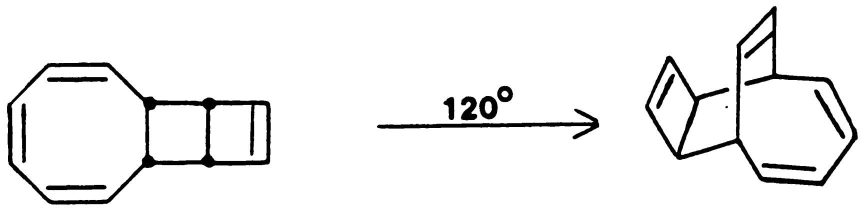
(26)

It is clear that the hydrocarbons, **14**, **22**, **58**, and **64** have arisen through the carbene intermediate while the pyrazoles **54** and **55** were formed either through the cyclization of salt or diazo intermediate and subsequent [1,5] hydride shift.



A Look at the Plausible Mechanisms for the Formation of Tetraenes 14 and 22

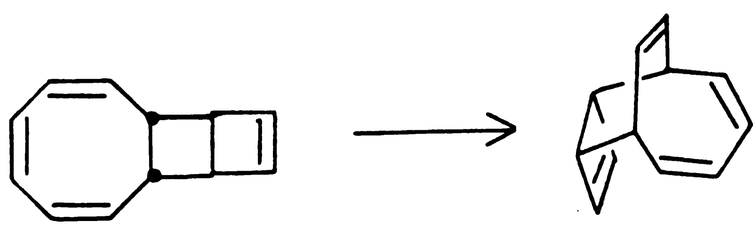
Paquette has reported that pyrolysis of cis, syn, cis-tricyclo[8.2.0.0^{2,9}]dodeca-3,5,7,11-tetraene 1 at 120° afforded the exo-tetraene 14 (Equation 27).[9]



(27)

1 14

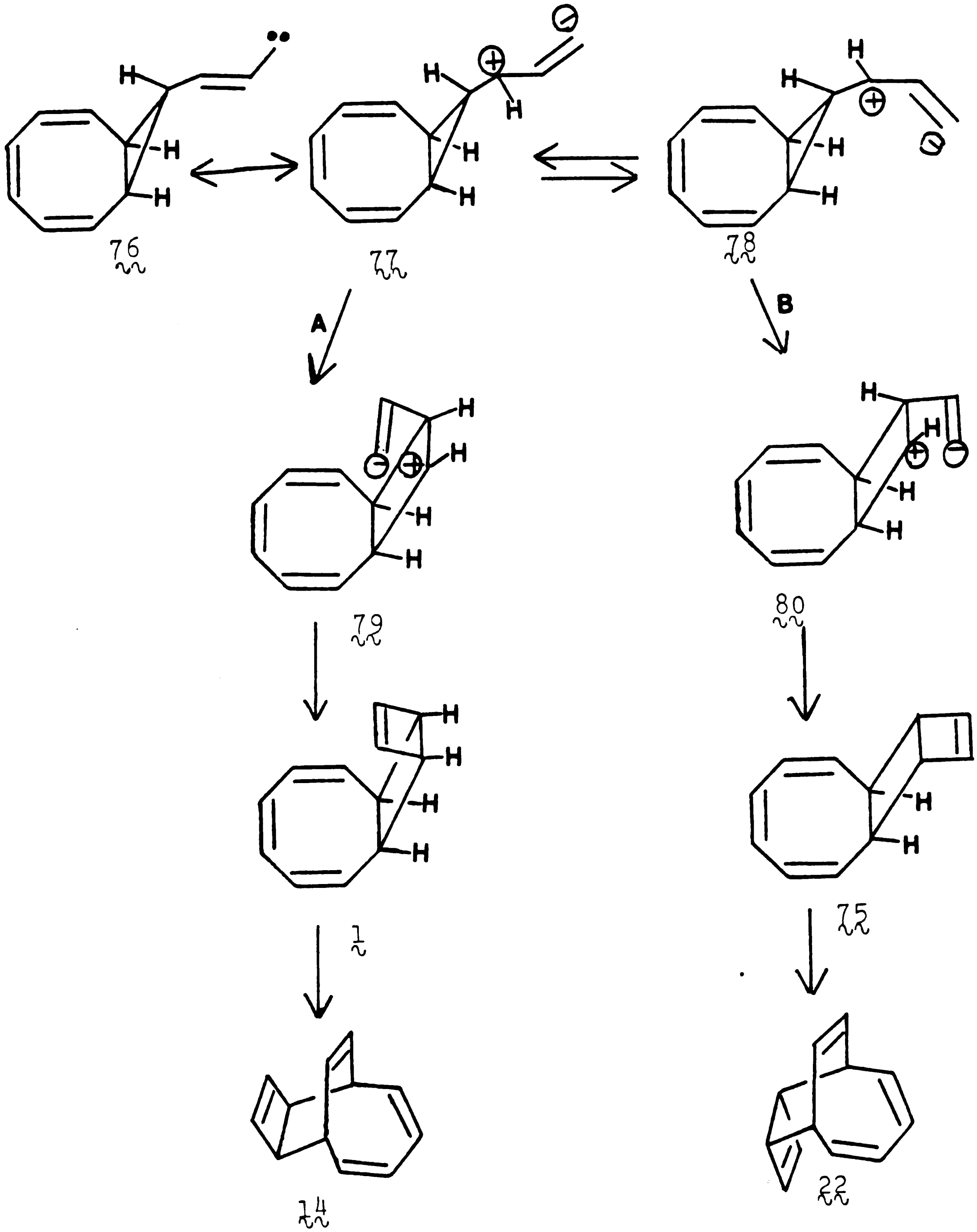
It seems likely that the anti-isomer 75 would isomerize to endo-tetraene 22 in an analogous fashion (Equation 28).



(28)

75 22

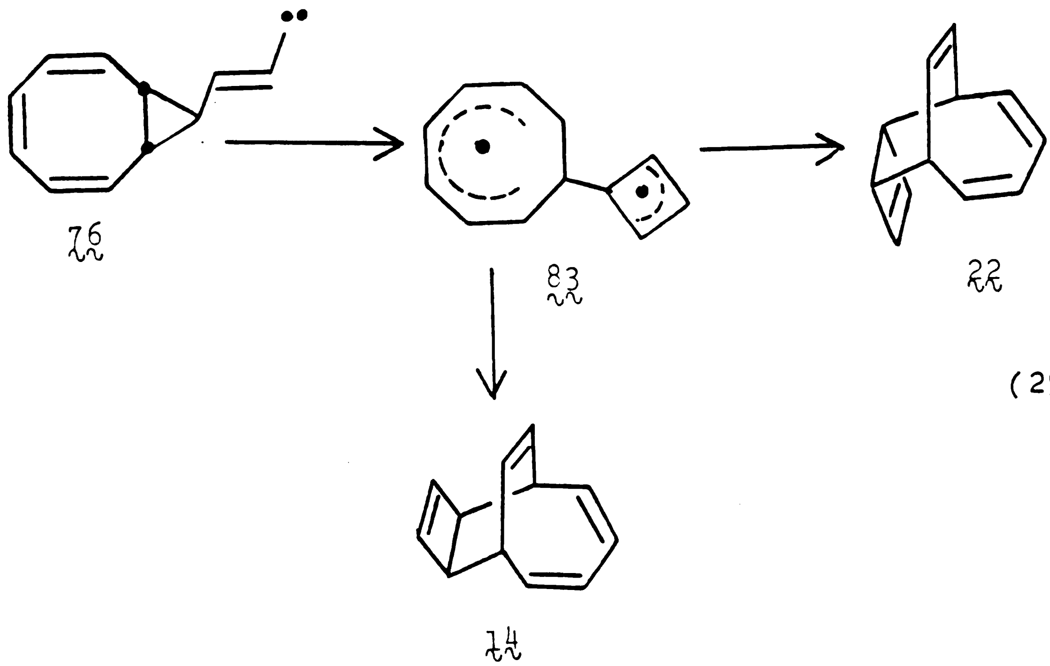
Formation of primary products 1 and 75 from carbene 76 may have arisen according to the following mechanism (Scheme 1). The bisected cyclopropyl carbonium ion 77, the mesomeric structure of carbene 76, is in conformational equilibrium with the bisected cyclopropyl carbonium ion 78. Although



Scheme 1. A plausible mechanism for the formation of tetraenes 14 and 22 from carbene 76.

the conformer 77 seems favored over conformer 78 because of its transoid arrangement, the intermediate 80 would be favored over 79 because the double bond is anti to the eight membered ring. The stereoselectivity of the reaction toward the formation of the endo-tetraene 22 as the major product requires that if the reaction goes through this mechanism, the pathway B would be favored over pathway A.

On the other hand, the carbene intermediate 76 could have generated the diradical intermediate 83 which upon subsequent cyclization could lead to tetraenes 14 and 22 (Equation 29).[9]



(29)

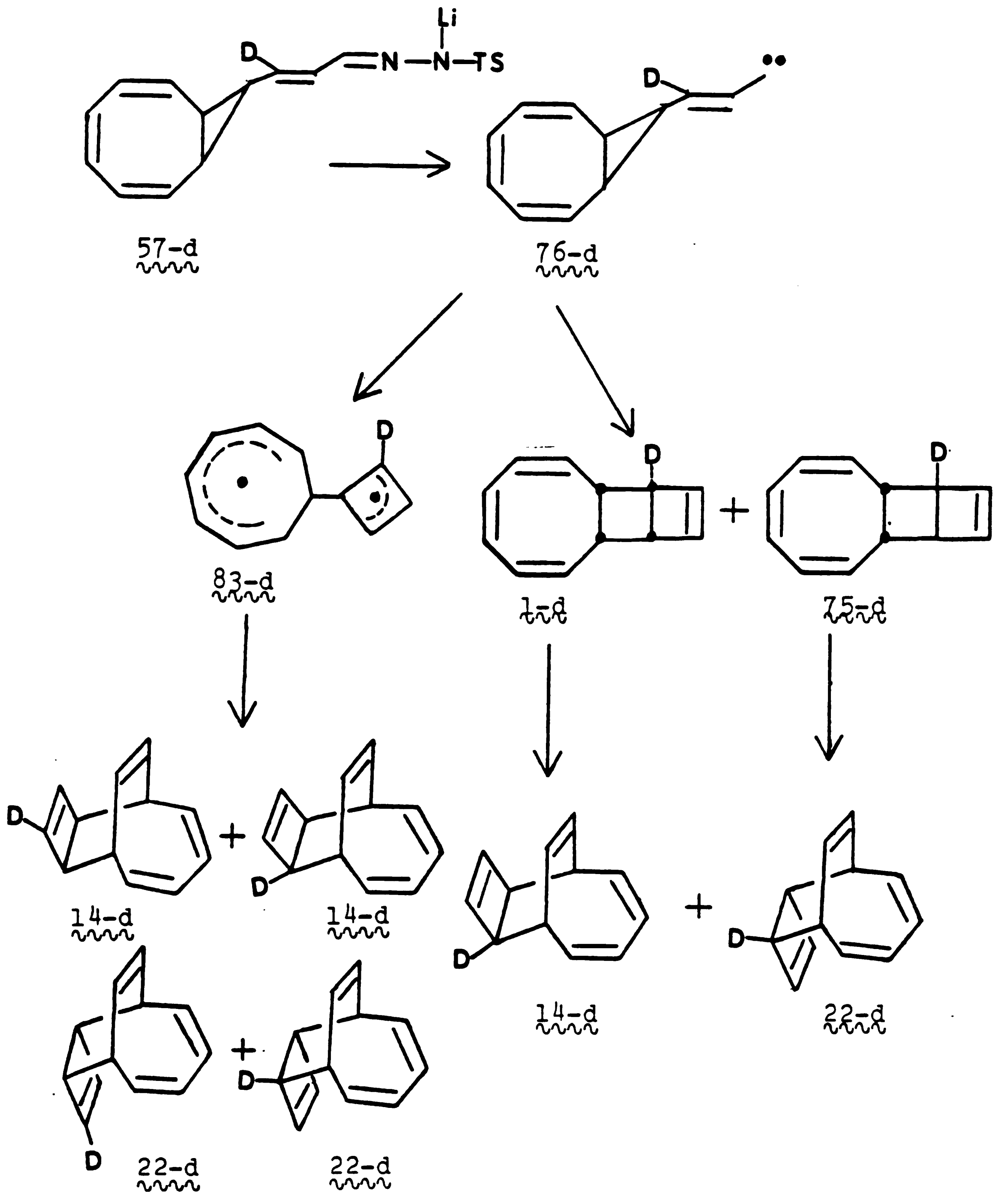
An important experiment which can distinguish between these mechanisms, would be the thermal decomposition of tosylhydrazone salt 57 with deuterium at the β-position (Scheme 2). The formation of tetraenes through Scheme 1 would result in compounds 14 and 22 with deuterium on aliphatic carbons, while intermediate 83 will end up with scrambling of deuterium at both aliphatic and olefinic carbons. Deuterated tosylhydrazone salt 57-d could easily be prepared as follows (Figure 12). Unfortunately, this experiment has not been performed, but work is currently in progress.

A Close Look at the Mechanism to Hydrocarbons 58, 64 and Pyrazoles 54, 55

A straightforward mechanistic pathway leading to diene 58 might be through the intramolecular Diels-Alder addition of compound 85, which could have been formed from a suprafacial [1,5] sigmatropic shift of cyclopropene 51 (Figure 13). To test this, we decided to look at the pyrolysis of cyclopropene 51.

Thermolysis of anti-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]-nona-2,4,6-triene 51. Preparation of Pentacyclo[6.4.0.-$0^{2,4}.0^{3,10}.0^{5,9}$]dodeca-6,11-diene 86

Many attempts at pyrolysis of cyclopropene 51[23] using different methods either gave the starting material or polymers. We found that the best method for pyrolysis



Scheme 2. Thermal decomposition of deuterated tosylhydrazone salt 57-d.

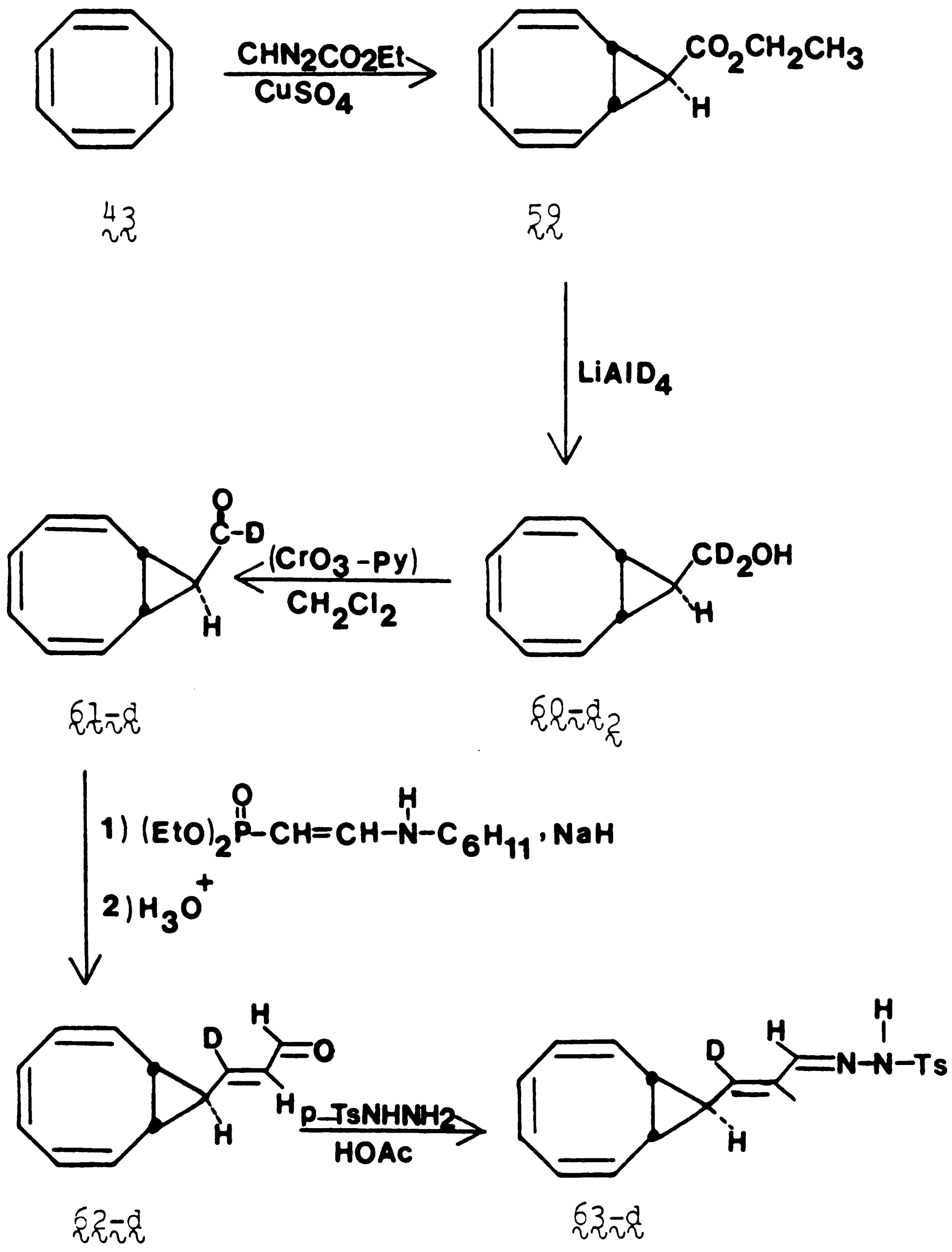


Figure 12. Proposed procedure for preparation of Deuterated Tosylhydrazone Salt 57-d.

