A NEW ENTRY TO THE $(CH)_{12}$ HYDROCARBON ENERGY SURFACE

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THOMAS JOEL REITZ
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This is to certify that the

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A NEW ENTRY TO THE $(CH)_{12}$ HYDROCARBON

ENERGY SURFACE

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Thomas Joel Reitz

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Donald G Farnum
Major professor

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ABSTRACT

A NEW ENTRY TO THE $(CH)_{12}$ HYDROCARBON ENERGY SURFACE

BY

Thomas Joel Reitz

Pyrolysis of the dry lithium salt of _trans_-β-[anti-9-bicyclo-[6.1.0]nona-2,4,6-trienyl]acrolein tosylhyrazone resulted in the formation of three $(CH)_{12}$ hydrocarbons, characterized as: _exo_ and _endo_-tricyclo$[4.4.2.0^{2,5}]$dodeca-3,7,9,11-tetraenes and the previously unreported diene, pentacyclo$[6.4.0.0.^{2,12}0.^{3,7}0^{4,11}]$dodeca-5,9-diene.

The tosylhydrazone deuterated β to the tosyl group was also prepared and its pyrolysis products were studied. Some mechanistic considerations of the formation of the thermolysis products were examined.

We have also looked at the thermolysis of some _anti_-9-bicyclo-[6.1.0]nona - 2,4,6-triene derivatives. We have found rearrangement to the corresponding bicyclo[4.2.1] system to be general for derivatives with extended π-electron withdrawing ability.

In the second part of this work we attempted to isomerize anti-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]nona-2,4,6-triene to truncated tetrahedrane. Some photochemical and transition metal catalyzed isomerizations were tried.

A NEW ENTRY TO THE $(CH)_{12}$ HYDROCARBON ENERGY SURFACE

By

Thomas Joel Reitz

A DISSERTATION

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TO MY PARENTS

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Finally, I thank my parents for their continual support, confidence and prayers.

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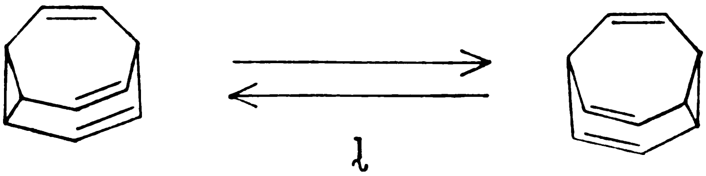
Introduction

Mapping of the interconversions of stable molecules residing on the potential energy surfaces describing $(CH)_n$ hydrocarbons has been the goal of various research groups.[1,2,3,4] Some of the findings for $(CH)_8$,[1] $(CH)_{10}$ [2] and $(CH_{12}$ [3] hydrocarbons are illustrated in Figures 1, 2 and 3 respectively. Two recent review articles have helped to organize much of this material. Masamune and Darby[4a] reviewed [10] annulene and other $(CH)_{10}$ hydrocarbons, and Scott and Jones[4b] examined a number of other $(CH)_n$ compounds. Also Balaban[5] has published a series of computer generated valence isomers of $(CH)_n$ cyclopolyenes (where n = 2, 3, 4 or 5,[5a] and where n = 6 [5b]) which conveniently acts as a compendium for these compounds.

Much of the work to date in studying $(CH)_n$ formations and transformations have centered on the $(CH)_8$ and $(CH)_{10}$ energy surfaces. A few contributions are of particular note. The prediction[2c] and subsequent synthesis[2p] of bullvalene (1) validated the concept of "fluxional" molecules, whereby very rapid valence tautomerization results in the interchange of carbon atom positions within a molecule. Fluxional molecules are members of a repeatedly appearing class of compounds capable of undergoing degenerate rearrangements. They have the distinction of rearranging extremely fast, i.e., too fast for individual



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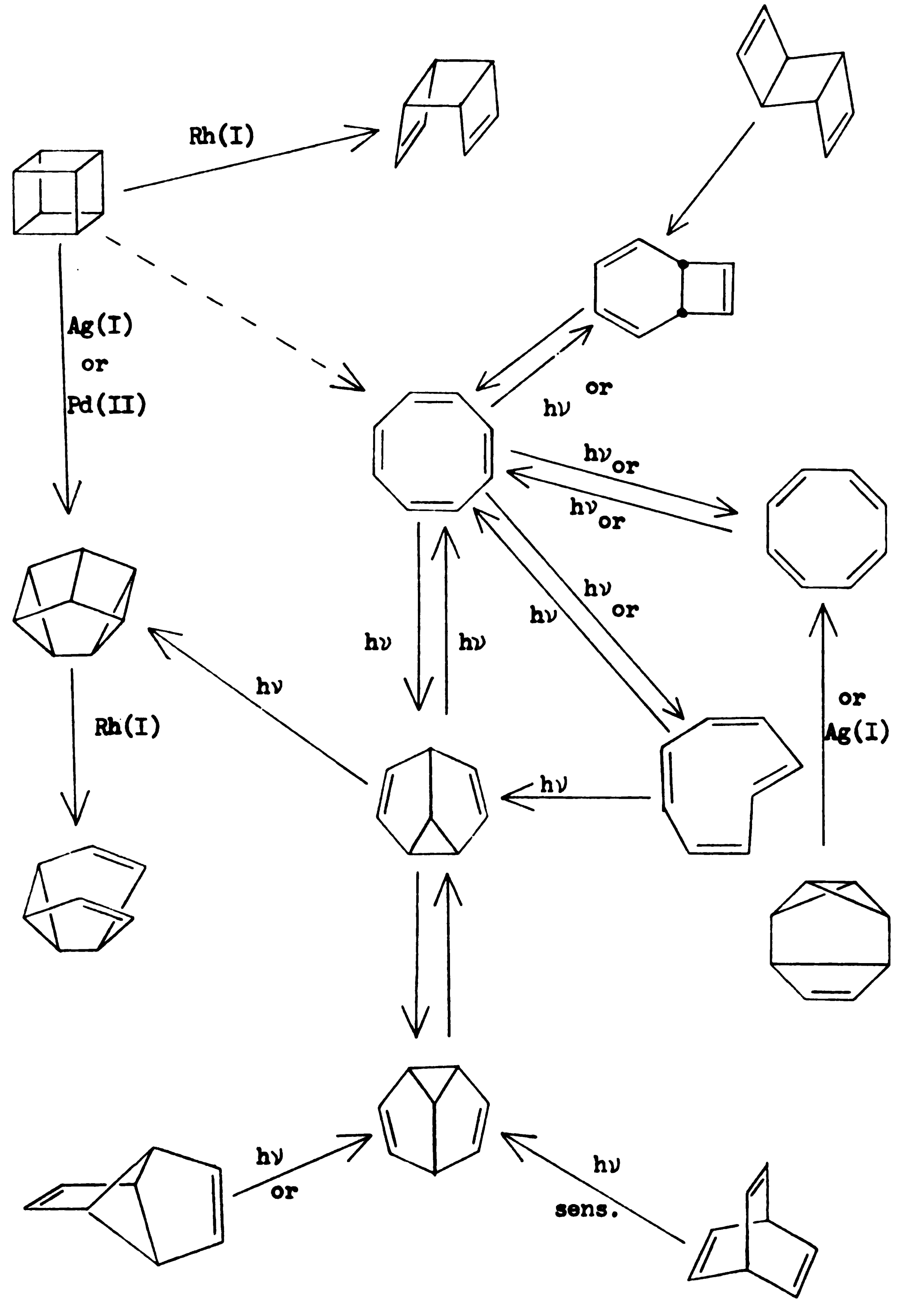


Figure 1. Interconversions of $(CH)_8$ Isomers.

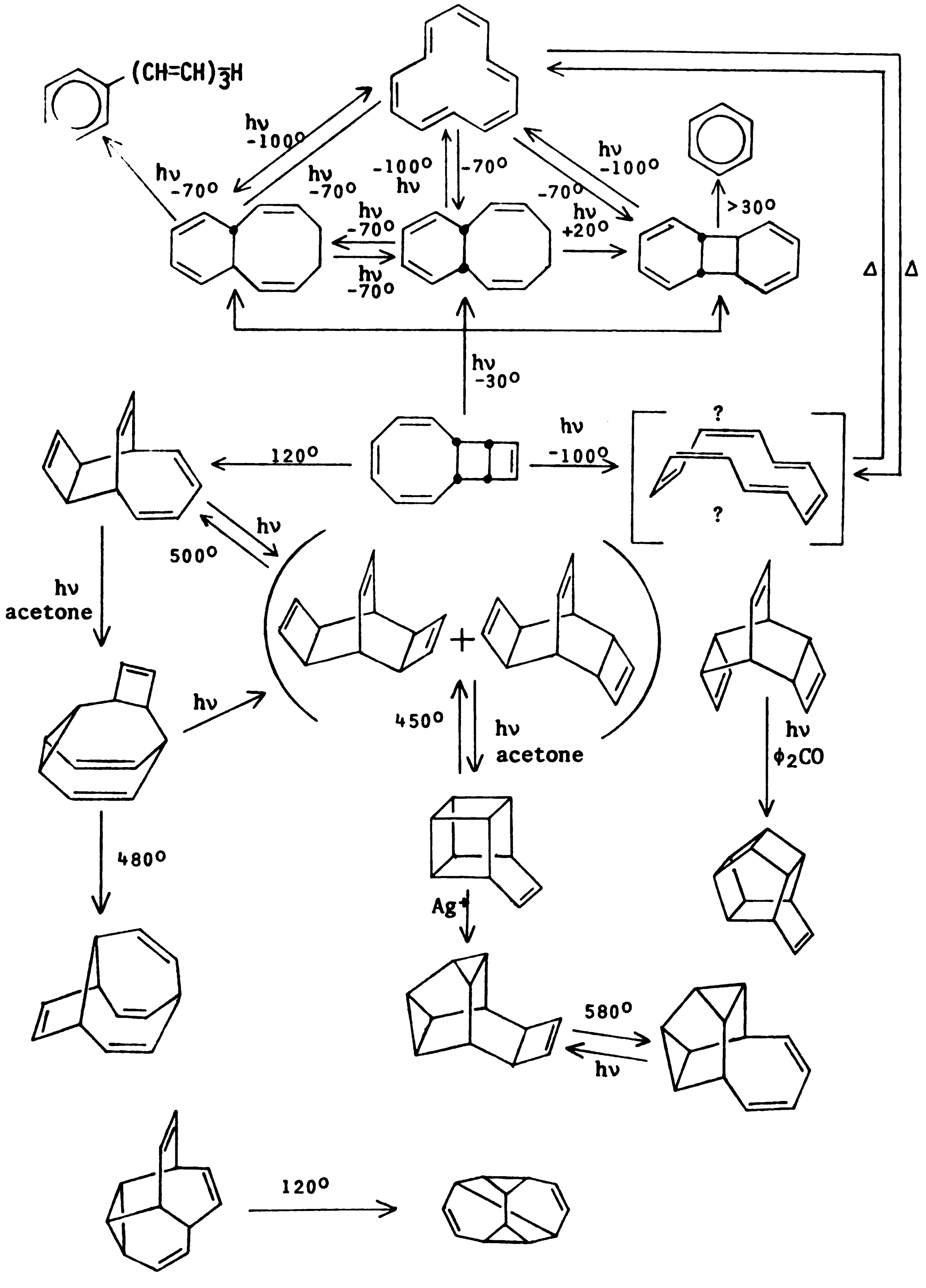
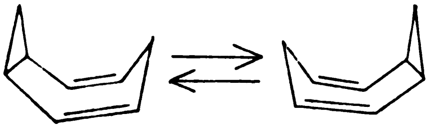


Figure 3. Interconversions of $(CH)_{12}$ Isomers.

valence isomers to be observed on an nmr time scale. In bullvalene all ten carbons become identical through a series of degenerate Cope rearrangements. In general fluxional molecules possess a homotropilidene unit (2). The rate of this reaction is enhanced when the geometry



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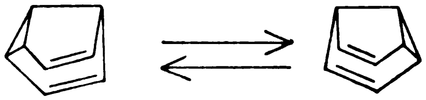

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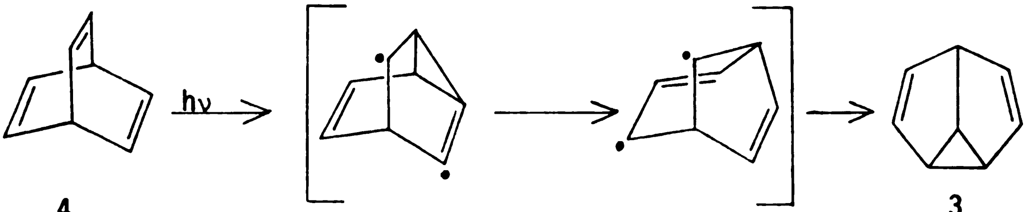
is rigid, as in semibullvalene (3), where the ends of the homotropilidene unit are tied together.[6]

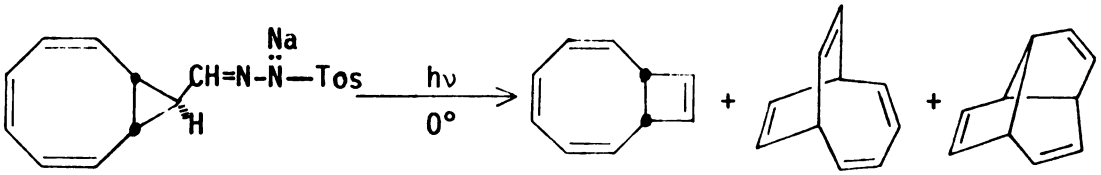
Sensitized irradiation of barrelene (4) led to semibullvalene (3).[1b] Subsequent recognition of the generality of this photosiomerization has led to formulation of the general di-π- methane



4 3 (1)

rearrangement mechanism.[7]

Before one can look at transformations within an energy surface, one must, of course, synthesize a member of that surface. Various approaches have been used to synthesize these compounds. If one member is of particular interest, a directed synthesis might be attempted (more will be said of this approach later); often, however, a general synthesis has been used to generate a mixture of members.[2h,i,j,l] For instance decomposition of tosylhydrazone salt 5 both photochemically[8] (eq. 2) and thermally[2h] (eq. 3) has led to a number of different $(CH)_{10}$ isomers.



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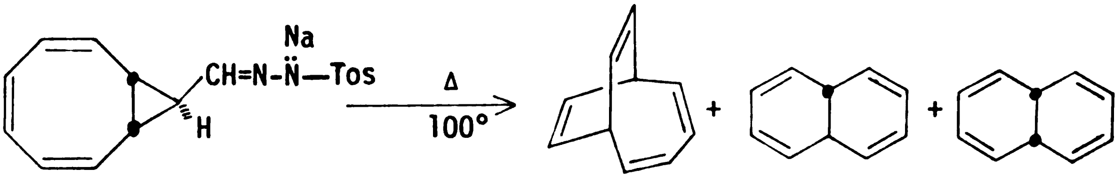

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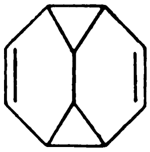
(3)

Once a member of an energy surface is in hand, its rearrangements can be probed. The most common methods for doing this are to look at the compounds formed from its thermal or photochemical isomerization. A very instrumental factor in this area has been the predictive role orbital symmetry[9] has been found to play in determining what reaction paths a molecule may follow.

After products have been identified, an intermediate or series of intermediates can be proposed to explain the course of the isomerization. Testing of these proposals generally includes labeling experiments, trapping experiments, and/or synthesis and subsequent isomerization of key intermediates. A common method of synthesizing thermally labile "intermediates" has been low temperature photolysis. Prior to its observation and isolation,[2ℓ] tetracyclo$[4.4.0.0.^{2,10}0^{5,7}]$-deca-3,8-diene (6) had been proposed to be a key intermediate in some



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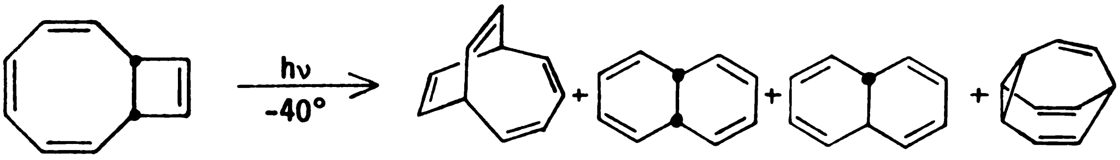
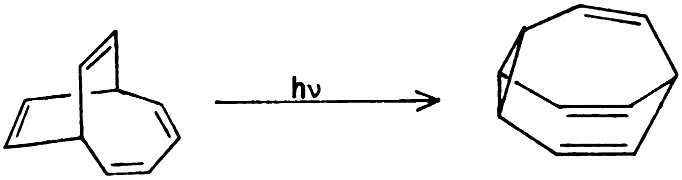
interconversions of $(CH)_{10}$ isomers.[10] While investigating the photochemistry of cis-bicyclo[6.2.0]deca-2,4,6,9-tetraene (7) at -40° followed by room temperature workup (eq. 4), Masamune and coworkers



7 8

(4)

noticed that the photolysis time did not significantly alter the product distribution. The fact that 8 was photochemically labile under these conditions[2d,g,l] (eq. 5) indicated that there must have been an

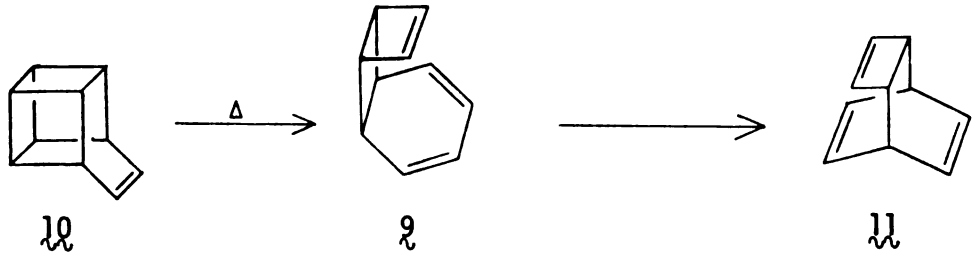


8 1

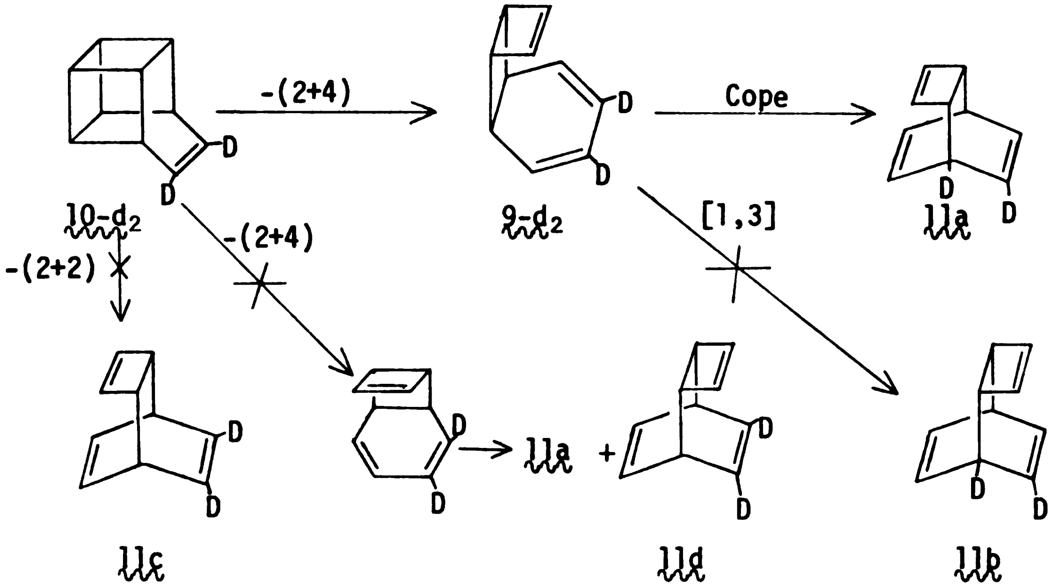
(5)

intermediate which was photochemically inert but thermally labile. Workup of the reaction at -80° did indeed give 6 and its facile thermal conversion to 8 was confirmed.[2ℓ]

Another often proposed intermediate[11] in $(CH)_{10}$ interconversions was <u>cis</u>,<u>syn</u>,<u>cis</u>-tricyclo[4.4.0.$0^{2,5}$]-3,7,9-decatriene (9). For instance, basketene 10 is known to rearrange thermally to Nenitzescu's hydrocarbon 11.[2a,b,k] Deuterium labeling,[12] kinetic studies,[12] and

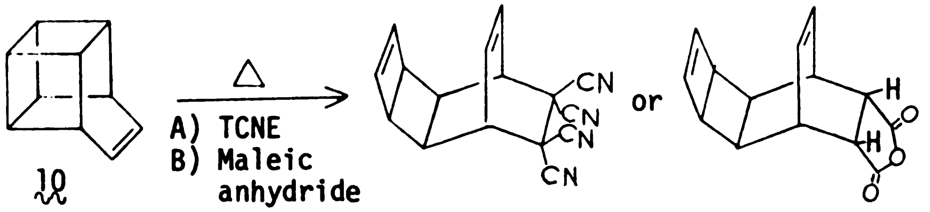


trapping experiments[13] have shown that this rearrangement cannot involve a simple retro 2 + 2 reaction. Thermolysis of dideuterated basketene 10-d$_2$ gave only 11a (eq. 6), which is consistent with the intermediacy of 9. Deuterium labeling also helped differentiate between two possible



(6)

courses for the rearrangement of 9 to 11. An allowed Cope rearrangement is consistent with rearrangement of 9-d$_2$ to 11a, while a forbidden [1,3] sigmatropic shift of 9-d$_2$ would lead to 10b and not the observed 11a.[12] Also, heating basketene (10) with tetracyanoethylene or maleic anhydride gave adducts (eq. 7) which are consistent with a Diels-Alder addition to



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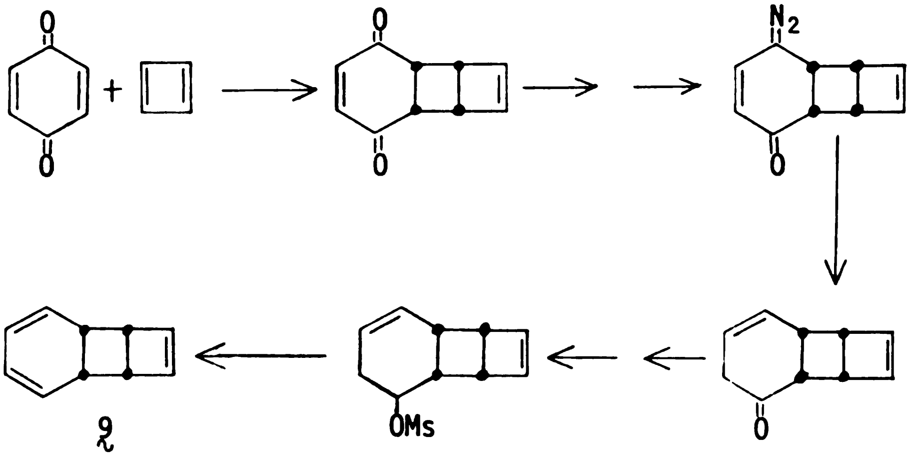
9.[13] Compound **9** later became available through a directed synthesis. Vedejs prepared **9** (eq. 8) and observed its facile thermal rearrangement



(8)

to **11** (at 70° $\tau_{1/2}$ = 28 min).[2r]

Our interest lies in contributing to the understanding of the $(CH)_{12}$ energy surface. Although this system has not been investigated as thoroughly as the lower $(CH)_n$ families, much interesting chemistry has been uncovered. These findings, illustrated in part in Figure 3,[3] have been the subject of a recent review;[4b] therefore, I will not treat that work here, but concentrate on later work. A listing of $(CH)_{12}$ isomers which have been synthesized, but have not yet been fit into their places on the energy surface, is given in Figure 4.

