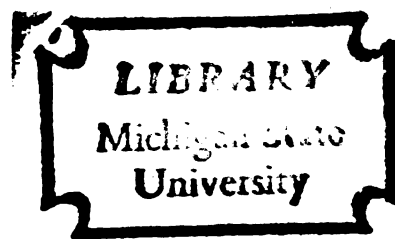


MOLECULAR REARRANGEMENTS OF DERIVATIVES OF
HEXAMETHYLBICYCLO[3.2.0]HEPTA-3,6-DIEN-2-ONE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY

SHIN LEE

1977



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ABSTRACT

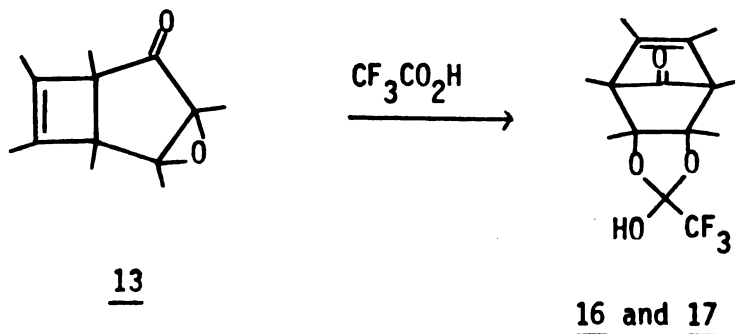
MOLECULAR REARRANGEMENTS OF DERIVATIVES OF HEXAMETHYLBICYCLO(3.2.0)HEPTA-3,6-DIEN-2-ONE

by

Shin Lee

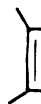
In this theses, synthesis, acid-catalyzed and photoinduced rearrangements of hexamethylbicyclo(3.2.0)hepta-3,4-epoxy-6-en-2-one (13) and the synthesis and acid-catalyzed rearrangements of 4,4-dichloro-1,3,5,6,7,8-hexamethyltricyclo(4.2.0.0^{3.5})octa-7-en-2-one (50) were investigated.

Treatment of 13 with trifluoroacetic acid resulted in a high yield of a mixture of two stereoisomeric compounds to which structures 16 and 17 are assigned.



The mechanism proposed for this reaction involves protonation of the carbonyl oxygen, a circumambulatory-type rearrangement and addition of the trifluoroacetic acid.

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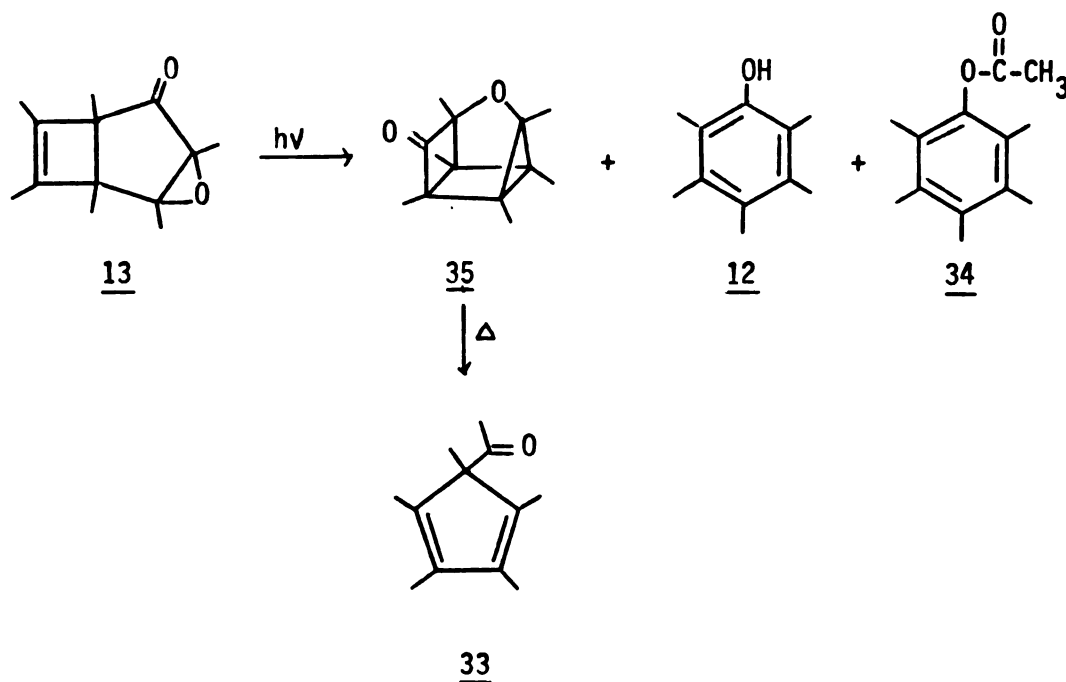


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Irradiation of 13 in ether through Pyrex resulted in the formation of 35 (70%), 12 (8%) and 34 (5%). The unusual strained cage structure of 35 is tentatively assigned on the basis of the spectral data and its subsequent thermal reaction to 33.



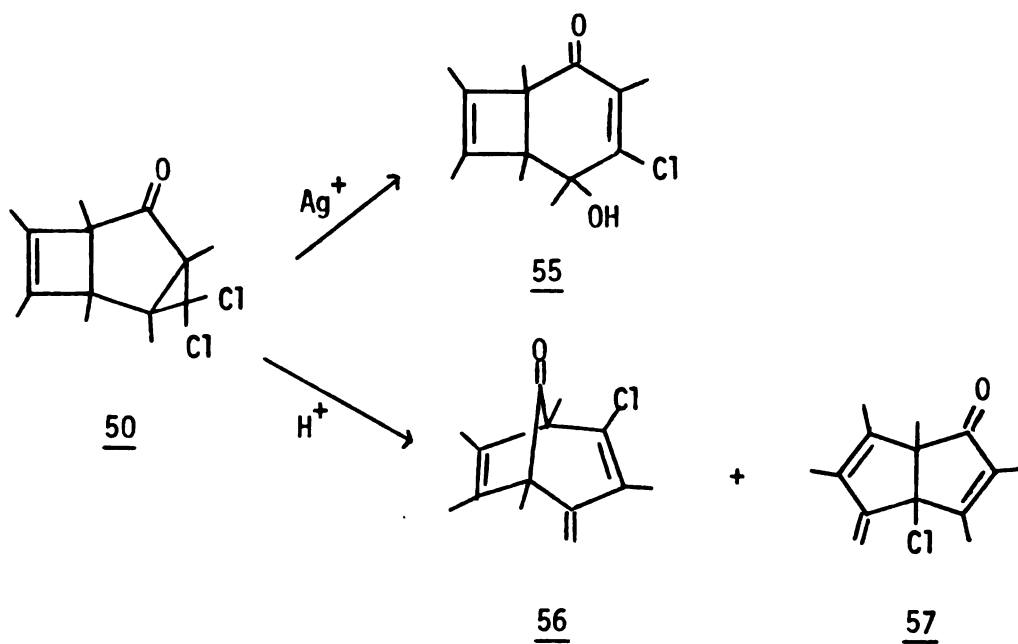
The mechanism proposed for the formation of 35 involves cleavage of the epoxide C-C bond. Mechanisms for the formation of 12, 34 and 33 are also proposed.

Treatment of 50 with aqueous silver perchlorate resulted in the exclusive formation of ring expansion product 4-chloro-5-hydroxy-1,3,5,6,7,8-hexamethylbicyclo(4.2.0)octa-3,7-dien-2-one (55).

Treatment of 50 with methanolic sulfuric acid resulted in the formation of compound 56 (10%) and 57 (72%) which are tentatively assigned the structures shown.



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The mechanism proposed for the formation of 56 involves a circum-ambulatory type rearrangement whereas the formation of 57 involves a homotropylium cation rearrangement.

MOLECULAR REARRANGEMENTS OF DERIVATIVES OF
HEXAMETHYLBICYCLO[3.2.0]HEPTA-3,6-DIEN-2-ONE

by

Shin Lee

A THESIS

Submitted to
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in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

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ACKNOWLEDGMENTS

The author is deeply grateful to Professor Harold Hart for his guidance and encouragement throughout the course of this study.

Appreciation is extended to Michigan State University, National Science Foundation and National Institute of Health for financial support in the form of teaching and research assistantships.

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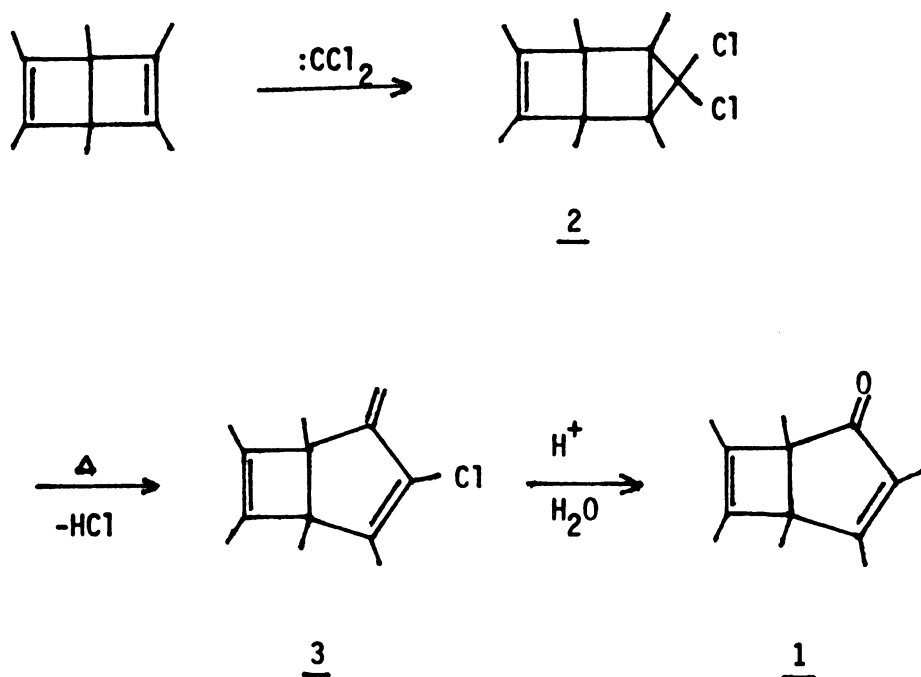
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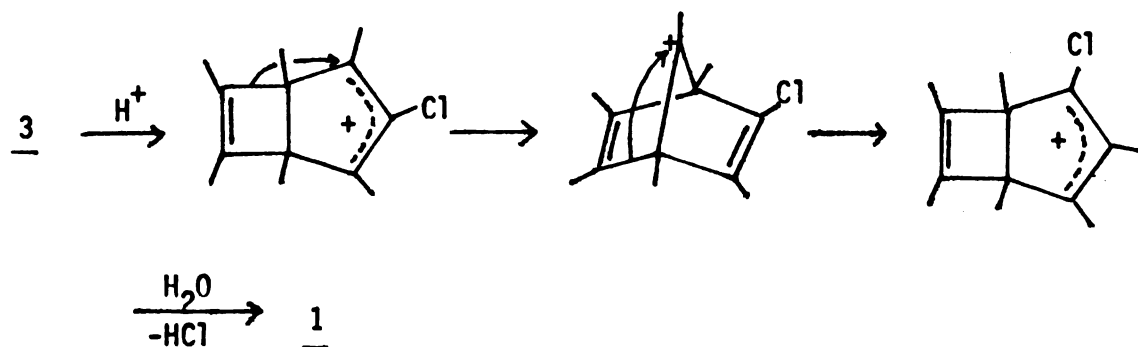
INTRODUCTION