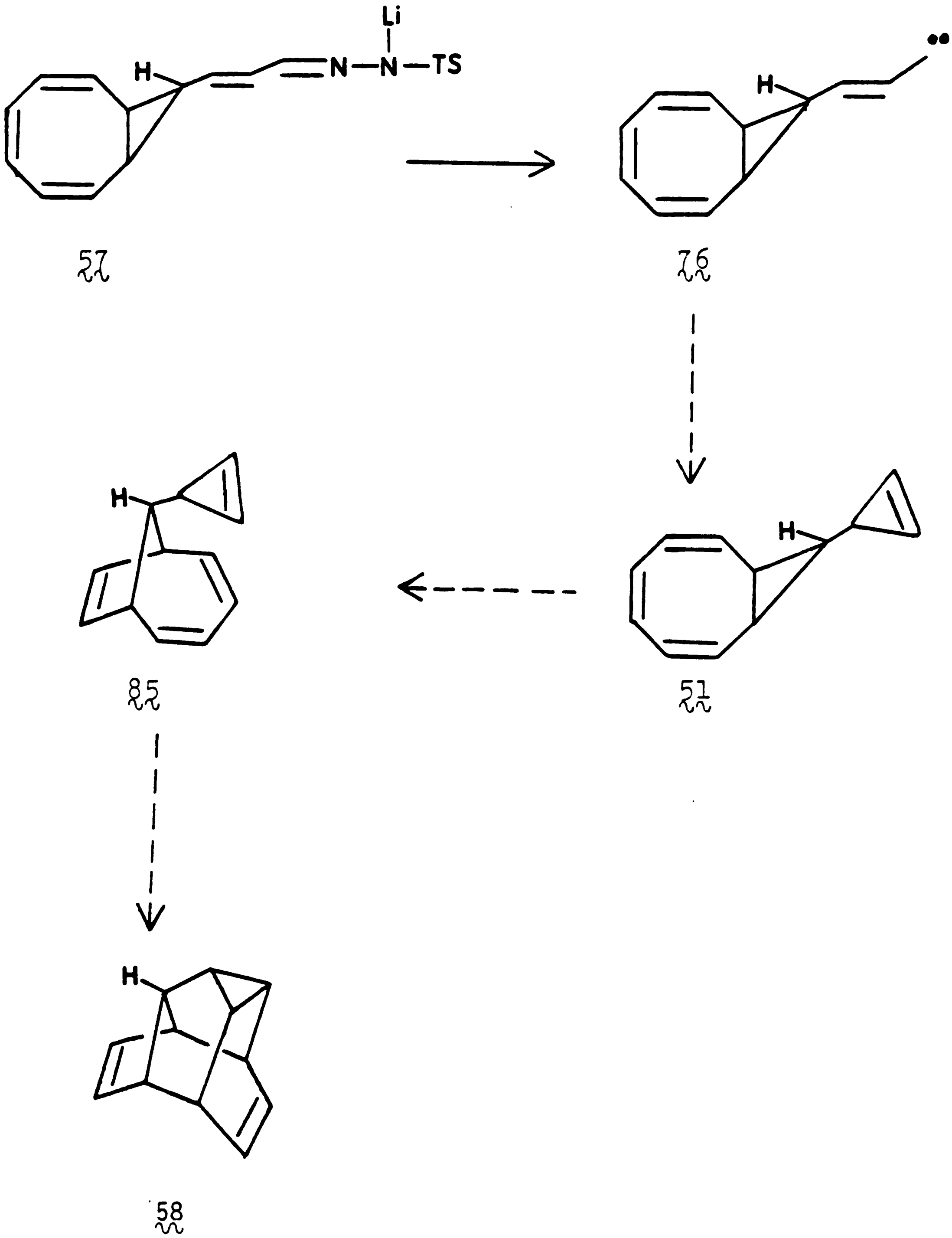
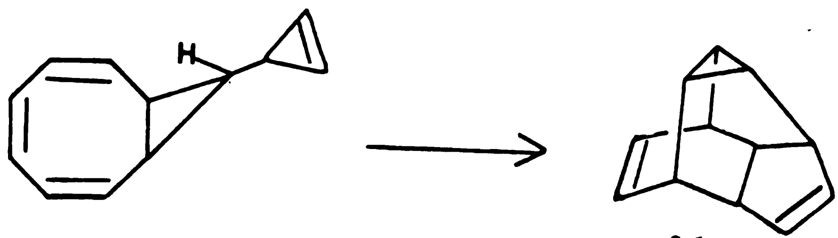


Figure 13. A plausible mechanism for the formation of diene 58.

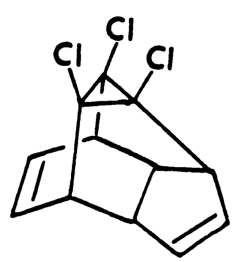
of hydrocarbon 51 was to add its solution in tetrahydrofuran to a hot flask connected to a hot column containing glass beads, both at 300° under an argon stream. The volatiles were pumped and collected in a trap kept in liquid nitrogen. Gas chromatographic separation gave hydrocarbon 86, a new $(CH)_{12}$ member, in 2.6% yield (Equation 30).



(30)

51 86

Hydrocarbon 86 was identified as pentacyclo[$6.4.0.0^{2,4}.0^{3,10}.0^{5,9}$]dodeca-6,11-diene (Balaban's number, 2-1-0-2)[4b] because of the closely parallel of its proton nmr spectrum to that of the known compound 87.[37]



87

The mass spectrum of hydrocarbon 86 showed the molecular ion peak of 156. The 250 MHz proton nmr spectrum (δ, $CDCl_3$) (Figure 14) of compound 86 consisted of peaks at: 0.75-0.90 (m,2H), 1.75 (ddd,J=7.9, 4.9 and 4.1 Hz,1H), 1.85 (dd,J=6.2 and 3.3 Hz,1H), 2.35 (ddd,J=7.5, 6.2, and 5.1 Hz,

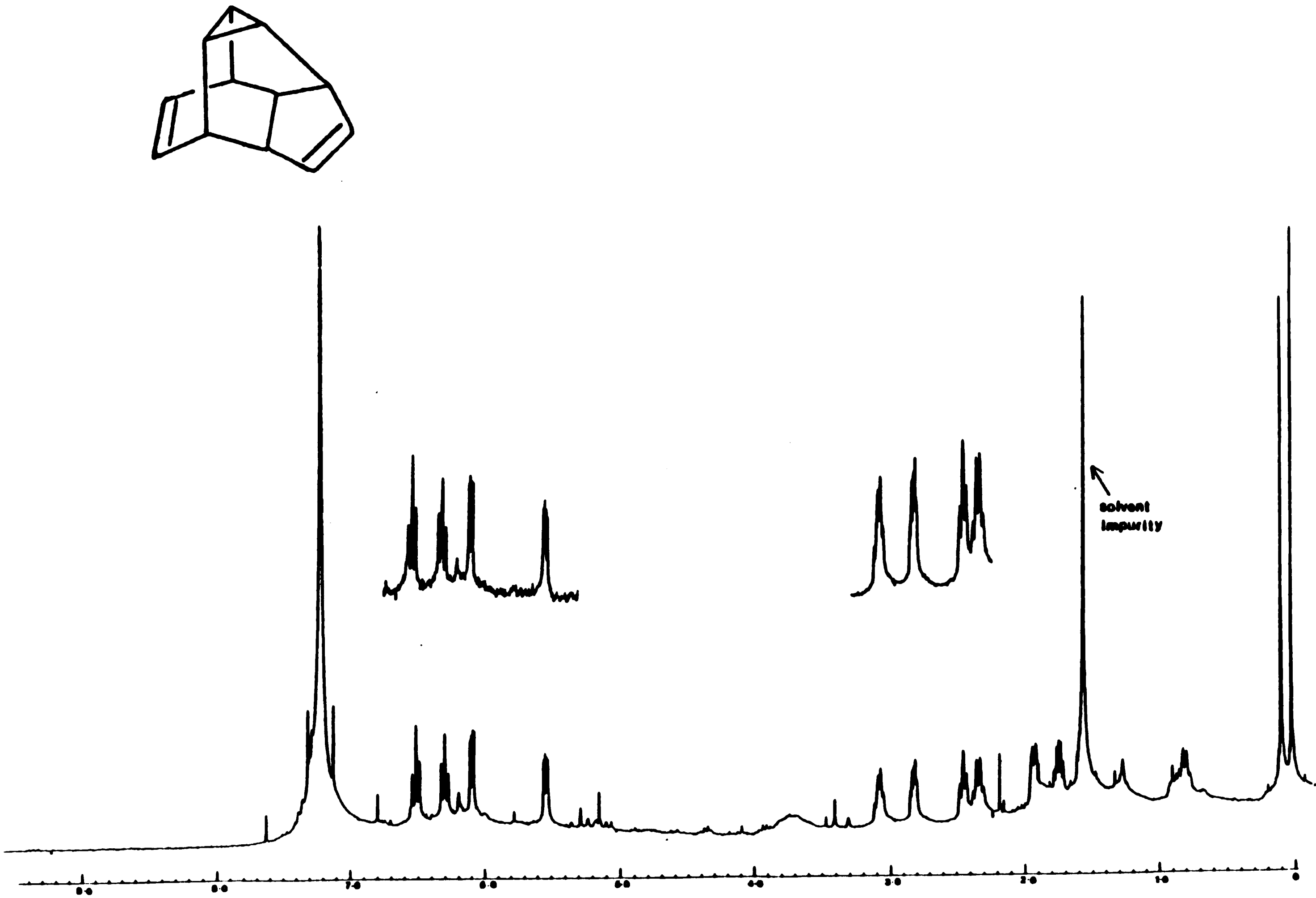


Figure 14. 250 MHz proton nmr spectra of compound 86.

1H), 2.48 (dd,J=7.9 and 6.2 Hz, 1H), 2.82 (dd,J=5.1 and 3.2 Hz,1H), 3.06 (dd,J=7.5 and 5.8,1H), 5.55 (dd,J=5.0 and 3.3 Hz,1H), 6.12 (dd,J=5.0 and 3.3 Hz,1H), 6.33 (dd,J=7.9 and 5.8 Hz,1H), and 6.55 (dd,J=7.9 and 6.2 Hz,1H).

Proton chemical shift and coupling constant assignments in compound **86** were made in the same way as that of the similar structure **87**.[37] Figure 15 shows the chemical shift and coupling constant assignments in compound **86** and the reported assignments for compound **87**.[37] Because of its similarity to compound **87**,[37] the proton chemical shift assignment for compound **86** was straightforward except for the cyclopropane hydrogens. Indeed, the three cyclopropane protons appeared at 1.75 and 0.75-0.9 ppm as a doublet of doublet of doublets and a multiplet in a ratio of 1:2. A molecular model showed that, of the three cyclopropane ring protons, H_3 and H_4 have dihedral angles near 90° with their respective vicinal protons, H_{10} and H_5, while H_2 had a dihedral angle with the bridgehead proton H_1 near 0°. As a consequence, the single proton at 1.75 ppm was assigned to H_2 which showed a large vicinal coupling of 7.9 Hz to the bridgehead proton H_1. The difference in chemical shift could arise from the diamagnetic anisotropy effect of the double bond C_{11}-C_{12} which is experienced differently by H_2 and $H_{3,4}$.[38]

The formation of hydrocarbon 86 can be explained according to the mechanism proposed by Mock for the formation

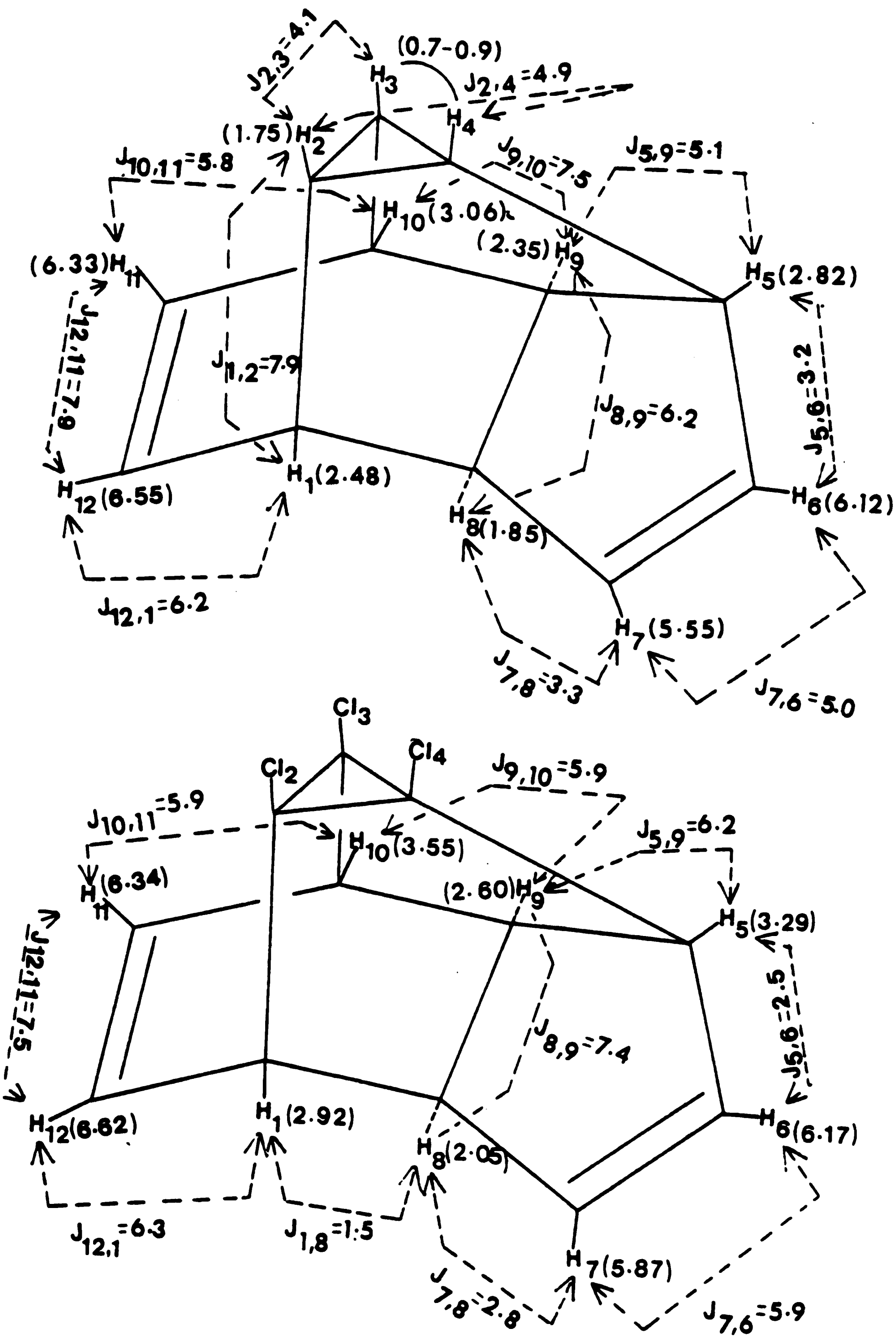


Figure 15. Proton chemical shift and coupling constant assignments in 86 (top), and reported assignment in compound 87 (bottom).

of the similar compound **87** as follows[37] (Figure 16). The intermediates **88** and **89** may be produced by disrotatory ring closure of initial product **52**.[37] From these two, only **89** can feasibly undergo an internal cycloaddition to give **86**.[37]

Incidently, the retention time for compound **86** was exactly the same as that of the unidentified minor compound from the pyrolysis of salt **57**. If this compound is **86**, one can definitely say that it could have come from cyclopropene hydrocarbon **51**. This in turn means that the cyclopropene hydrocarbon **51** has been generated from the pyrolysis of salt **57**, but rearranged to **86** under the pyrolytic conditions.

As we discussed, cyclopropene **51** cannot be the precursor for the formation of polycyclic **58**. Other possibilities for the formation of hydrocarbons **58**, **64** and pyrazoles **54** and **55** are shown in Scheme 3. The formation of epimeric pyrazoles **54** and **55** could have come from, (1) cyclization of diazointermediates **91** and **92** (path F) which were formed either by a step-wise [1,5] shift of diazo intermediate **90** (path B) or from the two <u>syn</u> and <u>anti</u> tosylhydrazone salts **93** and **94** (path D) which were generated from a step-wise [1,5] shift of salt **57** (path C), or (2) a step-wise [1,5] shift of pyrazole **95** (path E). All these pathways seem possible for the formation of pyrazoles **54** and **55**. The two hydrocarbons **58** and **64** could have come from the carbenes **96** and **97** which may