In 1974 Daub completed the set of tetracyclo[4.4.2.0.^{2,5}0^{7,10}]-dodecatrienes (**12**)-(**14**) [3b] by synthesizing the *endo,endo* isomer (**12**).[3a]

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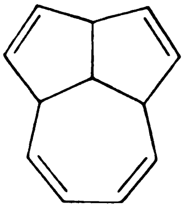

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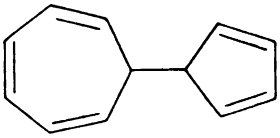

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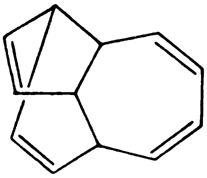

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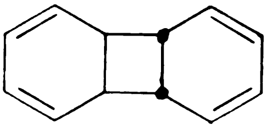

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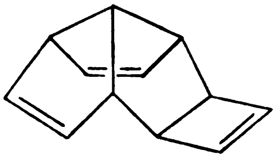

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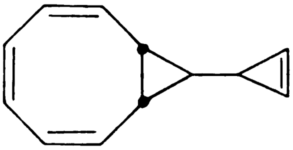

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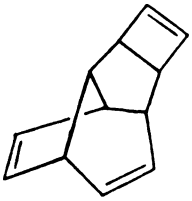

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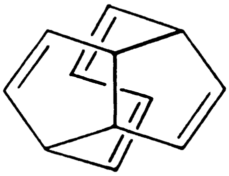

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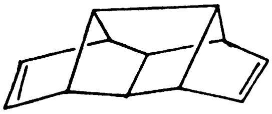

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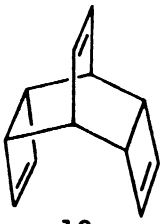
Figure 4. Uncharted $(CH)_{12}$ Isomers.



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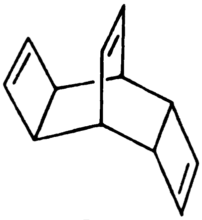

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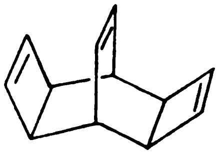

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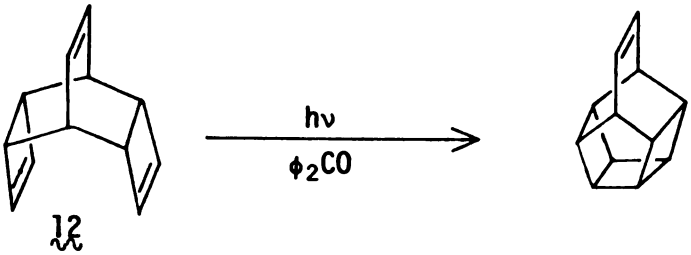
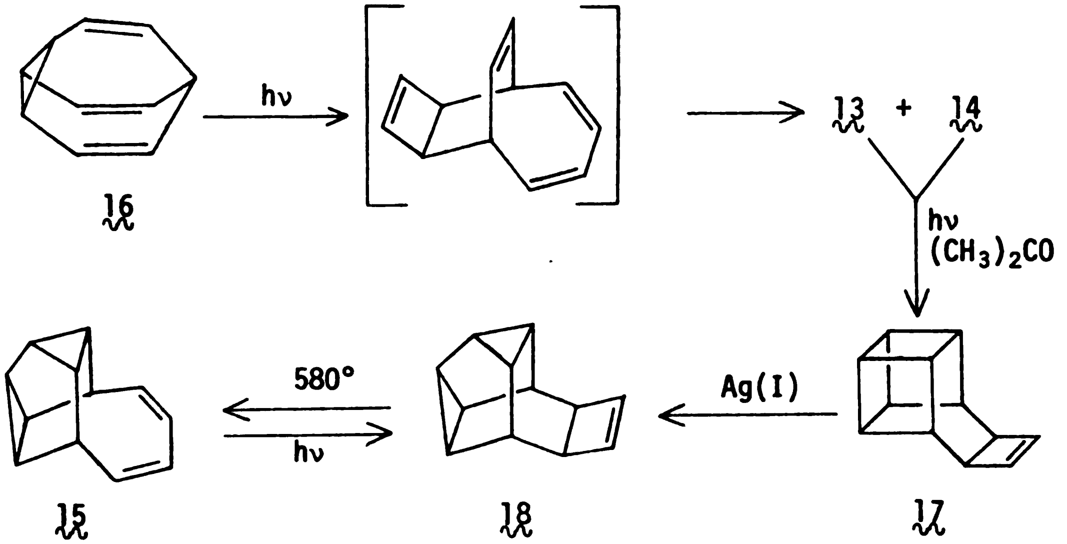
He showed that 12 on sensitized irradiation (eq. 9) went to the known cage compound.[3a]



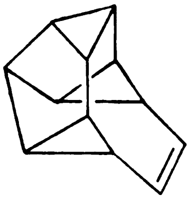
(9)

Paquette, who has probably contributed the most to describing the $(CH)_{12}$ energy surface, prepared pentacyclo[6.4.0.^{6,11}0.^{7,9}0^{11,12}]dodeca-2,4-diene (15) through a four-step directed bond reorganization of tetracyclo[5.3.2.0.^{2,5}0 ^{6,8}]dodeca-3,9,11-triene (16) [3c] (eq. 10).



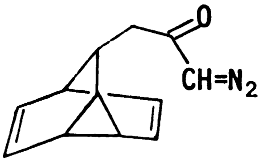
(10)

Conversion of 17 to 18 is an example of the well precedented[14] (σ2a + σ2a) bond relocation process which simultaneously converts a set of four multiply fused cyclobutane rings to two pairs of cyclopropane and cyclopentane rings. Compound 18, though resistant to thermal rearrangement, did partially rearrange to 15 at 580°. However, no evidence for the hexacyclic hydrocarbon 19 was observed.[3c]



19

Vedejs has reported an elegant synthesis of pentacyclo-$[5.5.0.0.^{2,12}0.^{6,8}0^{3,9}]$dodeca-4,11-diene (20) using the diazo compound 21.[3d] While conceptually diene 20 has the possibility of undergoing a retro-Diels-Alder to give 22, which in turn could undergo a Cope rearrangement leading to 23, a potential photochemical precursor of



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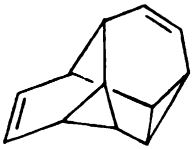

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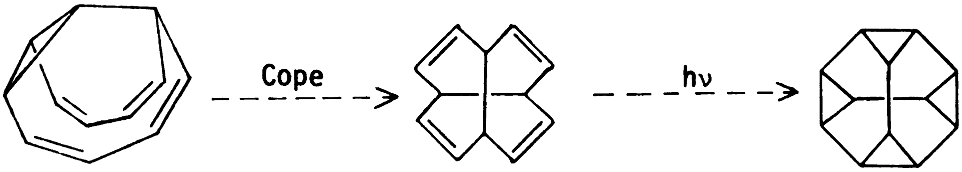
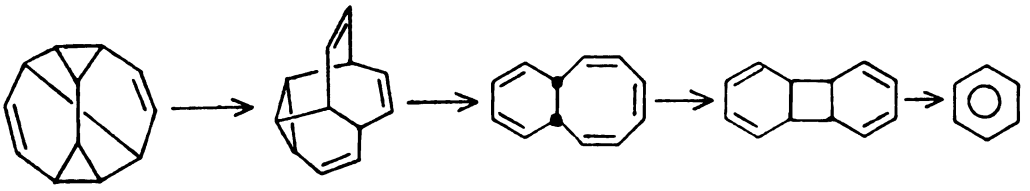


22 23 24

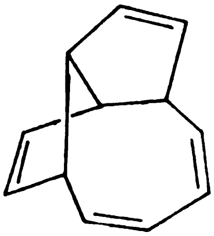
truncated tetrahedrane 24, pyrolysis above 160° gave only benzene. A mechanism leading to benzene was proposed (eq. 11). As a test,


(11)

20 25

tetracyclo[5.5.0.0.^{2,4}0^{3,10}]dodeca-2,4,6,9,11-pentaene 25 was prepared. Thermolysis of 25 above 160° did indeed give benzene, but more significantly, reaction at temperatures between 120° and 150° resulted in complete conversion of 25 to 20.[3d]

Two new $(CH)_{12}$ hydrocarbons have recently been synthesized in our lab: tricyclo[7.3.0.0^{4,12}]dodeca-2,5,7,10-tetraene (26) [15] and anti-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]nona-2,4,6-triene (27).[16] Tetraene 26 could undergo a series of degenerate Cope rearrangements, one of which is illustrated in equation 12. An added feature is that each Cope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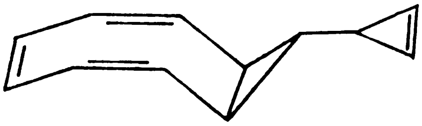
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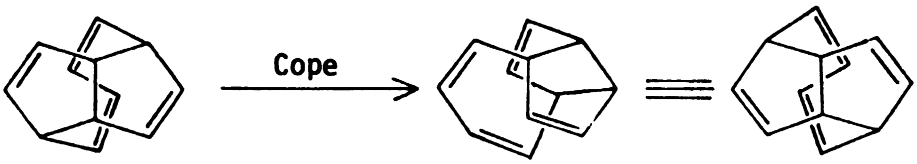

(12)

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rearrangement interchanges enantiomers. Initial work (up to 141°) shows 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.[15]

Two hydrocarbons of particular interest to us are "truncated tetrahedrane" (24) (so named for its tetrahedral symmetry), and its valence tautomer 29. Compound 24 is of much theoretical interest, owing to its cage-like array of cyclopropane rings. The quadruple trishomobenzene nature of 24 makes it and 29 an ideal system (Fig. 5) for testing the theory of homoaromaticity in neutral molecules. The possibility of such stabilization existing in molecules with three properly

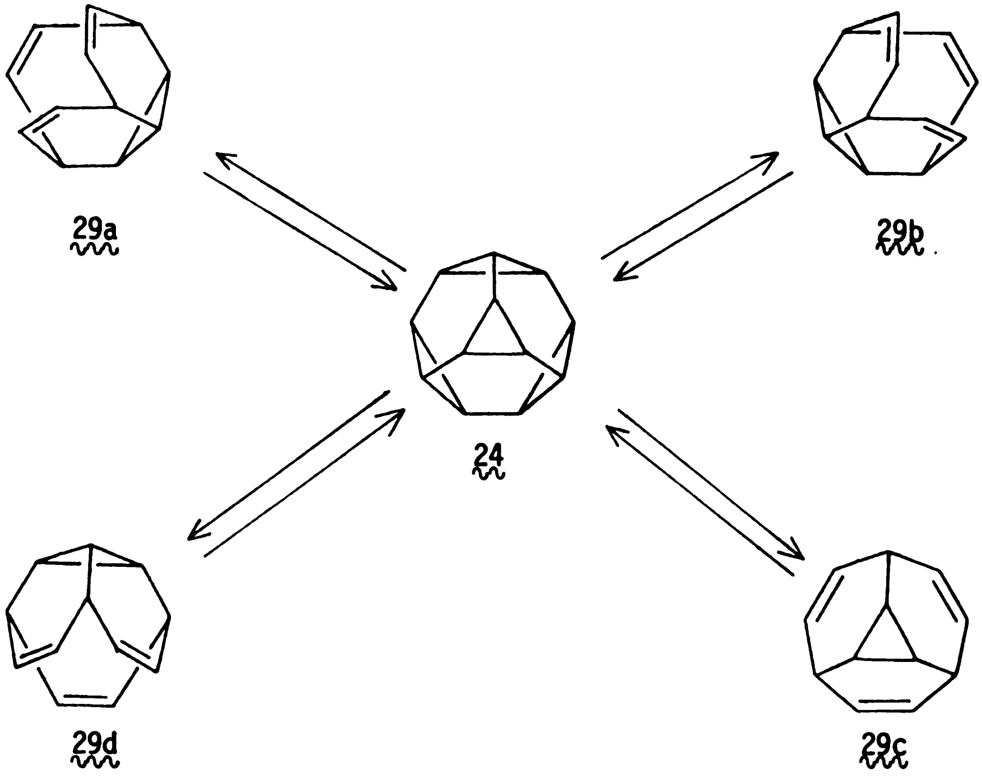
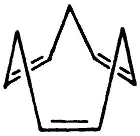


Figure 5. Thermally Allowed ($\pi_{2s} + \pi_{2s} + \pi_{2s}$) Interconversions.

disposed double bonds, such as syn-cis,cis,cis-1,4,7-cyclononatriene (30) and triquinacene (31) has prompted a great deal of work with these compounds and their valence isomers 32 and 33.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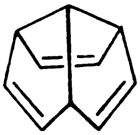
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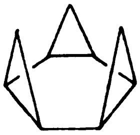
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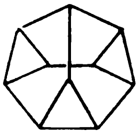

33

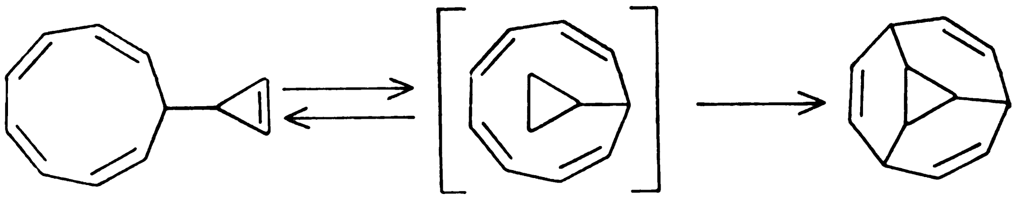
The most direct measure of homoconjugative interaction is the difference in the ionization potentials of the interacting bonds, relative to the ionization potentials of isolated, noninteracting systems. Through the technique of photoelectron spectroscopy (PES) [2ℓ] such measurements of the magnitude of homoconjugative interaction have become feasible and are now available for a number of molecules.[22]

Compounds 30,[23] 31,[24] and 33 [24b,25] have been prepared. Each has been studied by PES (references 22a, 22c and 22e respectively), but only in the case of 30 do the authors suggest a strong through bond homoconjugative interaction. By comparing Dreiden models (perhaps a naive approach, but still useful) of 30 and 31 we can see that incorporation of the sp^3 carbon in triquinacene forces the π-orbitals farther apart relative to those in 1,4,7-cyclononatriene; and thus is consistent with less interaction as shown by PES. A Dreiden model of 29 shows, however, that incorporation of a cyclopropane moiety results in a geometric arrangement of π-bonds similar to that of cyclononatriene. On this basis we would predict some homoaromatic stabilization for compound 29.

It is not clear what predictions concerning stabilization within truncated tetrahedrane (24) can be made. There is some evidence for homoconjugative stabilization between two adjacent eclipsed cyclopropane rings.[22e] The results of PES on diademane (33) were interpreted to show less stabilization than expected. The authors suggested that this observed destabilization was due to the inductive effect of the central sp^3 carbon atom, which ties the cyclopropane rings together. This effect would be absent in truncated tetrahedrane (24) and we might expect to see a stabilization due to the six sets of eclipsed cyclopropane rings.

Assuming the degenerate isomerization of 29 will take place as in Figure 5, we would like to see if truncated tetrahedrane (24) is only a transient intermediate in this rearrangement or if indeed there is enough stabilization within 24 to see or isolate it.

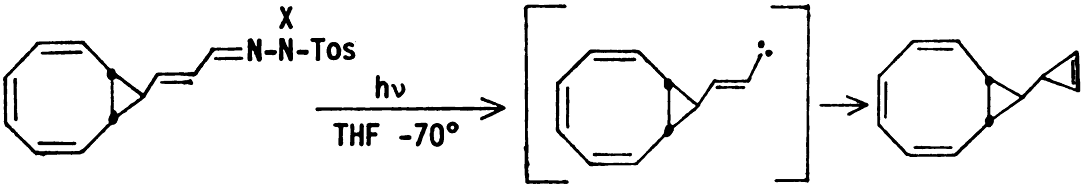
The original intent of this project was the conversion of Raghu's cyclopropene 27 to 1-(3-cyclopropeno)-cyclonona-2,4,6,8-tetraene (34), an intermediate which could interconvert with other $(CH)_{12}$ isomers. In particular, we envisioned geometrical isomerization followed by a $(\pi_{2s} + \pi_{2s} + \pi_{2s})$ cycloaddition leading to 29 (eq. 13).



(13)

34 29

Cyclopropene 27 was available from low temperature decomposition of tosylhydrazone salt 36 (eq. 14).[16] We felt thermal decomposition of 34



(14)

35 X = H

36 X = Na

27

might also lead to a mixture of other known and yet unknown interesting $(CH)_{12}$ hydrocarbons.

With these considerations in mind, we undergook the synthesis of large quantities of tosylhydrazone 35 and looked at its photochemical and thermal decomposition in an attempt to find and study numerous $(CH)_{12}$ entries.

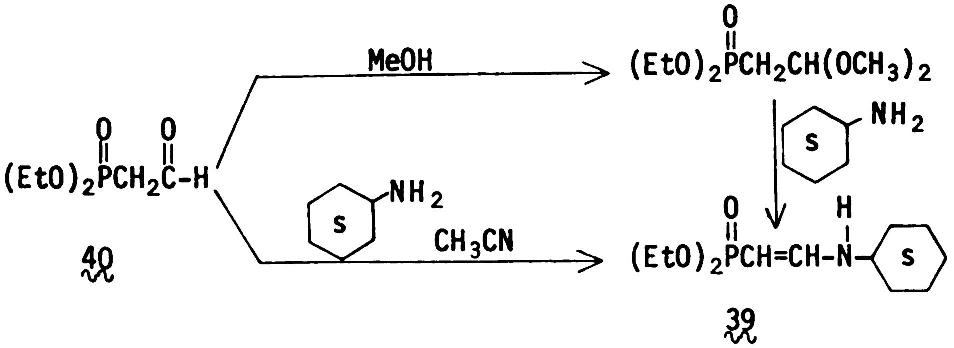
Results and Discussion

Part A

Synthesis of *Trans*-β-[*anti*-9-bicyclo[6.1.0]-2,4,6-trienyl]acrolein Tosylhydrazone (**35**).

Our first major concern was the synthesis of a large quantity of tosylhydrazone **35**. The general procedure, as illustrated on the next page, was adapted from Raghu's thesis.[16] Some minor modifications to the reported procedure are described in the Experimental. The only step which required detailed investigation was the *ca.* 50% conversion of aldehyde **37** to extended aldehyde **38**. Since a 6:1 molar ratio of enamine reagent to aldehyde was required for this conversion, we set about preparing large amounts of this reagent (**39**).

The procedure for preparing formylmethylphosphonate (**40**) was adapted from the literature.[26] The next step was to react **40** with cyclohexylamine in methanol. We found that phosphonate **40** in the presence of methanol (eq. 15) formed the acetal, and subsequent reaction with cyclohexylamine was impeded. The use of acetonitrile as the solvent resulted in a much cleaner reaction. The enamine reagent was prepared in 80% yield as a white crystalline solid (mp 60-62°; lit.[26b] 58-61°) after recrystallization from ether.



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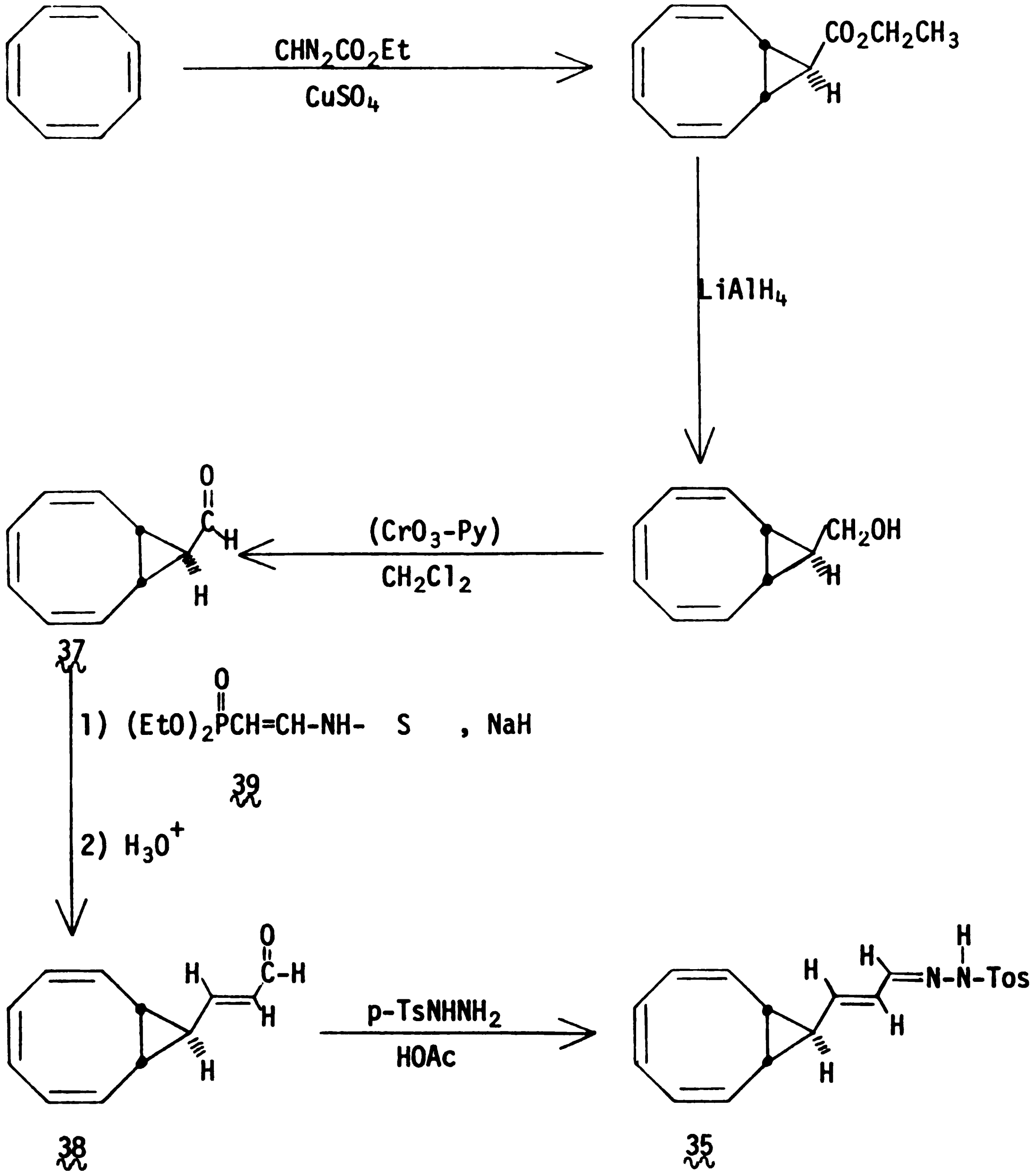
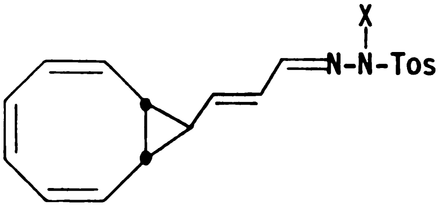


Figure 6. Preparation of Tosylhydrozone 35.