In an earlier attempt to synthesize hexamethyltropone by Dr. M. Nitta in this laboratory, compound 1 — a valence isomer of hexamethyltropone — was obtained. The reaction sequence for synthesizing compound 1 was as follows¹, starting from the commercially available hexamethyldewarbenzene:



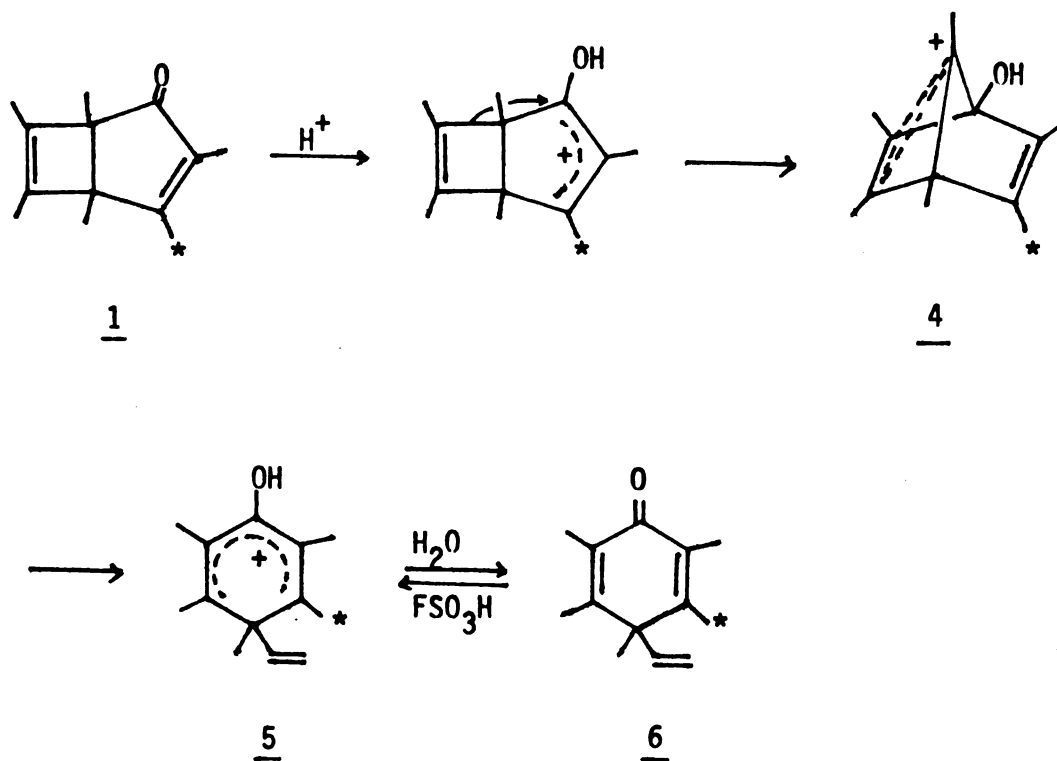
The dichlorocarbene adduct 2 was not isolated but spontaneously underwent dehydrochlorination to yield compound 3. Treatment of 3 with cold, concentrated methanolic sulfuric acid gave the bicyclic dienone 1 in

85% yield. The conversion of 3 to 1 involves a sequence of 1,2-shifts:



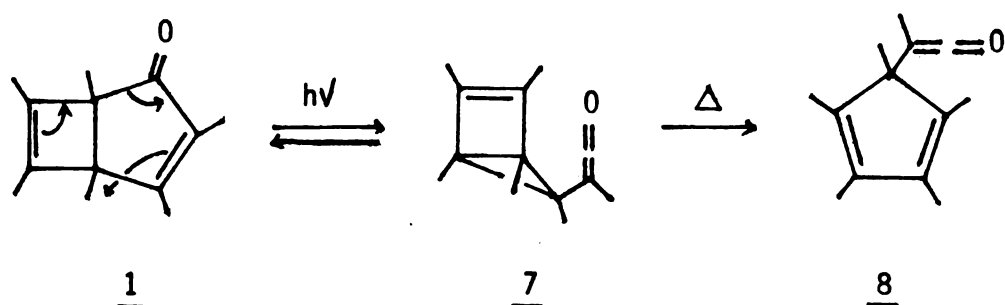
Compound 1 showed some interesting acid-catalyzed² (Scheme 1) and photoinduced³ (Scheme 2) rearrangements.

Scheme 1

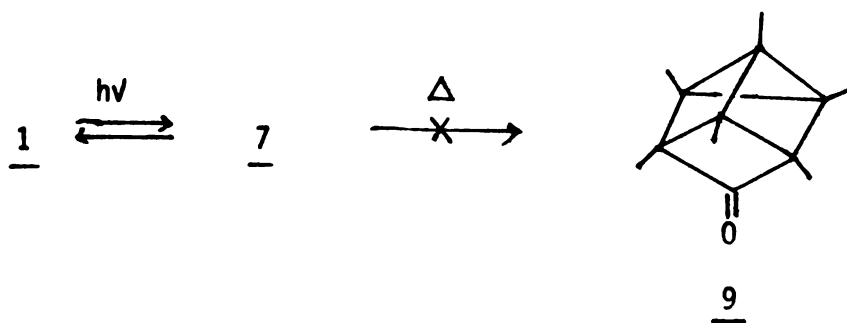


The proposed mechanism for the formation of 6 in FSO_3H involves a 1,2-shift to the OH-bearing carbon to give 4, which further rearranges to 5.

Scheme 2



The formation of 8 by the photolysis of 1 can be rationalized by an electrocyclic photorearrangement followed by ring opening of the bicyclic ketene intermediate 7. An anticipated intramolecular cycloaddition product, the tetracyclic cyclobutanone 9, was not obtained in this reaction.



Small-ring compounds have been notorious for undergoing molecular rearrangements, and the versatile rearrangements of compound 1 stimulated our interest to further study the chemistry of some of its derivatives. That this would be a promising area was already clear from a study of the epoxyketone 10³. Irradiation of the β,γ -epoxyketone

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11

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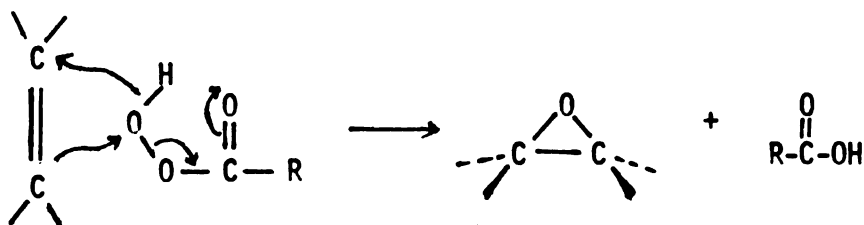
between C-4 and C-6 followed by bond cleavage between C-1, C-7 and C-5, C-6 and bond formation between C-3 and C-6 could give 11. r-hydrogen abstraction followed by aromatization would then lead to the observed products, pentamethylphenol and ketene.

I will discuss, in this thesis, the acid-catalyzed and photo-induced rearrangements of the α,β -epoxy derivative of compound 1 and the acid-catalyzed rearrangements of a dichlorocarbene adduct of compound 1.

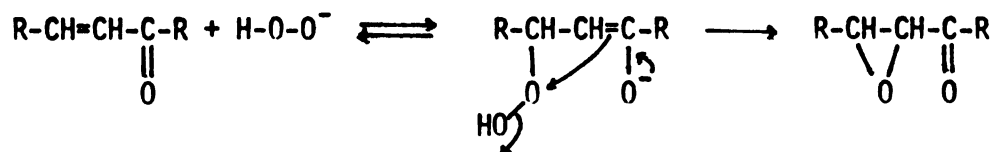
RESULTS AND DISCUSSION

1. Epoxidation of Hexamethylbicyclo(3.2.0)hepta-3,6-dien-2-one (1) via Alkaline Hydrogen Peroxide vs m-Chloroperbenzoic Acid

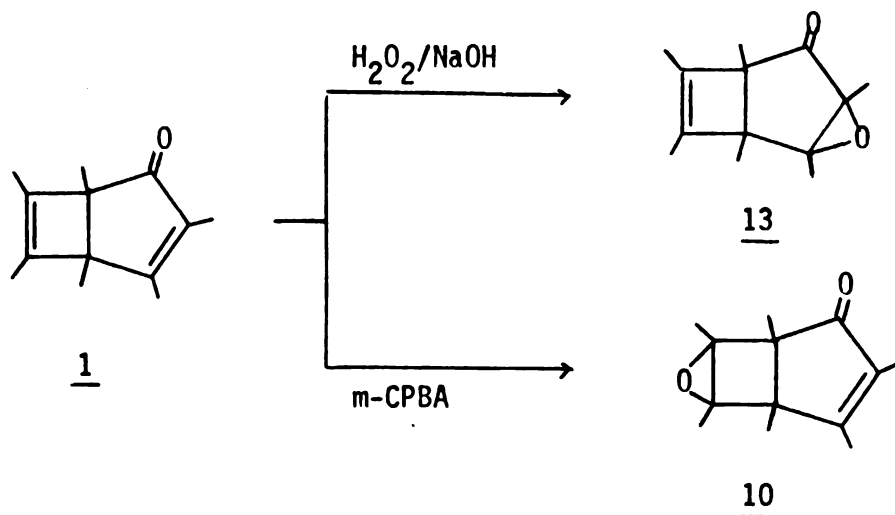
It is well established⁴ that the epoxidation reactions of olefins by peracids proceed by electrophilic attack of the peracid upon the double bond. When the olefinic bond is conjugated with an electron-