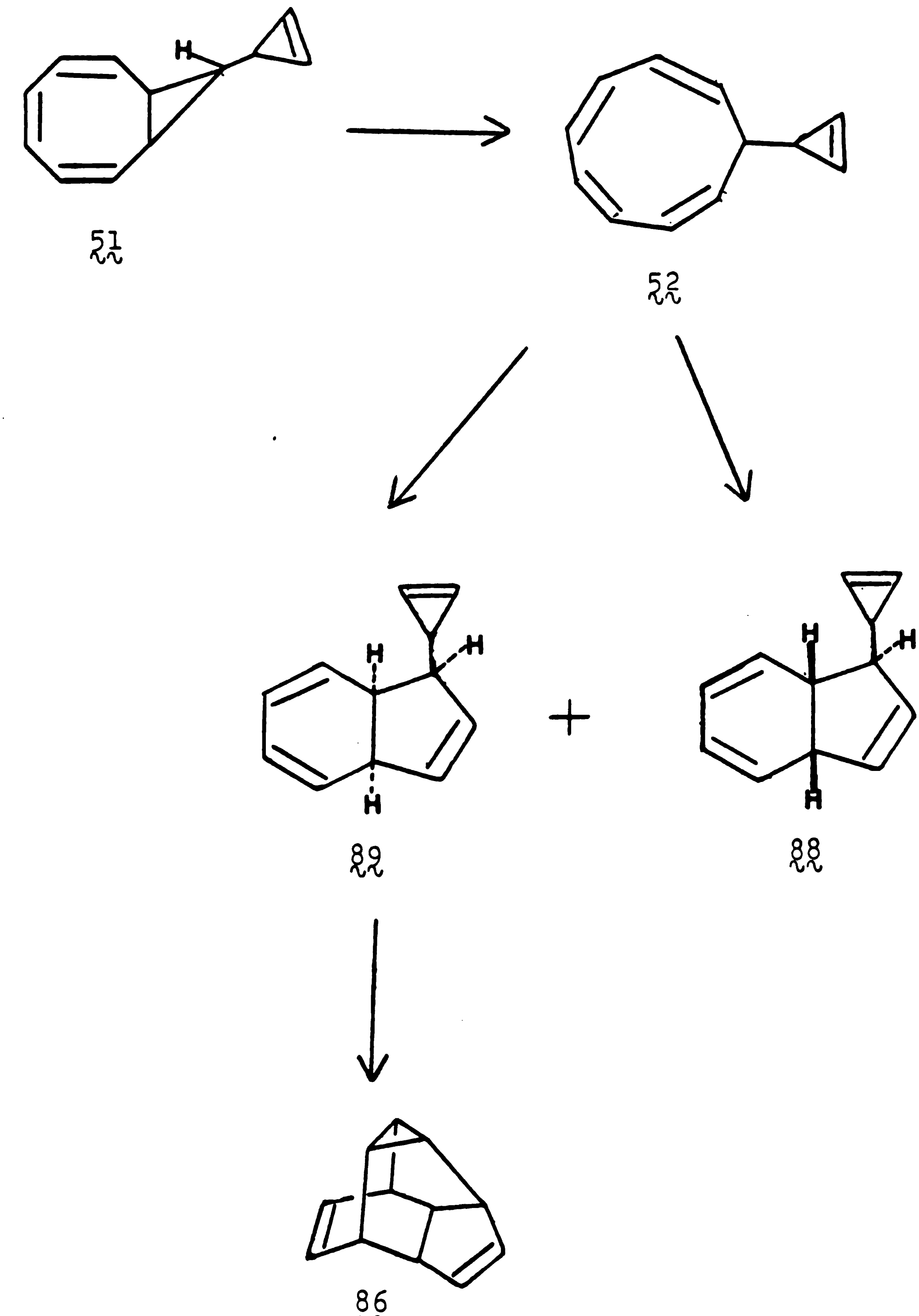
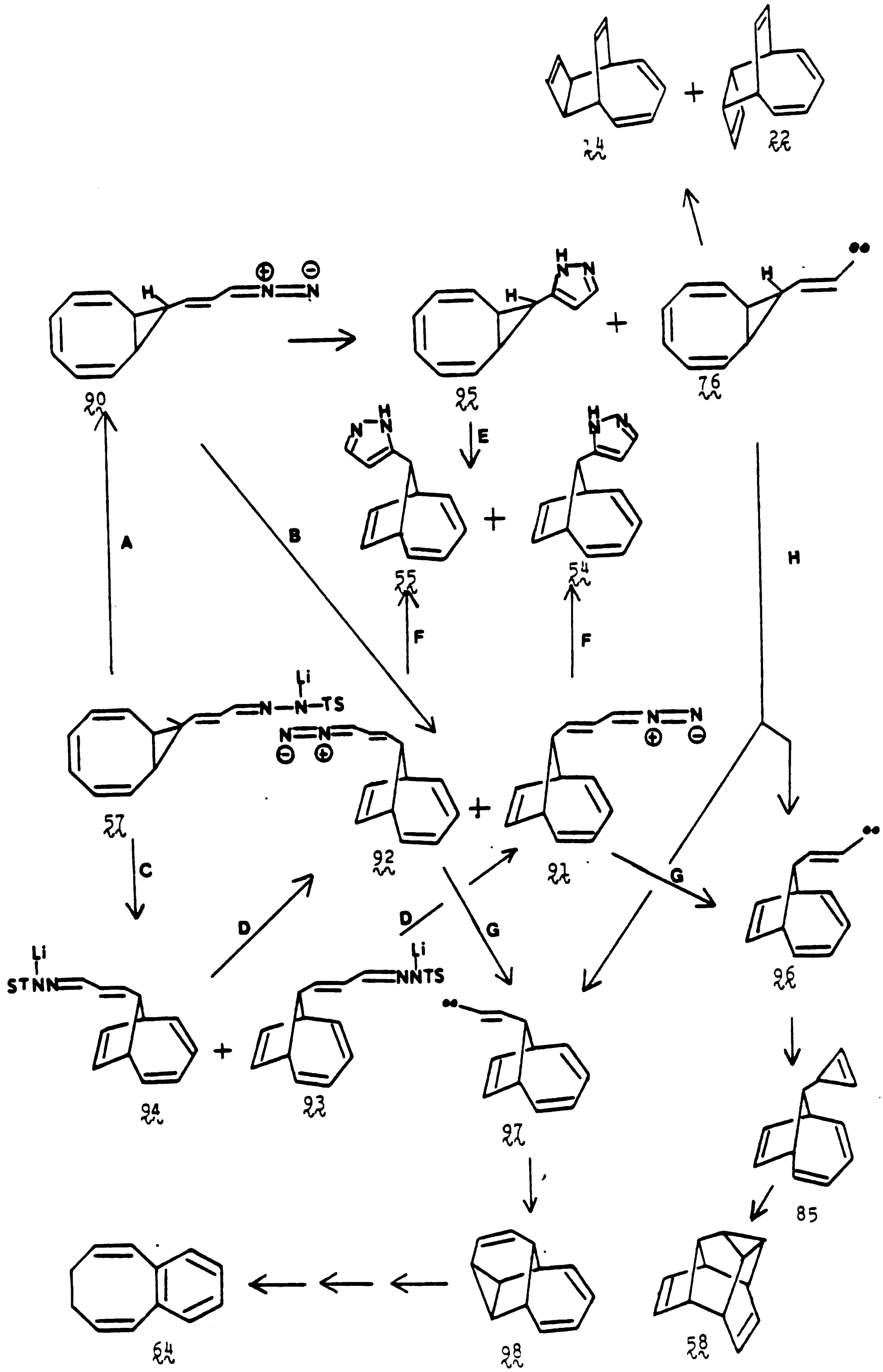
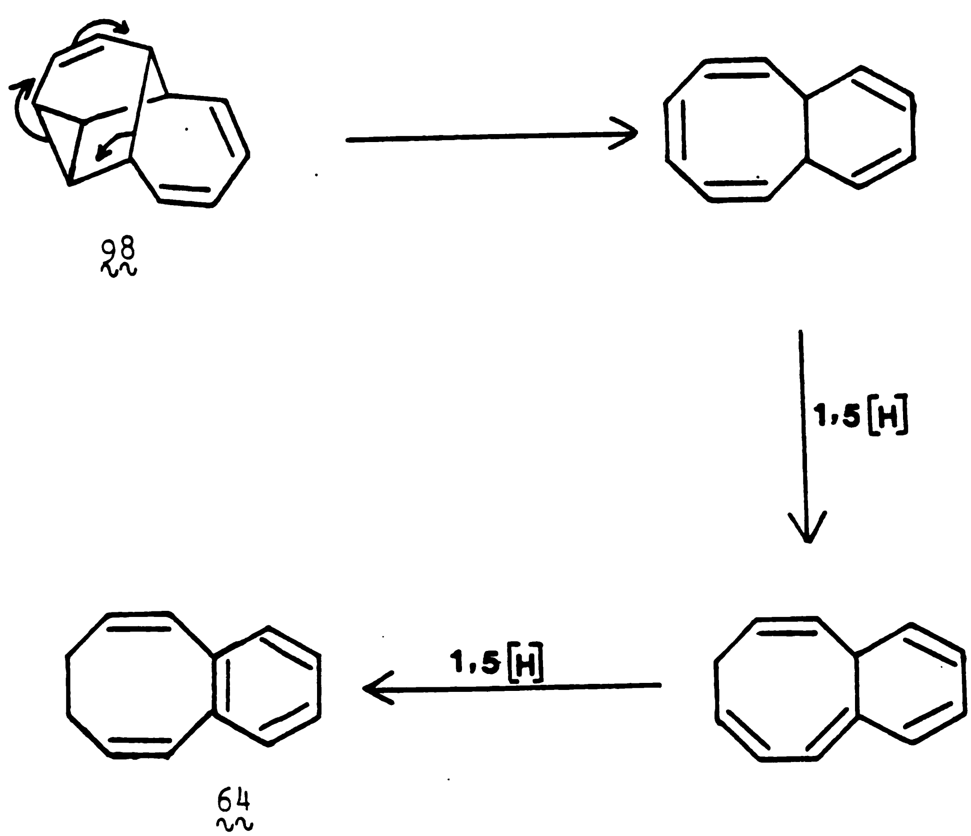


Figure 16. A plausible mechanism for the formation of compound 86.



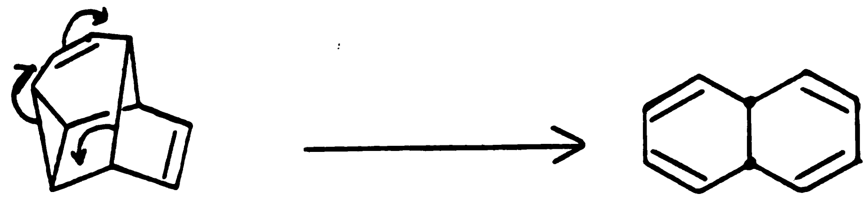
Scheme 3. Thermal decomposition of tosylhydrazone salt 57.

have been formed either from a step-wise [1,5] shift of carbene 76 (path H) or from the diazo intermediates 91 and 92 (path G). From these two (path H and path G), the first path which requires a [1,5] shift of a short-lived species such as vinyl carbene 76 through a step-wise process seems less likely. As a consequence, carbenes 96 and 97 as the precursors for the formation of hydrocarbons 58 and 64 (and probably tetraenes 14 and 22) were formed from the rearranged tosylhydrazone salts 93 and 94. Although we did not find any evidence for the presence of compound 98, the formation of hydrocarbon 64 may have come through this primary product as follows (Equation 31).



(31)

Such a rearrangement has been reported in case of a similar compound 99 which underwent a fast reverse Diels-Alder reaction at 100° and gave dihydronaphthalene 100[3c] (Equation 32).

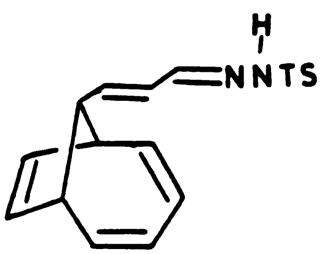


99

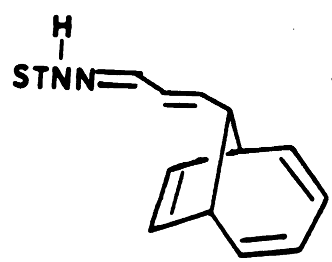
100

(32)

At this stage, one experiment which seemed worthwhile was to prepare the tosylhydrazones 65 and 101 and look at the thermal and photochemical decomposition of their salts 93 and 94.



65

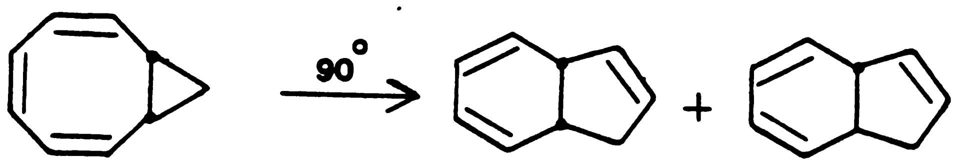


101

The results of these experiments were thought to be helpful in determining the way in which hydrocarbons 11, 22, 58, and 64 were formed from the pyrolysis of the tosylhydrazone salt 57. The most straightforward procedure for preparation of tosylhydrazones 65 and 101 seemed to be available from the thermal rearrangement of tosylhydrazone 63.

Thermal Rearrangement of [6.1.0] System.

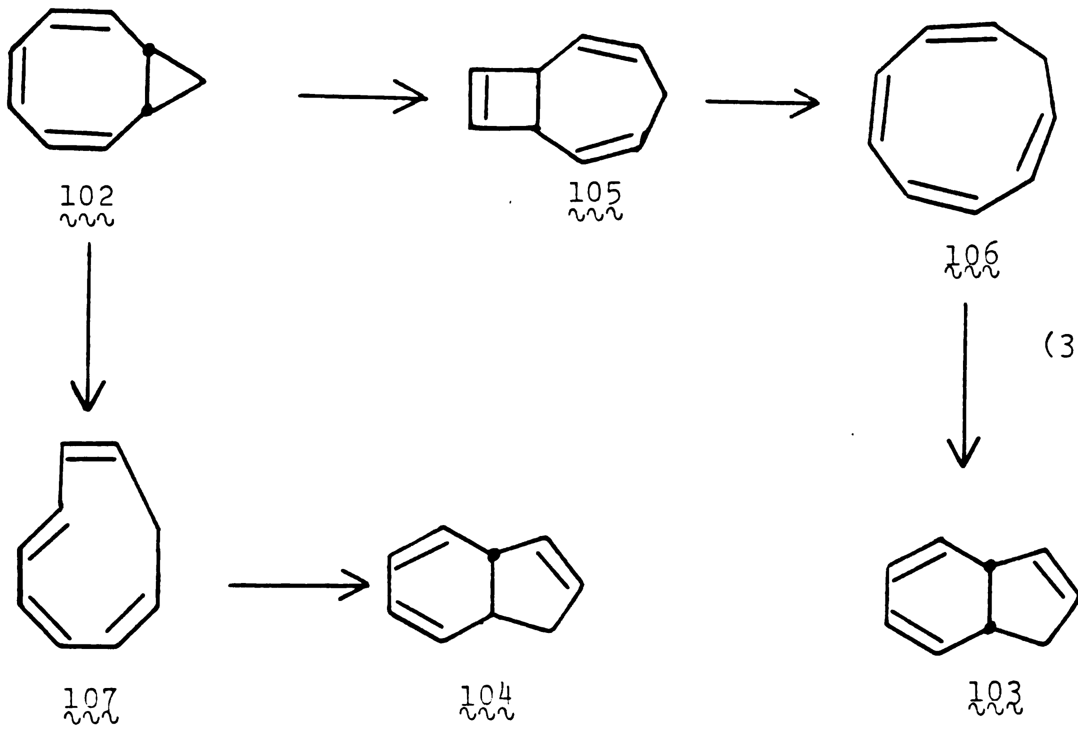
Thermal rearrangement of bicyclo[6.1.0]-2,4,6-triene and its 9-substituted derivatives have been reported in the literature. Vogel and collaborators synthesized cis-bicyclo [6.1.0]nona-2,4,6-triene 102 in 1961, and discovered its rearrangement to a 9:1 mixture of cis and trans dihydro-indene 103 and 104 at 90°[39] (Equation 33).



(33)

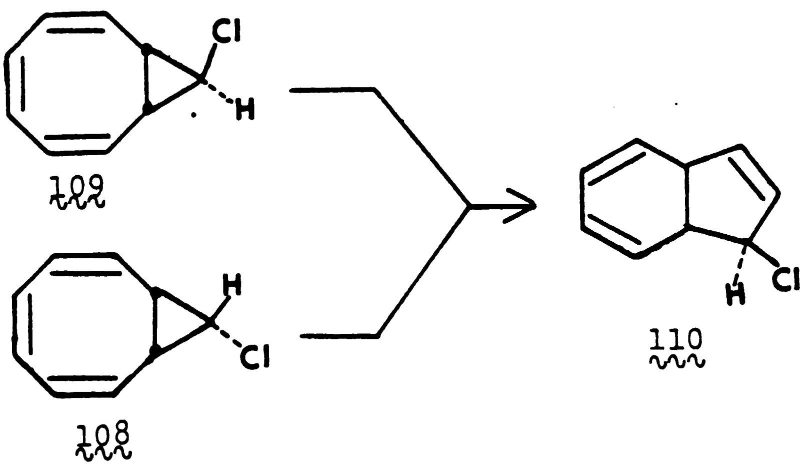
102 103 104

Labeling experiments showed that the formation of cis isomer 103 may occur through the valence isomers bicyclo-[5.2.0]nona-2,5,8-triene 105 and cis, cis, cis, cis-cyclo-nonatetraene 106[40] while the trans isomer 104 is formed through the cis,trans,cis,cis-cyclononatetraene 107 (Equation 34). Thermolysis of syn and anti 9-chloro-bicyclo-[6.1.0]nona-2,4,6-trienes 108 and 109 led[41] to the formation of compound 110 (Equation 35). Despite this evidence, deuterium labeling studies showed conclusively that 108 and 109 reacted by different mechanisms[41]

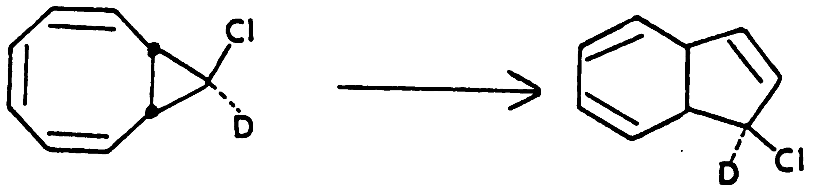


(34)

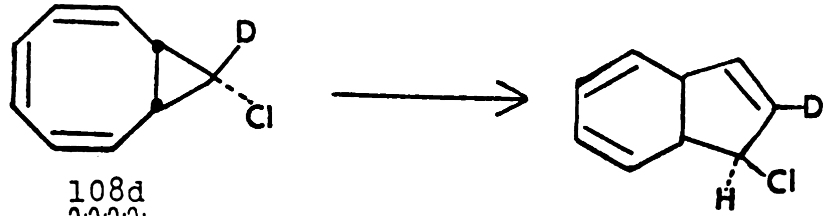
(Equations 36,37).