The aldehyde on treatment with one-half molar excess of crystalline enamine reagent gave the unsaturated aldehyde in 68% yield. The tosylhydrazone could then be made conveniently and in good yield.

Thermal Decomposition of Tosylhydrazone 35.

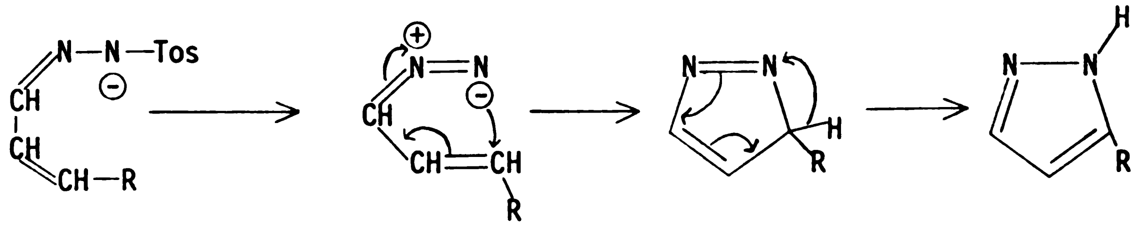
We were now in a position to look at the thermal decomposition of tosylhydrazone salt 42. Raghu[16] had found that pyrolysis of 36 under a



42 X=Li

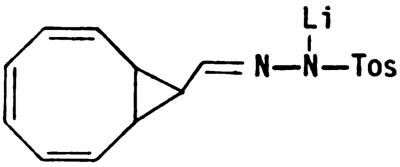
36 X=Na

variety of conditions (varying solvents and temperatures) yielded a pyrazole, rather than any $(CH)_{12}$ hydrocarbons. This rearrangement, though well precedented[27] for the case of α:β unsaturated diazo compounds (eq. 16), was disappointing. We felt that this rearrangement

 (16)

might be slowed down in the absence of solvent, so that pyrolysis of the dry salt[2i] would enable us to siolate some $(CH)_{12}$ hydrocarbons.

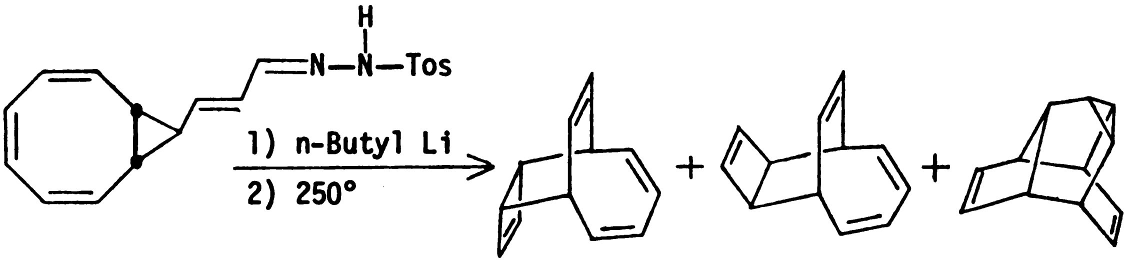
A simple method of testing this idea would be to pyrolize the solid salt in the gc injector port and look at the volatile products as they emerged from the gc column. We first examined the pyrolysis of tosylhydrazone salt 41 and found retention times for the products to be



41

consistent with reported[2i] gc data for this decomposition. We then tried this method with tosylhydrazone salt 42. Indeed combined gas chromatography/mass spectrometry (gc.ms) of the volatiles collected from this decomposition gave a series of peaks of molecular weight 156 (consistent with $C_{12}H_{12}$).

We found that the best method for preparative pyrolysis of 42 was to drop the dry salt into a column of hot glass beads maintained at 250° in a tube oven. The volatiles were then pumped through the column at 250° and collected in a trap at -78°. Gas chromatographic collection from a series of columns gave three major $(CH)_{12}$ products: 43, 44 and 45 in a ratio of 3.0:1.2:1.0 respectively (eq. 17).



(17)

35 43 44 45

<u>Endo</u> and <u>exo</u>-tricyclo[4.4.2.$0^{2,5}$]dodeca-3,7,9,11-tetraenes 43 and 44.

Compounds 43 [17] and 44 [28] have been reported by Paquette, while 45 is a new $(CH)_{12}$ member. All three compounds gave practically identical mass spectra, with a parent peak at m/e 156, corresponding to $C_{12}H_{12}$, and fragment ion peaks at m/e 155, 141, 129, 128, 115, 91 (base peak) and 78 among others. In fact comparison of these spectra with those of two other $(CH)_{12}$ hydrocarbons prepared in this lab[15,16] showed quite similar characteristics. This similarity, though at first glance surprising, accentuates the fact that these $(CH)_{12}$ hydrocarbon isomers do lie on a common free energy surface. Thus, fragmentation in the mass spectrometer can follow from a common high energy structure.

In conjunction with other spectral techniques, carbon-13 nuclear magnetic resonance has been used quite successfully in structure determination of some polycyclic hydrocarbon compounds.[29] The number and intensity of lines in a proton decoupled cnmr spectrum can give important clues to the symmetry of the compound in question. For instance, the cnmr spectra of compounds **43** and **44** consist of six equally intense peaks, indicating either a plane or C_2 axis of symmetry. As will be shown below, the simplicity of the pnmr spectra and the presumption in each case of a symmetrically substituted cyclobutene moiety indicated the presence of a plane of symmetry for tetraenes **43** and **44**.

The exo isomer (**44**) was identified by comparison of its pnmr chemical shifts with the literature values.[28,30] It gave peaks at δ5.96-5.0 (4 H, m), 5.83 (2 H, sharp singlet, indicative of a symmetrical cyclobutene[31]), 5.47-5.3 (2 H, doublet of doublets), 3.25 (2 H, singlet) and 2.57 (2 H, pseudo triplet). Its proton decoupled cnmr spectrum, showing lines for four different olefinic carbons (δ139.0, 136.7, 125.0 and 120.6) and lines for two aliphatic carbons (δ50.4 and 36.1) is consistent with this assignment. The presence of a cyclobutene moiety is likewise indicated by the two relatively low field lines in the cnmr spectrum at δ139.0 and 50.4.[1b]

The assignment of **43** as the endo isomer of **44** was made on the basis of its spectral similarity to **44** and by comparison of its pnmr spectrum to one supplied by Paquette for this previously synthesized but unreported compound.[30] Its ultraviolet spectrum consists of maxima at 263.5 mu (ε ∿ 3,000), 273 mu (ε ∿ 2,900) and 283 mu (ε ∿ 1,300). This is quite similar to the exo isomer which gave maxima at 258.5 mu (ε 4600), 268.5 mu (ε 5000) and 280 mu (ε 2700).[28a]

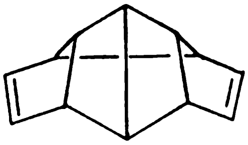
The proton decoupled cnmr of endo isomer **43** is likewise similar to the exo compound, showing lines for four olefinic carbons (δ140.0, 134.5, 126.7 and 123.3) and lines for two aliphatic carbons (δ48.6 and 34.7). Again the relatively low field peaks at δ140.03 and 48.65 reveal the cyclobutene.

Pentacyclo[6.4.0.0.^{2,12}0.^{3,7}0^{4,11}]dodeca-5,9-diene (**45**).

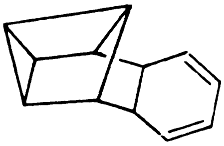
The structure of **45** was more difficult to assign. The pnmr spectrum, consisting of peaks at δ5.85 (2 H, dd, J = 4.4 and 3.0 Hz), 5.30 (2 H, d, J = 1.0 Hz), 2.67-3.34 (5 H, broad multiplet) and 1.78 (3 H, m), showed **45** to be a diene, and suggested the presence of a cyclopropane ring. The proton decoupled cnmr of **45** showled lines at δ 134.3, 130.9, 66.0, 62.4, 41.6, 36.1 and 26.4 with the third and seventh line of approximately one-half the intensity of the other five. From this and the symmetry within the pnmr spectrum we could see that diene **45** contained a plane of symmetry reflecting five pairs of carbons and bisecting two others.

Using Balaban's planar trivalent multigraph of order 12,[5b] one can reduce the number of possible dienes from 110 (not counting geometric isomers) to 16 based on symmetry alone. These 16 possibilities, named using Balaban's nomenclature[32] (β,t,q,s; where β is the number of double bonds, t is the number of three-membered rings, q is the number of four-membered rings and s is a serial number) are shown on the next page. Since the ultraviolet spectrum of **45** shows no absorption above 250 nm and since pnmr decoupling experiments show the olefinic peaks are not coupled to each other, we can say that diene **45** is not a conjugated diene and that its plane of symmetry must bisect each double bond.[33] These two criteria eliminate all but seven of the possibilities. Three others can easily be ruled out from the pnmr spectrum. Isomer 2-2-3-4 requires an even integration ratio in the aliphatic region whereas diene **45** shows a 5:3 ratio. Also isomers 2-2-3-6 and 2-3-0-2 require a cyclopropene which is lacking in our compound. This reduces the possibilities to 2-0-3-5, 2-1-0-2, 2-1-2-9 or 2-2-21.

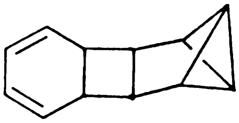
Structures 2-0-3-5 and 2-2-2-1 can be eliminated easily. Both contain symmetrically substituted cyclobutenes which characteristically gave a sharp singlet for the olefinic signal between δ5.8 and 6.3 in the pnmr.[31] Neither of the olefinic signals in the spectrum for **45** would correspond, since one is highly coupled and the other, though a broadened singlet, is beyond the normal range of a cyclobutene. Likewise, symmetrically (σ) substituted cyclobutenes gave characteristic chemical shifts[34] (*ca*. 140 and 49 ppm) in cnmr spectra. Such signals are absent in the cnmr spectrum of **45**. The bicyclobutane moiety of 2-2-2-1 would also give characteristic pnmr[31] and cnmr[34] peaks which are not apparent in the spectra of **45**.



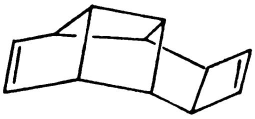
2-0-2-3



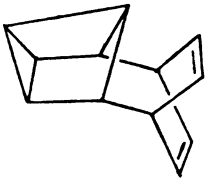
2-1-2-5



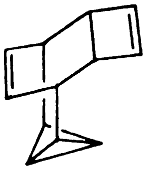
2-2-2-3



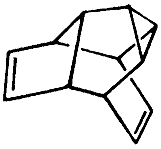
2-0-3-5



2-1-2-9



2-2-2-1



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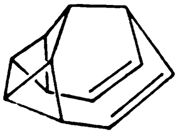

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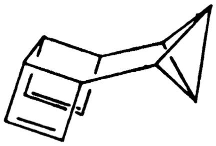
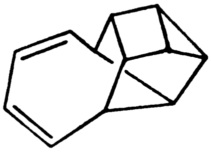
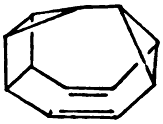


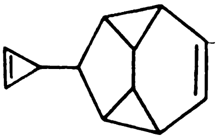
2-2-3-1



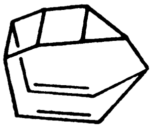
2-1-1-11



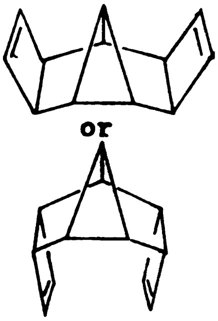
2-2-1-6



2-3-0-2

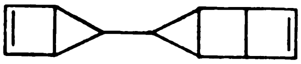


2-1-2-1

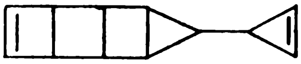


or

2-1-2-2



2-2-3-4

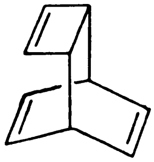


2-2-3-6

Figure 7. Possible^{5b} Structures for **45** Based on CNMR Symmetry Considerations.

A gated decoupled cnmr spectrum 45 [35] showed a doublet for the carbon at 26.4 ppm with a coupling constant (J_{C-H}) of 173 Hz. This J value is consistent with reported coupling constants for a hydrogen on a cyclopropane ring.[36] Both remaining possible structures, 2-1-0-3 and 2-1-2-9, contain a cyclopropane ring.

If 2-1-2-9 were the structure of 45, we would expect the olefinic region of the pnmr spectrum to be more complex. Molecular models show the geometry of the 2,5-cyclohexadiene unit of structure 2-1-2-9 to be quite similar to that in "Nenitzescu's" hydrocarbon 46 and homobarrelene 47. The pnmr spectrum of each of these compounds gives two sets of doublets (46: δ6.0, J = 5, 7 Hz; 6.35, J = 7.5, 5 Hz, and 47: δ6.58 and 5.97)[37] for the 2,5-cyclohexadiene moiety.



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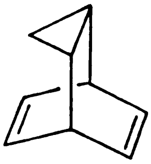
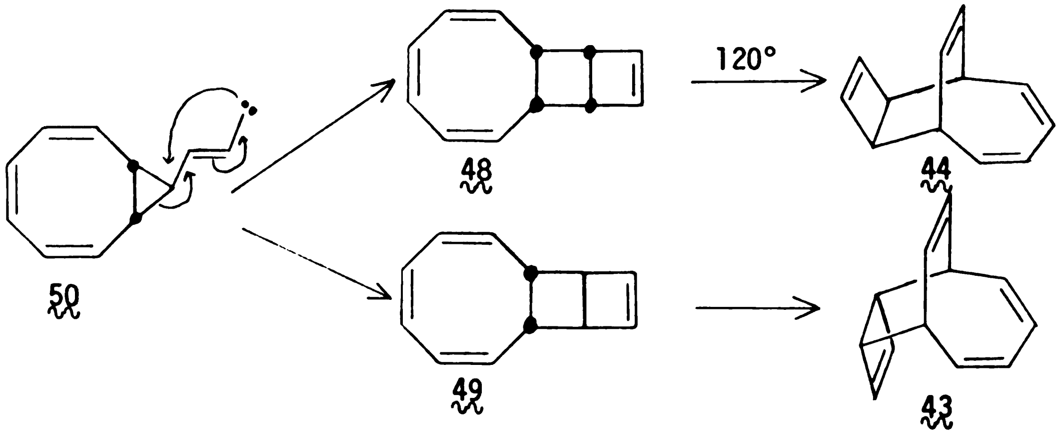


47

The protons on the 1,4 positions of these cyclohexadiene units appear as multiplets at δ3.25-3.5 and δ3.62 respectively. Compound 45 does have hydrogens in this region, but if 2-1-2-9 were the structure we would expect more of the saturated protons to appear separated from the allylic protons. As it is, we have a five hydrogen multiplet from δ2.5-3.3 in the spectrum of 45. While 2-1-2-9 has only two allylic hydrogens, structure 2-1-0-3 has four and is more in line with the five downfield aliphatic protons for 45. These considerations and the straightforward mechanistic path leading to structure 2-1-2-9 led us to conclude that the structure of 45 was as assigned.

A Look at a Possible Mechanism to 43 and 44.

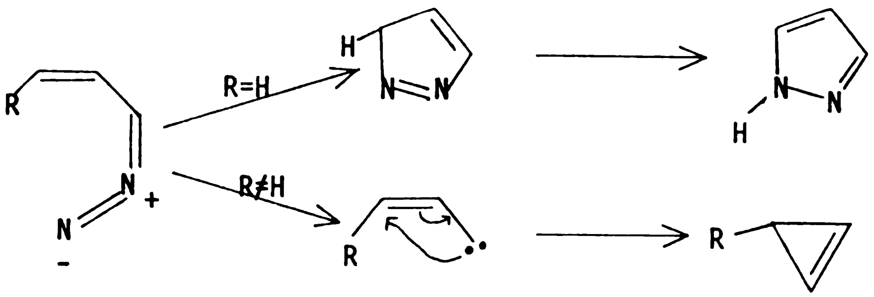
Cis,syn,cis-tricyclo[8.2.0.$0^{2,9}$]dodeca-3,5,7,11-tetraene (48) is known to thermolize selectively to tetraene 44. It seems likely that the anti isomer 49 would isomerize to 43 in an analogous fashion. Thus, it seemed clear from the start that a mechanism which led from dry salt 42 to a mixture of 48 and 49 would plausibly explain the formation of tetraenes 44 and 43. We envisioned (eq. 18) formation of carbene 50



(18)

followed by the novel ring expansion with concomitant cyclization to give 48 and 49. These can then isomerize to 44 and 43 respectively.

Carbenes are certainly known to arise from thermal decomposition of tosylhydrazone salts.[38] The second step, however, to our knowledge, is unprecedented for α,β unsaturated carbenes. Cyclization of carbenes, generated from photochemical decomposition of tosylhydrazone salts of α,β unsaturated carbonyl compounds, is known to give cyclopropenes.[38] Thermal decomposition of such salts also results in cyclopropene formation. However, when R = H (eq. 19), pyrazole[27] formation (through cyclization of the intermediate diazo compound) is predominant. Ring



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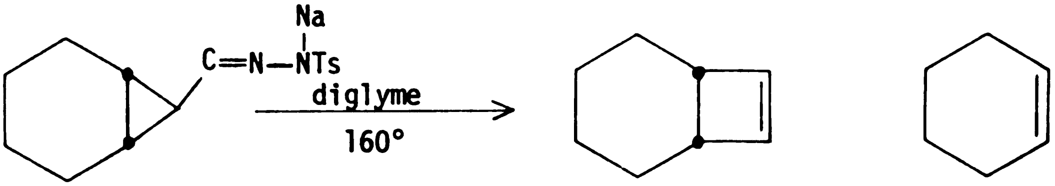
expansion of cyclopropylcarbenes to give cyclobutenes is also known[39] (eq. 20), but the presence of the conjugated double bond adds an



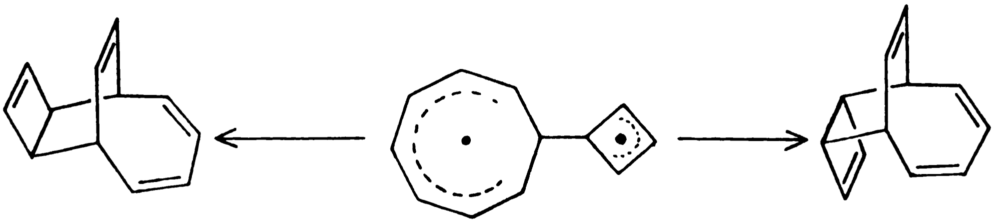
(20)

40

20

unknown dimension to our system.

The literature is indefinite on the course of rearrangement of 48 to 44. Clearly the selectivity of this isomerization precludes 48 opening to diradical 51, since the subsequent recyclization would be required to be sterochemically unidirectional from the symmetrical intermediate 51 (eq. 21). Paquette discussed two other possible



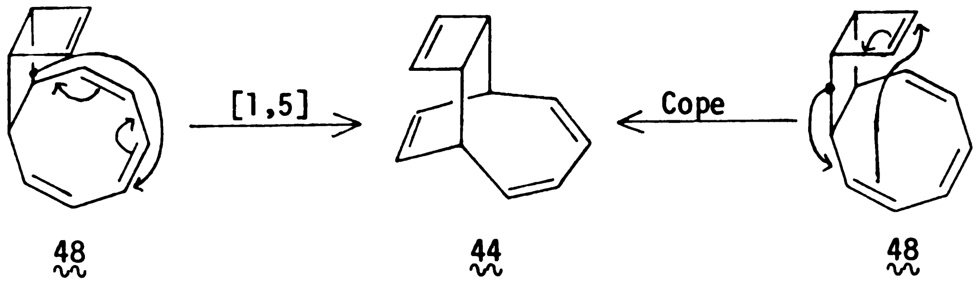
(21)

44

51

43

mechanisms. First, a suprafacial [1,5] sigmatropic shift and second, a Cope rearrangement (eq. 22). These mechanisms are distinguishable with

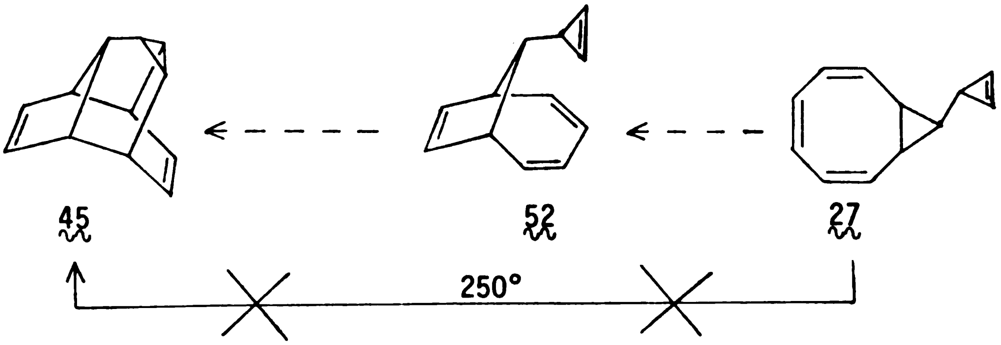


(22)

labeling and in a later section we will discuss an experiment which we thought would settle this question. However, our scheme requires the intermediacy of 48; and, as we will see, a mechanism for the rearrangement of 42 to 44 which avoids 48 can be postulated.

Some Mechanistic Thoughts on the Formation of 45.