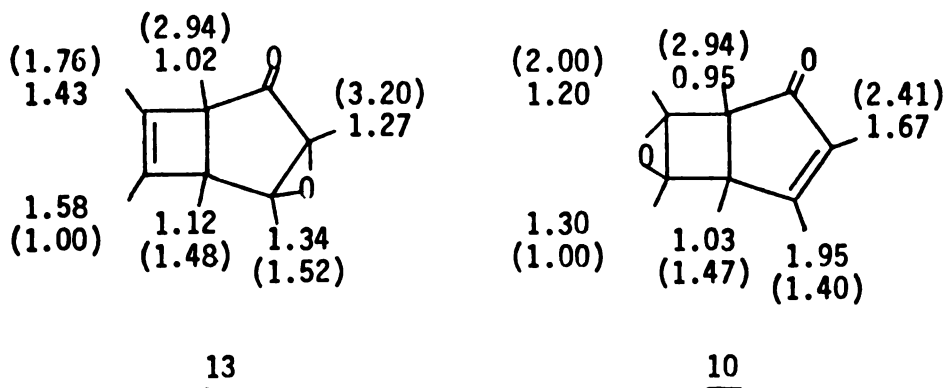
withdrawing group such as carbonyl, nucleophilic epoxidation by means of alkaline hydrogen peroxide is often used.



Thus, the epoxidation of the $\alpha,\beta;\beta',\gamma'$ -unsaturated ketone 1 with alkaline hydrogen peroxide or with m-chloroperbenzoic acid led to two different monoepoxides, 13 and 10 respectively.



The chemical shifts and europium shift slopes of 13 and 10 are shown on the structural formulas. The signal at the C-4 position of 13 and 10 was assigned by epoxidizing compound 1^{*} (labeled with a CD₃ group at the C-4 position). The remaining peaks are readily assigned from their chemical shifts and from their Eu-shift slopes. The configurations of these epoxides (exo or endo) were not determined, but only one isomer was formed in each case. I will return to this question of stereochemistry shortly.

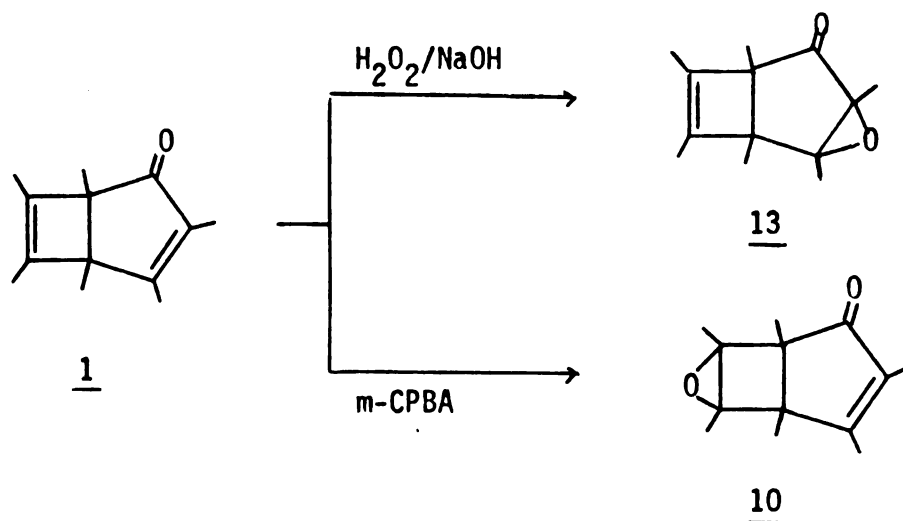




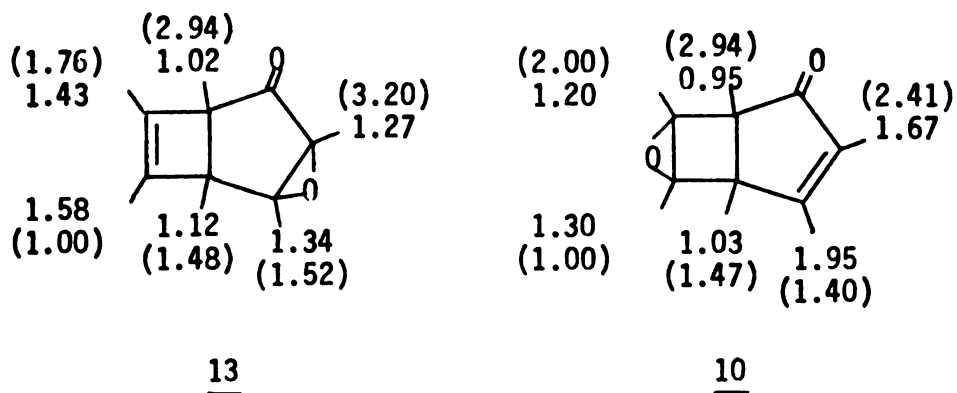
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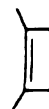
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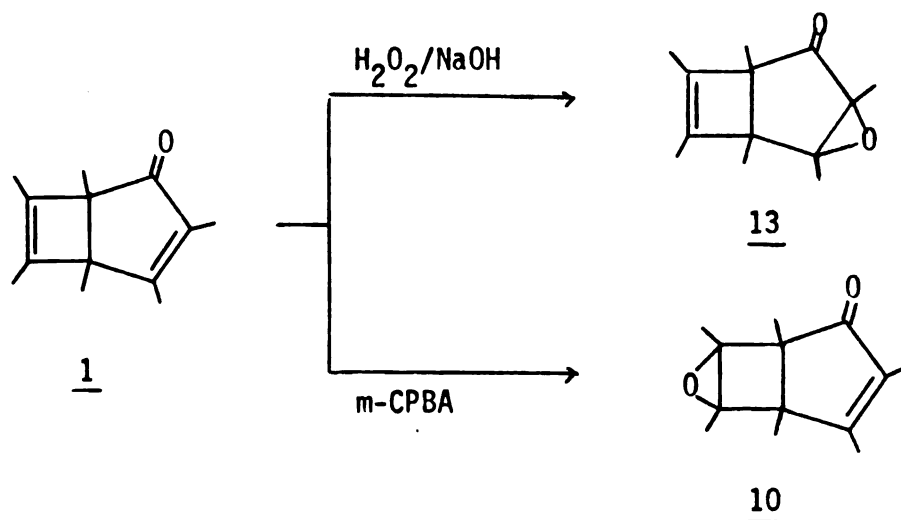




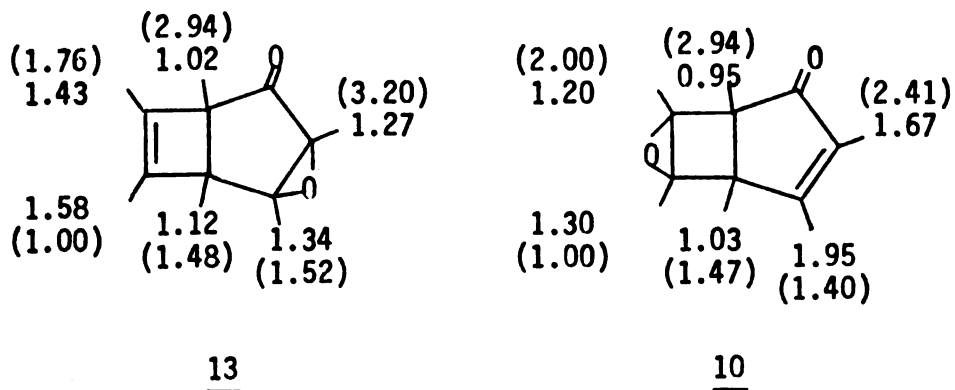
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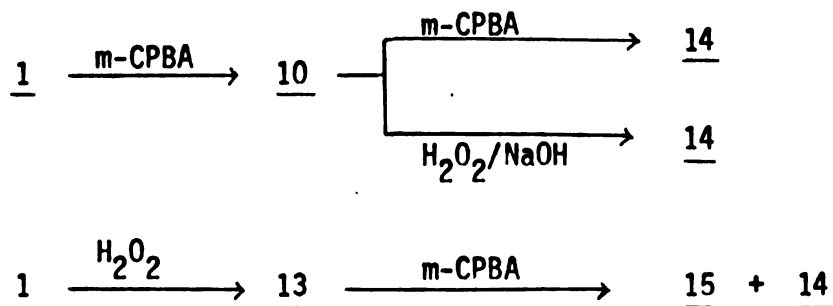
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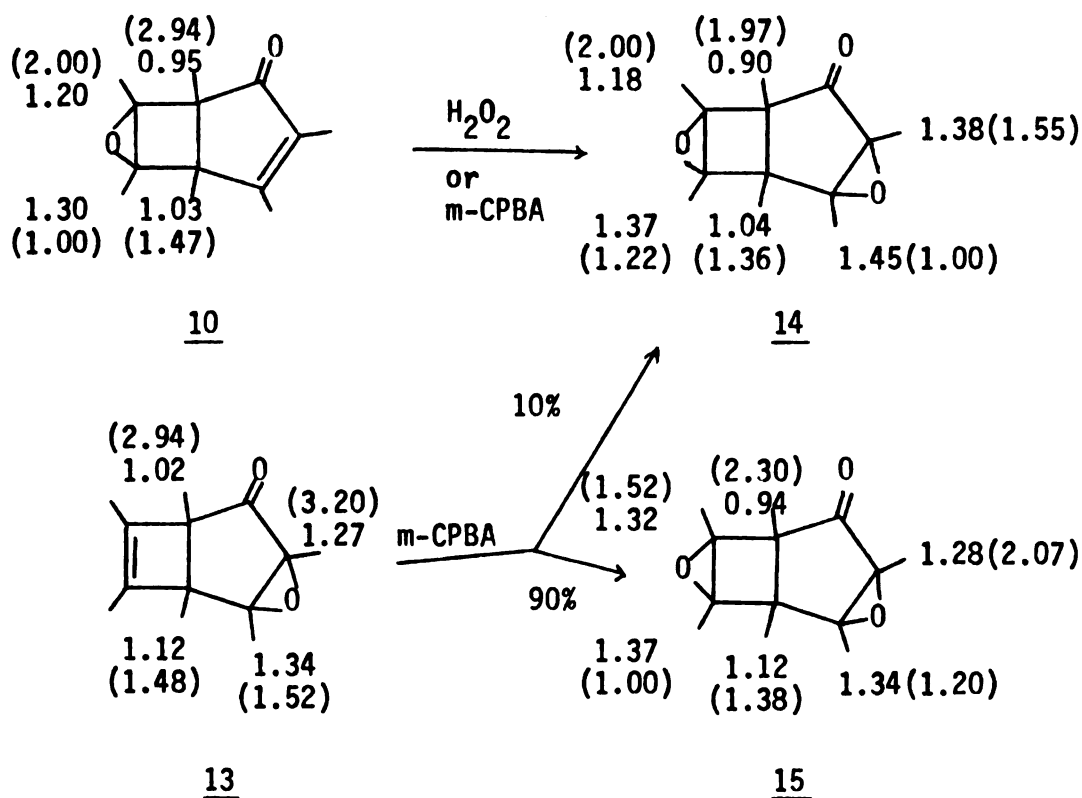
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When an excess of *m*-chloroperbenzoic acid was used, a single diepoxide 14 was formed from 1. Treatment of 10 with alkaline hydrogen peroxide also gave exclusively 14. However, treatment of 13 with *m*-chloroperbenzoic acid gave a mixture of two stereoisomeric diepoxides 15 and 14 in a ratio of 9 to 1.