(35)

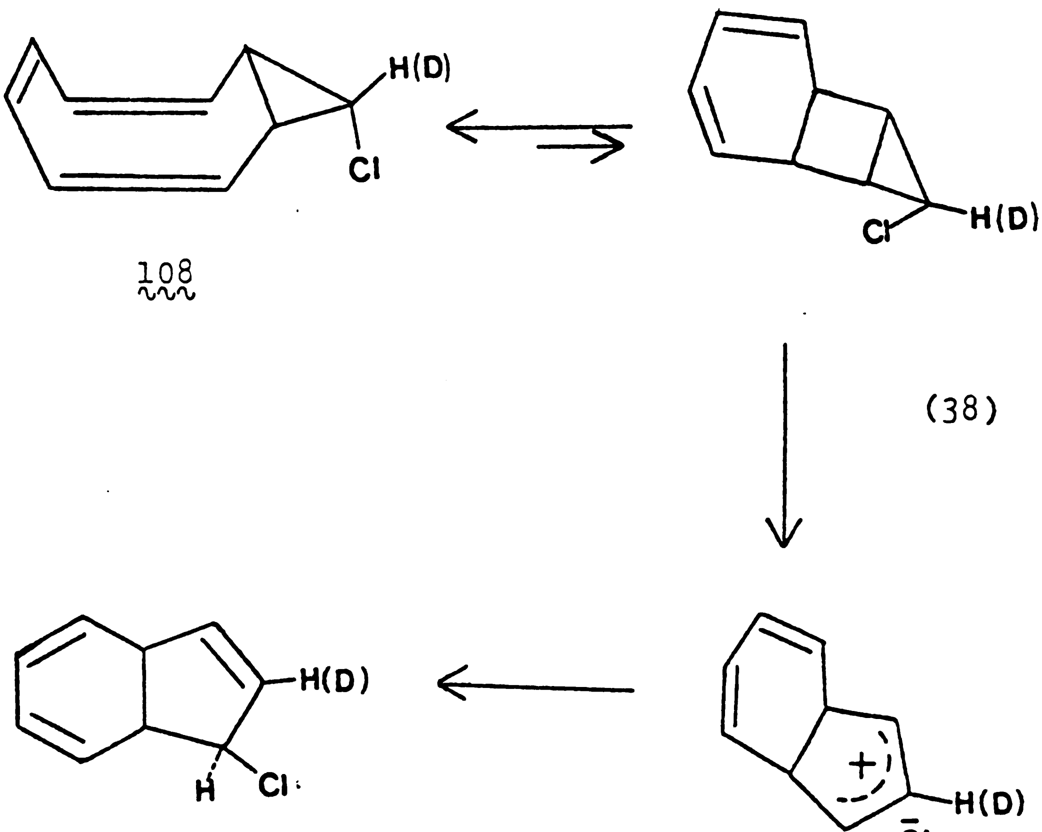


109d 110d (36)



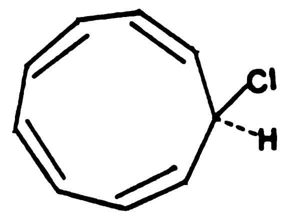
108d 111 (37)

The formation of compound 111 was explained according to Vogel and Kiefer's postulated mechanism (Equation 38),



108 111 (38)

while it was proposed that compound **110d** was formed through the intermediate **112**.[41]

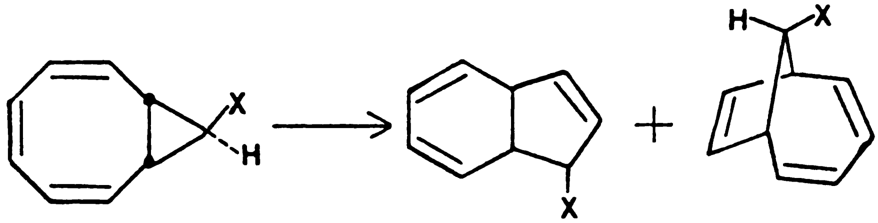


112

Several other anti C-9-substituted derivatives (CN, OCH_3, CO_2CH_3, C_6H_5) have been reported to rearrange to the dihydroindene systems.[42] In the case of anti-9-substituted fluoro and dimethylamino derivatives, the rearrangement surprisingly led[43] to a mixture of dihydroindenes and syn-9-fluoro and dimethylamino [4.2.1]nona-2,4,7-trienes (Figure 17). The formation of the syn epimer was consistent with a suprafacial [1,5] sigmatropic shift.[43]

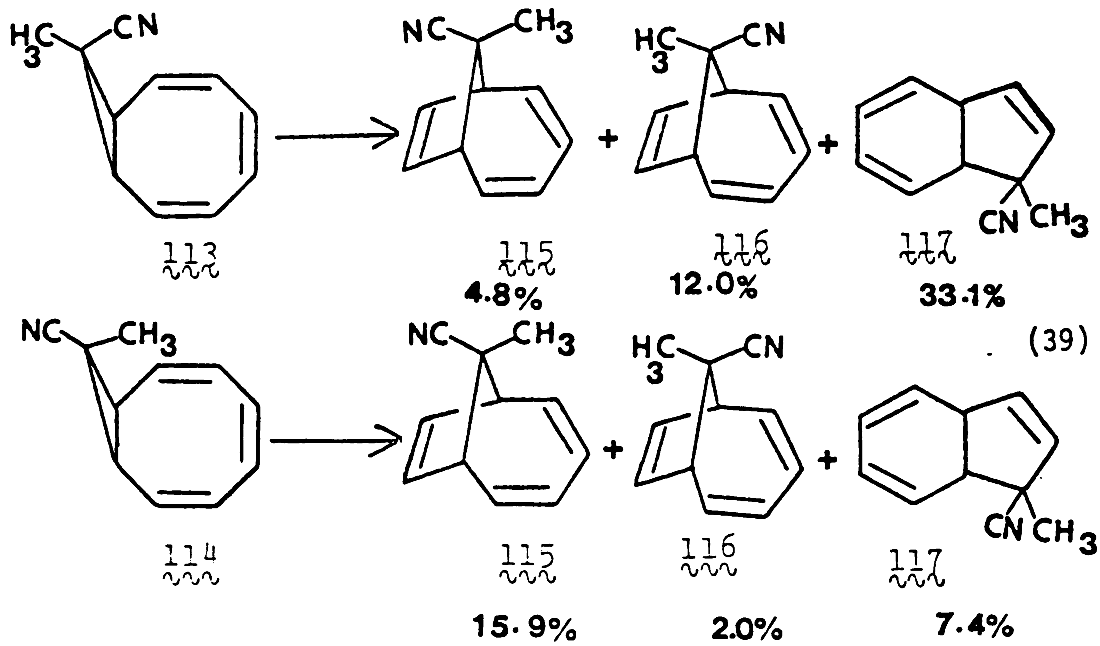
Some 9-cyano-9-methyl derivatives also rearranged to the [4.2.1] systems.[44] However, the [1,3] path was preferred over the [1,5] shift[44] (Equation 39). An explanation for these results has been presented in terms of a stepwise biradical mechanism.[44]

Compound **118** has also been reported[45] to thermolize to the corresponding [4.2.1] system **119** (Equation 40). Thermolysis of tosylhydrazone **63** in the presence of sodium methoxide in tetraglyme has been reported by T. Reitz[11] to lead to a mixture of dihydroindene and bicyclo[4.2.1]

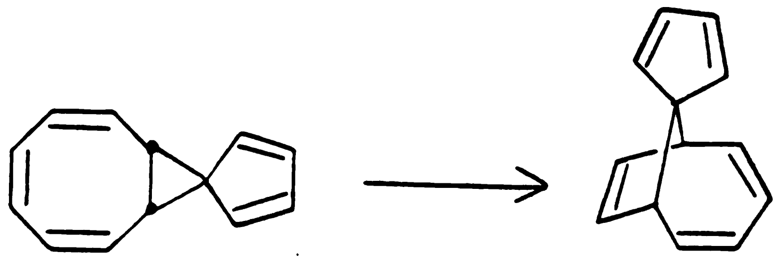


X = CN	x	
OCH_3	x	
CO_2CH_3	x	
C_6H_5	x	
F	x	x
NMe_2	x	x

Figure 17. Rearrangement of some [6.1.0] derivatives to the dihydroindene and [4.2.1] systems.

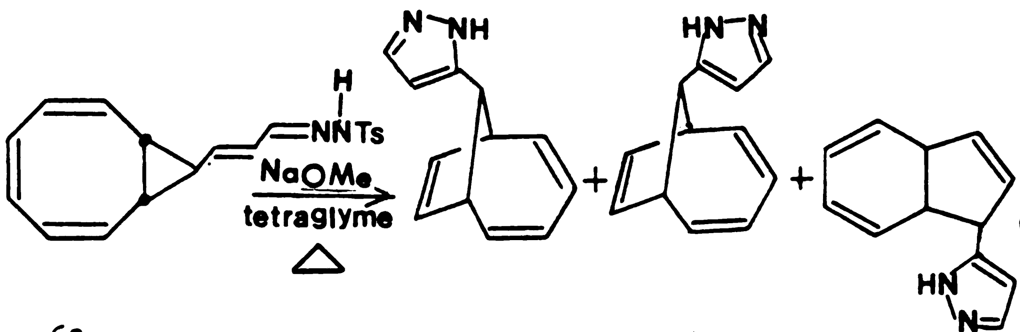


(39)



118 119 (40)

system with the syn pyrazole 54 as the major product (Equation 41).



(41)

63 55 54 56

These results and also the formation of pyrazoles 54 and 55 in the pyrolysis of the tosylhydrazone lithium salt 57 showed that the isomerization of the [6.1.0] system to [4.2.1] might be general for substituents having π-electron accepting groups. As a result, we thought that the most straightforward method for the preparation of tosylhydrazones 65 and 101 might be through the thermolysis of tosylhydrazone 63.

Thermal Rearrangement of Tosylhydrazone **63**. Preparation of Trans-β-[syn-bicyclo[4.2.1]nona-2,4,7-trienyl]Acrolein Tosylhydrazone **65**

Tosylhydrazone **63** was thermolized in refluxing chloroform. The progress of the reaction was monitored by proton nmr spectroscopy by observing the disappearance of the doublet at 1.6 ppm belonging to cyclopropane ring and formation of two singlets at 5.1 and 5.2 ppm characteristic of the [4.2.1] systems.[33,34] Integration at these two peaks showed the presence of two epimers in a ratio of 3:1. Separation of these two isomers by column chromatography failed due to the polymerization of products. The major product was separated by fractional crystallization as a light creamy solid (yield, 49%), and was identified as the _syn_-tosylhydrazone **65** from its spectroscopic information. MP 151-158°, mass spectrum m/e, M^+ 340, ir (Nujol): 3100, 1670, 1550, 1350, 1175, proton nmr (δ,$CDCl_3$): 2.44 (shs,3H), 3.0 (t,J=6.0 Hz,1H), 3.18 (m,2H), 5.2 (shs,2H), 5.3-6.1 (m,6H), 7.1-7.9 (m,6H), proton decoupled ^{13}C nmr (δ,$CDCl_3$): 150.1 (1C), 144.0 (1C), 142.8 (1C), 135.3 (1C), 134.2 (2C), 129.5 (2C), 127.8 (2C), 127.0 (1C), 126.0 (2C), 123.0 (2C), 47.3 (2C), 39.8 (1C), and 21.5 (1C). The assignment of this isomer as the _syn_ epimer was based on the observed coupling constant (J=6.0 Hz) for the bridge proton at 3.0 ppm.[33,34]

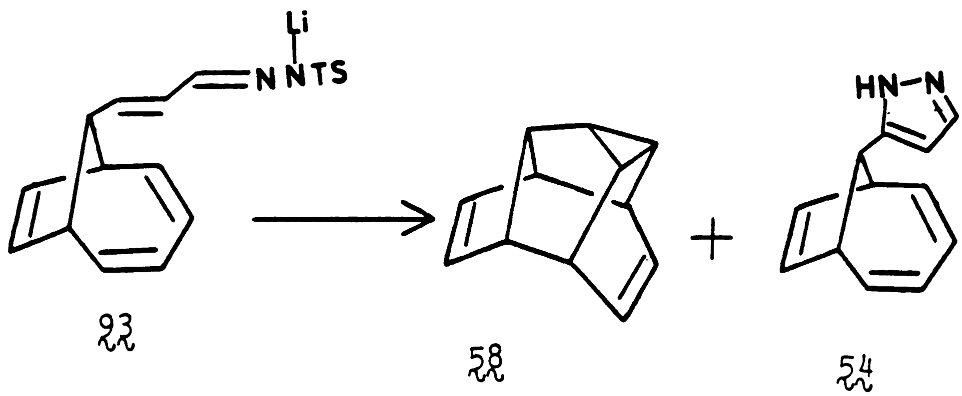
Unfortunately, attempts to isolate the anti epimer 101 failed because of its contamination with some syn epimer. Proton nmr did not detect the presence of any dihydroindene tosylhydrazone derivatives.

The formation of both epimers suggested that the rearrangement occurred either through a nonconcerted biradical mechanism or a combination of nonconcerted and concerted allowed [1,5] sigmatropic shifts resulting in the formation of syn-epimer 65 as the major product.

Pyrolysis of Trans-β-[syn-bicyclo[4.2.1]nona-2,4,7-trienyl] Acrolein Tosylhydrazone Lithium Salt 93. Preparation of Diene 58 and Pyrazole 54

Thermal decomposition of the tosylhydrazone lithium salt 93 was carried out in a similar way to that of salt 57 at 250°. GC/MS analysis of the volatiles showed one single peak with a parent peak of 156 corresponding to $(CH)_{12}$ hydrocarbons (yield, 2.0-2.5%). Proton nmr showed this compound to be diene 58. The less volatile product was identified as the syn-pyrazole 54 according to its mass and proton nmr spectra (yield, 13.2%) (Equation 42).

These results clearly showed that the decomposition of salt 93 has produced the diazo intermediate 91 which could give pyrazole 54 by cyclization, or diene 58 through carbene 96 and cyclopropene 85 followed by intramolecular



(42)

Diels-Alder reaction (Figure 18).

This experiment also ruled out the formation of tetraenes 14 and 22 through the carbene intermediate 96. As a result, both tetraenes 14 and 22 could have arisen through the carbene 76 in the pyrolysis of tosylhydrazone salt 57.

Photolysis of the Sodium Salt of Trans-β-[syn-bicyclo-[4.2.1]nona-2,4,7-trienyl]Acrolein Tosylhydrazone 65. Preparation of Diene 58

Photolysis of the sodium salt of tosylhydrazone 65 either in refluxing tetrahydrofuran through a Pyrex filter using a sun lamp or in tetrahydrofuran at room temperature through a quartz filter using a 200 W mercury lamp gave the pyrazole 54 in 37% and 28% yield, respectively. Nevertheless, the photolysis in tetrahydrofuran at 0° through a Pyrex filter gave the diene 58, obtained in 31-33% yield (Equation 43).

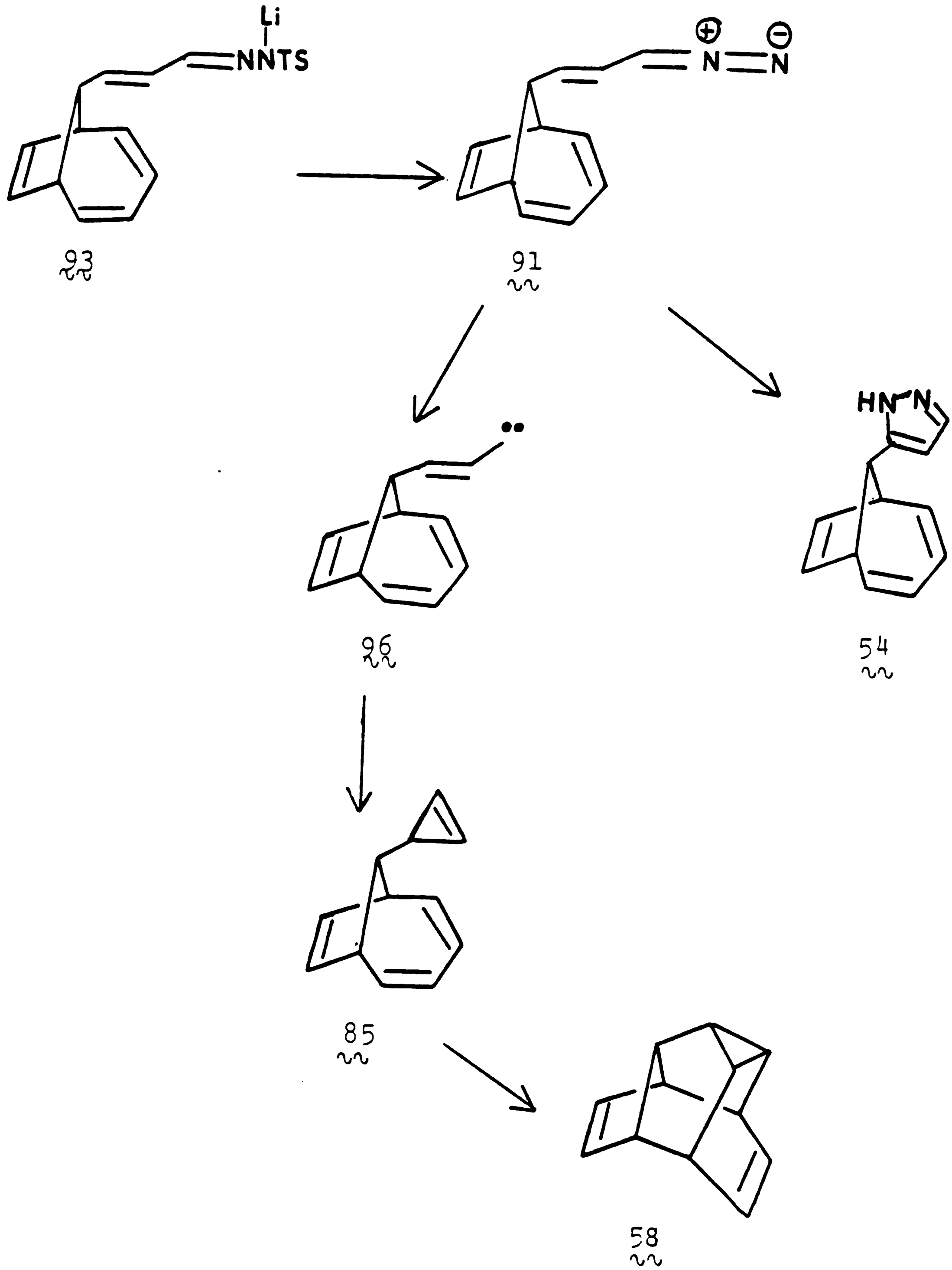
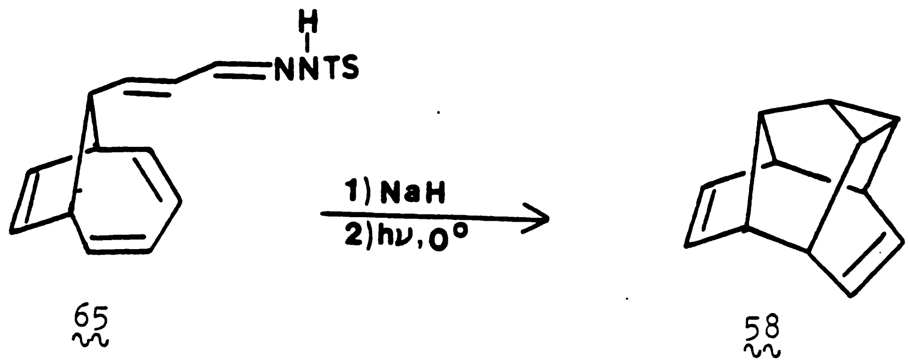


Figure 18. Mechanism for the formation of diene 58 and pyrazole 54 from the pyrolysis of salt 93.