Diene 45 can be seen (eq. 23) as an intramolecular Diels-Alder addition product of cyclopropene 52, which could arise from a suprafacial [1,5] sigmatropic shift of cyclopropene 27. To test this we

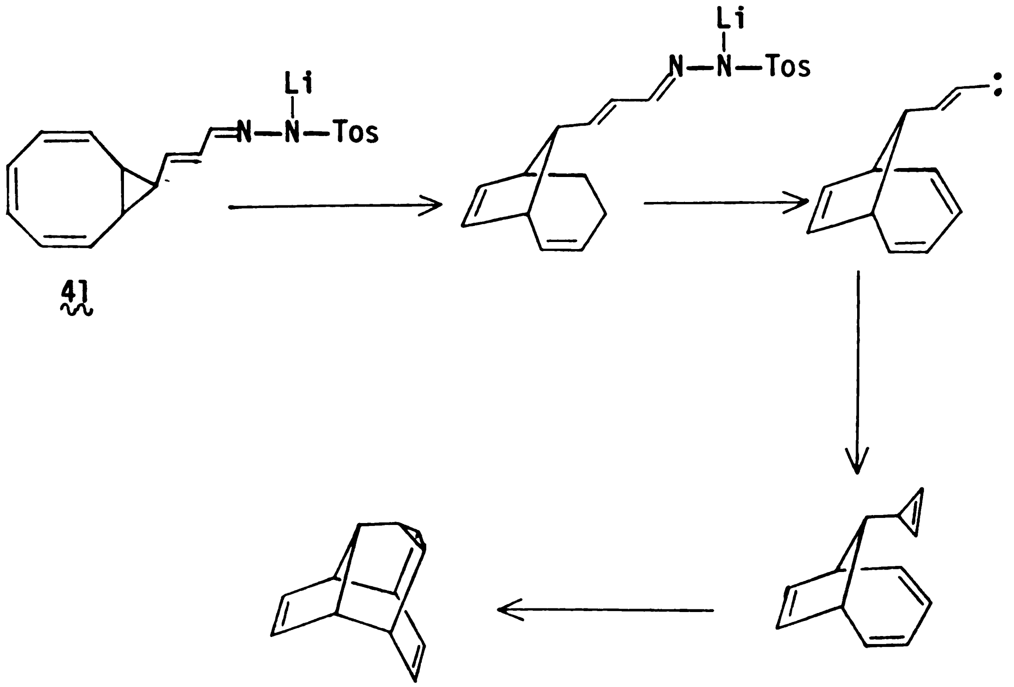


(23)

pyrolized 27 at 250°. To our surprise, gas chromatographic analysis of the volatile products showed no peak corresponding to 45.

An alternate approach, which still invokes the intermediacy of 52, would be to do the [1,5] shift prior to carbene formation (eq. 24).

This shift, though thermally allowed, has rarely been observed in the



41

52

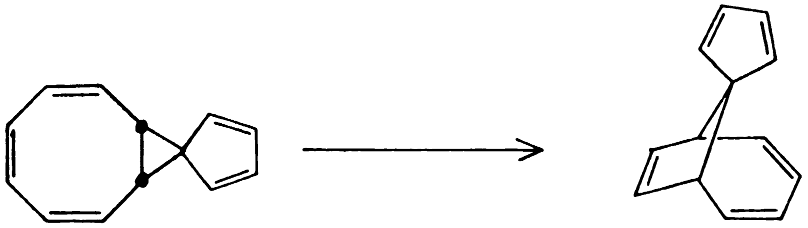
45

(24)

bicyclo[6.1.0] system. This would still allow for the formation of 45 from an intramolecular Diels-Alder addition of 52, but would be consistent with the failure of 27 to rearrange to 45.

Rearrangement to the [4.2.1] System.

A few examples of what is formally a [1,5] sigmatropic shift have been reported in the literature. Compound 53 thermolysed to the corresponding [4.2.1] system[40] (eq. 25). The anti-9-fluoro and dimethylamino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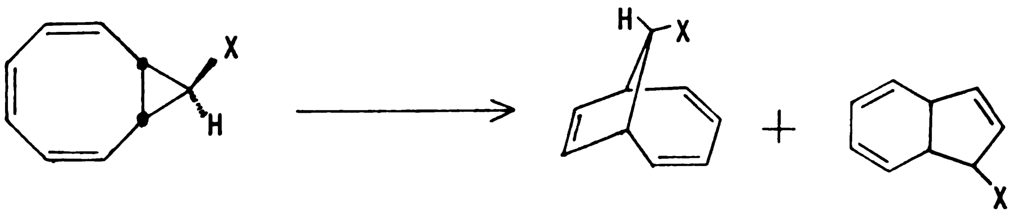
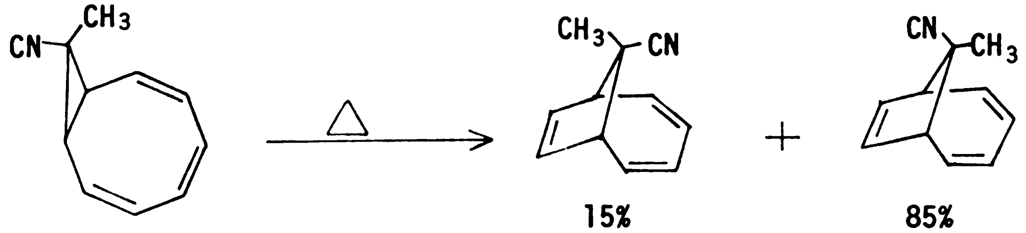
(25)

derivatives (eqs. 26 and 27) have been reported[41] to give the corresponding [4.2.1] products as well as dihydroindenes, while the methoxy



X = F	33%	67%	(26)
X = NMe_2	60%	40%	(27)
X = OMe	0%	100%	(28)

derivative (eq. 28) gave only the dihydroindene isomer.[41] It should be noted (see footnote 42) that the authors reported observing only the <u>endo</u> [4.2.1] epimers (eqs. 26,27), consistent with a suprafacial [1,5] sigmatropic shift. Some 9-cyano, 9-methyl or cyano derivatives also rearranged to the [4.2.1] system.[43] These however gave a majority of the [1,3] product (eqs. 29,30). An explanation for these latter results



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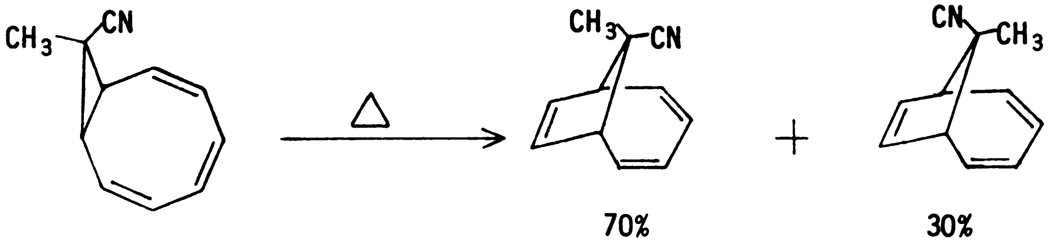
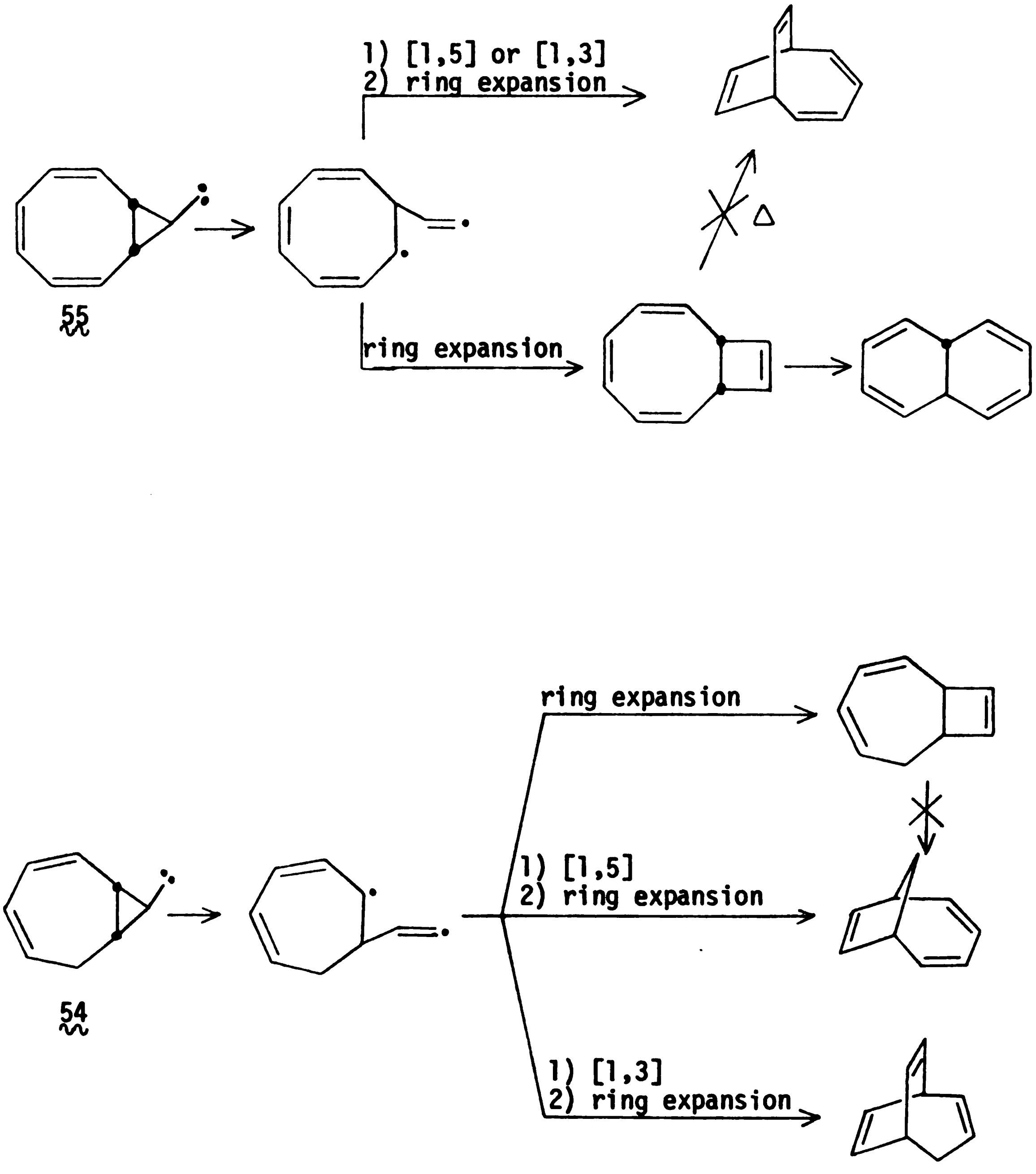


(30)

has been presented in terms of a stepwise biradical mechanism.[44] However, it has also been noted[45a] that configuration interaction analysis predicts stabilization for a polar (as is the case above) [1,3] sigmatropic shift with retention.

Biradical mechanisms were also proposed for the decomposition of two similar cyclopropyl carbenes.^{2i} The general scheme favored (Scheme 1) was fragmentation of the carbene to give a diradical which reclosed

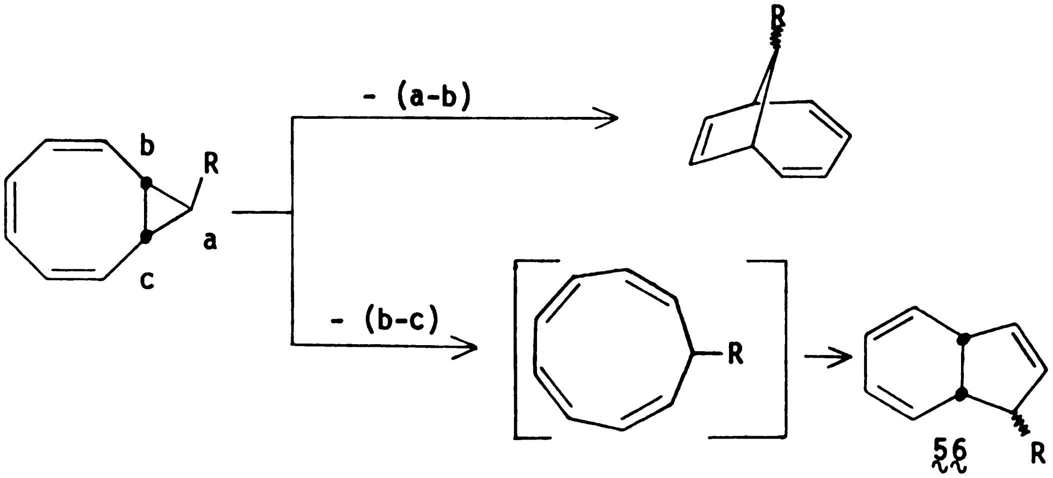


Scheme 1.

at all possible positions to give the observed products. It should be noted that the unsymmetrical nature of 54 allows differentiation between the [1,5] and [1,3] shift. This distinction is absent in the symmetrical [6.1.0] system 55.

Rearrangements of the [6.1.0] System.

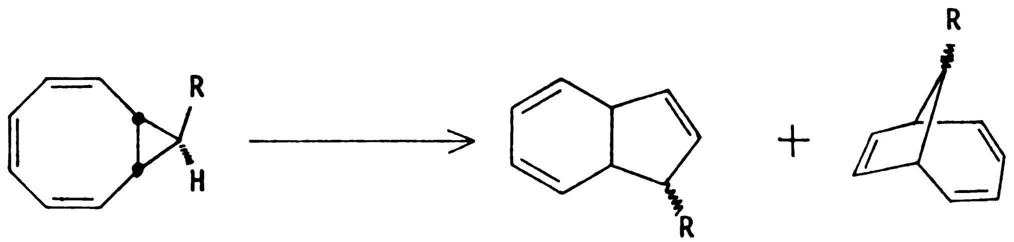
The question then arose whether the carbene itself was needed for rearrangement to the [4.2.1] system or if this isomerization could have occurred prior to decomposition to the carbene. A wide variety of anti-9-substituted [6.1.0]nona-2,4,6-trienes have been reported to thermolize to cis-dihydroindenes 56. A study has shown that electron withdrawing groups decrease the rate of this isomerization.[47] It seemed, however, from the few examples available of more heavily substituted derivatives that π-electron withdrawing groups favored a peripheral-bond (a-b) cleavage rather than a cross-linked (b-c) scission (eq. 31).



56

(31)

We decided to look at the thermal rearrangement of some anti-9-substituted [6.1.0] trienes available to us. In order to use the obvious symmetry differences inherent in the dihydroindene and [4.2.1] systems, we analyzed the thermal products of compounds 57 (a-g) by cnmr. The results of this work are summarized in Figure 8.



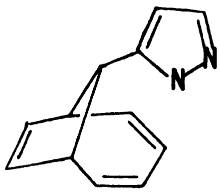
a.	CO_2Et	X	
b.	CH_2OH	X	
c.	CHO (37)	inconclusive	
d.	CH=N-NH-Tos	inconclusive	
e.	CH=CH-CH_2OH	X	
f.	CH=CH-CHO (38)		X
g.	CH=CH-CH=N-NH-Tos (35)		X

Figure 8. Rearrangements of Some [6.1.0] Derivatives to the Dihydroindene and [4.2.1] Systems.

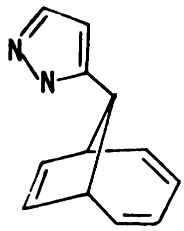
Derivatives for R = H, Cl, OCH_3, ϕ, CN, CO_2CH_3 are reported[47] to give dihydroindene products. The aldehyde (c) and corresponding tosylhydrazone (d) either decomposed or gave very messy inconclusive spectra. Both alcohol (b) and extended alcohol (e) thermolized to the dihydroindene. However, both the extended aldehyde (f) and its corresponding tosylhydrazone (g) cleanly rearranged to a mixture (ca. 3:2 and 1:1 respectively) of epimeric [4.2.1] products. This epimeric mixture was surprising and its implied significance will be discussed later.

A Closer Look at the Pyrazole Formed from Decomposition of 42.

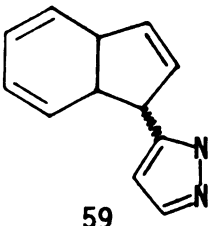
When it became clear that derivatives with extended conjugation were isomerizing cleanly to the [4.2.1] system, we decided to take a closer look at the pyrazole formed on decomposition of the lithium salt of tosylhydrazone 35. Indeed, after column chromatography of the products of thermolysis of 42 in tetraglyme, cnmr analysis showed evidence for the two epimeric bicyclo[4.2.1]pyrazole derivatives 58a and 58b. The major component gave a proton decoupled cnmr spectrum



58a



58b

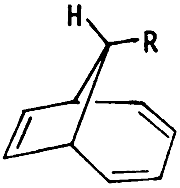


59

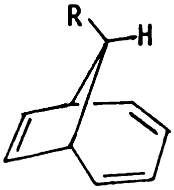
consisting of four equally intense lines at δ134.8, 125.7, 122.4 and 45.9 and a sixth line of half the intensity of the others at δ35.5. The spectrum also included three broadened small peaks at ca. 104, 134 and 146 corresponding to carbons-4, 5 and 3 respectively for the pyrazole ring.[29a] A second fraction gave a cnmr spectrum corresponding to a mixture of the [4.2.1] epimer and a dihydroindene (59).

A General Scheme for the Decomposition of 42.

Orbital symmetry considerations fail to explain the formation of the epimeric mixtures of [4.2.1] derivatives. The formation of isomer 60a could involve either a thermally allowed [1,5] sigmatropic shift

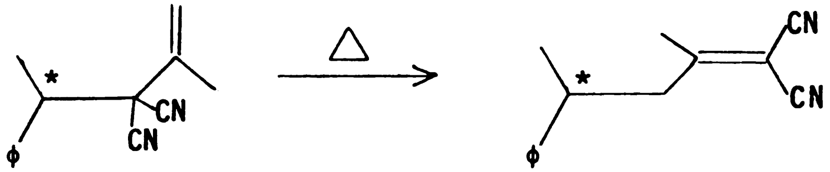


60a



60b

with retention of configuration or a [1,3] shift with inversion of configuration. The thermal formation of isomer 60b, however, is orbital symmetry forbidden. This could suggest a biradical mechanism. Alternatively a [1,3] sigmatropic shift with retention could take place.[45] Such rearrangements are not unknown.[46] Compound 61 (eq. 32) has been shown to undergo a [1,3] sigmatropic shift with retention of

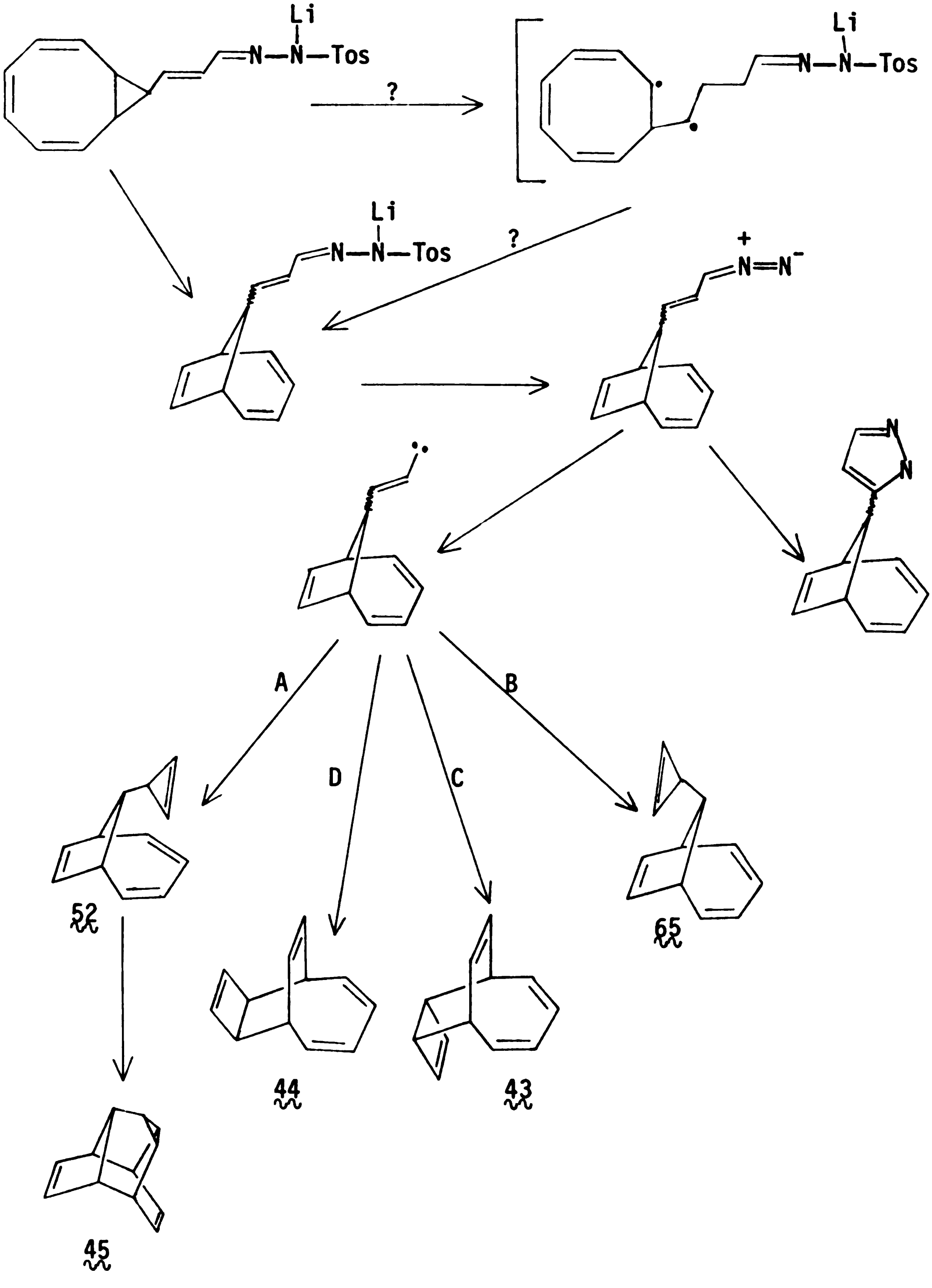


61

(32)

configuration.[46a] Berson et al. also described some concerted [1,3] sigmatropic shifts with retention in cases where the inversion pathway is blocked.[46b]

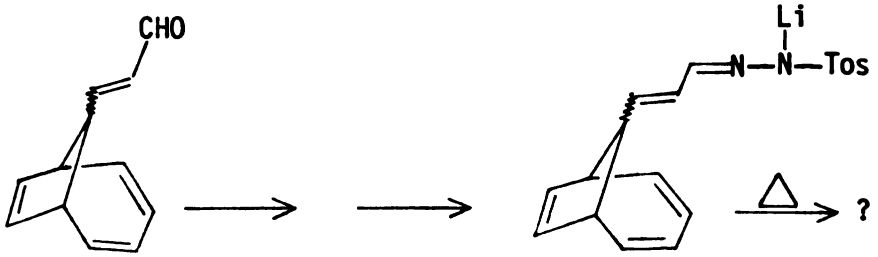
Consequently, the general scheme (Scheme 2) which best explains this and the previous results would be isomerization of the tosylhydrazone lithium salt (42) to the epimeric [4.2.1] compounds 63. This could involve either a peripheral bond cleavage to a triply-allylic diradical which recloses at either the 3 or 5 position or [1,3] and [1,5] sigmatropic shifts with retention. Decomposition of the [4.2.1] tosylhydrozone salt proceeds to the corresponding diazo compound which either cyclizes with a hydrogen shift to the pyrazole 63 or looses nitrogen to give a carbene 64. The epimeric carbenes can cyclize to the corresponding cyclopropenes (path A and B); the endo isomer 52 can give 45 by a Diels-Alder, while evidence for the exo isomer 65 is not observed (perhaps because it has no low energy path of isomerization available except for polymerization). The carbenes can also ring expand[39] with



Scheme 2. Decomposition of Tosylhydrazone 42.

cyclization to give tetraenes 43 and 44. Since the MO's of a carbene are orthogonal, it is not possible to predict using Woodward-Hoffmann rules the stereochemistry of this isomerization. Consequently we can not determine if the two tetraenes are derived from different, epimeric [4.2.1] carbenes or if both can arise from the same isomer.