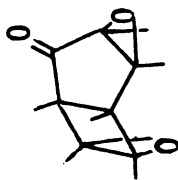
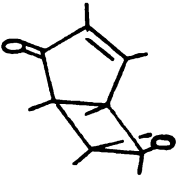
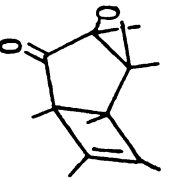
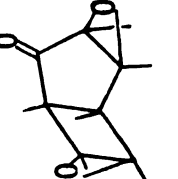
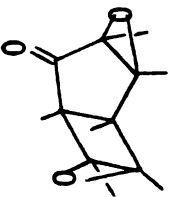
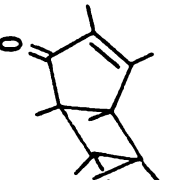
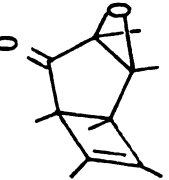
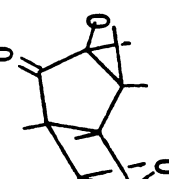
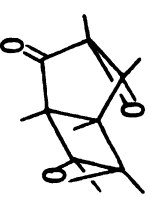
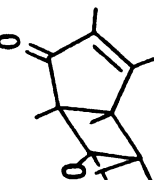
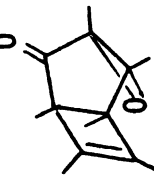
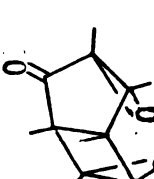
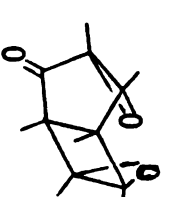
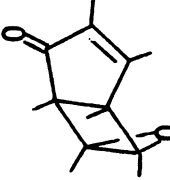
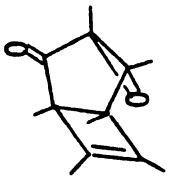
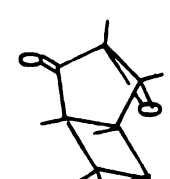
The chemical shifts and europium shift slopes of 14 and 15 are tentatively assigned as shown on the structural formulas.



The signal at the C-4 position of 14 and 15 was assigned by epoxidizing compound 13^{*} (labeled with a CD₃ group at the C-4 position). The remaining peaks were assigned by comparing with those of the monoepoxides from which they were derived.

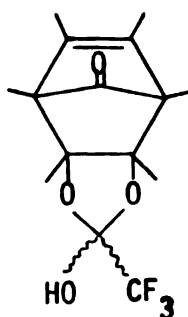
The configurations of these diepoxides (exo or endo) could not be determined. However, once the configuration of one of the diepoxides is determined, the configurations of the other diepoxide and the two monoepoxides 13 and 10 will be known. There are all together four sets of possible configurations of these epoxides (Table 1). Set 3 and Set 4 are least likely considering the unfavored diepoxide structure (15 in Set 3 and 14 in Set 4) with both epoxy groups having endo positions. The fact that the chemical shifts of the methyls at C-3 and C-4 of 14 (δ 1.38, 1.45) are at lower field than those of 13 (δ 1.27, 1.34) and 15 (δ 1.28, 1.34) is consistent with the configurations assigned in Set 1 in which the two methyls in 14, being close to the endo epoxy group, would be shifted to lower field. For this reason Set 1 is favored. However, the configuration of 14 in Set 1 does not explain why the europium shift slope of the C-7 methyl (2.00) is larger than that of the C-1 methyl (1.97). However in Set 2, the configuration assigned to 14 places the C-7 methyl group in an endo position, possibly closer to the binding site of the carbonyl group and europium shift reagent than the C-1 methyl group, offering an explanation for the larger europium shift slope of the C-7 methyl. Thus Set 2 remains a possibility.

Table 1. Possible Configurations of 10, 13, 14 and 15

	<u>14</u>	<u>10</u>	<u>13</u>	<u>15</u>
Set 1				
Set 2				
Set 3				
Set 4				

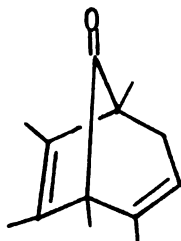
2. Acid-Catalyzed Rearrangement of Hexamethylbicyclo[3.2.0]hepta-3,4-epoxy-6-en-2-one (13)

Treatment of 13 with trifluoroacetic acid at 0°C for 1 hr gave a mixture of two stereoisomeric compounds to which structures 16 and 17 are assigned. It was not possible to separate the two isomers. The



two isomers: 16 and 17

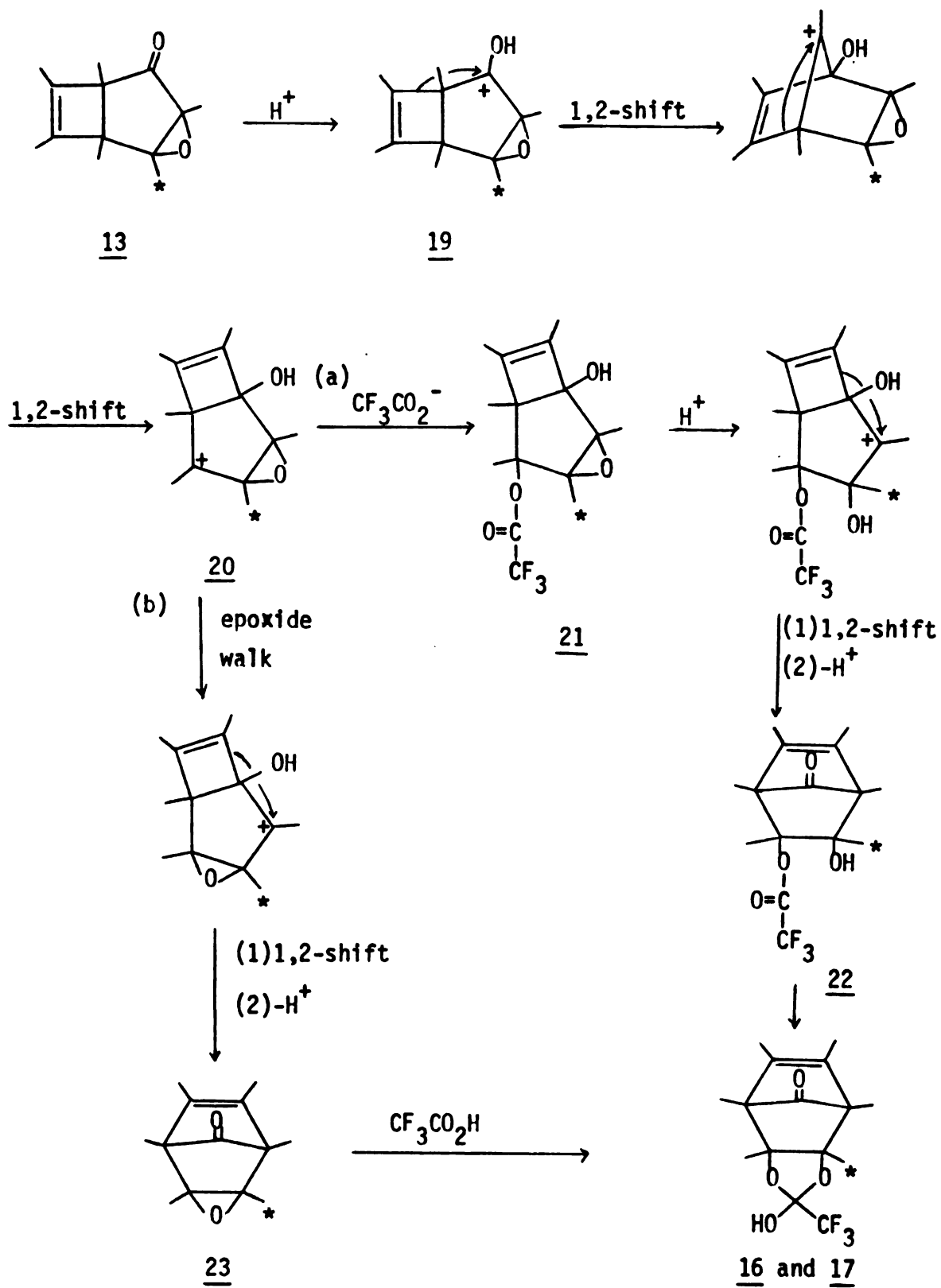
structures of these isomers were assigned based on their spectral properties though the configuration of each isomer could not be determined. The molecular formula $C_{15}H_{19}O_4F_3$ was confirmed by a mass spectrum (parent peak m/e 320) and elemental analysis. The ir spectrum showed a strong O-H stretching band at 3400 cm^{-1} ; the $\nu_{C=O}$ at 1755 cm^{-1} and uv maxima at 214 nm (ϵ 1,030) and 232 nm (ϵ 590) indicate that there is no conjugation in the molecule, and the position of the carbonyl absorption is consistent with its location in a strained five-membered ring. For example, compound 18² has a carbonyl absorption at 1753 cm^{-1} .