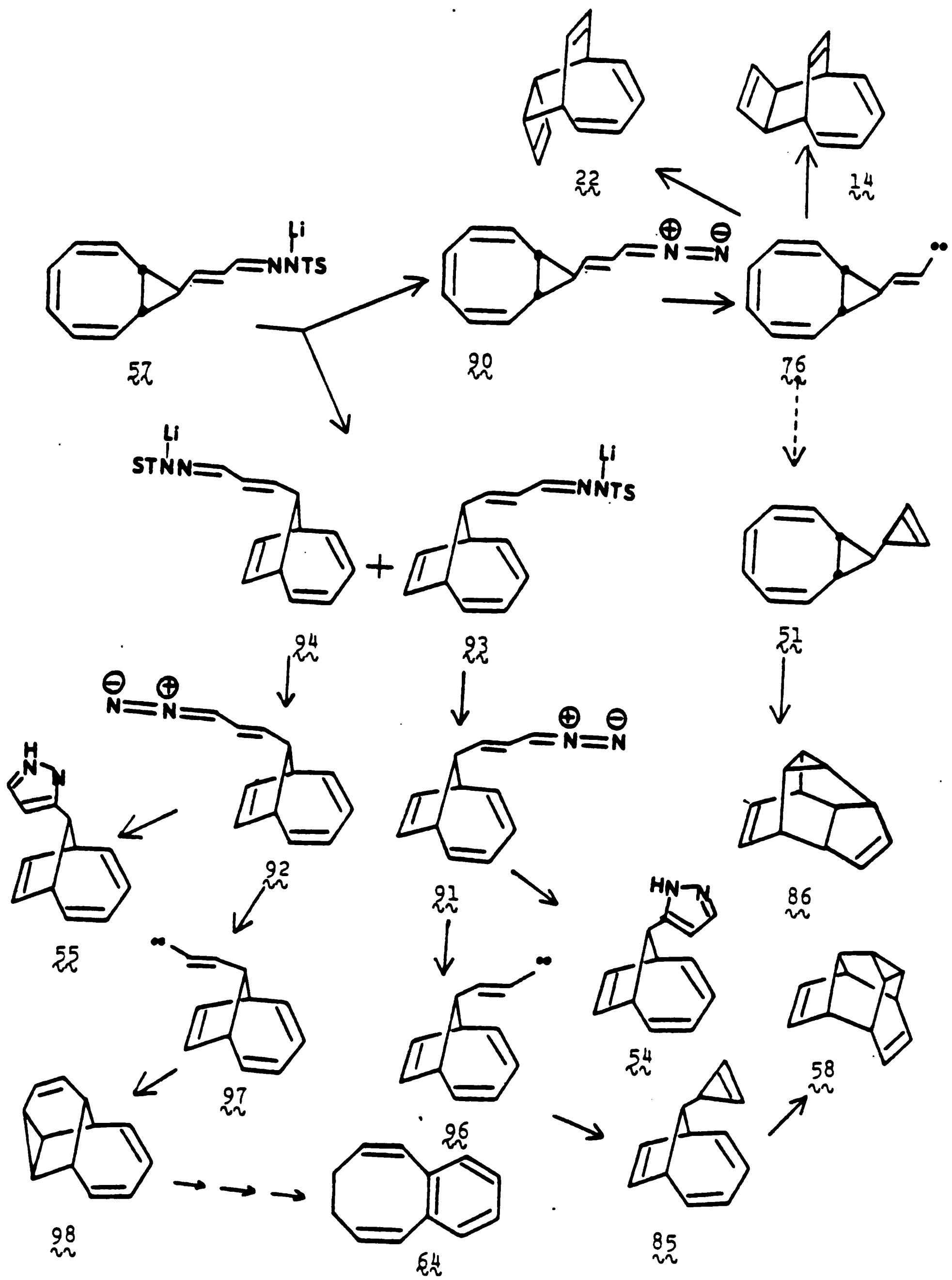


(43)

GC/MS and nmr analysis showed no evidence for the presence of any other $(CH)_{12}$ hydrocarbons.

The formation of diene 58 and pyrazole 54 from the pyrolysis of tosylhydrazone salt 93 clearly evidenced the diazo compound 91 and carbene 96 as the primary intermediates. In addition, the formation of diene 58 from the photolysis of the sodium salt of tosylhydrazone 65 also indicated the formation of carbene 96 as the primary product. This information showed that the generation of pyrazole 54 and diene 58 most likely arose from tosylhydrazone salt intermediate 93 in the pyrolysis of the tosylhydrazone lithium salt 57 (Path D, Scheme 3). These results also emphasized that the _exo_ and _endo_ tetraenes 14 and 22 were formed from the carbene 76 in the pyrolysis of salt 57. If we were able to obtain the other _anti_ epimer 101, we would be in a position to generate the hydrocarbon 98 (a new $C_{12}H_{12}$ member) photochemically and check its pyrolysis to hydrocarbon 64.

Consequently, the general scheme (Scheme 4) which best



Scheme 4. Decomposition of tosylhydrazone lithium salt 57.

explains the pyrolysis of tosylhydrazone lithium salt 57 would be both decomposition to carbene 76, and isomerization to the epimeric [4.2.1] tosylhydrazone salts 93 and 94. Carbene 76, then rearranges to both tetraenes 14 and 22, and probably to cyclopropene 51 which, on subsequent pyrolysis, gives hydrocarbon 86. Decomposition of tosylhydrazone salts 93 and 94 then proceeds to corresponding diazo compounds 91 and 92 which cyclize with a [1,5] hydrogen shift to the pyrazoles 54 and 55. Decomposition of diazo compounds 91 and 92 by loss of nitrogen gives two epimeric carbenes 96 and 97. The carbene 96 can cyclize to the corresponding cyclopropene 85, and finally to the diene 58 by an intramolecular Diels-Alder reaction. On the other hand, carbene 97 can lead to the formation of hydrocarbon 98 which subsequently undergoes a retro-Diels-Alder followed by two consecutive [1,5] hydrogen shifts under the pyrolytic conditions leading to hydrocarbon 64.

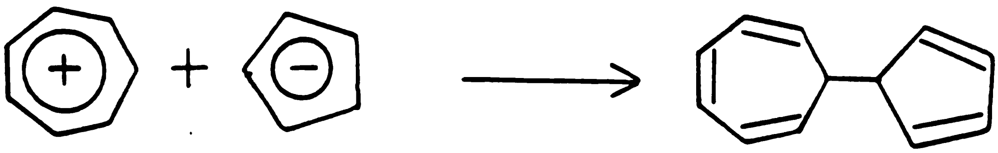
Summary

In continuation of our research group efforts toward the generation of new entries into the $(CH)_{12}$ energy surface, we were able to regenerate the recently prepared $(CH)_{12}$ member, and proved its structure to be the diene 58 using high resolution 250 MHz carbon and proton nuclear magnetic resonance spectroscopy. We also prepared a new $(CH)_{12}$ representative 86 from the known cyclopropene hydrocarbon 51. We have been able to find evidence for the formation of a new $(CH)_{12}$ member 98 as the primary product leading to hydrocarbon 64. We have developed the general thermal rearrangement of bicyclo [6.1.0] to bicyclo [4.2.1] systems for derivatives with strong π-electron accepting capabilities. Using this rearrangement, we prepared pure tosylhydrazone 65 and prepared diene 58 from it by either thermal or photochemical decomposition of its salt. These results clearly showed that tetraenes 14 and 22 have arisen from a different carbene intermediate than diene 58 in the pyrolysis of tosylhydrazone salt 57.

RESULTS AND DISCUSSION

PART B

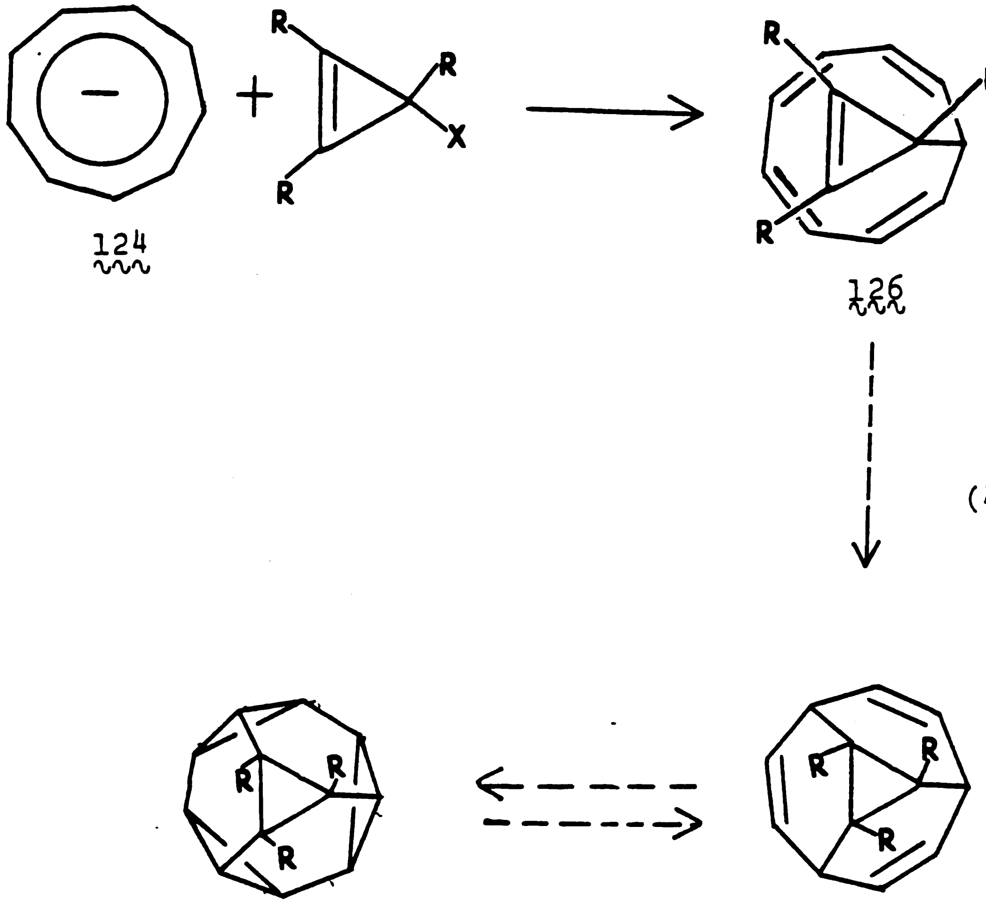
One of the earlier preparations of a $(CH)_{12}$ hydrocarbon involved[46] the reaction of tropylium ion 121 with the cyclopentadiene ion **122** (Equation 44).



(44)

121 **122** **123**

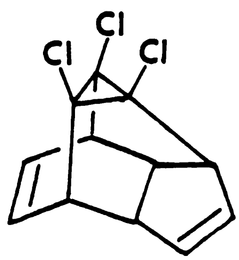
It was thought[37] that the reaction between the known higher and lower homologues of these 6π electron aromatic ions, namely between the cyclononatetraenide **124** and cyclopropenium ions, should likewise produce a $(CH)_{12}$ species. It was expected that the initial product **126**, which should be a highly reactive species, would readily undergo an internal Diels-Alder reaction to produce tetracyclododecatriene **127**, as a potential precursor of the truncated tetrahedrane **128** (Equation 45). Reaction between lithium cyclononatetraenide **124** and tetrachlorocyclopropene **125** (R = X = Cl) had been shown by Mock to give compound **87** as an unanticipated



124 126 128 127

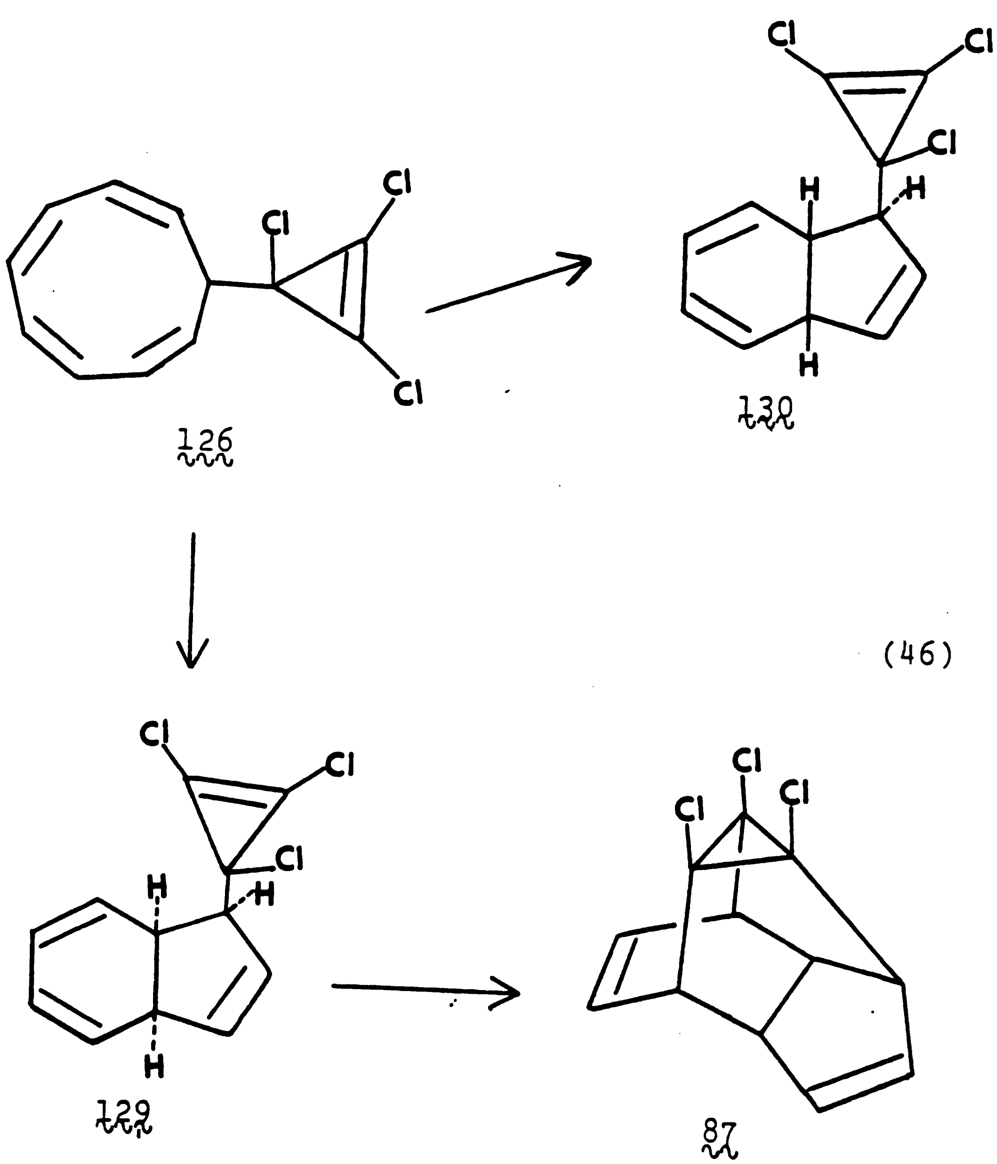
(45)

product.[37]



87

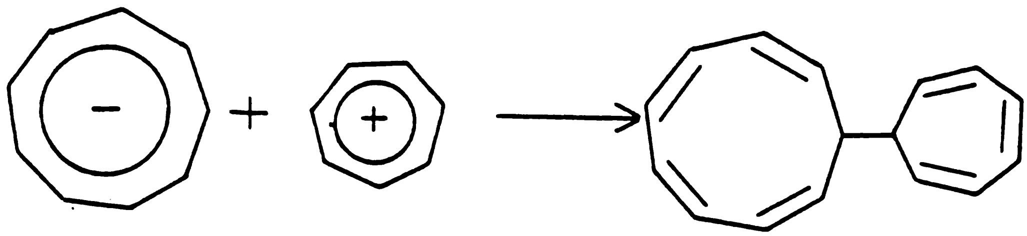
Formation of compound 87 was rationalized as follows[37] (Equation 46).



(46)

Formation of 87 showed that, under the reaction conditions, ring contraction of 126 proceeded in preference to intramolecular Diels-Alder addition to give 127.

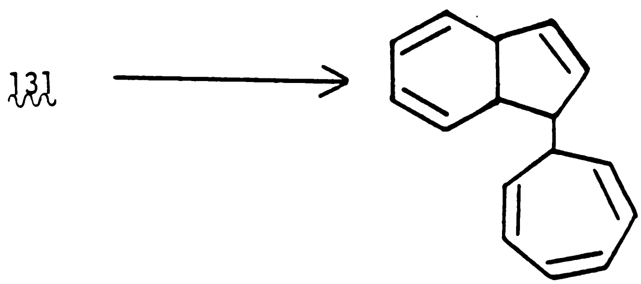
In this work, we decided to try to obtain compound 136, under suitable conditions. A product similar to 126 had been isolated below room temperature[47] (Equation 47).



(47)

124 121 131

At room temperature, compound 131 rearranged to 132[47] (Equation 48).