We have shown that the isomerization of the [6.1.0] system to the [4.2.1] is general for π-electron accepting groups, but we have not determined if this rearrangement occurs prior to or after carbene formation. An important experiment would be to look at the thermal decomposition of the epimeric tosylhydrazone salts 63, prepared from the epimeric mixture of [4.2.1] extended aldehyde 62. The formation of



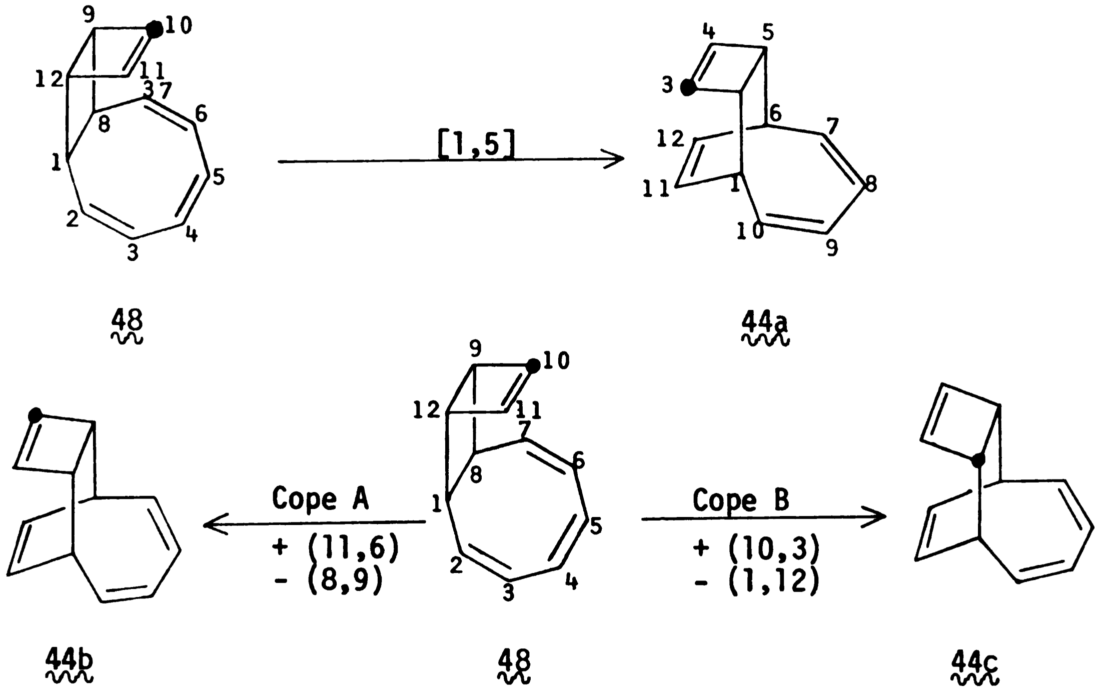
63 63

products 43, 44 and 45 would be strong evidence for the intermediacy of 63 in the decomposition of the [6.1.0] tosylhydrazone salt 42.

If this were shown to work we would also be in a position to answer another important question. Separation of the epimers of 62 and subsequent decomposition of each epimer of tosylhydrazone salt 63 would tell us if tetraenes 43 and 44 arise from different [4.2.1] carbenes or if both can follow from the same carbene. Unfortunately these experiments have not been performed, but work is currently in progress to answer these questions.

Deuterium Labeling as a Mechanistic Probe: [1,5] or Cope?

While working from the assumption that 44 arose from cis,syn,cis-bicyclo[6.4.0.$0^{9,12}$]dodeca-2,4,6,10-tetraene 48, we noticed that proper deuterium labeling would distinguish between the [1,5] sigmatropic shift and the Cope rearrangement for this isomerization. As illustrated in Figure 9, if 49-d were deuterated at the 10 position, the resulting



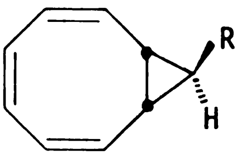
●Designates deuterium

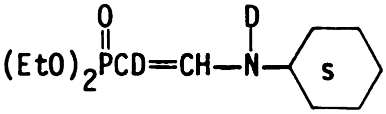
Figure 9. Course of Carbon-10 in a [1,5] and Cope Rearrangement of 48.

cis,exo-bicyclo[4.4.2.$0^{2,5}$]dodeca-3,7,9,11-tetraene would be labeled exclusively at the 3 position for a [1,5] sigmatropic shift, while a Cope rearrangement would lead to scrambling of the deuterium between the 2 and 4 positions. Analogous results would be observed for deuteration at the 9 position, i.e. 9 goes to 2 for a [1,5] and 9 goes to 3 and 5 for a Cope.

Preparation of Deuterated Tosylhydrazone.

In an attempt to clarify some of these mechanistic considerations, we prepared deuterated tosylhydrazone 35-d and looked at its decomposition products. The key step in its synthesis was the use of the





39-d

37-d R = CHO

38-d R = CH=CD-CHO

35-d R = CH=CD-CH=N-NH-Tos

deuterated enamine reagent 39-d in extending the aldehyde.

White crystalline 39-d was prepared in ca. 58% yield (mp 60-62°) by stirring 39 with sodium deuteroxide. Mass spectrometry of 39-d showed ca. 67% d_2, 28% d_1 and 5% d_0. The pnmr showed a 1-proton doublet in the vinyl region ($\delta 6.82$, $J_{P-C=CH} = 16$ Hz) (unfortunately the NH proton in 39 and 39-d is obscured). This led us to believe 39-d to be at least 90% deuterated at the carbon next to phosphorus.

In any event treating aldehyde 37 with the anion of the deuterated enamine reagent followed by mild acid hydrolysis gave the deuterated extended aldehyde 38-d (mp 87-89°) (Figure 10). The pnmr showed ca. 80% deuteration with the olefinic region ($\delta 6.23$, m) integrating to 1.2

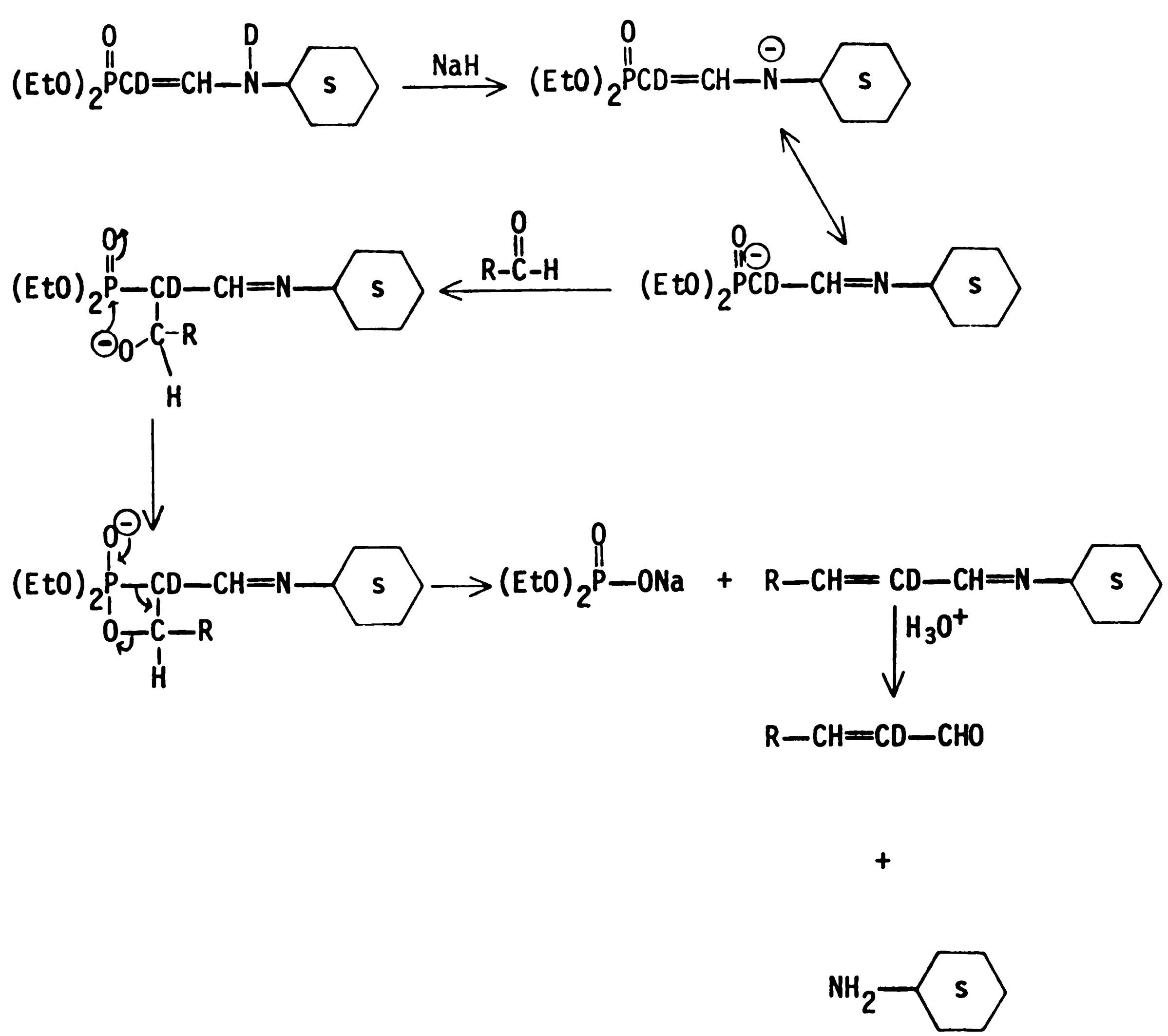


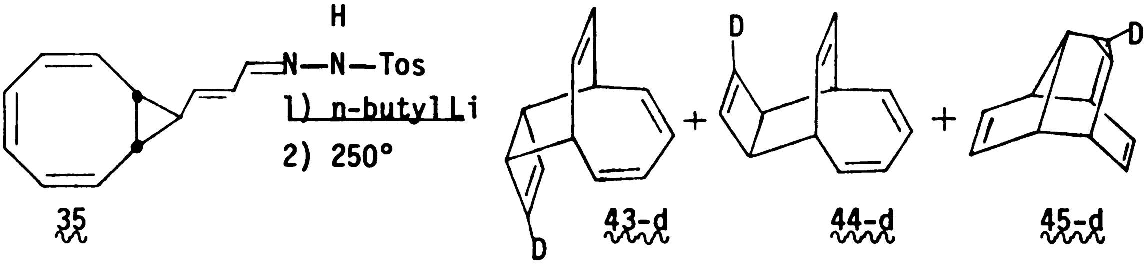
Figure 10. Mechanism for the Reaction of Aldehyde 37 with Deuterated Enamine Reagent (39-d).

protons and the aldehyde proton (δ9.22) changing from a sharp doublet to a broad singlet. The mass spectrum showed ca. 75% deuterium incorporation. The cnmr shows loss of the line at 130.6 ppm.

The deuterated tosylhydrazone 35-d was prepared as a white fluffy solid in an analogous fashion to the undeuterated compound. The pnmr spectrum showed the deuterium content to be essentially unchanged (ca. 80%, by loss of 0.8 protons in the olefinic region). The mass spectrum showed a molecular ion at m/e 341 (consistent with $C_{19}H_{19}DN_2O_2S$). Likewise, except for the absence of the peak at 124.4 ppm the proton decoupled cnmr was unchanged from that of the undeuterated compound.

Thermal Decomposition of Deuterated Tosylhydrazone 42-d.

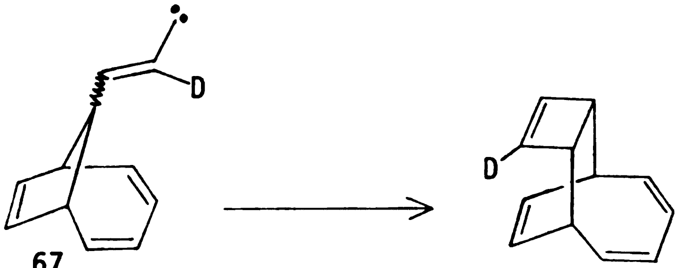
The lithium salt of the deuterated tosylhydrazone 42-d was prepared and decomposed in an analogous fashion to the undeuterated compound. Separation and isolation by preparative gas chromatography gave the epimeric deuterated tetraenes 43-d and 44-d and the deuterated diene 45-d (eq. 33). Each showed a M^+ peak at m/e 157 which is consistent with the molecular formula $C_{12}H_{11}D$. Since these compounds lose hydrogens easily in the mass spectrometer to form aromatic species, (in fact the P-1 peaks were larger than the M^+ peak) a calculation of deuterium content was not possible.[71]



(33)

Position of Deuterium in Deuterated 43 and 44.

Positional assignment of the deuterated tetraenes was relatively straightforward. In each case integration of the pnmr spectrum showed reduction of the sharp singlet for the vinyl cyclobutene position from 2.0 to 1.2 protons. There was no evidence for deuterium scrambling in either spectrum. Thus, if tetraene 44 did result from isomerization of 49 we could rule out the Cope rearrangement path in favor of the [1,5] sigmatropic shift. Likewise, the origin of 43-d and 44-d from ring expansion and cyclization of 67 (eq. 34) is consistent with the



67

(34)

deuterium labeling study.

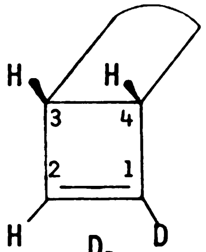
Carbon nuclear magnetic resonance spectra confirmed these assignments (see Table 1, page 44). Proton decoupled cnmr spectra of the deuterated tetraenes showed in each case two sets of doublets corresponding to the cyclobutene carbons. It should be noted here that in this context a doublet does not imply one signal split by spin-spin splitting into two equally intense peaks. It stands for two peaks resulting from different chemical shifts due to isotope effects. The origin of these splitings is discussed in the next section.

Interpreting CNMR Spectra of Deuterated Compounds.

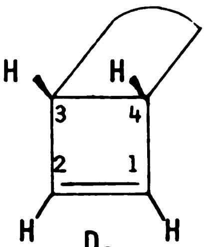
The carbon nuclear magnetic resonance spectra of these deuterated compounds can be somewhat confusing. Deuterium substitution is known to affect the chemical shifts of neighboring carbons. Carbons α to a deuterium (i.e. attached to a deuterium) are reported to shift 0.2 to 0.5 ppm relative to the hydrogen analog, while carbons β to a deuterium have been shown to move upfield (-ppm) ca. 0.12 ± 0.04 ppm.[48] Often, especially when no other hydrogens are at the α position, deuterium substitution causes the α carbon signal to disappear in the cnmr spectrum.[49] This is due primarily to the increased relaxation time of the deuterated carbon, plus a decreased NOE, and finally the spin-spin spliting (D has a quantum number of 1) of the carbon into a triplet.[49b]

The cnmr spectra of compounds **43-d**, **44-d** and **45-d**, in which *ca.* 80% of the molecules are deuterated, showed no lines for carbons α to a deuterium. Doublets were observed for the carbons β to the deuterium. One line resulted from the unshifted β carbons of the undeuterated molecules and the other line from the shifted (*ca.* -0.1 to -0.2 ppm) β carbons of the deuterated molecules. Symmetry within these molecules must also be taken into account.

For example, we might predict the following for a symmetrically substituted cyclobutene which is 80% deuterated and 20% undeuterated (analogous to **43-d** and **44-d**). The signal for carbon-1 of the D_1 molecule would disappear. β shifts for the D_1 molecules would cause



D_1
80%

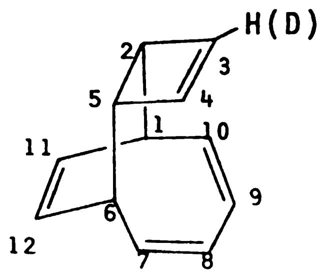


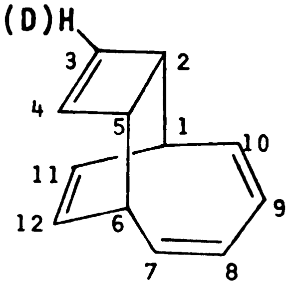
D_0
20%

carbons-2 and -4 to move *ca.* -0.1 ppm relative to carbons-1,2 and -3,4 respectively of the D_0 molecules. Since γ shifts are reported to be only -0.02 to -0.04, we would expect the resonance for carbon-3 of the D_1 molecules to essentially coincide with the resonance for carbons-3,4 for the D_0 molecules. Thus we predict a two-line spectrum for each β carbon.

Assignment of Position of Deuterium in Diene **45-d**.

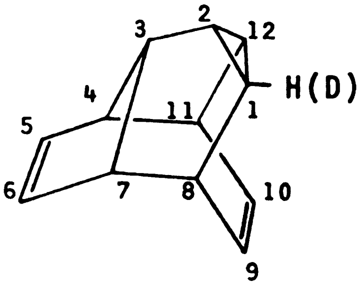
Analysis of the cnmr spectrum was necessary to assign the position of deuterium incorporation in the diene product. See Table 1 for a comparison of cnmr chemical shift data for deuterated and nondeuterated





*	CH ppm	CD ppm	CH ppm	CD ppm
3,4	140.02	140.03	139.19	139.23
		139.84		139.03
	134.59	134.52	136.89	136.93
	126.85	126.83	125.18	125.20
	123.31	123.30	120.78	120.78
2,5	48.64	48.62	50.54	50.54
		48.52		50.40
1,6	34.68	34.67	36.58	36.34

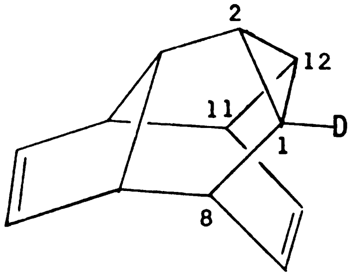
*	CH ppm	(I)	CD ppm	J_{C-H}
	134.33	1	134.29	163
	130.90	1	130.88	162
3	66.03	.5	66.04	135
4,7	62.38	1	62.34	140
8,11	41.61	1	41.54	
			41.47	
1,12	36.10	1	36.01	
			35.93	
2	26.40	.5	26.21	173
			26.06	



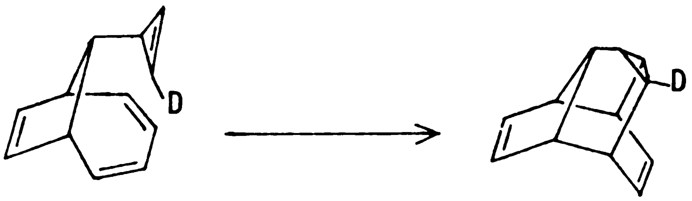
* Tentative assignment of carbons

TABLE 1. Comparison of CNMR Data for Deuterated and Undeuterated Pyrolysis Products. See footnote 75.

45. The proton decoupled cnmr spectrum showed two distinct sets of doublets (ca. 41.5 and 36 ppm) and a third barely observable doublet at ca. 26 ppm. Since the signal for a carbon next to a deuterium is known to "disappear" in a cnmr spectrum, we would expect carbon-2 or carbon-3, if deuterated, to disappear. Each of the other carbons is symmetrically equivalent to one other carbon, so deuteration at one of these positions would cause some change, but not a disappearance of the corresponding signal. Since no signal disappears in the cnmr spectrum of 45-d relative to that of 45, we can say that the deuterium in 45-d is not at position 2 or 3. Likewise, since neither of the lines corresponding to an olefinic carbon is affected, the deuterium is not on or adjacent to an olefinic carbon. That leaves only carbon-1. We would expect deuterium at carbon-1 to result in three different β-shifts. Theoretically (for an 80% deuterated mixture) carbon-2 should be split into a doublet of relatively intensity 4:1. Intensity values in these spectra are unreliable due to noise and phase inconsistencies, but the proposed 4:1 ratio is consistent with the poorly resolved doublet at ca. 26 ppm. From symmetry considerations and from the percentage of deuterated molecules we would expect doublets for carbons-1,12 and for carbons-8,11 in ratios of 2:1 and 3:2 respectively. The observed doublets at ca. 36 ppm and ca. 46.5 ppm respectively are consistent with this prediction. Also assignment of deuterium at carbon-1 is entirely consistent with a



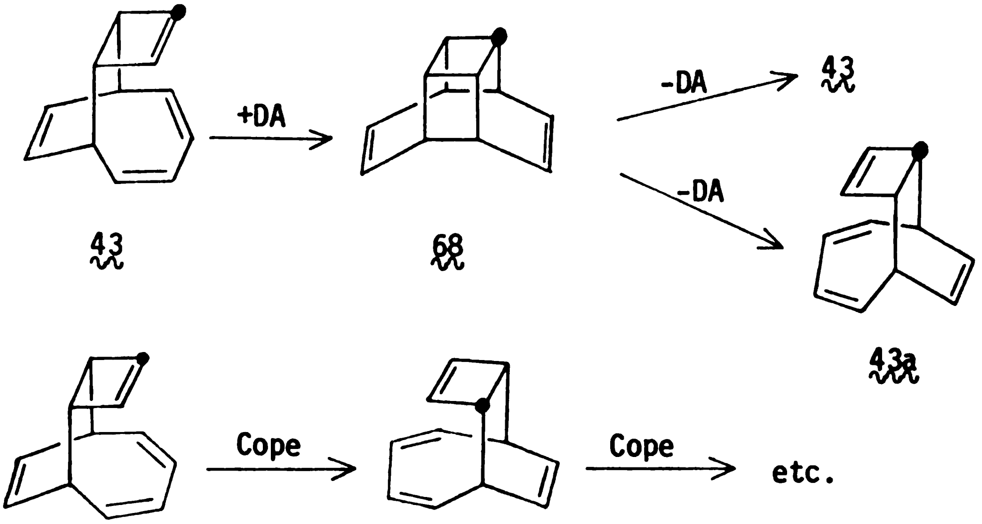
mechanism in which **45-d** arises from an internal Diels-Alder addition of **52-d** (eq. 35).



52-d **45-d**

Heating of Tetraene **43**: Possibility of Fluxional Character.