An ^{19}F NMR spectrum gave two signals with an area ratio of 10 to 9 corresponding to the magnetically different CF_3 groups in the two isomers 16 and 17. A PMR spectrum of the mixture in CCl_4 showed a singlet for the four aliphatic methyls at δ 1.20 and another singlet for the two vinyl methyls at δ 1.67. However, europium shift reagent resolved the signal at δ 1.20 into two singlets, thus gave a spectrum with three singlets of equal intensity with europium shift slopes of 2.36, 1.47 and 1.00 (two vinyl methyls). These three singlets were not resolved further by shift reagent but were broadened owing to the presence of the two isomers. Use of acetone- d_6 as the solvent resolved the PMR spectrum of the mixture into two sets of signals corresponding to compounds 16 and 17, with relative areas of 10:9. Compound 16 had three equal singlets at δ 1.12, 1.33 and 1.70 whereas compound 17 had three equal singlets at δ 1.15, 1.20 and 1.70.

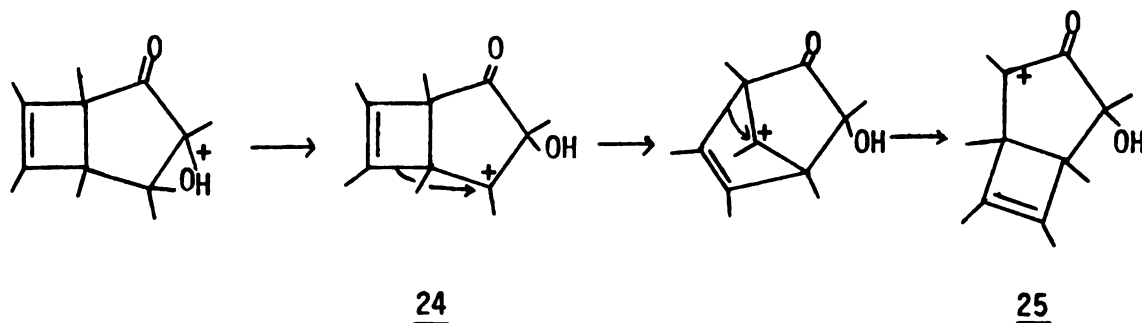
When the mixture of 16 and 17 was treated with a 7% solution of K_2CO_3 in aqueous MeOH for 4 hours the starting material was recovered quantitatively. The difficulty in the hydrolysis of 16 and 17 is consistent with the structure assigned. Although the structures of 16 and 17 are not rigorously proved, it is difficult to imagine an alternative structure which will satisfy the symmetry demands of the NMR spectra, and will also be consistent with the carbonyl absorption in the ir.

A plausible mechanism for the formation of 16 and 17 from 13 in TFA is shown in Scheme 4.

Scheme 4

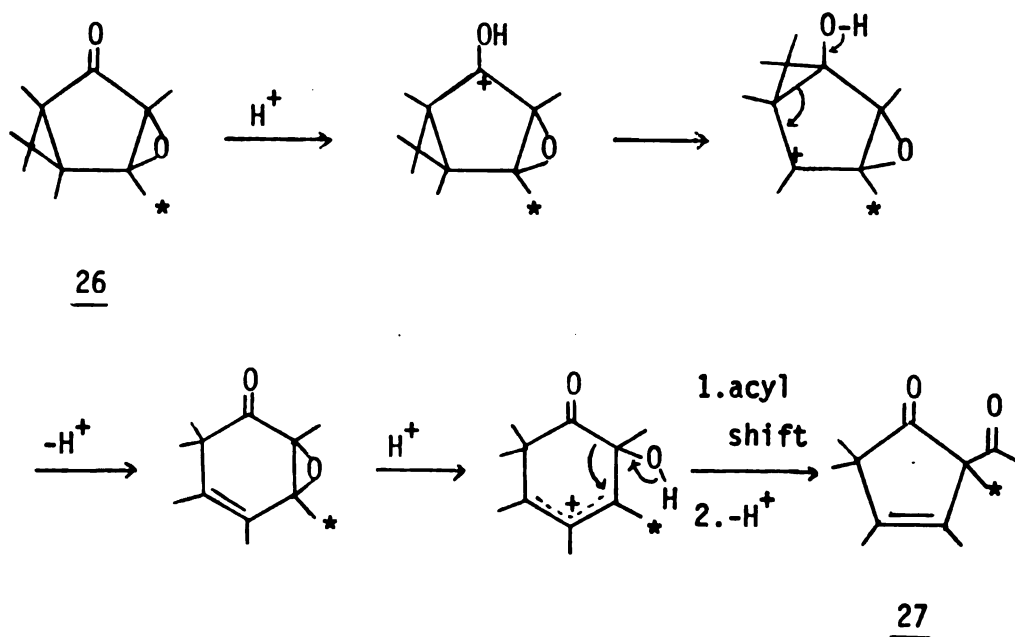
Protonation of the carbonyl oxygen and two 1,2-shifts gave cation 20, then followed by either route (a) or route (b) could lead to the final products. In route (a), 20 was first attacked by trifluoroacetate ion to give 21. Reprotonation followed by 1,2-shift and deprotonation gave 22, which on cyclization would give 16 and 17. In route (b), 20 could undergo epoxide walk process followed by 1,2-shift and deprotonation to give 23 which could be attacked by TFA to give 16 and 17.

The first step involves the protonation of the carbonyl oxygen. In general, the acid-catalyzed rearrangement of epoxy ketones is initiated by protonation of the epoxy oxygen atom⁵. However, if epoxide were protonated first, ring opening would occur in such a manner as to place the positive charge remote from carbonyl group to give ion 24. The subsequent rearrangements could not lead to the products observed but would only lead to carbonium ion 25 which is unfavored by having the positive charge α to the carbonyl group.

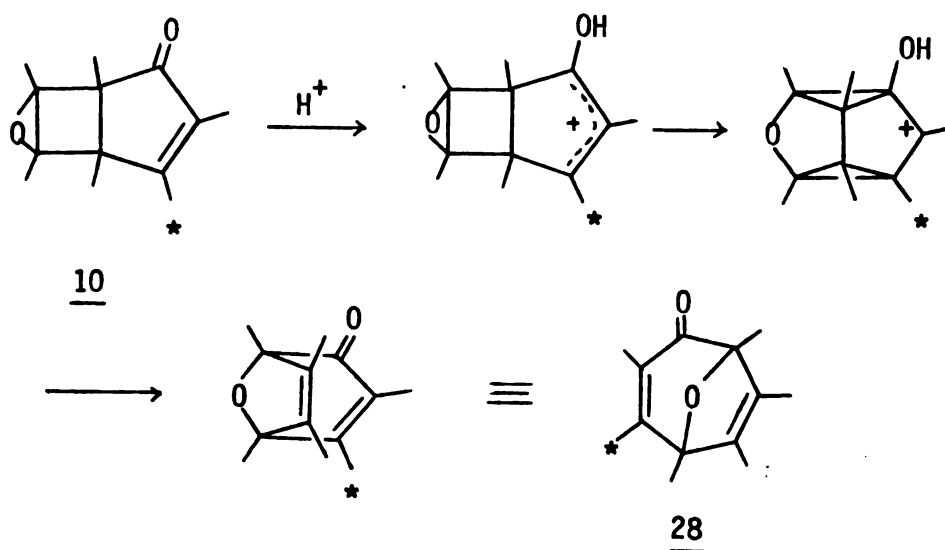


A few examples of the protonation of the carbonyl oxygen in an epoxyketone are known. For example, a competitive protonation at each oxygen of the epoxyketone 26 was reported by Hart and Huang⁶.

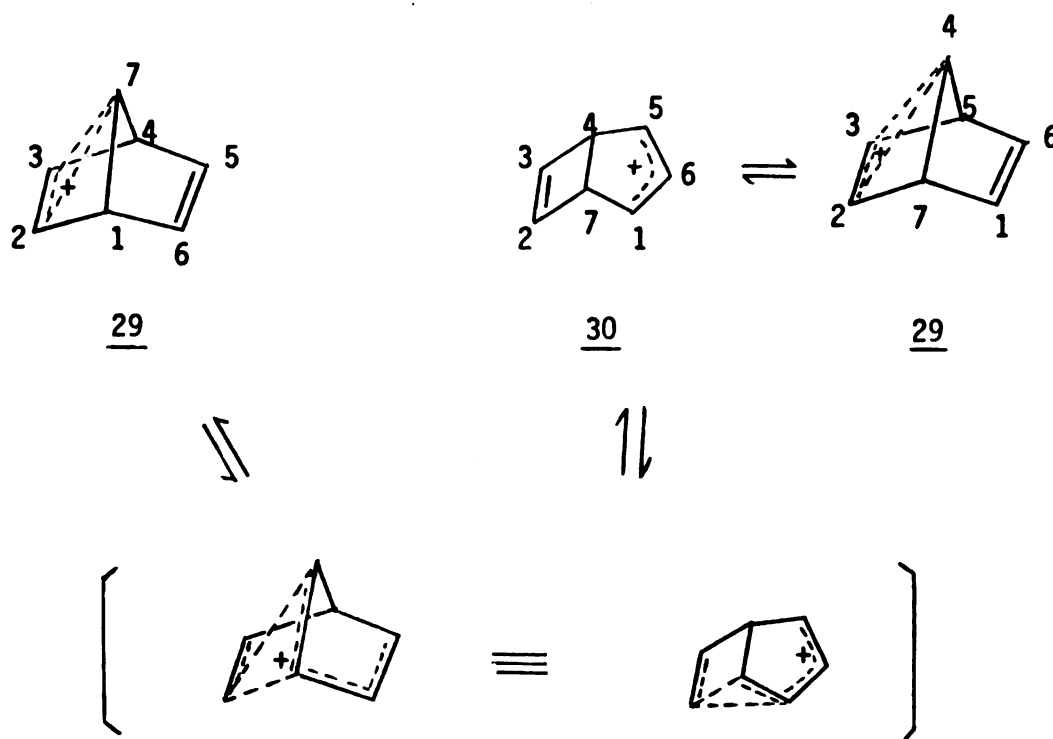
The formation of 27 from 26 involved initial protonation at the carbonyl oxygen, a mechanism consistent with labeling experiments.