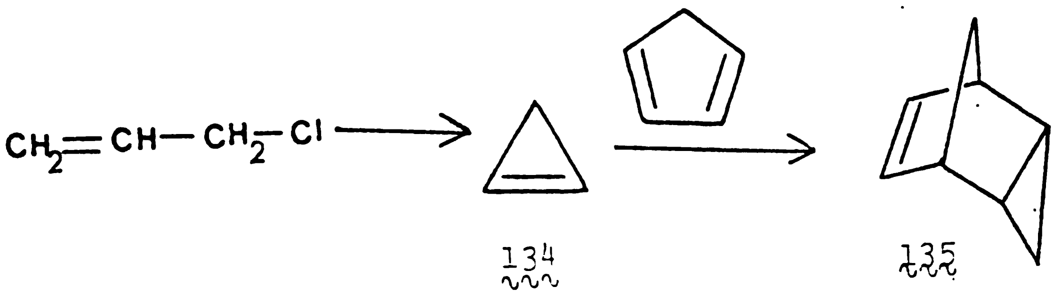


(48)

132

We thought that by keeping the tetraene intact in 126, by controlling the reaction temperature, it might undergo addition to the cyclopropene ring in a Diels-Alder fashion instead of undergoing ring contraction. In addition, Mock's isolation of compound 87 as the only product in very low yield[37] (2%) prompted us to reinvestigate the reaction. Although the reaction was done several times, either at 0° or -78°, nothing could be obtained except compound 87 in the reported yield.

At this stage, we decided to use 3-chlorocyclopropene 133 instead of tetrachlorocyclopropene. We thought this might give us a better electrophile which in turn might show different results. Generation of 3-chlorocyclopropene was attempted by treatment of 1,3-dichloropropene with strong base. A similar reaction was reported in the literature for preparation of cyclopropene by treatment of allyl-chloride with sodium amide[48] (Equation 49).

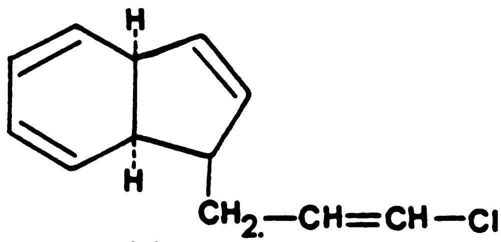


(49)

The generated cyclopropene was trapped with cyclopentadiene and resulted in the Diels-Alder adduct 135.[48]

Treatment of 1,3-dichloropropene with n-butyl lithium at -40° and subsequent reaction with cyclononatetraenide at -78°, after purification gave a yellow oil in 30% yield. This product was identified as compound 137 from its spectroscopic data.

MS, m/e 192 (194-Cl isotope), ir (neat): 3100, 2900, 1650, 180-MHz proton nmr (δ, $CDCl_3$): 2.39 (dd, J=7.5 and 9.0 Hz, 2H), 2.65-2.75 (m, 2H), 3.59 (bd, J=12.0 Hz, 1H), 5.47 (m, 1H), 5.55-5.95 (m, 6H), proton decoupled ^{13}C nmr (δ, $CDCl_3$):



137

134.1 (1C), 132.3 (1C), 129.6 (1C), 128.9 (1C), 126.0 (1C), 120.9 (1C), 120.7 (1C), 119.0 (1C), 54.5 (1C), 44.0 (1C), 41.9 (1C), and 31.7 (1C). Partially proton coupled ^{13}C nmr transformed those singlets at 54.5, 44.0, 41.9, and 31.7 ppm to a doublet, doublet, doublet, and a triplet, respectively. This spectrum clearly showed that the carbon corresponding to 31.7 contained two hydrogens. The assignment for cis-ring fusion was made on the basis of diallylic proton coupling (J=12.0 Hz) at 3.59 ppm.[49]

This experiment showed that 3-chlorocyclopropene had not been formed under the reaction conditions. This result prompted us to prepare 3-chlorocyclopropene separately, and then look at its reaction with lithium cyclonononatetraenide.

Treatment of 1,3-dichloropropene with sodium amide at 60-90°, after distillation resulted in recovered starting material. In addition, treatment with potassium t-butoxide[50] led to a messy mixture which showed no evidence for the presence of 3-chlorocyclopropene in its nmr spectrum. Because of time limitations, we stopped these experiments, although synthetic approaches toward the cyclopropenium ion from other methods is currently in progress in our group.

EXPERIMENTAL

General - Melting points were taken in open capillaries with a Thomas-Hoover apparatus. The NMR spectra were recorded on a Varian T-60 (60 MHz), Bruker WH 180 MHz, Varian CFT-20, and Bruker WM 250 spectrometer operating at 250 MHz for ^1H and 62.86 MHz for ^{13}C. Chemical shifts are reported in ppm downfield from internal standard tetramethylsilane. The J values are given in Hz. Gas chromatography/mass spectral data were obtained on a Finnigan 4021 with INCOS System equipped with a 1/8 in. x 6 ft glass column packed with 4% OV-225 on Chromasorb G. The compositions reported were calculated by comparing the peak of 1,2,3,4-tetramethyl benzene as internal standard with the peak areas (determined by weight). Gas chromatography separations were achieved at 120° using an F & M Model 700 chromatograph equipped with a thermal conductivity detector. Helium was used as the carrier gas at flow rates 35-40 ml/min. An injector temperature of 240° and a detector temperature of 250° were used in all cases. The column employed was a 1/4 in. x 6 ft aluminum column packed with 4% OV-225 on Chromosorb G, acid washed and silanized. The concentration of N-butyllithium, used for preparation of the salts of tosylhydrazone, was determined according to the procedure described by Kofron.[51]

9-Carbethoxy bicyclo[6.1.0]-2,4,6-triene[23] 59

Ester 59 was prepared in 47% yield by treatment of cyclooctatetraene with ethyl diazoacetate in the presence of copper sulfate, (bp 88-90° at 0.8 mm). Proton nmr (δ,CCl_4): 1.25 (5,J=7 Hz,3H), 1.3 (t,J=5 Hz,1H), 2.05 (d,J=5 Hz,2H), 4.1 (q,J=7 Hz,2H), 5.9 (s,2H), and 6.0 (s,4H).

9-Hydroxymethyl bicyclo[6.1.0]nona-2,4,6-triene 60[23]

Alcohol 60 was prepared in 77% yield by reduction of ester 59 with lithium aluminum hydride in ether. Recrystallization of crude alcohol from hexane was found to be cleaner than from methanol-water mixture. Mp 60-61°, proton nmr (δ,CCl_4): 0.78 (t,J=5.0 and 6.0 Hz,1H), 1.4 (d,J=5.0 Hz,2H), 3.6 (d,J=6.0 Hz,2H), 4.55 (bs,1H, washed with D_2O), 5.9 (s,2H), and 6.0 (s,4H).

Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde 61[23]

Oxidation of alcohol 60 with chromium trioxide and pyridine in methylene chloride yielded aldehyde 61 (75.3%, bp 58-62° at 0.25 mm). Proton nmr (δ,CCl_4) 1.7 (dt,J=6.0 and 5.0 Hz,1H), 2.24 (d,J=5 Hz,2H), 5.9 (s,2H), 6.0 (s, 4H), and 9.74 (d,J=6 Hz,1H).

Diethyl-2,2-diethoxyethylphosphonate 138[52]

Compound 138 was prepared (70% yield, bp 100-102°, 0.8 mm) by treatment of triethylphosphite with bromoacetaldehyde diethylacetal. Proton nmr (δ,CCl_4): 1.22 and 1.34 (2t,J=7 Hz,12H), 2.17 (dd,J=19 and 6 Hz,2H), 3.6 (2q,J=7 Hz,4H), 4.1 (2q,J=7 Hz,4H), and 4.9 (q,J=6 Hz,1H).

Diethylformylmethylphosphonate 139[52]

Treatment of compound 138 with hydrochloric acid, gave, after work up and distillation, compound 139 in 76% yield (bp 100-103° at 0.8 mm). Proton nmr (δ,$CDCl_3$): 1.35 (t,J=7 Hz,6H), 3.11 (dd,J=22 and 3.5 Hz,2H), 4.2 (2q,J=7 Hz,4H), and 9.7 (dt, J=3 and 1 Hz, 1H).

Diethyl-2-(cyclohexylamino)vinylphosphonate 140[11]

Treatment of compound 139 with cyclohexylamine in dry acetonitrile according to the described procedure did not result in compound 140. We found that the presence of unreacted amine prevents the crystallization of product. As a result, we improved the procedure as follows.

After treatment of compound 139 with fresh cyclohexyl amine at 0-5° in dry acetonitrile, the flask was left under aspirator vacuum at 100° for one hour. The residue was then taken up in 300 ml ether and dried over anhydrous sodium sulfate. The ether was partly evaporated so that the volume of the solute to the solvent became 1:1. This solution was then put in the freezer (-40°) for several days. Crystallization yielded compound 140 as a white solid (70% yield mp 60-62°). Proton nmr (δ,$CDCl_3$): 1.0-2.1 (m overlapped with a triplet at 1.3 (J=7 Hz, 17H), 4.0 (quintuplet, J=7 Hz, 4H), 4.8-5.2 (bs, NH), and 6.6-7.4 (m, 2H).

Trans-β-[anti-9-bicyclo[6.1.0]nona-2,4,6-Trienyl]Acrolein 62[11]

Condensation of compound 140 with aldehyde 61 in the presence of sodium hydride according to the reported procedure resulted in the formation of extended aldehyde 62 in low yield (∿20%) contrary to the reported 68% yield.[11] When the mixture of aldehyde and enamine was stirred overnight and the final dark solution was concentrated before working up the yield increased to the reported value. Mp 88-90°, proton nmr (δ,$CDCl_3$): 1.69 (m, 1H), 1.9 (d, J=5 Hz, 2H), 5.9 (s, 2H), 6.0 (s, 4H), 6.25-6.45 (2d, J=7.5 Hz, 2H), and 9.4 (d, J=7.5 Hz, 1H).

Trans-β-[anti-9-bicyclo[6.1.0]nona-2,4,6-trienyl]Acrolein Tosylhydrazone 63

Tosylhydrazone 63 was prepared in 84% yield by treatment of aldehyde 62 with p-toluenesulfonhydrazide in the presence of acetic acid in ethanol. Mp 149-150°, proton nmr (δ,$CDCl_3$): 1.2 (m, 1H), 1.65 (d, J=5 Hz, 2H), 2.4 (s, 3H), 5.7-6.4 (m, 8H), and 7.3-8.1 (m, 6H).

Preparation of Tosylhydrazone Lithium Salt 57

In a 100 ml three necked round-bottomed flask equipped with a magnetic stirrer, 100 ml dropping funnel, and nitrogen inlet, was placed 0.5 g (1.47 mmoles) tosylhydrazone 63 in 10 ml anhydrous tetrahydrofuran. The flask was flushed with nitrogen and the solution was cooled to -78° in a dry ice-acetone bath. 1.0 ml of n-butyl lithium in hexane (1.47 N) was slowly added through the dropping funnel. A tannish yellow color developed, and a precipitate fell out immediately. After the addition was finished, the solution was kept at -78° for 15 min, then slowly warmed to room temperature, and allowed to stir another 15 min. 60 ml pentane was added and the mixture was filtered. The lithium salt was obtained as a yellow solid in a nearly quantitative yield. This salt is stable in air and can be stored for a long time.

Pyrolysis of Tosylhydrazone Lithium Salt **57**. Preparation of Exo-tricyclo[$4.4.2.0^{2,5}$]dodeca-3,7,9,11-tetraene **14**, Endo-tricyclo[$4.4.2.0^{2,5}$]dodeca-3,7,9,11-tetraene **22**, pentacyclo[$6.4.0.0^{2,12}.0^{3,7}.0^{4,11}$]dodeca-5,9-diene **58**, 1,2-Benzocycloocta-1,3,7-triene **64**, and 9-syn and anti(5-pyrazola)bicyclo[4.2.1]nona-2,4,7-triene **54** and **55**

Tosylhydrazone lithium salt **57** (0.5 g, 1.44 mmoles) was placed in a bent Pyrex tube with a male ground glass joint and attached to the pyrolysis apparatus (Figure 19). The system was opened to vacuum (ca. 0.03 mm Hg), and the sand bath heated to 250°. The lithium salt was added in small portions to the flask containing hot glass beads. Periodically, approximately 5 to 10 glass beads were added to the flask to give fresh surface. New beads were allowed to warm up for about 20 minutes, before addition of more lithium salt. After addition of all lithium salt (approximately 2 hours), the system was cooled to room temperature, the vacuum was disconnected, and nitrogen was slowly allowed into the apparatus. It was observed that some less volatile compounds were deposited on the extension tube. This portion was separately washed into a flask with methylene chloride. The contents of the liquid nitrogen trap were washed with methylene chloride into another flask. This solution was concentrated on a rotary evaporator and subjected to gc/ms analysis. Five peaks were evident at 9.2, 12.8, 16.6, 18.3, and 33.4 minutes in

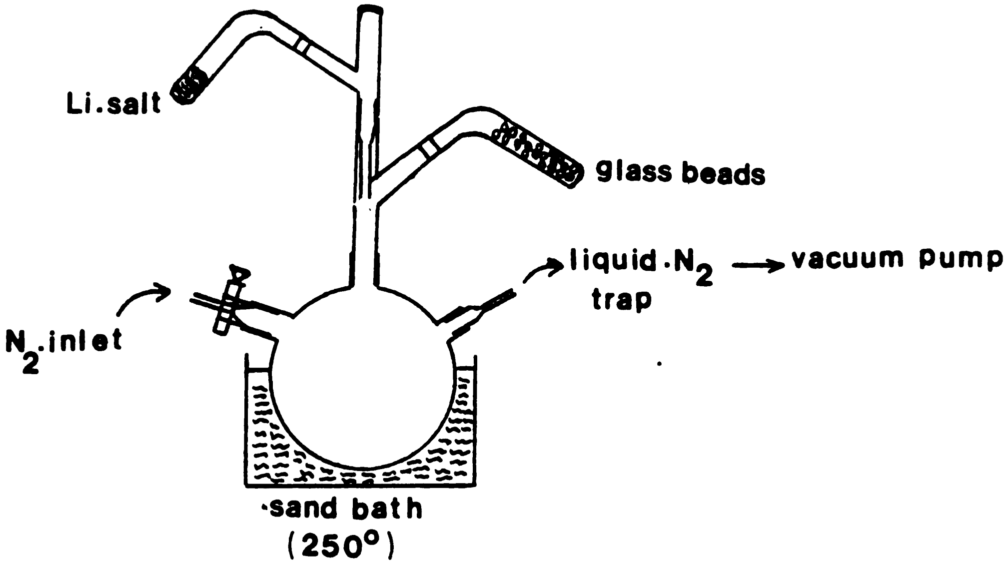


Figure 19. Pyrolysis apparatus for decomposition of dry salt 57.

a ratio of 1.2:6.8:7.5:13.5:3.3, respectively. Mass spectra exhibited parent peaks of 156 for $(CH)_{12}$'s. All these compounds were separated on preparative columns. There was not enough of the first compound to be identified. The second compound was isolated as a white solid (3% yield), and identified to be diene 58. Mp 67-68°[11], ms (m/e, %): 156 (20), 155 (49), 154 (16), 153 (31), 152 (28), 141 (39), 129 (20), 128 (41), 127 (18), 115 (31), 91 (100), 78 (13), 77 (7), 250 MHz proton nmr (δ,$CDCl_3$): 1.75 (dt, J=7.0 and 4.7 Hz, 1H), 1.91 (ddd, J=7.0, 5.5, and 1.5 Hz, 2H), 2.9 (m, 2H), 3.15 (ddd, J=9.3, 5.5, and 1.5 Hz, 2H), 3.35 (dt, J=5.5 and 4.7 Hz, 1H), 5.45 (t, J=1.2 Hz, 2H), 6.05 (dd, J=5.8 and 2.8 Hz, 2H), proton decoupled ^{13}C nmr (δ, $CDCl_3$): 134.8 (2C), 131.3 (2C), 66.3 (1C), 62.6 (2C), 41.8 (2C), 36.1 (2C), 26.6 (1C), proton coupled ^{13}C nmr (δ,$CDCl_3$): 134.6 (d, J=160.9 Hz, 2C), 131.1 (d, J=156.4 Hz, 2C), 66.2 (d, J=137.8 Hz, 1C), 62.3 (d, J=137.8 Hz, 2C), 41.6 (d, J=135.9 Hz, 2C), 36.06 (d, J=166.5 Hz, 2C), and 26.4 (d, J=171.1 Hz, 1C).

The third compound was isolated as a clear liquid (yield 3.3%) and identified from its nmr as the known exo-tetraene 14.[9b] Ms (m/e, %): 156 (47), 155 (68), 153 (43), 152 (31), 141 (51), 128 (59), 115 (46), 91 (100), 78 (16), 60 MHz proton nmr (δ,CCl_4): 2.57 (m, 2H), 3.25 (bs, 2H), 5.3-5.4 (dd, J=5 and 2.5 Hz, 2H), 5.83 (shs, 2H), and 5.0-5.9 (m, 4H).

The fourth compound was isolated as a white solid (yield 6%), and identified as endo-tetraene **22**.[14] Ms (m/e, %): 156 (6), 155 (47), 154 (22), 153 (44), 152 (29), 141 (47), 129 (30), 128 (62), 115 (48), 91 (100), 78 (16), 60 MHz proton nmr (δ,CCl_4): 2.82 (bs, 4H), 5.4-5.6 (m, 6H), and 6.04 (shs, 2H).

The last compound was isolated as a yellow liquid (yield 1.5%). The spectral data showed it to be 1,2-benzocyclo-octa-1,3,7-triene **64**.[24] MS (m/e, %): 156 (34), 155 (22), 154 (12), 153 (23), 152 (19), 141 (29), 129 (20), 128 (100), 115 (22), 250 MHz proton nmr (δ, $CDCl_3$): 2.29 (m, 4H), 5.92 (m, 2H), 6.52 (d, J=12.3 Hz, 2H), 7.13 (m, 2H), 7.22 (m, 2H), proton decoupled ^{13}C nmr (δ, $CDCl_3$): 143.6 (2c), 136.7 (2c), 131.2 (2c), 130.6 (2c), 124.3 (2c), and 25.4 (2c).