The geometry of tetraene **43** offers the possibility for two different degenerate rearrangements. (See Figure 11; for convenience in following these rearrangements carbon-3 is labeled •). A Diels-Alder addition of the cyclobutene vinyl group to the diene portion of **43** would



43 **68** **43** **43a**

Figure 11. Possible Degenerate Rearrangements of **43**.

lead to **68** of C_{2v} symmetry. Adduct 68 could then undergo a retro Diels-Alder reaction either back to starting tetraene **43** or on to the degenerate isomer **43a**. A Cope rearrangement of **43** would also lead to a degenerate rearrangement. However, when the pnmr of 43 was recorded at several temperatures between 25° and 150°, the spectra obtained were independent of sample temperature.

Deuterated **43** offered a much more delicate probe for these rearrangements. Degenerate isomerization by either a Cope or Diels-Alder reaction would lead to scrabling of deuterium between the vinyl and saturated positions of the cyclobutene ring (follow the labeled • carbon in Figure 11). Still, when **43-d** was heated at 75° for 20 days and pnmr spectra run periodically, no scrambling of deuterium was observed. Likewise, when **43-d** was heated in hexadeutero dimethyl sulfoxide at 200° overnight, no deuterium scrambling was observed. However, on prolonged heating at 200° the sample decomposed (turned dark brown) and showed a sharp singlet in the pnmr at δ7.2 (conceivably benzene) and a broad multiplet at *ca*. δ4.

On the off-chance that the assignment of tetraenes **43** and **44** was reversed, we tried the same experiment as above on **44-d**. As expected, heating at 75° for two weeks resulted in no change in the pnmr spectrum of **44-d**.

Summary.

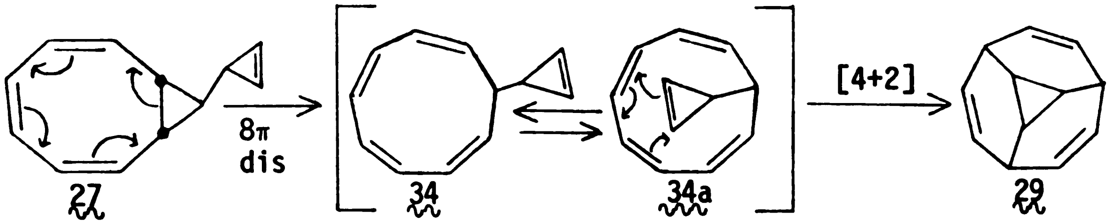
In conclusion we have generated a new entry into the $(CH)_{12}$ energy surface. In doing so, we were able to prepare one new $(CH)_{12}$ representative and synthesize two others by a new route. In the preparation of this $(CH)_{12}$ precursor we have developed a practical synthetic process for making large quantities of the reagent used to extend an aldehyde to an

α,β-unsaturated aldehyde. We have also been able to deuterate this reagent and thus incorporate a deuterium label into our system. We have found carbon nuclear magnetic resonance quite useful not only for structure assignment but also for observing symmetry within our molecules. And, finally, we have shown a general alternate path for bond cleavage in the bicyclo[6.1.0]triene system for derivatives with strong π-electron acceptor capabilities.

Results and Discussion

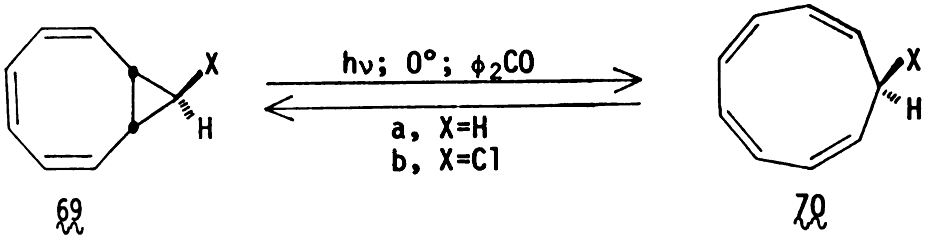
Part B

As we have seen, conceptually the conversion of Raghu's cyclopropene **27** to the truncated tetrahedrane valence isomer **29** is relatively straightforward (eq. 36). The first step would involve a photochemically



(36)

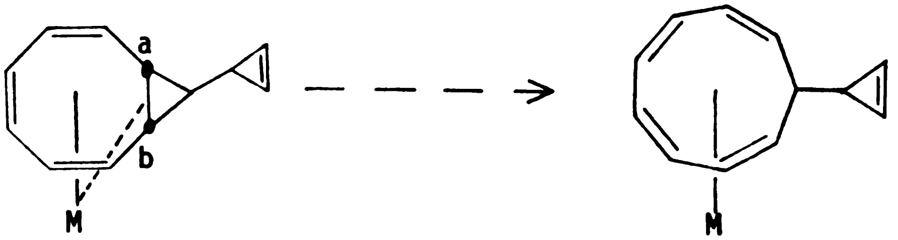
allowed 8π disrotatory ring opening of a cis-bicyclo[6.1.0] ring system to an "all-cis" cyclononatetraene. This indeed has been realized for the parent compound (eq. 37); a photostationary state consisting



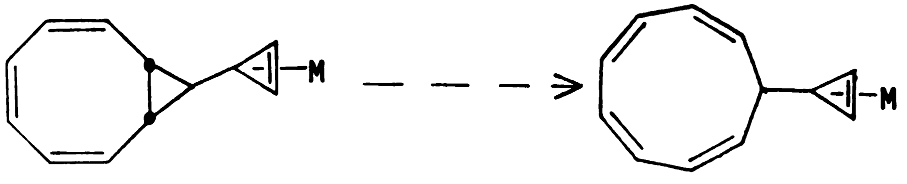
(37)

predominantly of **69a** (**69a**/**70a** $\simeq$ 8) was reached rapidly on irradiation of **69a** (through Pyrex in ether at 0°) in the presence of benzophenone.[50] Likewise, the anti-9-chloroderivative **69b** isomerized cleanly when irradiated (through Pyrex in petroleum ether at 0° for 1.5 hr) in the presence of benzophenone to give a crude photolysate consisting (nmr) of ca. 65% **69b** and 35% **70b**.[51] However irradiation of **27** in the presence of benzophenone under similar conditions (through Pyrex, in pentane, at 0°, with a 200 W Hanovia lamp) failed to give product resulting from opening of the [6.1.0] system, but gave back only starting material. When the filter was changed from Pyrex to quartz, irradiation resulted in loss of starting material, but left only a polymeric residue (Rf = 0). Also photolysis through Pyrex at -78° with a 200 W Hanovia lamp or through Pyrex at -78° with a 450 W Hanovia lamp resulted in each case in no reaction. Warming and continued photolysis of the latter experiment gave a polymeric product deposited on the glass wall of the immersion well.

Since direct photolysis of **27** did not seem to be leading toward anything successful, and increased usage of transition metal catalysts were appearing in the literature,[52] we directed our work toward this latter approach. We envisioned three approaches to this problem: first of all, the metal could complex to some part or all of the triene π-system (**27-M**) and then open the "a-b" (eq. 38) cyclopropane bond to give the "all-cis" cyclononatetraene (**34-M**). Secondly a metal that stabilizes cyclopropenes (eq. 39) could be used and then harsher conditions than were previously available could be tried to open the [6.1.0] system.



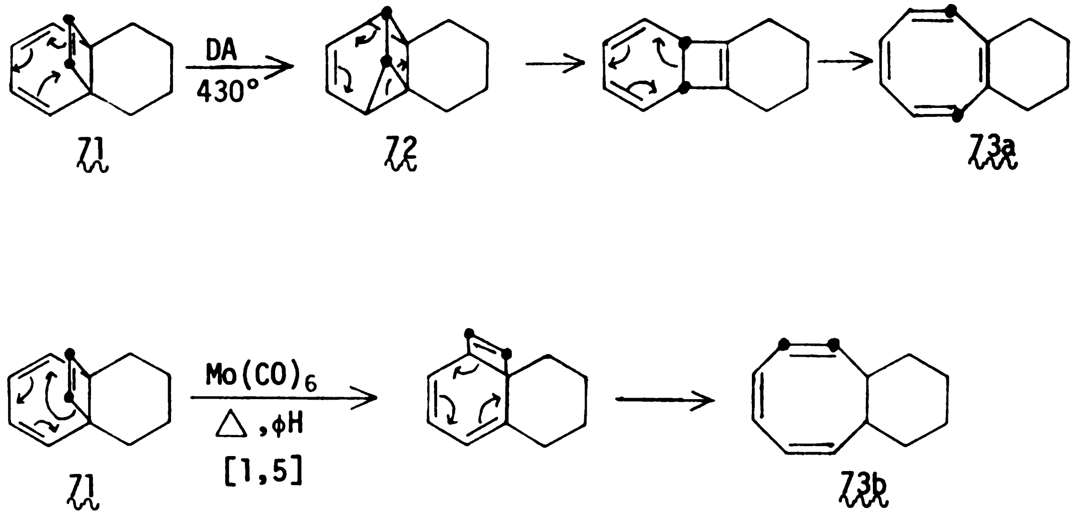
27-M **34-M** (38)



27-M' **34-M'** (39)

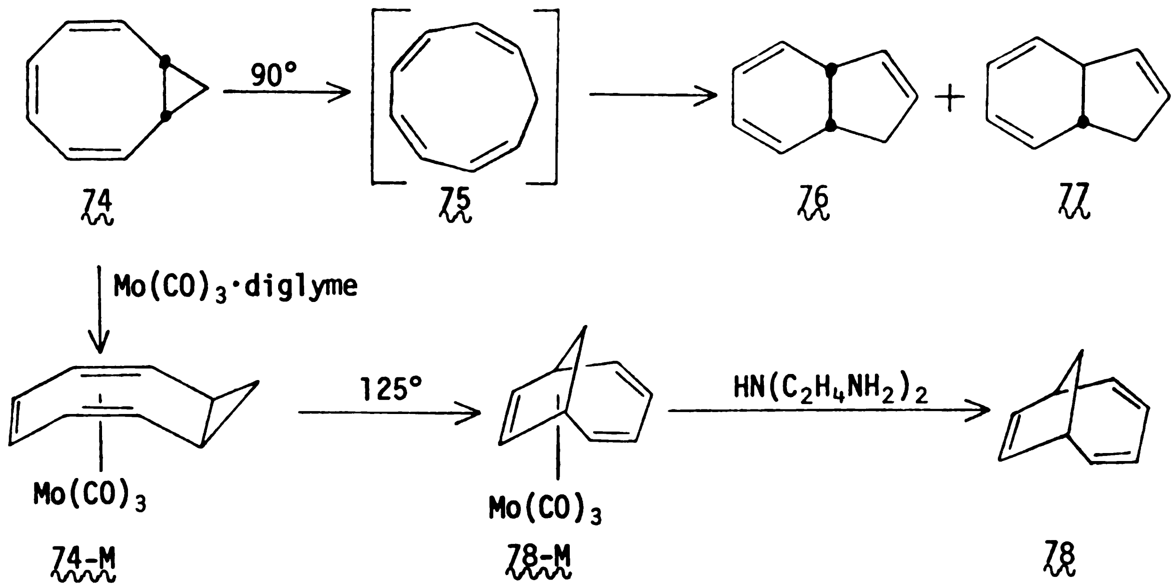
Finally a metal catalyst which could complex to both the triene system and the cyclopropene could be conceived. It was the first approach with which this work was primarily concerned.

There are a number of examples in the literature of metal carbonyls and in particular molybdenum carbonyls which complex to π-systems and alter their reactivity.[52] For example (eq. 40), Paquette has shown that thermal activation of [4.4.2] propella-2,4,11-triene 71 proceeds by



(40)

intramolecular (4 + 2)π cycloaddition with formation of transient cis^2-bishomobenzene 72 and ultimately a cyclooctatetraene (73a) of isomeric structure.[53] However, in the presence of the transition metal catalyst $Mo(CO)_6$, the kinetically preferred Diels-Alder reaction could be blocked and redirected toward a second process, a [1,5] sigmatropic shift, to give the positionally isomeric cyclooctatetraene 73b [54] (notice the two routes of carbons 11 and 12, labeled •). Similarly, while bicyclo-[6.1.0]nona-2,4,6-triene 74 thermolyses at 90° presumably through the "all-cis" cyclonona-2,4,6,8-tetraene to give a 9:1 mixture of cis- and trans-dihydroindenes 76 and 77 respectively[55] (eq. 41), in the presence



(41)

of diethyleneglycol-dimethylether-tricarbonylmolybdenum (0) ^{56} triene 74 gave the metal complex 74-M which on heating at 125° resulted in product 78-M, formally resulting from a [1,5] sigmatropic shift.^{57}

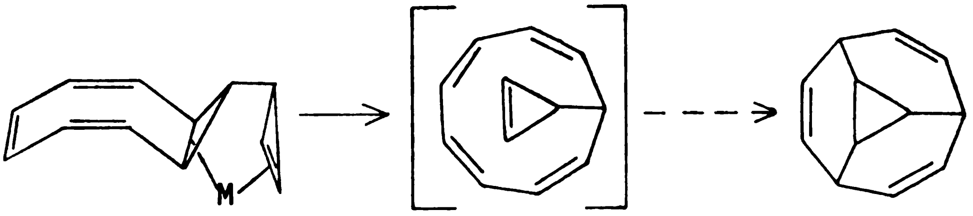
We felt that, because of the large π-character in this system (27) and the known propensity of molybdenum carbonyls to complex to π-systems and alter their reactivity, the use of a molybdenum carbonyl complex would be worth investigating. To this end cyclopropene 27 was stirred with a catalytic amount of $Mo(CO)_6$ in pentane or tetrahydrofuran at temperatures from 0° to refluxing. A sample without $Mo(CO)_6$ was run in each case as a blank. The reactions were monitored by HPLC and TLC. In no case did the sample with $MO(CO)_6$ behave differently than the blank sample. It should be noted that $Mo(CO)_6$ is very uv active and the HPLC has a uv detector. $Mo(CO)_6$ elutes nearly with the solvent front in HPLC and in relatively large concentrations can interfere with later components. On TLC it gave a spot ca. 0.8 (silica gel/hexane) which sublimes rapidly off the plate.

Since it appeared that the use of $Mo(CO)_6$ was leading nowhere, we decided to try the more reactive $Mo(CO)_3$·diglyme complex.^{58}

$Mo(CO)_3$·diglyme is very oxygen sensitive, and for this reason, its preparation and subsequent reactions were performed under nitrogen and using degassed solvents. When a solution of 27 in pentane was stirred in the presence of a catalytic amount of $Mo(CO)_3$·diglyme at temperatures ranging from -78° to refluxing, the only change was a gradual loss of cyclopropene 27 (presumably due to polymerization). No new spots of Rf similar to 0.3 (TLC) and no different peaks on the uv plot (HPLC) showed up during the course of this reaction.

We also decided to look at the photolysis of tosylhydrazone salt 36 in the presence of $Mo(CO)_3$·diglyme. Under conditions where the only difference was the addition of catalyst, the only product observed was cyclopropene 27. It is not clear whether or not solubility of the catalyst was the problem at this low temperature (-78°). Unfortunately at higher temperatures the cyclopropene decomposes rapidly in the presence of the sodium methoxide present to generate the tosylhydrazone salt.

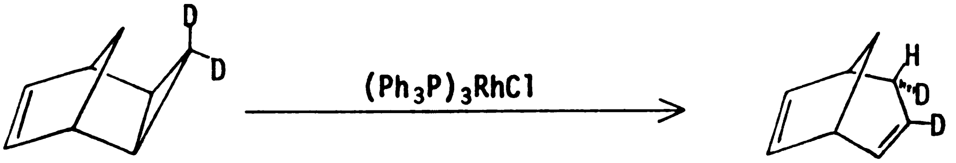
Some initial work has also been done on trying to complex a metal first to the cyclopropene double bond and then open the cyclopropene bond (eq. 42). Katz has reported what would formally be such a



27-M 29

(42)

reaction for 79 (eq. 43). However, when Raghu tried this, cyclopropene



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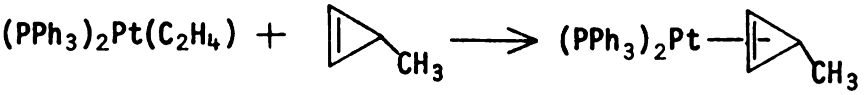
(43)

27 failed to isomerize.[16]

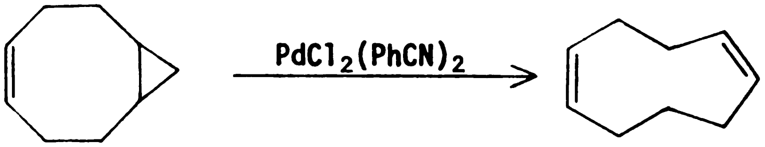
The zero-valent platinum complex $(PPh_3)_2Pt(C_2H_4)$ has been shown to exchange ethylene for cyclopropenes[60] (eq. 44). Preliminary work in



(44)

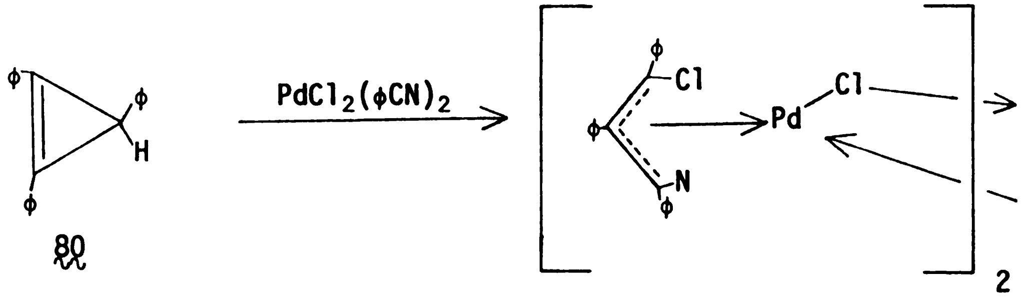
this lab by Bing Lam on forming a $(PPh_3)Pt(0)$-cyclopropene 27 complex was unsuccessful.[61]

A palladium (II) metal catalyzed isomerization of an unconjugated cyclopropyl derivative has been reported[62] (eq. 45). However when we



(45)

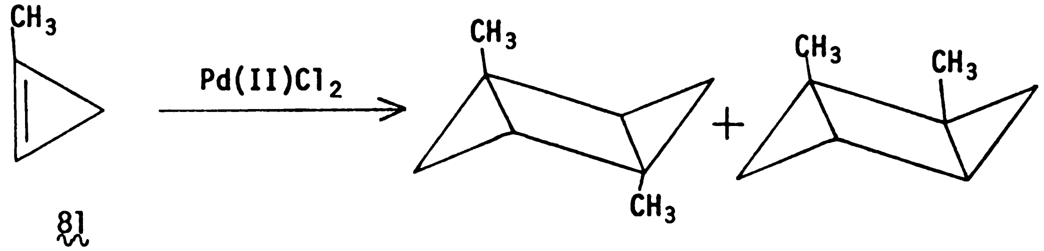
tried this catalyst with 27 at room temperature, polymerization occurred. In order to see if complexation had indeed occurred, the experiment was repeated at lower temperatures. The reaction between 27 and $PdCl_2(PhCN)_2$ was followed by low temperature nmr. Cyclopropene 27 was unchanged at -60°, but upon warming to -50° the peak representing the cyclopropene vinyl hydrogens disappeared. They did not reappear on cooling to -60°. The low solubility at these temperatures made the nmr spectra difficult to analyze. It is possible that the Pd(II) opened the cyclopropene ring to form a π-allyl complex. Such a reaction has been reported for a highly substituted cyclopropene[63] (**80**) (eq. 46). Also and probably



80

(46)

more likely is that Pd(II) catalyzed the cyclodimerization of **27**, as was the case for 1-methylcyclopropene[64] (**81**) (eq. 47). This is all very

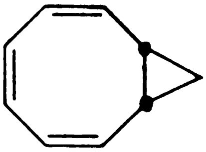


81

(47)

speculative, however, for the only analysis we did on the products was TLC. No spots of Rf similar to starting cyclopropene **27** (0.33) were observed (the only spots observed were near the origin; Rf ∿ 0). Since this did not seem to be leading to desired products, further analysis was abandoned. It is interesting that these latter authors also report some cyclodimerization of **112** in the presence of $Mo(CO)_6$.

It is clear that much work can still be done with the isomerization of cyclopropene **27**. Any of the above reactions could be studied in more detail. It would be very helpful if a stable metal-cyclopropene complex would be isolated and its reactions studied. Reaction of cis-bicyclo[6.1.0]nona-2,4,6-triene (**74**) with $Fe_2(CO)_9$ [65] or irradiation of



74

the polyolefin in the presence of $Fe(CO)_5$ [66] is reported to give a number of iron carbonyl-complexes. The use of dimetal catalysts such as $Fe_2(CO)_9$, $[CPFe(CO)_3]_2$ and $[CpMo(CO)_3]_2$ (CP = cyclopentadiene) appear promising and will be looked at. Regretably, this project has so far failed to relate 27 to truncated tetrahedrane or any other $(CH)_{12}$ isomer. However, it is my firm conviction that conditions can be found which will favor isomerization yet restrict cyclopropene polymerization.

Experimental

General. Melting points were taken either in open capillaries with a Thomas-Hoover apparatus or on a Reichert hot-stage microscope and are uncorrected. Ultraviolet spectra were run in hexane on a Unicam SP800 spectrophotometer. Solvents for chromatography were treated as follows: pentane and hexane were washed with concentrated sulfuric acid, saturated bicarbonate and water, dried with calcium chloride and distilled; methylene chloride was dried with calcium chloride and distilled. Tetrahydrofuran was distilled from sodium with benzophenone.

Proton nuclear magnetic resonance (pnmr) spectra were run on Varian T-60 (60 MHz) or HA-100 (100 MHz) instruments. Variable temperature pnmr spectra were recorded on a Varian A-56/60 instrument. Chemical shifts are reported in ppm downfield from internal standard tetramethylsilane (TMS = $\delta 0.0$). Chemical shifts and coupling constants are believed accurate to ±0.01 ppm and ±0.5 Hz respectively.

Carbon-13 nuclear magnetic resonance spectra (cnmr) were taken on a Varian CFT-20 spectrophotometer. Sample tubes were prepared in one of three ways. For small samples (2-20 mg) the compound to be examined was vpc collected in 3 mm glass tubing, sealed at one end and approximately 40 ul of carbontetrachloride added (CCl_4 used as both solvent and internal reference with $\delta CCl_4 = 96.0$). The 3 mm glass tube was then wrapped with Teflon tape and inserted snugly into a standard 8 mm cnmr tube filled with deuterium oxide (D_2O as deuterium lock). Data for small samples were collected overnight (approximately 50,000 pulses). Medium size samples (50-300 mg) were prepared in regular 4 mm nmr tubes with carbon tetrachloride as the solvent and internal reference. The nmr tube was then wrapped with Teflon tape and placed into a standard

8 mm cnmr tube filled with D_2O. Larger samples (500 mg - 1 g) were prepared in 8 mm tubes with deuterochloroform as both solvent and deuterium lock and TMS as the internal reference. Chemical shifts were reported in ppm downfield of TMS (δ0.00) and are believe accurate to ±0.05 ppm. In the cases where CCl_4 (δ96.00 ppm) was used as the internal standard, chemical shifts were corrected and reported in ppm from TMS.