An exclusive protonation at the carbonyl oxygen of an epoxy ketone had also been suggested³ in the acid-catalyzed rearrangement of compound 10 to 28.



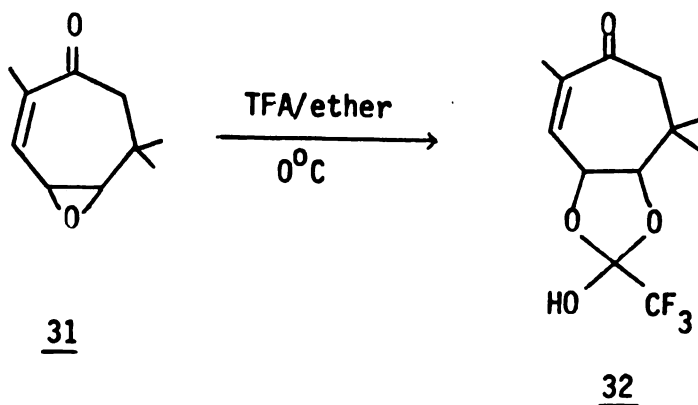
The rearrangement of 19 to 20 in Scheme 4 by two 1,2-shifts is a process closely related to the circumambulatory process which was postulated by Winstein and coworkers⁷ to rationalize the 5-carbon degenerate rearrangement (shown by deuterium labeling) of the 7-norbornadienyl cation 29. The suggested mechanism involved a shift of C-2 from C-1 to C-7 (or by symmetry, C-3 from C-4 to C-7) to form



30, which through the reverse process was reconverted to 29, but with the carbon skeleton in a different sequence. In this process the bond vinyl group (C-2, C-3) maintains its identity, but circumambulates about the five-membered ring.

Finally, there is precedent for the unusual ortho ester type of

functionality postulated for 16 and 17. A cyclization process of trifluoroacetic acid with epoxide similar to the present case had been found in the acid treatment of 31 with TFA⁸. Compound 32 was the major product of the reaction. The driving force of this reaction is still unknown.



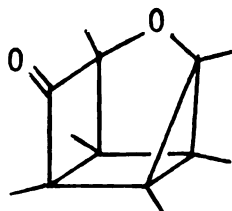
When 13 labeled with a CD_3 group at the C-4 position was subjected to the same acid rearrangement conditions, the products were found to be 16 and 17 with one of the four aliphatic methyls labeled. This result is consistent with the proposed mechanism.

3. Photolysis of 13

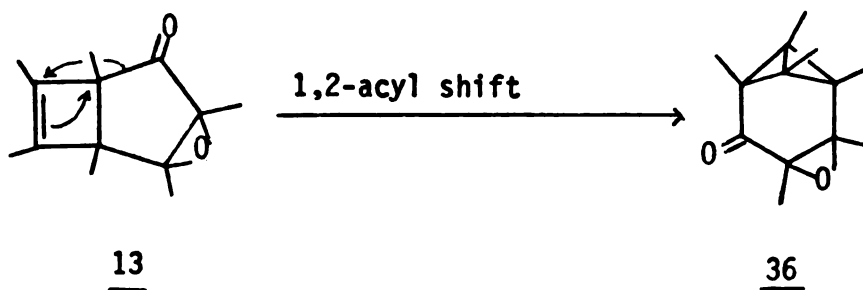
The extensive rearrangements of aliphatic α,β -epoxyketones upon ultraviolet light irradiation are attributable to transformations of the $n \rightarrow \pi^*$ excited state⁹. Compound 13 has an $n \rightarrow \pi^*$ absorption at λ_{max} 315 nm (ϵ 320); thus a pyrex filter was used for the irradiation of 13.

The photolysis of 13 in ether through Pyrex was followed by vpc. The peak corresponding to 13 disappeared completely in about 18 hr. During that period, one major peak corresponding to 33 and two minor peaks corresponding to 12 and 34 were growing in area. However, the NMR spectrum of the crude reaction mixture did not show the signals corresponding to 33. It showed mainly the signals corresponding to another compound 35, along with those corresponding to 12 and 34. Obviously the photolysis of 13 gave 35 (70%), 12 (8%) and 34 (5%) as products but the major product 35 decomposed thermally on being subjected to gas chromatography, to give compound 33. Attempts to isolate 35 by using tlc plates failed due to its decomposition on the plates.

By comparing the spectral data with those of the authentic samples, compound 12 was identified as pentamethylphenol, compound 34 as pentamethylphenyl acetate and compound 33 as 1-acetyl-pentamethylcyclopentadiene. Compound 35 is tentatively assigned the unusual strained cage structure shown, on the basis of the following spectral data, and on its subsequent thermal reaction to give 33. The NMR spectrum of 35 showed that all of the methyl groups were aliphatic

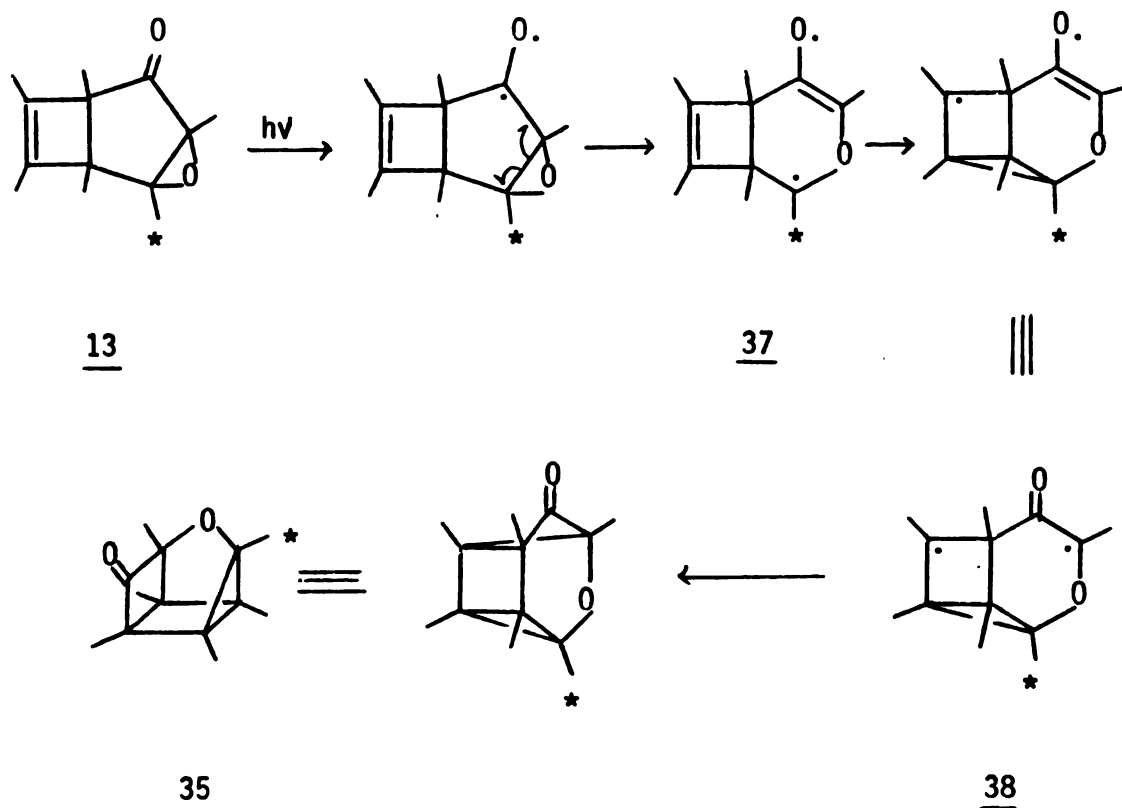
35

(all signals at $\delta \leq 1.26$). Europium shift reagent removed the accidental degeneracy of the two methyls at δ 1.00 and the two methyls at δ 1.26 to give a spectrum with six singlets, showing that each methyl group was unique and that there could be no symmetry in the molecule. The ir band at 1760 cm^{-1} is attributed to the cyclobutanone absorption. These spectral data severely restrict the possible structures. For example, an alternative structure with all methyls aliphatic could arise by a 1,2-acyl shift (oxa-di- π -methane rearrangement¹⁰) of 13:

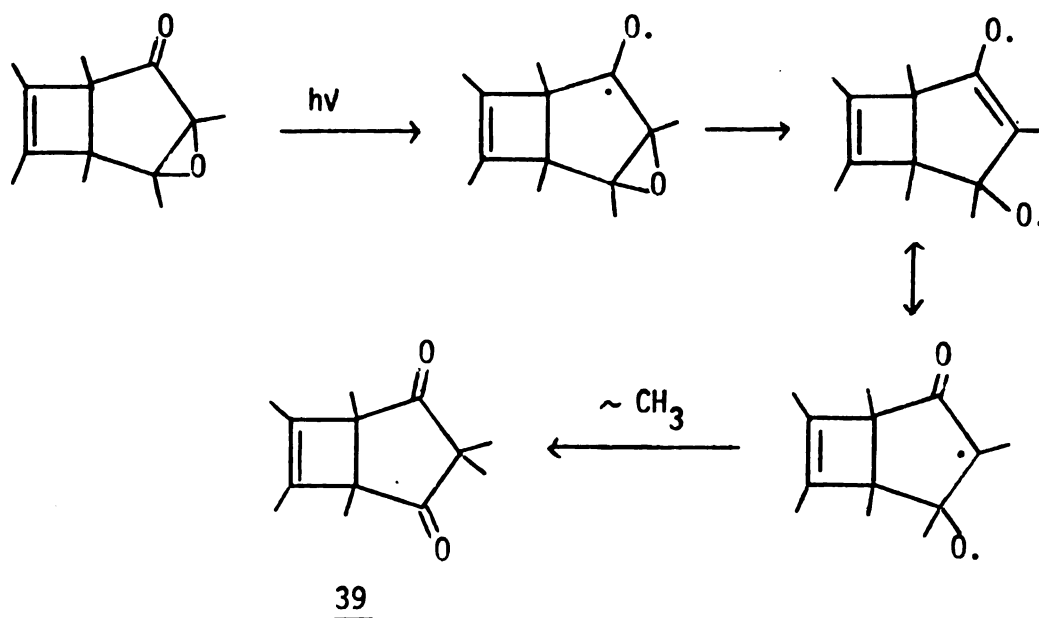
1336

However, although 36 has six unique methyl groups and therefore could be consistent with the NMR spectrum, it is not consistent with a carbonyl frequency at 1760 cm^{-1} .