Spin Decoupling Studies of Diene **58**

Using 250 MHz proton nmr, decoupling experiments were carried out at seven positions. Irradiation at 1.75 ppm caused the doublet of doublet of doublets at 1.91 ppm, and doublet of triplets at 3.35 ppm to collapse to a doublet of doublets (J=5.5 and 1.5 Hz) and a triplet (J= 5.5 Hz). Irradiation at 1.91 ppm caused the doublet of triplets at 1.75 ppm to collapse to a distorted doublet (J=4.7 Hz) and also caused some change in the multiplet at 2.9 ppm. Irradiation at 3.35 ppm collapsed the doublet of triplets at 1.75 ppm and doublet of doublet of doublets at 3.15 ppm to a triplet (J=7.0 Hz) and a doublet of doublets (J=9.3 and 1.5 Hz). These results clearly showed that the proton at 1.75 ppm had vicinal coupling relations both with two protons at 1.91 ppm (with J=7.0 Hz) and the single proton at 3.35 ppm (with J=4.7 Hz). Thus, the signals at 1.75 were assigned to cyclopropane ring proton H_2. Irradiation at 2.9 ppm caused the doublet of doublet of doublets at 1.91 ppm, doublet of doublet of doublets at

3.15 ppm, and doublet of doublets at 6.05 ppm to collapse to a doublet of doublets (J=7.0 and 1.5 Hz), a broad doublet (J=5.5 Hz), and a sharp singlet respectively. As a result, the two protons at 1.91 ppm must have vicinal coupling relation with the two protons at 2.9 ppm (with J=5.5 Hz). These two protons were assigned to the H_1 and H_{12} of the cyclopropane ring. The additional coupling (J=1.5 Hz) may be either a long range or a second order coupling. On the basis of these results, the two protons at 2.9 ppm was also found to have vicinal relations both with the pairs at 3.15 ppm (J=9.3 Hz) and 6.05 ppm (J=5.8). So these two were assigned to the bridgehead protons H_8 and H_{11}, while the signals at 6.05 ppm were assigned to protons H_9 and H_{10}. Since the doublet of doublets at 6.05 ppm collapsed to a singlet after irradiating at 2.9 ppm, the second coupling (J=2.8 Hz) should have arisen from the long range allylic coupling of H_{10} with H_8. The assignment of signals at 6.05 ppm to H_9 and H_{10} were supported by irradiating at these signals and observing some distortion in the multiplet at 2.9 ppm as the only change in the spectrum. Irradiation at 3.15 ppm collapsed the doublet of triplets at 3.35 ppm and the triplet at 5.45 ppm to a doublet (with J=4.7 Hz) and a sharp singlet, respectively. So, it was realized that this pair should also be related vicinally to the single proton at 3.35 ppm. This pair was assigned to the bridgehead protons H_4 and H_7, while the two olefinic at 5.45 ppm were assigned to H_5 and H_6. Collapse of the triplet at 5.45 ppm to a singlet after irradiation at 3.15 ppm, clearly showed that this triplet must have been the overlap of two doublets of doublets, one resulted from vicinal coupling of H_5 with H_4 (J = 1.5 Hz), and the other from long range allylic coupling of H_5 with H_4 (J = 1.2 Hz).

The less volatile part was flash chromatographed on silica gel with ether elution. The first eluting material, which was not characterized, was observed by its nmr spectrum to be an aromatic compound. The second eluting compound was obtained as a yellow greasy material (6.7 mg, yield 2.2%). This compound was identified as anti-pyrazole 55 from its spectroscopic data. MS (m/e, %): 184 (16), 183 (19), 169 (9), 156 (12), 128 (9), 115 (40), 91 (35), 40 (100), 60 MHz proton nmr (δ, $CDCl_3$): 2.95 (s, 1H), 3.12 (d, J=6.0 Hz, 2H), 5.08 (s, 2H), 5.6-6.1 (m, 5H), 6.98-7.1 (m, 2H), proton decoupled ^{13}C nmr (δ, $CDCl_3$): 137.75 (2C), 124.26 (2C), 121.21 (2C), 50.08 (2C), and 40.22 (1C). Because of a noisy baseline, the peaks belonging to the pyrazole ring were not observed.

The third eluting material was separated as a yellow greasy compound (17.5 mg, yield 6.1%). This compound was identified as the syn-pyrazole 54 from its spectroscopic information. MS (m/e, %): 184 (16), 183 (22), 169 (10), 156 (13), 128 (10), 115 (37), 91 (34), 40 (100), 60 MHz proton nmr (δ, $CDCl_3$): 3.1-3.4 (m, 3H), 5.12 (s, 2H), 5.8 (bs, 5H), 7.1 (m, 1H), 11.0 (bs, 1H), proton decoupled ^{13}C nmr (δ, $CDCl_3$): 145.69 (small), 135.44 (2c), 134.48 (small), 126.09 (2c), 122.87 (2c), 104.20 (small), 46.37 (2c), and 36.07 (1c).

Anti-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]nona-2,4,6-triene 51.[23] Low temperature Photolytic Decomposition of Tosylhydrazone Sodium Salt 49

This procedure was adapted from Raghu's thesis.[23] The tosylhydrazone 63 (340 mg, 10 mmoles) was dissolved in 60 ml dry tetrahydrofuran and was placed in a Pyrex tube equipped with a magnetic stirrer and nitrogen inlet. Sodium methoxide (54 mg, 10 mmoles) was added to this and allowed to stir for 10 minutes. The tube was then placed next to a Pyrex immersion well in a dry ice-acetone bath. The solution was photolyzed using a 200 W Hg vapor lamp for 2.5 hours. The solution was 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 combined pentane extracts were washed with 100 ml cold water to remove most of the tetrahydrofuran. The solution was dried over anhydrous sodium sulfate and then rapidly filtered through silica gel (∿20 g) to remove unreacted tosylhydrazone. The solution was concentrated to 5 ml on a rotary evaporator and the rest of solvent was removed at -30° using a high vacuum pump to give 58 mg of a light yellow oil (yield, 37%). This compound was shown to be cyclopropene **51** according to its nmr spectrum. 60 MHz proton nmr (δ, $CDCl_3$) showed peaks at: 0.8-1.0 (m, 1H), 1.2 (d, J=5.5 Hz, 2H), 1.8 (m, 1H), 5.8-6.0 (d, 6H), and 7.2 (shs, 2H).

Pyrolytic Attempts at Isomerizing Compound **51**

Method A

A 60 cm Pyrex tube, packed with 25 cm of glass beads, and fitted with a serum cap at the top was connected from the bottom to a trap kept in liquid nitrogen. The system was opened to vacuum (ca. 0.3 mm Hg), and the tube was heated to 300° with an tube oven. Hydrocarbon **51** (52 mg, 0.3 mmoles) was dissolved in 2 ml dry tetrahydrofuran and was injected through the serum cap in small portions. After finishing the addition (around two hours), the oven was cooled to room temperature, and the vacuum was disconnected. The contents of the trap were rinsed with pentane into a flask. Most of the solvent was removed on a rotary evaporator and the rest was taken off at -30° using a high vacuum. Proton nmr spectrum showed it to be the recovered starting material. Gc/ms analysis showed no evidence for any other $(CH)_{12}$ hydrocarbons.

Method B

A 250 ml round bottomed three necked flask equipped with a serum cap and stopper, and containing glass beads was connected to a trap kept in liquid nitrogen. The flask was opened to vacuum (ca. 0.3 mm Hg), and heated to 300° in a sand bath. Hydrocarbon **51** (52 mg, 0.3 mmoles) was dissolved in 2 ml dry tetrahydrofuran, and was injected through the serum cap. After injecting all the solution (ca 2 hrs), the flask was cooled to room temperature, and the vacuum was disconnected. Proton nmr spectrum of the contents of the trap revealed only the starting material.

Method C

Hydrocarbon **51** (53 mg, 0.3 mmoles) was dissolved in pentane (10 ml) and the solution was placed in a 60 cm Pyrex tube. The tube was sealed under nitrogen and was placed in the oven and then rapidly heated to 260°. The solution was allowed to stand at this temperature for 5 minutes. It was observed that a polymeric material was deposited on the tube wall which was not soluble in organic solvents. The nmr spectrum of the concentrated solution was quite messy and gc/ms analysis showed no evidence for $(CH)_{12}$ hydrocarbons.

Method D

Preparation of Pentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{5,9}]dodeca-6,11-diene 86 - A 60 cm pyrex tube, packed with 25 cm of glass beads was connected to a 250 ml round bottomed three necked flask containing glass beads, serum cap, and argon inlet. The top of the column was connected to the trap kept in liquid nitrogen (Figure 20).

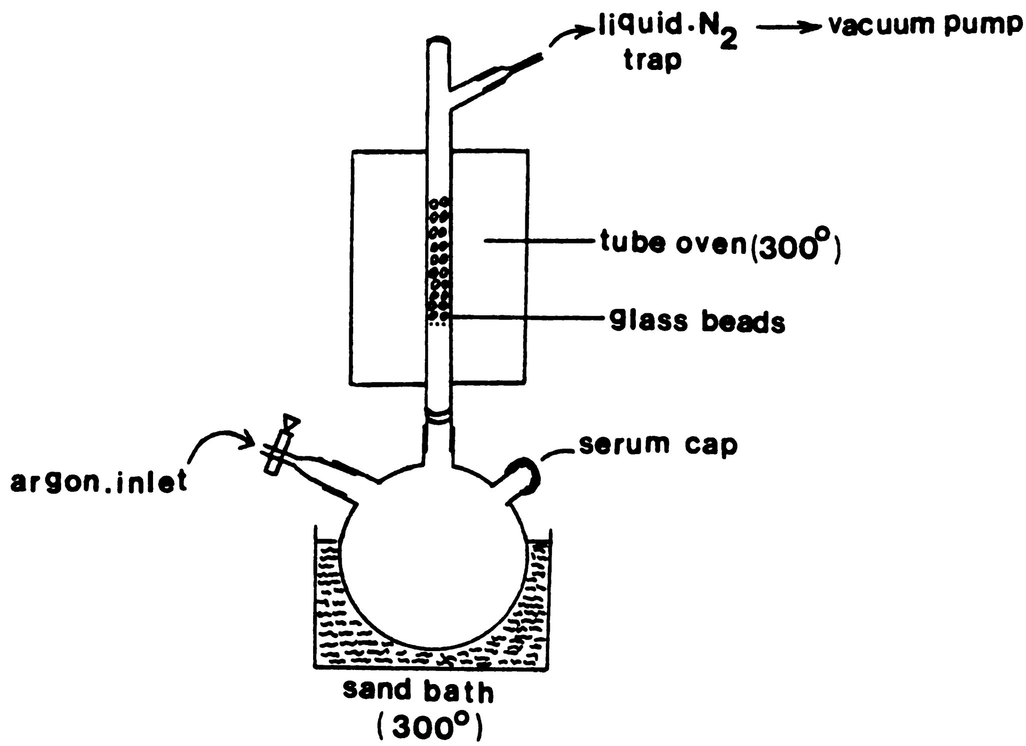


Figure 20. Pyrolysis apparatus for isomerization of compound 51.

Argon was allowed to flow into the apparatus and the system was opened to vacuum (ca. 0.3 mm Hg). The flask and tube were then heated to 300° with a sand bath and tube oven respectively. Hydrocarbon 51 (52 mg, 0.3 mmoles) was dissolved in 2 ml dry tetrahydrofuran and was injected through the serum cap into the hot flask. After injecting all the solution (2 hours), the system was cooled to room temperature, and the vacuum was disconnected. The contents of the trap were rinsed with pentane into a flask and the solution was concentrated at -20° using a high vacuum pump. Gc/ms analysis showed two peaks at 9.20 and 11.40 minutes in a ratio of 14.0:3.2. Mass spectra taken at these peaks showed a parent peak of 156 corresponding to $(CH)_{12}$ hydrocarbons. The first compound was collected by preparative gas chromatography as a colorless liquid (1.5 mg, yield 2.6%). This compound was identified as polycyclic 86 from its spectroscopic data. MS (m/e, %): 156 (10), 155 (11), 141 (11), 128 (14), 115 (15), 91 (100), 78 (16), 250 MHz proton nmr (δ, $CDCl_3$): 0.7-0.9 (m, 2H), 1.75 (ddd, J=7.9, 4.9, and 4.1 Hz, 1H), 1.85 (dd, J=6.2 and 3.3 Hz, 1H), 2.35 (ddd, J=7.5, 6.2, and 5.1 Hz, 1H), 2.48 (dd, J=7.9, and 6.2 Hz, 1H), 2.82 (dd, J=5.1, and 3.2 Hz, 1H), 3.06 (dd, J=7.5 and 5.8 Hz, 1H), 5.55 (dd, J=5.0 and 3.3 Hz, 1H), 6.12 (dd, J=5.0 and 3.2 Hz, 1H), 6.33 (dd, J=7.9 and 5.8 Hz, 1H), and 6.55 (dd, J=7.9 and 6.2 Hz, 1H).

Preparation of Trans-β-[syn-9-bicyclo[4.2.1]nona-2,4,7-trienyl]Acrolein Tosylhydrazone 65

Tosylhydrazone 5 (1.0 g, 2.9 mmoles) was refluxed in 50 ml chloroform overnight. Solvent was removed by rotary evaporator and the residue was crystallized in a mixture of methylene chloride and carbon tetrachloride to give 240 mg of a light yellow solid. The mother liquid was concentrated and crystallized in a mixture of methylene chloride and hexane to give another 220 mg of the solid (49%, mp 151-153°). This compound was identified as the titled compound 65 from its spectra. MS (m/e, %): 340 (2.4), 278 (9.8), 249 (4), 185 (63), 168 (10), 156 (24), 155 (11), 141 (17), 129 (17), 115 (28), 91 (100), 81 (24), 77 (12), ir (Nujol), 3100, 1670, 1550, 1390, 1350, 1310, 1180, 60 MHz proton nmr (δ, $CDCl_3$): 2.4 (s, 3H), 3.0 (t, J=6.0 Hz, 1H), 3.18 (m, 2H), 5.1 (shs, 2H), 5.7-6.0 (m, 6H), 7.1-8.0 (m, 6H), proton decoupled ^{13}C nmr (δ, $CDCl_3$): 150.1 (1C), 144.0 (1C), 142.8 (1C), 135.3 (1C), 134.2 (2C), 129.5 (2C), 127.8 (2C), 127.0 (1C), 126.0 (2C), 123.0 (2C), 47.3 (2C), 39.8 (1C), and 21.5 (1C).

The filtrate was concentrated and was shown by nmr to be a mixture of compound 65 and its epimeric compound 101. Fractional crystallization failed to separate these epimers.

Preparation of Trans-β-[syn-9-bicyclo[4.2.1]nona-2,4,7-trienyl]Acrolein Tosylhydrazone Lithium Salt **93**

Tosylhydrazone lithium salt **93** was prepared according to the procedure described for the lithium salt **57** and obtained in a nearly quantitative yield.

Pyrolysis of Tosylhydrazone Lithium Salt **93**. Preparation of Diene **58** and Pyrazole **54**

Tosylhydrazone lithium salt **93** (0.5 g, 1.44 mmoles) was pyrolyzed at 250° in the same way described for lithium salt **57** (Figure 17). Gc/ms analysis of voltailes showed a single peak at 12.8 minutes with a parent peak of 156. Proton nmr spectrum showed this to be the diene **58** (yield, 1.9-2.3%). Analysis of the less volatiles showed the presence of the pyrazole **54** (yield 13.2%).

Photolysis of Sodium Salt of Tosylhydrazone **65**. Preparation of Pyrazole **54**

In a 500 ml round bottomed three necked flask equipped with a magnetic stirrer, condenser, and nitrogen inlet, was placed a solution of tosylhydrazone **65** (100 mg, 0.27 mmoles) in 10 ml dry tetrahydrofuran. Ninety-nine percent sodium hydride (7.0 mg, 0.27 mmoles) was added to this solution and the mixture was allowed to stir for 15 minutes. The flask was then placed close to a sun lamp and was irradiated for one hour. During this time, the solution began to reflux. The solution was filtered to remove the unreacted salt and the filtrate was concentrated at -20° using a high vacuum pump. Mass spectra and proton nmr showed the product to be the pyrazole 54 (20 mg, 37%).

Photolysis of the Sodium Salt of Tosylhydrazone 65 Through a Quartz Filter Using a 200 W Hg Vapor Lamp. Preparation of Pyrazole 54

A solution of tosylhydrazone 65 (100 mg, 0.2 mmoles) in 60 ml tetrahydrofuran was placed in a Pyrex tube containing a magnetic stirrer, and nitrogen inlet. The tube was flushed with nitrogen and 99% sodium hydride (7 mg, 0.27 mmoles) was added to the solution and allowed to stir for 15 minutes. This solution was then placed close to a quartz immersion well and photolyzed for one hour using a 200 W Hg vapor lamp. The solution was then poured to a mixture of 200 ml 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 combined pentane extracts were washed with 100 ml cold water to remove most of the tetrahydrofuran. The solution was dried over anhydrous sodium sulfate. The solution was filtered and most of the solvent was removed on a rotary evaporator. The rest of the solvent was removed at -30° using a high vacuum pump. Mass spectra and nmr showed the product to be the pyrazole 54 (15 mg, yield 28%).

<u>Low Temperature Photolysis of the Sodium Salt of Tosylhydrazone 65 Through a Pyrex Filter with 200 W Hg Vapor Lamp. Preparation of Diene 58</u>

This experiment was carried out in the same way as described above with the exceptions that the reaction was run at 0° and irradiation was done through a Pyrex filter. Gc/ms analysis of the product showed a single peak at 12.8 minutes with a molecular ion peak of 156 (yield 31-33%). The proton nmr spectrum was identical with that of diene 58.

<u>Pentachlorocyclopropane 141[53]</u>

Compound 141 was prepared by treatment of trichloroacetic acid sodium salt with trichloroethylene, obtained in 22.4% yield (bp 35° at 1.0 mm Hg). Ir (neat): 3000, 960, 930, 900, 770, proton nmr (δ, CCl_4): 3.8, sharp singlet.

<u>Tetrachlorocyclopropene 125[53]</u>

Compound 125 was prepared by treatment of compound 141 with potassium hydroxide, and then hydrochloric acid, obtained in 80% yield (bp 129-131 at 745 mm Hg). IR (neat): 2300, 1150, 1050, and 750.

Anti-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene **142**[54]

Compound **142** was prepared in 24% yield (bp 31-32° at 0.3 mm) according to the described procedure. Proton nmr (δ, CCl_4): 1.8 (d, J=4.0 Hz, 2H), 2.4 (t, J=4.0 Hz, 1H), 5.9 (s, 2H), and 5.95 (s, 4H).