Mass spectra (ms) were run by Mrs. Ralph Guile on a Hitachi RMU-6 spectrophotometer with an ionizing voltage of 70 eV. A Perkin-Elmer model 900 gas chromatograph interfaced with the RMU-6 was used for a coupled gas chromatography-mass spectrometry (gc-ms) experiment; the column used for this was a 1 m x 2 mm glass column packed with 20% FFAP on 60-80 mesh Chromosorb W.

All other gas chromatographic separations were achieved using an F & M model 700 chromatograph equipped with a thermal conductivity detector. Helium was used as the carrier gas at flow rates of 70-90 ml/min; the injector temperature was 220° and the detector temperature 250°. The columns used were 6' x ¼" aluminum columns packed with the following materials:

column A: 10% DC-710 on 60-80 mesh Chromosorb W
column B: 10% Carbowax on 60-80 mesh Chromosorb W
column C: 20% SE-30 on 60-80 mesh Chromosorb W
column D: 20% DC-710 on 30-60 mesh Chromosorb P
column E: 20% FFAP on 60-80 mesh Chromosorb W

With an appropriate modification to the injector port, solid phase pyrolyses of tosylhydrazone salts were performed on the F & M 700 gas chromatograph. Into a 2 mm standard melting point capillary was placed about 2 cm of the salt to be pyrolized. The ends were sealed and the capillary placed into the shaft of the solid injector. Pushing in the plunger of the injector caused the capillary tube to be crushed and the salt pyrolized at 250° in the injector port. Columns and column temperatures for the individual salts are reported in the body of the Experimental.

High pressure liquid chromatographs were run on a Nester Faust Model 1240 Liquid Chromatograph using a 19" steel column packed with 18-32 micron mesh silica gel with hexane as the solvent.

Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde (37).

The procedure for oxidizing alcohol 82 with chromium trioxide and pyridine in methylene chloride was taken from Raghu's[16] thesis. For a cleaner workup, the following procedure was used. After the washing steps and drying of the CH_2Cl_2 solution with magnesium sulfate, the solvent was evaporated using a rotary evaporator. The residue was taken up in ether and filtered with suction through a Büchner funnel filled with celite. The ether was removed and the residue distilled to give the aldehyde 37. Its spectral properties were identical to Raghu's.[16]

Diethyl-2-(cyclohexylamino)vinylphosphonate (39). Preparation of the Enamine Reagent.

This procedure was adapted from that of Nagata and Hayase[26a] and later Nagata, Wakabayashi and Hayase.[26b] Into a 500 ml three-necked round-bottomed flask fitted with a magnetic stirrer, dropping funnel, and nitrogen inlet were placed 149.4 g (0.83 moles) of diethyl formylmethylphosphonate (40) [26] and 625 ml of dry acetonitrile. The solution was cooled to 0-5° with ice cooling and the system was flushed with nitrogen. Freshly distilled cyclohexylamine (95 ml, 0.83 moles) was added over a period of 10 minutes with the temperature maintained at 0-5°. The solution turned yellow upon addition of cyclohexylamine. The mixture was stirred at room temperature for an additional 15 minutes. The acetonitrile was removed on a rotary evaporator, the residue taken up in 300 ml of ether and dried over anhydrous sodium sulfate. The ether was partly evaporated and the solution was left to crystallize in the freezer (-40°). Crystallization yielded 173 g (80% yield) of white crystalline enamine reagent, mp 60-62°.[26b] IR, NMR and UV spectral data were consistent with literature values.[26] The mass spectrum showed: (m/e, %) 262(7), 261(44), 260(45), 232(42.5), 219(15), 218(100), 216(15), 204(12), 190(22), 180(52), 162(21), 152(35), 144(14), 125(35), 124(75), 123(34), 122(21), 106(32), 98(46), 97(15) and 96(25) among others.

Trans-β[anti-9-bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein (38). Preparation of the Extended Aldehyde Using the Enamine Reagent 39 and Aldehyde 37.

The procedure for extending the aldehyde was adapted from Nagata and Hayase[26] and Raghu's thesis.[16] Into a 100 ml three-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel, and nitrogen inlet, were placed 4.34 g (1.03×10^{-1} moles) of sodium hydride (57% oil dispersion) and 150 ml of anhydrous tetrohydrofuran. The flask was flushed with nitrogen and brought to 0° with an ice bath. A solution of 26.8 g (1.03×10^{-1} moles) of enamine reagent in 50 ml dry THF was added dropwise to the stirred mixture while maintaining the temperature at 0-5°. The mixture was further stirred for 15 minutes at 0-5° to ensure complete reaction. A solution of 10.0 g

(6.85 x 10^{-2} moles) of bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde (**37**) in 100 ml dry THF was added dropwise to the mixture at a rate such that the temperature did not exceed 5°. The mixture was stirred for an additional 2 hours at room temperature. During this time the solution became quite dark, almost black, and a gummy precipitate of sodium diethylphosphate was observed. The mixture was poured into cold water and extracted with three 100 ml portions of ether. The combined ether layers were washed twice with saturated aqueous salt solution, dried over anhydrous sodium sulfate, and the solvent was rotovaped off. The residue was dissolved in 300 ml benzene and transferred to a 2-l round-bottomed flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet. To this was added 900 ml of 1% oxalic acid (1.36 g oxalic acid dihydrate/100 ml H_2O). This mixture was stirred overnight under nitrogen. The benzene layer was separated and the aqueous layer was extracted twice with 300 ml portions of ether. The combined organic layers were washed with 200 ml water, 200 ml of saturated salt solution, and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residue was chromatographed on Florisil (80 grams). The column was prepared with hexane as the solvent. The residue was dissolved in methylene chloride and adsorbed on about 1 gram of Florisil, the methylene chloride was evaporated and the residue was added to the top of the column as a Florisil plug. The product was eluted first with hexane (ca. 1500 ml) and later with methylene chloride (ca. 1000 ml). The solvent was evaporated and the residue was recrystallized from hexane to give 8.03 g (68% yield) of the unsaturated aldehyde **38** as shiny white plates (MP 88-90°).[16] Spectral data were identical to those reported by Raghu.[16] The cnmr proton decoupled spectrum showed lines at: (δ, $CDCl_3$ = 76.9) 192.7(1C), 160.8(1C), 130.3(1C), 128.7(2C), 126.5(2C), 125.0(2C), 32.0(1C) and 29.7(2C).

Trans-β-[*anti*-9-bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein Tosylhydrazone (**35**).

Tosylhydrazone **35** (mp 149-150°) was prepared from the extended aldehyde **38** as in Raghu's thesis.[16] Spectral data (pnmr and ms) were identical to those reported.[16] The cnmr proton decoupled spectrum showed lines at: (δ, $CDCl_3$ = 76.9) 150.3(1C), 146.2(1C), 143.9(1C), 135.3(1C), 129.5(2C), 128.0(2C), 127.7(2C), 127.2(2C), 124.9(2C), 124.4(1C), 32.2(1C), 28.1(2C) and 21.4(1C).

Lithium Salt **42** of Tosylhydrazone **35**.

To a flamed out 100 ml round-bottomed flask with a serum capped side arm was added 2 g (5.89 x 10^{-3} moles) tosylhydrazone **35** and 50 ml anhydrous tetrahydrofuran. The flask was flushed with nitrogen and the solution was cooled to -78° with a Dry Ice/acetone bath. N-butyl lithium (1.66 N) was slowly added through the serum cap with a syringe. A tannish yellow color developed where the n-butyl lithium hit the solution and a white precipitate fell out almost immediately. After the addition of 2 ml of n-butyl lithium, the solution became quite thick and the stirrer stopped. The Dry Ice/acetone bath was removed and the addition was continued until the solution maintained a tannish color. About 3 to 3.5 ml (approximately 1.5 to 1.8:1.0 molar ratio of base to tosylhydrazone respectively) was required. Jones[2i] suggested for a similar reaction that n-butyl lithium be added until a purple color was maintained. It was found by this researcher that a purple color did develop on addition of greater than a 2-fold excess of n-butyl lithium;

however pyrolysis of the resulting salt did not seem to work as well. Most of the tetrahydrofuran was removed on a rotary evaporator. The remaining traces of solvent were removed by attaching the flask overnight to a vacuum pump (∿0.1 mm Hg). The resulting gray to brown lithium salt was not characterized but was pyrolized as soon as possible after removal from the vacuum pump. On standing in the air for ten minutes, the salt turned black and sticky.

Preliminary Work to Preparative Pyrolyses.

A. Method of Jones, Reich and Scott.[2i]

Decomposition of Dry Salt **41**. The flask containing the lithium salt **41** [2i] (15 mmoles) was connected via a curved adaptor to a trap. A high vacuum was applied and the trap cooled to -78°. The flask was placed into an oil bath at 70° and the temperature was gradually raised to 110-110° at which time decomposition set in. Ether was added to the trap and the products were analysed by gas chromatography (column D, 110°). Relative retention times for the mixture of $(CH)_{10}$ hydrocarbons formed were consistent with those in the literature.[2i]

Decomposition of the Dry Salt **42**. Compound **42** was pyrolyzed in an identical fashion as salt **41**. Vpc analysis (column D, 110°) of the contents of the trap showed no peaks other than solvent. The residue in the pyrolysis flask was quenched with water and extracted with ether. The residue gave an nmr and ms similar to those of the pyrazole reported by Raghu.[16]

B. Gas Chromatographic Pyrolyses of Tosylhydrazone Salts.

Decomposition of the Dry Salt **41**.[2i] Capillary tubes containing the lithium salt **41** (the sodium salt gave similar results) were crushed at 250° in the injector port of the gas chromatograph. The volatile products were observed through their separation at various temperatures (column D). In each run much highly volatile material came off first. In one run (125°) six additional peaks in the ratio of 6:1.3:1:11:10.3:5.3 with retention times of 1.9, 4.8, 5.8, 7.9, 10.3 and 12.4 min. respectively were observed. By comparison cyclooctatetraene had a retention time of 1.6 min. under similar conditions (same column and temperature, but not with the solid injector). No effort was made to identify the different components.

Decomposition of the Dry Salt **42**. Capillary tubes containing the lithium salt **42** were crushed at 250° in the injector port of the gas chromatograph. Other than the initial very volatiles, peaks were observed (column D, 160°) at 3.3, 4.0, 7.7, 8.8, 12.5 and 14.6 minutes in a ratio of 2:1.5:7:10:3.75:1 respectively. For comparison napthalene came off at about 3.5 min and 1,5,9-cyclododecatriene at 3.9 and 4.6 minutes.

C. Pyrolysis in Sand Bath.

Decomposition of the Dry Salt **42**. A two-necked round-bottomed flask fitted with a short path and a bent adaptor closed at one end was placed in a sand bath. A receiver with a vacuum attachment was connected to the short path. Lithium salt **42** (14.8 mmoles) was placed into the bent adaptor. A vacuum (*ca.* 0.1 mm) was applied and the trap cooled to -78°. The sand bath was heated to about 300°. The lithium salt 42 was added in small portions to the hot glass surface of the round-bottomed flask. The volatiles (collected in the Dry Ice/acetone trap) were taken up in pentane and subjected to gc analysis (column D, 150°). Peaks were evident at 3.7, 7.2, 8.5 and 12.2 minutes in a ratio of 1:13:17:2 respectively. The volatiles were also analyzed by gc/ms (column E, 160°). Peaks were evident at 4.1, 5.0, 6.4, 7.2 and 8.4 minutes in a ratio of 1:7.5:10.5:30:1.5 respectively. Mass spectra taken at approximately 5, 6.2, 6.9 and 7.9 minutes were essentially identical and showed a parent peak of 156 corresponding to $(CH)_{12}$'s.

Endo-tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene (43), *exo*-tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene (44),[28] pentacyclo[6.4.0.0.^{2,12}0.^{3,7}0^{4,11}]-dodeca-5,9-diene (45). Pyrolysis of Tosylhydrazone Salt 42.

The lithium salt 42 (5.9 x 10^{-3} moles) was placed in a bent Pyrex tube with a male ground glass joint and attached to the pyrolysis apparatus (Figure 12). The system was opened to vacuum (*ca.* 0.1 mm Hg) and the oven heated to 250°. The lithium salt was added in small portions to the top of the column of hot glass beads. Periodically approximately 5 to 10 glass beads were added to the top of the column to give a fresh hot surface. New beads were allowed to warm up for about 10 minutes before addition of more lithium salt. After the addition of all the lithium salt (approximately four hours) the vacuum was disconnected and nitrogen was slowly allowed into the apparatus. It was observed that most of the volatile products were collected on the tube leading into the round-bottomed flask in the liquid nitrogen bath. The contents of this tube and the Dry Ice/acetone trap were rinsed with pentane into the round-bottomed flask which contained about 0.2 g

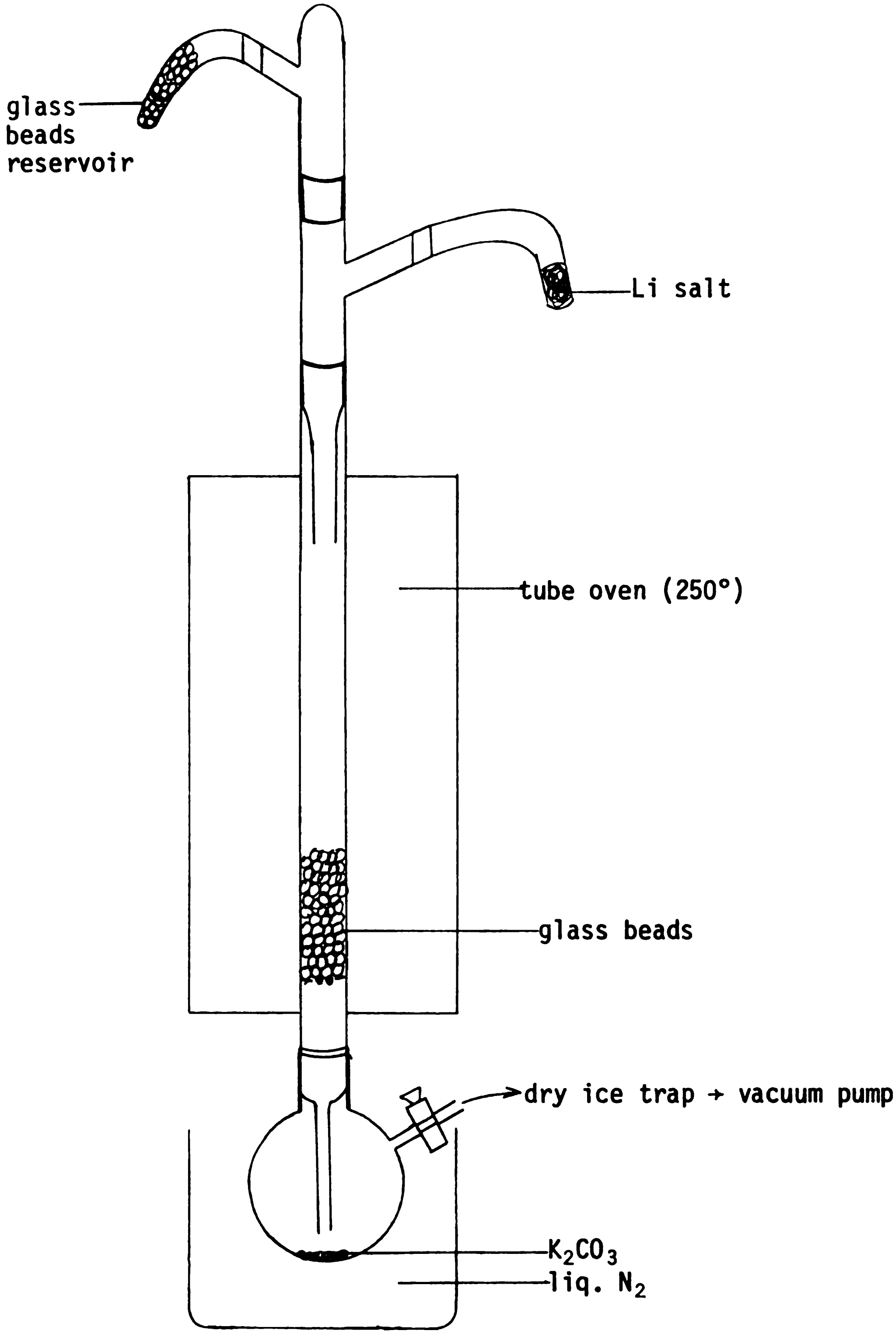


Figure 12. Pyrolysis Apparatus for Decomposition of Dry Salts.

potassium carbonate. The pentane solution was concentrated on a rotary evaporator and the components separated and collected by vpc.

Column A at 135° (∼75 ml/min) gave two major $(CH)_{12}$ peaks (MW 156 by mass spectroscopy): 18.7 and 22.6 minutes in relative amounts of 41.3% and 58.7% respectively. The second component was isolated as a white fluffy camphor smelling solid., *ca*. 40 mg (*ca*. 5% yield). The spectral data showed this to be tetraene 43: ms (m/e, %): 156(11), 155(17), 154(9), 153(10), 141(18), 129(13), 128(21), 115(26), 91(100), 78(27) and 77(15) among others; pnmr[30] (δ, CCl_4): 6.04 (2 H, sharp s, olefinic cyclobutene); 5.63-5.4 (6 H, unsymmetrical m) and 2.82 (4 H, broad s, H ½ = Hz); proton decoupled cnmr (δ, CCl_4 = 96.0): 140.0 (2C), 134.5 (2C), 126.9 (2C), 123.3 (2C), 48.6 (2C) and 34.69 (2C); uv (λ_{max}, ε): 263.5 (∼2,980), 273 (∼2,860) and 283 (∼1,315).

The other, earlier, component from column A was reinjected and collected from column B (125°, ∼ 80 ml/min) to give two more $(CH)_{12}$ components: 9.1 and 11.3 minutes in relative amounts of 53 and 47% respectively. The second of these two components was isolated from column B as a clear liquid (∼20 mg, ∼2.2% yield) and identified from its spectral properties as the known[28,30] tetraene 44 (mp lit.[28a] 8-11°): ms (m/e, %): 156(13), 155(19), 154(19), 153(15), 152(10), 141(21), 129(15), 128(23), 115(27), 91(100), 78(26) and 77(17) among others; pnmr (δ, CCl_4): 5.96-5.0 (4 H, m), 5.83 (2 H, sharp s, olefinic cyclobutene), 5.47-5.3 (2 H, dd, J = 5 Hz, 2.5 Hz), 3.25 (2 H, Bd s, H ½ = 3 Hz), 2.57 (2 H, pseudo triplet), irradiation at δ2.57 collapsed the dd centered at δ5.38 to a doublet (J = 5 Hz) and irradiation at δ5.38 collapsed the signal at δ2.57 to a poorly defined doublet (J = 8 Hz); proton decoupled cnmr (δ, CCl_4 = 96.0): 139.0 (2C), 136.7 (2C), 125.0 (2C), 120.6 (2C), 50.4 (2C) and 36.1 (2C).

The other, earlier, component from column B was reinjected into column C (115°, $\sim$80 ml/min) to give two more components (16.6 and 17.9 minutes in relative amounts of 17 and 83% respectively). The first peak was too small to characterize while the second has been identified as the hertofore unknown[67] $(CH)_{12}$ pentacyclic diene 45. Compound 45 was isolated in ca. 1% yield from column C as a white camphor smelling solid, mp 67-68°. Its spectral properties were: ms (m/e, %): 156(4), 155(8), 154(5), 153(3), 141(6), 128(9), 115(12), 91(100), 78(15) and 77(8) among others; pnmr (δ, CCl_4): 5.85 (2 H, dd, J = 4.4, 3.0 Hz), 5.30 (2 H, d, J = 1 Hz), 2.67-3.34 (5 H, bdm) and 1.78 (3 H, m); proton decoupled cnmr (δ, CCl_4 = 96.0): 134.3 (2C), 130.9 (2C), 66.0 (1C), 62.4 (2C), 41.6 (2C), 36.1 (2C) and 26.4 (1C); and ultraviolet: no absorption above 250 mμ.

Determination of Temperature Dependence of the NMR Spectrum of 43.

The pnmr spectrum of the sample 43, prepared above, was recorded in tetrachloroethylene solution (toluene as reference) at several temperatures between 25° and 150°. The solution was degassed and sealed under vacuum. The pnmr spectra so obtained were independent of the sample temperature.

Attempts to Deuterate Tosylhydrazone 42.

A. The tosylhydrazone (0.045 g, 1.32×10^{-4} moles) was dissolved in 0.5 ml tetrahydrofuran and 0.5 ml deuteromethanol. To this was added one equivalent of sodium methoxide. The mixture immediately turned yellow and after five minutes was orange. After 30 minutes the solution was quenched in water and was quickly extracted with methylene chloride.

The solvent was dried and evaporated. The pnmr showed no change from the starting material.[68]

B. Into a 10 ml round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet was added 0.5 g tosylhydrazone dissolved in 2 ml deuterochloroform. To this was added 3 ml of NaOD (prepared by adding a small piece of sodium metal to deuterium oxide). The mixture turned yellow upon addition of the base; and upon further stirring turned orange. The progress of the reaction was followed by pnmr. The spectra remained unchanged over a period of five days.

Preparation of Deuterated Enamine Reagent (39-d).

Into a 500 ml round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet was placed 50 g of 39 (0.193 moles) dissolved in 200 ml carbon tetrachloride. To this was added 40 ml NaOD ($\sim$0.5 g metallic sodium in 40 ml D_2O). After two days the aqueous layer was removed and 20 ml of fresh NaOD was added. After a total of three days the aqueous layer was removed; the organic layer was washed with 10 ml D_2O and dried with anhydrous potassium carbonate. Recrystallization from D_2O saturated ether gave 29.2 grams (ca. 58% yield) of deuterated enamine reagent 39 (mp 60-62°). Mass spectrometry showed the product to be approximately 67% d_2, 28% d_1, and 5% d_0: (m/e, %) 264(5.5), 263(25), 262(11), 261(2), 234(39), 233(14), 221(10), 220(82), 219(31), 218(14.5), 206(14), 192(22), 182(33), 181(23), 164(23), 163(11.5), 154(32), 153(18.5), 127(39), 126(100), 125(67), 124(30), 123(18), 108(47) and 99(52) among many others. Other spectral data was: pnmr (δ, CCl_4): 6.82 (1 H, d, J = 16 Hz), 3.81 (4 H, quin, J = 7 Hz), 3.0 (1 H, bd s, tert. cyclohexyl) and 2.0-1.0 (16 H, m, including triplet centered at 1.25).