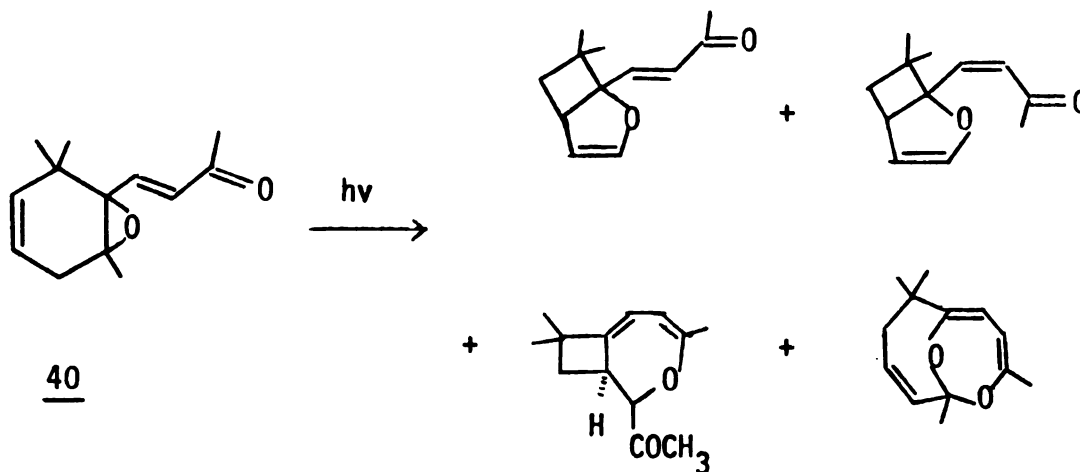
A plausible mechanism can be deduced for the formation of 35 and for its rearrangement to 33. The following mechanism is proposed for the formation of 35 from 13:



After electron promotion through the $n \rightarrow \pi^*$ state, the C-C bond in the epoxy ring was broken to give diradical 37. Participation of the β,γ -double bond formed 38. Ring closure to the diradical 38 would give 35. The feature of this mechanism that is unique is the C-C bond cleavage. Normally, one might have expected 13 to rearrange as follows⁹:

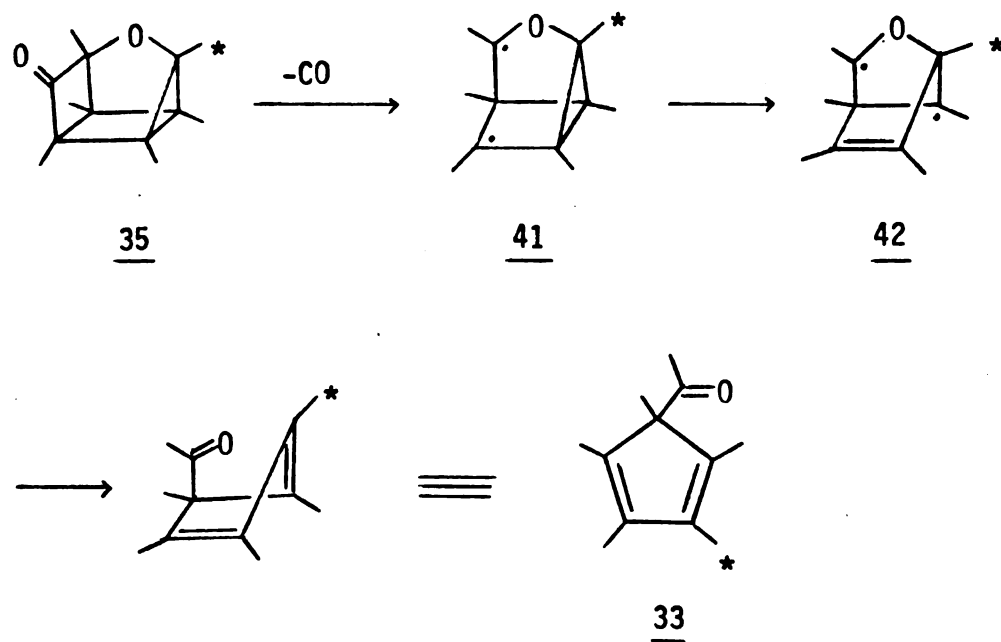


Indeed this was the process which was anticipated, but the properties of the product were clearly inconsistent with structure 39. However, there is precedent, though rare, for C-C bond cleavage in the ring opening of epoxides. For example, the photolysis of compound 40 which led to the formation of the four isomers seems to involve the C-C bond cleavage of the epoxide ring as the key step¹¹.

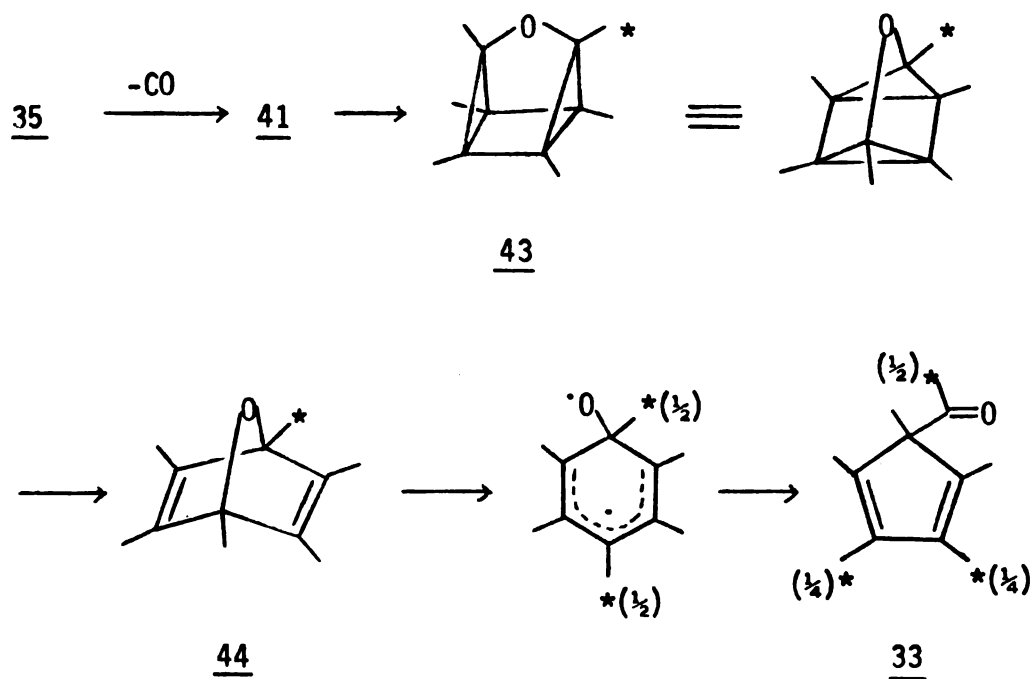


Three possible mechanisms to rationalize the thermal decomposition of 35 to 33 were considered:

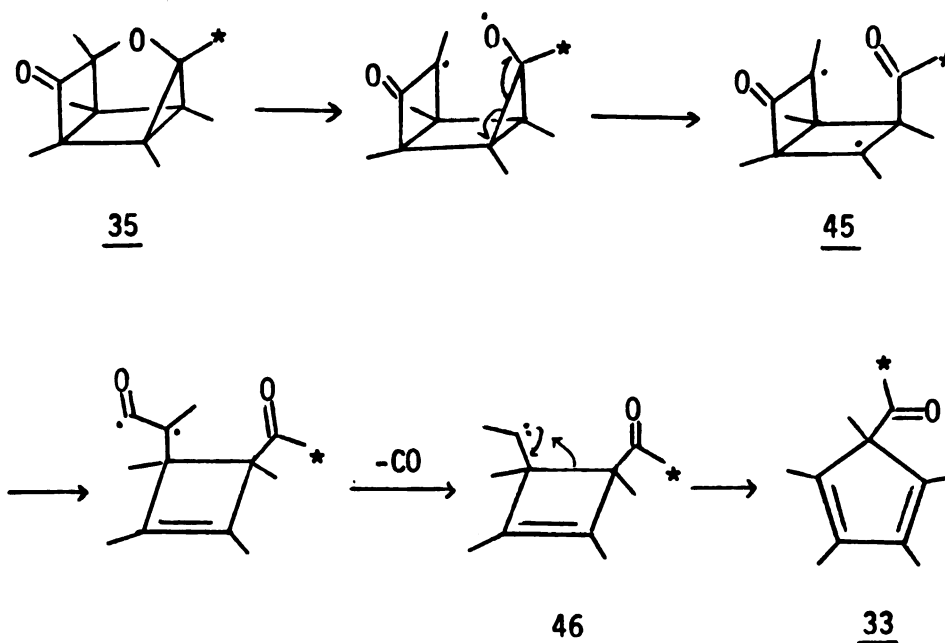
(A)



(B)



(c)