Preparation of 2,3,4-Trichloropentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{5,9}]dodeca-6,11-diene **87**.[37]

To a magnetically stirred mixture of 1.05 g lithium (cut into small pieces in an argon atmosphere, washed with cyclohexane, and added directly to the reaction flask containing solvent and argon atmosphere) and 50 ml of dry tetrahydrofuran was added 9.8 g (0.064moles)of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene **142** in 30 ml of tetrahydrofuran. The final black reaction mixture which contained a few particles of unreacted lithium was added with a syringe to a solution of 38.5 g (0.21moles)of tetrachlorocyclopropene **125** in 350 ml of tetrahydrofuran at 0° over a period of 15 minutes. The mixture was allowed to stand overnight at room temperature. The solvent was removed on a rotary evaporator, and the residue was treated with water and extracted with methylene chloride. The organic extract was dried over anhydrous sodium sulfate and concentrated on a rotary evaporator. A small amount of unreacted tetrachlorocyclopropene was removed using a high vacuum pump. The final thick oily black residue was taken up in carbon tetrachloride and submitted to column chromatography on 200 g of silica gel with carbon tetrachloride elution. Analysis of different fractions with TLC and nmr showed them to be polymeric materials. Elution was then continued with chloroform.

TLC showed some fractions contained a major compound. The nmr spectrum showed it to be the reported compound **87**. (53 mg, yield 1.8%). 60 MHz proton nmr (δ, $CDCl_3$): 2.0 (bd, J=7.0 Hz, 1H), 2.45 (ddd, J=7.0, 6.0 and 5.0 Hz, 1H), 2.8 (dd, J=6.0 and 2.0 Hz, 1H), 3.2 (dd, J=6.0 and 3.0 Hz, 1H), 3.40 (dd, J=6.0 and 6.0 Hz, 1H), 5.7 (dd, J=6.0 and 3.0 Hz, 1H), 6.0 (dd, J=6.0 and 3.0 Hz, 1H), 6.2 (dd, J= 7.0 and 5.5 Hz, 1H), and 6.4 (dd, J=7.0 and 6.0 Hz, 1H).

Temperature Effect on the Formation of Compound **87**

The cyclononatetraenide solution was prepared and then transferred to a dropping funnel containing a cooling jacket. This solution and the solution of tetrachlorocyclopropene in tetrahydrofuran were cooled to -78° using a dry ice-acetone bath. The cyclononatetraenide solution then was added to the flask over a period of 1.5 hours. The reaction mixture was allowed to stand at -78° for another 3 hours, and then gradually brought to room temperature. The mixture was then stirred for 2 days at room temperature. This solution was poured into 300 ml of ice water and 500 ml of ether. The ether layer was separated, and the aqueous layer was extracted with two 250 ml portions of ether. The ether extracts were combined, washed with 200 ml of ice water, and dried over anhydrous sodium sulfate. Ether was removed on a rotary evaporator, and the final black residue was submitted to chromatography on 200 g silica gel. Eluting with carbon tetrachloride and chloroform finally yielded the compound 87 in the same yield (1.8%).

Preparation of 1-Chloro-3-(dihydroindene)-1-Propene 137

Into a 500 ml round bottomed three necked flask equipped with magnetic stirrer, dropping funnel, dropping funnel with cooling jacket, and nitrogen inlet, was placed 3.4 g (0.03 moles) of 1,3-dichloropropene in 100 ml dry ether. The solution was cooled to -40° using a dry ice-acetone bath. 21 ml of n-butyl lithium (1.6 N) was added through the dropping funnel over one hour. A yellow color developed followed by the precipitation of lithium chloride. The mixture was then warmed to 0° and left standing for five hours. The mixture was then cooled to -78° in dry-ice-acetone bath and to this was added a solution of lithium cyclononatetraenide (prepared by treatment of 2.1 g (0.014moles)of _anti_-9-chloro-bicyclo[6.1.0]nona-2,4,6-triene with 0.25 g lithium in tetrahydrofuran) through the dropping funnel kept at -78° over a period of one hour. The mixture was then allowed to stir for another three hours at -78° and brought to room temperature, and left to be stirred overnight. The solution was poured over 200 ml of ice water and 600 ml ether. The ether layer was separated, and the aqueous layer was extracted with another 400 ml ether. The organic extracts were combined, washed with 200 ml ice water, and dried over anhydrous sodium sulfate. Solvent was removed on a rotary evaporator and the residue was submitted to chromatography on 50 gr aluminum oxide with carbon tetrachloride elution. The first fraction was separated and identified to be the unreacted compound **118**. The column was then eluted with chloroform to give another compound as a yellow liquid. This compound was identified as compound **137** (1.1 g, yield 30%). Ms (m/e, %): 192 (8), 155 (6), 143 (10), 129 (24), 117 (100), 115 (90), 91 (85), 77 (52), ir (neat): 3100, 2900, 1650, 180 MHz proton nmr (δ, $CDCl_3$): 2.39 (dd, J=9.0 and 7.5 Hz, 2H), 2.65-2.75 (m, 2H), 3.59 (bd, J=12.0 Hz, 1H), 5.47 (m, 1H), 5.5-5.95 (m, 6H), 6.05 (m, 1H), proton decoupled ^{13}C nmr (δ, $CDCl_3$): 134.1 (1c), 132.3 (1c), 129.6 (1c), 128.9 (1c), 126.0 (1c), 120.9 (1c), 120.7 (1c), 119.0 (1c), 54.5 (1c), 44.0 (1c), 41.9 (1c), and 31.7 (1c). Partially proton decoupled C nmr showed three doublets at 54.5, 44.0, 41.9 and a triplet at 31.7 ppm.

Attempts to Prepare 3-Chlorocyclopropene

A. Using Sodium Amide

Into a 100 ml round bottomed three necked flask equipped with magnetic stirrer, dropping funnel, nitrogen inlet was placed 4.0 g (0.1 mol) commercial sodium amide in 20 ml mineral oil. The flask was heated to 60°, and a solution of 11.1 g (0.1 mol) of 1,3-dichloropropene in 10 ml mineral oil was added dropwise through the dropping funnel over a period of one hour. The mixture was then heated to 80° and kept at that temperature for another one hour. The mixture was cooled to room temperature and the volatiles were distilled into a trap kept in liquid nitrogen using a high vacuum pump. Proton nmr spectrum of the volatile material showed it to be the starting material, 1,3-dichloropropene.

B. Using Potassium t-Butoxide

1.7 g (0.015 mol) of 1,3-dichloropropene in 10 ml ether was added dropwise to a rapidly stirring solution of 6.9 g (0.06 mol) of potassium t-butoxide in 15 ml ether at -10° over a period of one hour. The mixture was warmed to room temperature and allowed to stir for another six hours. The mixture was then filtered and the filtrate was concentrated at -30° using a high vacuum pump. The nmr spectrum of the residue was quite messy and did not show the peaks belonging to 3-chlorocyclopropene.

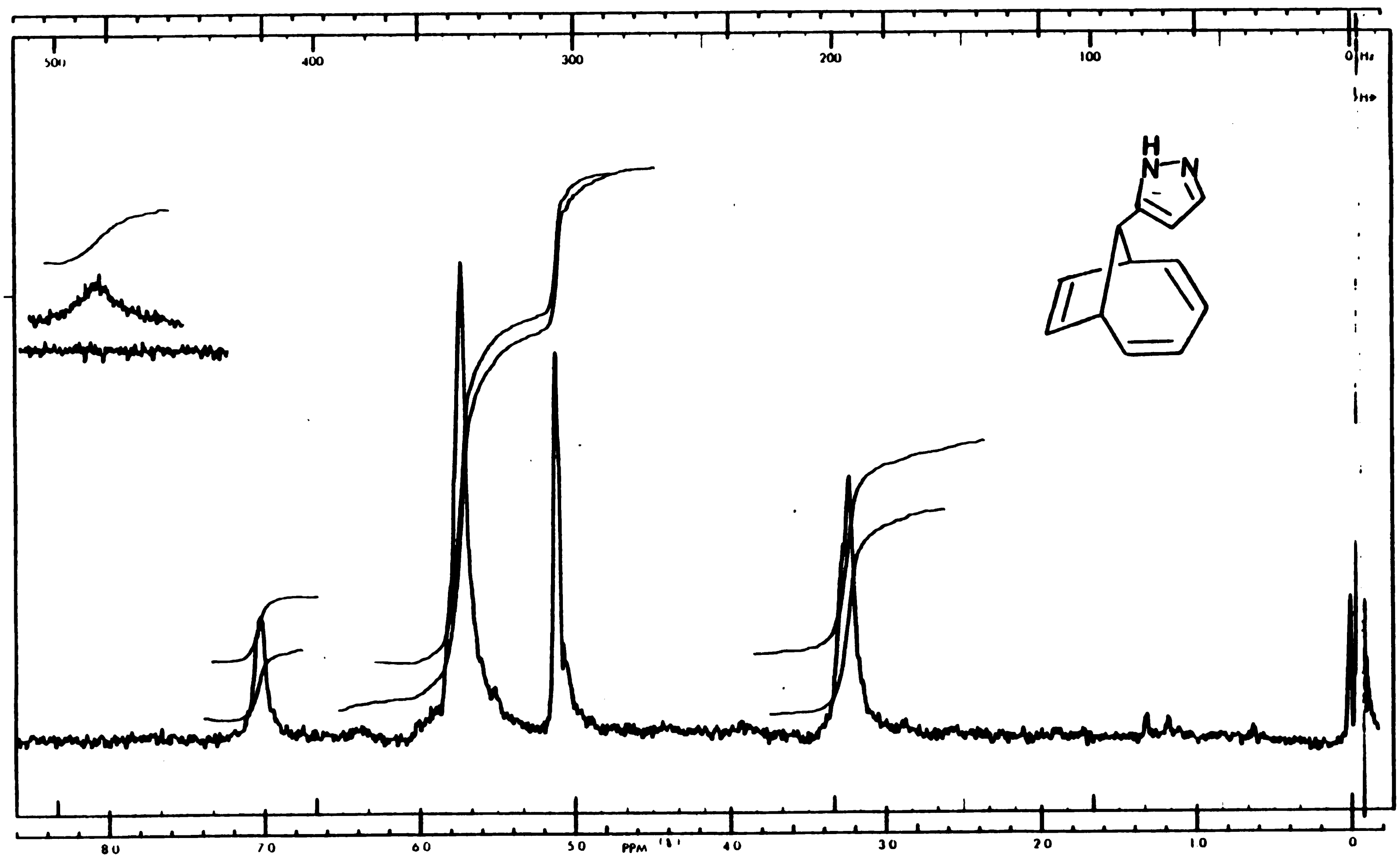


Figure 21. Proton nmr spectra of pyrazole 54.

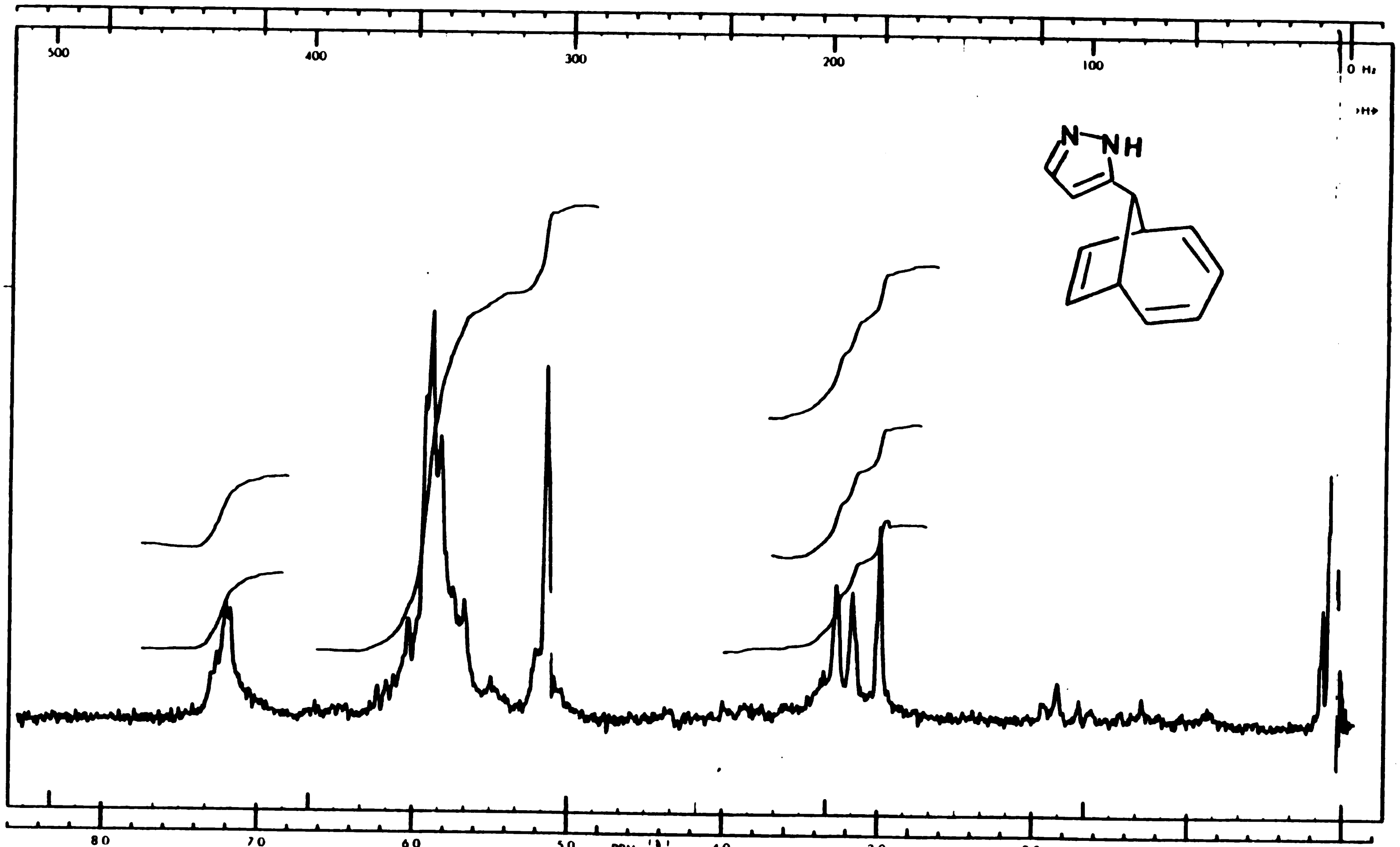


Figure 22. Proton nmr spectra of pyrazole 55.

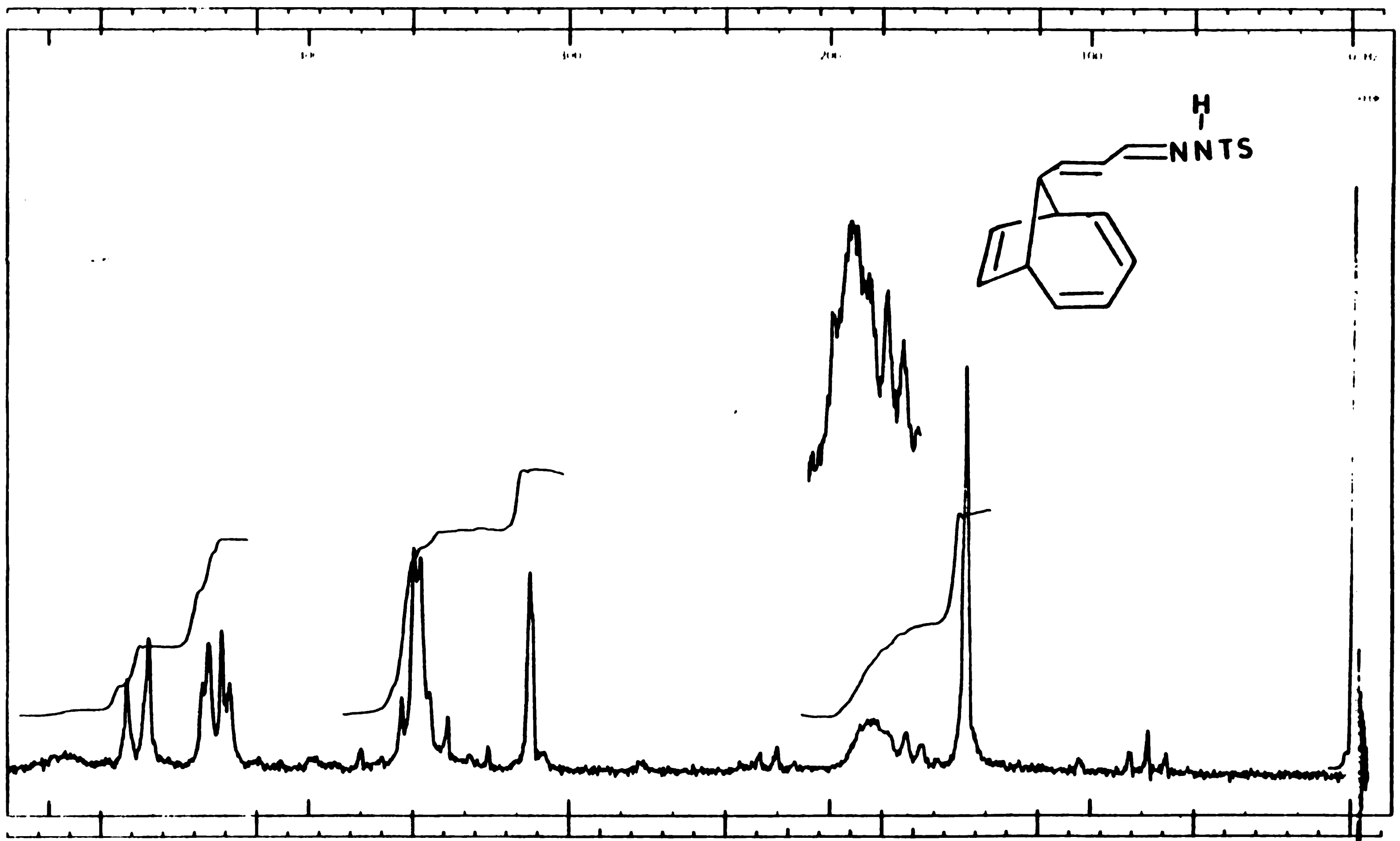


Figure 23. Proton nmr spectra of tosylhydrazone 65.

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