Trans-β-[anti-9-bicyclo[6.1.0]nona-2,4,6-trienyl]propenaldehyde-2-d (30-d). Preparation of Deuterated Extended Aldehyde.

Except for the use of deuterated enamine reagent, the preparation of the deuterated extended aldehyde was analogous to that of the undeuterated extended aldehyde (38). The product was isolated as white shiny crystals (mp 87-89°). The pnmr shows ca. 80% deuteration: δ(CCl$_4$) 9.22 (1 H, bd s, base was 10 Hz broad), 6.23 (∼1.2 H, m), 5.85 (6 H, sh s), 5.77 (2 H, bd s), 1.8 (2 H, d, J = 6 Hz) and 1.33 (1 H, dt, J = 9 Hz, J' - 4.5 Hz). The mass spectrum showed ca. 75% deuterium incorporation: (m/e, %) 174(3), 173(18.5), 172(13), 171(4), 170(2), 155(13.5), 154(19), 153(18), 144(40), 129(100), 128(98), 116(50), 115(64), 104(78), 96(85) and 82(58) among others. Its cnmr was (δ, CDCl$_3$ = 76.9) 192.4 (1C), 160.5 (1C), 128.4 (2C), 126.4 (2C), 124.8 (2C), 31.8 (1C), 29.5 (2C).[69]

Deuterated Tosylhydrazone 35-d. Preparation of Tosylhydrazone from Deuterated Extended Aldehyde 38-d.

The deuterated tosylhydrazone was prepared in an analogous fashion to the undeuterated compound 35. From 2 g of compound 38-d, prepared above, was obtained 2.67 g (68% yield) tosylhydrazone 35-d as a white fluffy solid after recrystallization from 95% ethanol. The pnmr spectrum showed the deuterium content to be essentially unchanged (ca. 80%): (δ, CDCl$_3$) 7.9-7.1 (6 H, m, becomes 5 H in D$_2$O), 5.9-5.7 (6 H, d), 6.1-5.1 (1.2 H, m), 2.37 (3 H, s), 1.58 (2 H, d, J = 5 Hz) and 1.4-0.9 (1 H, m). The mass spectrum was consistent with the pnmr results: M^+ m/e 341.[70] Except for the absence of the peak at 124.4 ppm the proton decoupled cnmr spectrum was unchanged from that of the undeuterated compound (**35**).

Lithium Salt **42-d** of Deuterated Tosylhydrazone **35-d**.

The lithium salt of the deuterated tosylhydrazone was prepared as above for the undeuterated salt **42**.

Decomposition of the Deuterated Dry Salt **42-d**. *Endo*-tricyclo-[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene-3-d (**43-d**), *Exo*-tricyclo-[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene-3-d (**44-d**), Pentacyclo-[6.4.0.0.^{2,12}0.^{3,7}0^{4,11}]-dodeca-5,9-diene-2-d (**45-d**).

The pyrolysis, separation and isolation was carried out as above for the analogous undeuterated compounds. Compounds **43-d** and **45-d** were isolated as white camphor smelling solids while compound **44-d** was isolated as a clear liquid. The mass spectrum of each of the three pyrolysis products showed a M^+ peak at a m/e of 157.[71] The pnmr and cnmr clearly showed the deuterium to be at a vinyl cyclobutene position in tetraenes **43** and **44** and at the "2" position in pentacyclic diene **45-d**. The nmr spectrum (δ, CCl_4) for compound **43-d** consisted of peaks at 6.04 (1.2 H, sh s), 5.63-5.4 (6 H unsymmetrical m) and 2.82 (4 H, broad s, H ½ = 5 Hz); compound **44-d** at 5.96-5.0 (7.2 H, m), 3.25 (2 H, s) and 2.57 (2 H, pseudo triplet); and for **45-d** 5.85 (2 H, dd, J = 4.4, 3.0 Hz), 5.28 (2 H, J = 1 Hz), 2.6-3.4 (5 H, bd m) and 1.6-3.0 (2.2 H, m). For a comparison of the proton decoupled ^{13}C-nmr of the deuterated and undeuterated pyrolysis products see Table 1. A gated decoupled cnmr spectrum of compound **45-d** showed the cyclopropyl carbon at 26.21 ppm (carbon-3) split into a doublet with a J value equal to 173 Hz.

Heating of Endo-tricyclo[4.4.2.$0^{2,5}$]dodeca-3,7,9,11-tetraene-3-d (43-d).

A. About 5 mg of tetraene 43-d was dissolved in carbontetrachloride and sealed in a piece of #3 Pyrex tubing. A sample was heated at 75° and periodically removed to run a pnmr spectrum. The integrated ratio of peak area was checked carefully. The spectra remained unchanged over a period of 20 days.[73]

B. A similar sample was prepared as above except that hexadeutero dimethylsulfoxide was used as the solvent. The sample was heated overnight at 200°. No scrambling of deuterium was observed, but on prolonged heating the sample gradually decomposed and resulted in a sharp singlet at δ7.2 (probably benzene) and a broad multiplet *ca.* δ4.

Anti-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]nona-2,4,6-triene (27).[16] Low Temperature Photolytic Decomposition of Tosylhydrazone 35.

This procedure was adapted from Raghu's thesis.[16] The tosylhydrazone (510 mg, 15 mmoles) was dissolved in dry tetrahydrofuran (60 ml) in a Pyrex test tube with a nitrogen inlet and exit. Sodium methoxide (81 mg, 15 mmoles) was added to this and nitrogen was bubbled through to stir the mixture. A blue precipitate fell out and over a period of a few minutes the solution turned from clear to yellow and on through the spectrum to red. In some runs a white precipitate of the sodium salt of the tosylhydrazone fell out but this gradually redissolved during the photolysis. The test tube was then placed next to a Pyrex immersion well in a Dry Ice/acetone bath. Nitrogen was constantly bubbled through the solution while it was photolyzed externally using a 200 W Hg vapor lamp. The course of the reaction was monitored by high pressure liquid chromatography (HPLC) on a silica gel column with hexane as the elutant.

A decomposition peak of the sodium salt came off after ∿6½ minutes and cyclopropene **27** eluted after 8 minutes (stroke 25). The photolysis was run until the ratio of the second to first peak reached a maximum (generally 6 to 9 hrs). 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 twice with cold water to remove most of the tetrahydrofuran. The solution was dried over anhydrous sodium sulfate and then rapidly filtered twice through silica gel (∿20 g) to remove unreacted tosylhydrazone. Evaporation of solvent gave a residue (ca. 100 mg) with spectral properties (ms, pnmr) identical to the literature,[16] however normally the cyclopropene was left in pentane and stored at -40° in a freezer until needed. The product does polymerize rapidly when neat, but was stable for a few months when stored in pentane in the freezer. Stirring in pentane at room temperature over a period of days showed a gradual decomposition to polymeric material. The presence of the cyclopropene could easily be checked by thin layer chromatography. It gave a Rf value of 0.34 on silica gel with hexane as the elutant.

Pyrolysis of Anti-9-(Δ^2-cyclopropeno)-bicyclo[6.1.0]nona-2,4,6-triene **27**.

A 60 cm Pyrex tube, packed with 25 cm of glass beads, fitted with a nitrogen inlet and dropping funnel at the top and a trap at the exit was heated to 200° in an oven. Approximately 100 mg of **27** dissolved in 5 ml pentane was passed through the column with a slow stream of nitrogen. The volatiles were collected in a Dry Ice/acetone trap. After addition of the solution of **27** the column was washed with an additional 10 ml of pentane. The condensed pentane was dried with anhydrous potassium carbonate, evaporated and the residue was subjected to vpc analysis (column A, 140°). Two peaks in the ratio of 1:3 with retention times of 6.4 and 10.8 minutes respectively were observed. Coinjection of compound 45 gave a vpc trace with a peak at 13.1 minutes in addition to the previous two. The two components of the pyrolysis mixture were collected by preparative gas chromatography (column A, 135°). The first component was tentatively identified from its spectral properties as cis-1-phenyl-1,3-butadiene: ms (m/e): M^+ = 130 (consistent with $C_{10}H_{10}$) and pnmr (δ, CCl_4): 7.05 (5 H, m), 6.05-6.7 (3 H, m) and 4.9-5.3 (2 H, m). Subjecting the second component to vpc analysis (column B, 115°) showed peaks in a ratio of 1:3 at 7.5 and 10.4 minutes respectively. Both latter components gave a M^+ peak at 156 m/e in the mass spectrophotometer. The pnmr spectrum of each was highly complex and probably indicated each to still be a mixture of $(CH)_{12}$ isomers or possibly a single isomer with no symmetry. There was not enough sample to pursue this further.

Preparation of Pyrazoles 58 and 59. Decomposition of Tosylhydrazone Salt 42 in Tetraglyme.

Tosylhydrazone lithium salt 42 (prepared above) was refluxed for 2 hrs in tetraglyme. The solution was cooled, water was added, and the mixture was extracted with ether. The ether layer was washed twice with water and was dried over magnesium sulfate. The ether was evaporated and the residue was chromatographed with ether on a silica gel column. The first eluting material was shown by proton decoupled cnmr to be a mixture. The [4.2.1] component gave lines at (δ, $CDCl_3$ = 76.9) 135.7 (2C), 124.1 (2C), 121.0 (2C), 49.8 (2C) and 4.0 (1C), while in the same spectrum the dihydroindene component showed lines at 133.0 (1C), 127.9 (1C), 126.2 (1C), 125.7 (1C), 121.4 (1C), 52.7 (1C), 44.7 (1C) and 43.8 (1C). The pyrazole carbons for each showed broad lines *ca*. 151, 133 and 102 ppm. The pnmr was quite messy but did show a singlet *ca*. $\delta 5$, typical of the [4.2.1] system. The second eluting material was clearly the other [4.2.1] pyrazole epimer. It showed lines in the proton decoupled cnmr at (δ, $CDCl_3 = 76.9$) 134.8 (2C), 125.7 (2C), 122.4 (2C), 45.8 (2C) and 35.5 (1C). The pnmr spectrum showed peaks at (δ, $CDCl_3$) 9.0 (1 H, bd s), 7.1 (2 H, bd s), 5.8 (4 H, bd s), 5.0 (2 H, sh s) and 3.4-3.1 (3 H, bd m).

Isomerization attempts on 27 were followed by high pressure liquid chromatography (HPLC) using a silica gel column with hexane as the eluting solvent or thin-layer chromatography (TLC) using silica gel plates with hexane again as the eluting solvent (Rf for 27 wa 0.33).

Photolytic Attempts at Isomerizing 27.

A. A solution of *ca*. 100 mg of 27 in 300 ml of purified pentane was irradiated at -78° with a 200 W Hg vapor lamp through Pyrex for 12.5 hrs. Periodic sampling and analysis by HPLC and TLC showed no change from starting material.

B. A solution of *ca*. 100 mg of 27 in 100 ml of purified pentane was irradiated through Pyrex in the presence of benzophenone sensitizer (10 mg, *ca*. 9%) at 0° with 200 W Hg vapor lamp. The reaction was monitored by TLC. After 3.5 hrs and development of no new spots, an additional 50 mg of benzophenone was added. After 10 hrs of irradiation and no apparent change from starting material, the filter was changed to quartz. After continued photolysis for 3 hrs TLC showed the loss of starting material but no new peak. Evaporation of the solvent left a hexane insoluble but chloroform soluble residue.

C. A solution of *ca*. 100 mg of **27** in 100 ml of purified pentane was irradiated at -78° with a 450 W Hg vapor lamp through Pyrex for 2 hrs. TLC and HPLC showed no new spots. The solution was allowed to warm to room temperature. Continued photolysis resulted in a polymer depositing on the wall of the immersion well.

Treatment of **27** with $PdCl_2(\phi CN)_2$.

A. An approximate equimolar amount of $PdCl_2(\phi CN)_2$ was added to a solution of **27** in deuterochloroform. A nmr was run on the resulting reddish brown solution. The peak at ∿7.0δ (cyclopropene vinyl H's) disappeared, the vinyl peaks at ∿6.8δ went to a broadened singlet with much fine structure, and the high field protons went to a series of ill-defined multiplets.

B. Deuterochloroform solutions of equimolar cyclopropene **27** and $PdCl_2(\phi CN)_2$ were mixed together under nitrogen at -60°. Nmr spectra were taken at various temperatures. Although solubility was poor at -60° and the resulting concentration was quite low, it appeared that the cyclopropene was present at -60° but on warming to -50° the peak at 7.0δ disappeared.

Attempts at Isomerizing **27** with $Mo(CO)_6$.[74]

A. A solution of *ca*. 100 mg of **27** in 15 ml purified pentane was prepared. To 10 ml of the solution was added 40 mg $(Mo(CO)_6$ and a nitrogen atmosphere was maintained. The remaining 5 ml of solution was maintained as a blank. The solutions were stirred at room temperature for one week with samples periodically removed from each and analyzed by TLC and HPLC. Except for a fast-eluting, very uv active fraction corresponding to $Mo(CO)_6$, no differences showed up between the samples with and without $Mo(CO)_6$. Although much of the sample had polymerized, evidenced by a precipitate, some cyclopropene was still present after one week (TLC, Rf $\sim$ .3).

B. A solution of 100 mg **27** and 70 mg $Mo(CO)_6$ in purified pentane was irradiated through Pyrex, with a 200 W Hg vapor lamp, at -78°, under nitrogen, for 1 hr. The solution was allowed to warm to room temperature and photolysis continued for another hour. TLC and LC showed no new nonpolymeric fractions. The nmr of the residue after evaporation showed some cyclopropene starting material plus other olefinic material (presumably polymer): (δ, CS_2) 7.0 doublet, J = 2 Hz, 5.8 unsym. doublet, in a ratio of 1 to 25.

Preparation of $Mo(CO)_3 \cdot$diglyme.

$Mo(CO)_3 \cdot$diglyme was prepared by the method of Coffield and Werner.[58] Diglyme, benzene and petroleum ether were each distilled under nitrogen from benzophenone ketal. A solution of 2.5 g $Mo(CO)_6$, 8.5 ml diglyme and 2.5 ml benzene was refluxed for seven hours and filtered hot over a layer of cellite filter aid. All operations were performed under argon to exclude oxygen. Cooling the clear yellow-brown solution produced a precipitate which was washed exhaustively with petroleum ether to remove unreacted $Mo(CO)_6$. The brownish-yellow crystals were dried in vacuum and transferred to a dry-box for storage until use. The $Mo(CO)_3$·diglyme was soluble in water to give a yellow solution but readily turns black in air.

Attempts at Isomerizing **27** in the Presence of $Mo(CO)_3$·diglyme.

A. A solution of 20 mg **27** in 25 ml purified pentane was degassed by a repetitive freeze-thaw process. After degassing, the solution was added under nitrogen to a round-bottomed flask containing *ca*. 5 mg $Mo(CO)_3$·diglyme and maintained at -78°. The process was monitored by HPLC. After 45 minutes and no apparent change, the solution was allowed to warm to room temperature. The solution was stirred for 8 hrs at room temperature, during which time the ratio of $Mo(CO)_3$·diglyme to cyclopropene increased gradually. A heat lamp was shone on the solution for 5 hrs. By this time no peak other than $Mo(CO)_3$·diglyme was apparent by HPLC.

B. Tosylhydrazone **35** (0.51 g) in 30 ml tetrahydrofuran was irradiated at -78° under argon in the presence of an equimolar quantity of sodium methoxide and a catalytic amount of $Mo(CO)_3$·diglyme. HPLC monitoring showed only the appearance of cyclopropene **27**. The reaction mixture was worked up as above for the same reaction without $Mo(CO)_3$·diglyme catalyst to give *ca*. 100 mg of cyclopropene **27**.

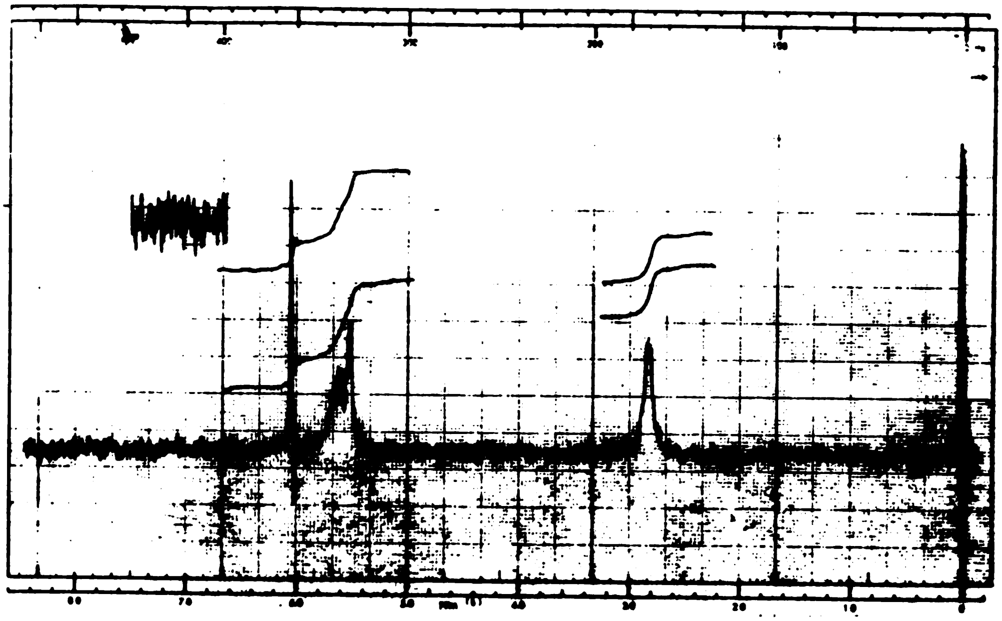


Figure 13. PNMR of Endo-Tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene (43).

Figure 14. PNMR of Endo-Tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene-3-d (43-d).

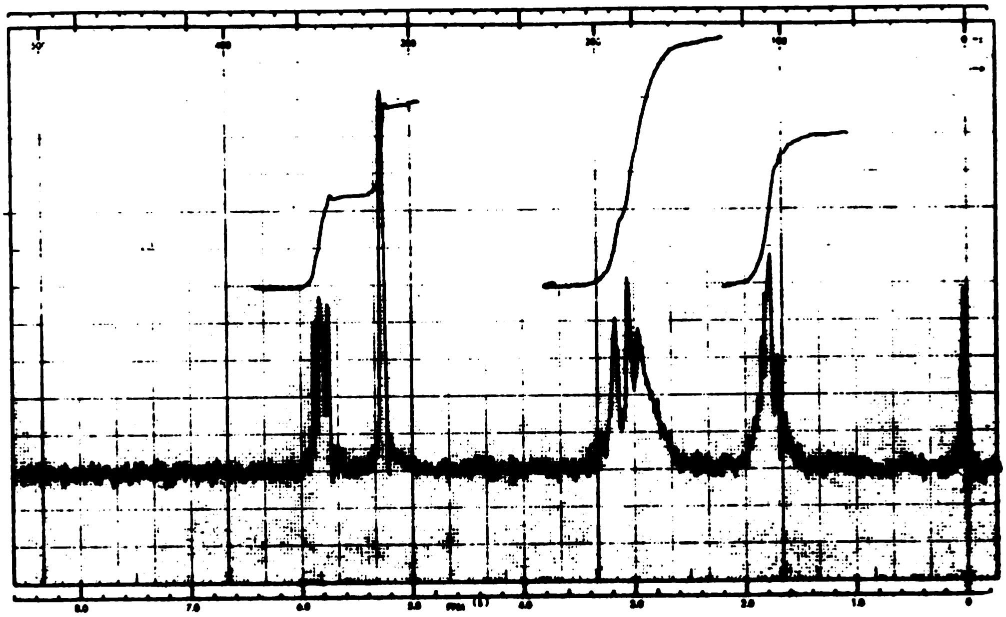


Figure 17. PNMR of Pentacyclo[6.4.0.0.^{2,12}0.^{3,7}0^{4,11}]dodeca-5,9-diene (45).

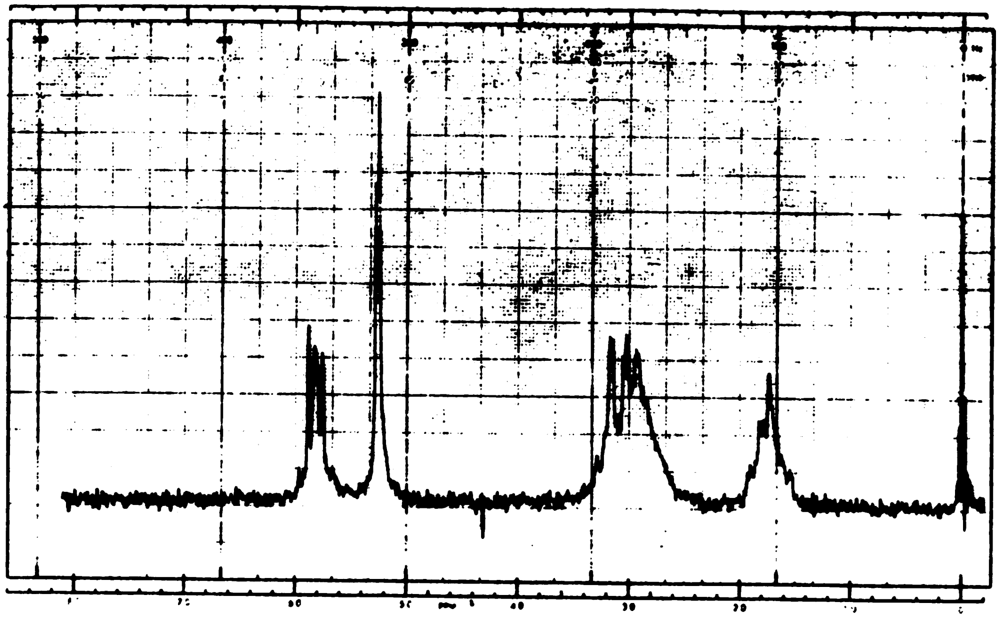


Figure 18. PNMR of Pentacyclo[6.4.0.0.^{2,12}0.^{3,7}0^{4,11}]dodeca-5,9-diene-2-d (45-d).

Footnotes

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68. The N-H peak is lost in the spectra of **35-d** but is presumably exchanged under these conditions.

69. Note the absence of a line at *ca*. 130.6 ppm.

70. The intensity of the M^+ and P-1 peaks was too small for a determination were of percent deuterium content.

71. Since these $(CH)_{12}$ and $C_{12}H_{11}D$ compounds loose hydrogens in the mass spectrometer easily to form aromatic species (in fact the P-1 peaks were larger than the M^+ peak), a calculation of deuterium content was not possible.[72]

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73. The exo-isomer, treated in the same manner, as expected, did not show deuterium scrambling.

74. We wish to thank Climax Molybdenum Company for a generous gift of $Mo(CO)_6$.

75. Although the precision for chemical shift data is only ca. ±0.05 ppm, the data in Table 1 is expressed to two significant figures, to better show the effects of deuterium isotope shifts.