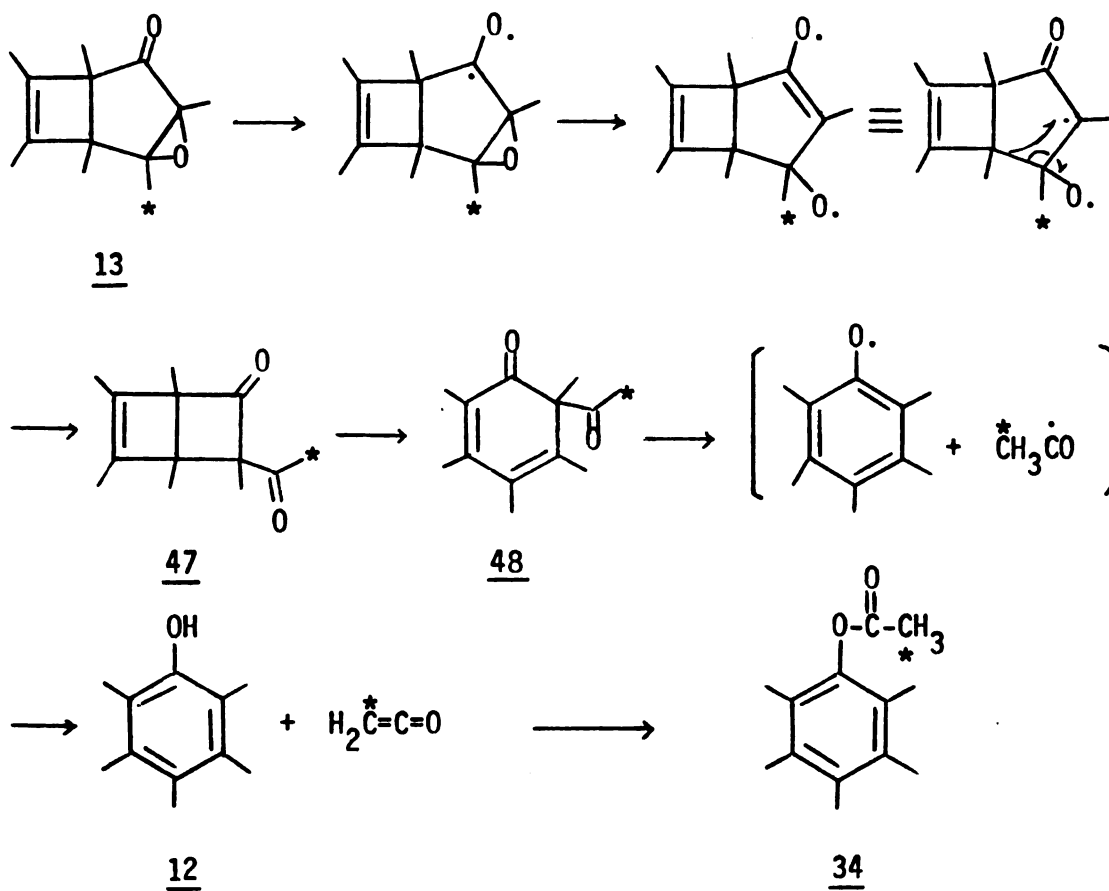
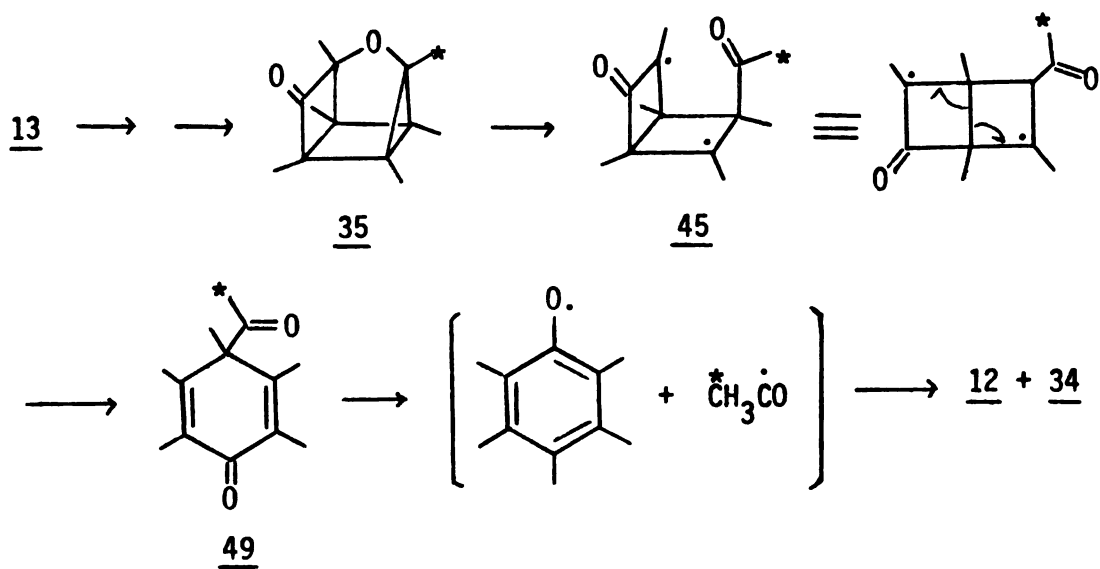
The first two mechanisms (A) and (B) involve decarbonylation as the initial step. In mechanism (A), cyclopropyl ring opening of 41 could give 42, and cleavage of the C-O bond could give 33. In mechanism (B), ring closure of the diradical 41 would give 43. Isomerization to 44 followed by cleavage of the C-O bond and ring contraction could give 33. Mechanism (C) involves cleavage of a C-O bond as the initial step. Opening of cyclopropyl ring followed by cleavage of the bond α to the carbonyl group and decarbonylation could give carbene 46, which could undergo ring expansion to give 33. Undoubtedly other mechanisms than those shown could also be devised, and some steps in the above mechanism could be coupled or concerted, rather than discrete.

In order to obtain additional mechanistic information, the photolysis was carried out by irradiating compound 13^{*} which was labeled at the C-4 position with a CD₃ group. Product 35^{*} lacked the NMR signal

of one of the methyl groups at δ 1.26, as shown by a europium-shifted spectrum. However careful examination of the NMR spectrum of compound 33^{*} obtained from the thermal decomposition of 35^{*} showed that the signal of the acetyl methyl group was reduced about 50% in area while the signals of all other methyls retained their full intensity. It is possible that the deuterated acetyl methyl was partly exchanged although how it was exchanged is still unknown. The labeling result rules out path (A) and (B) because both of these mechanisms would result in label (or partial label) at the vinyl methyls. Path (C), with a full label at the acetyl methyl group, is more favored to be correct.

The formation of the two minor photoproducts 12 and 34 from 13 can be rationalized by the mechanisms in schemes 5 and 6. Scheme 5 involves breaking of the epoxy C-O bond followed by ring contraction to give β -diketone 47. This feature of the mechanism is not too appealing, but if coupled with the next step might have a reasonable driving force due to relief of strain. Ring opening could give 48, which could easily eliminate one molecule of ketene to form 12. Compound 12 could recombine with ketene to form 34. Scheme 6 involves the formation of 35 as an intermediate. The same path as in the rearrangement of 35 in mechanism (C) to give 45, followed by ring opening could give 49, which could eliminate ketene to give 12 and 34.

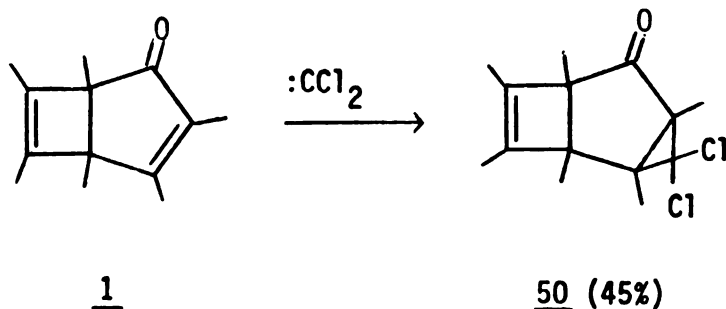
Scheme 5 and 6, which give the same labeling position in 34^{*} (at the acetyl group) by photolysis of 13^{*}, were both consistent with the experimental results.

Scheme 5Scheme 6

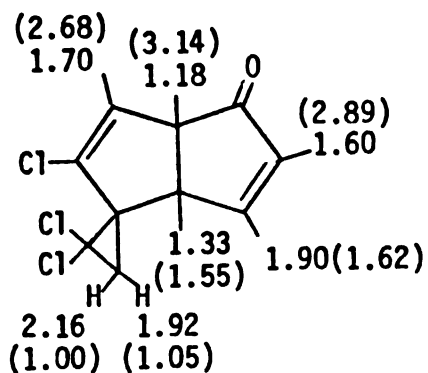
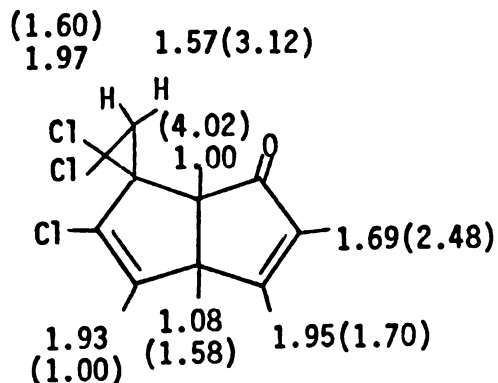
4. Addition of Dichlorocarbene to Hexamethylbicyclo(3.2.0)hepta-3,6-dien-2-one (1)

The method of generating of dichlorocarbene by the action of aqueous alkali on chloroform in the presence of triethylbenzylammonium chloride developed by Makosza and Wawrzyniewicz¹² was used for the addition of dichlorocarbene to compound 1. Three products, 50 (45%), 51 (3.8%) and 52 (3.3%) were obtained in this reaction.

Compound 50 was assigned the structure shown based on spectral properties. The molecular formula $C_{14}H_{18}OCl_2$ was confirmed by the mass spectrum and elemental analysis. The NMR spectrum showed two mutually coupled vinyl methyl groups (δ 1.43, 1.65), and the ir band at 1715 cm^{-1} and the uv maxima at 230 nm (ϵ 2,210) and 305 (440) indicated that the carbonyl group was unconjugated. Therefore the carbene must have added to the double bond in the five-membered ring.

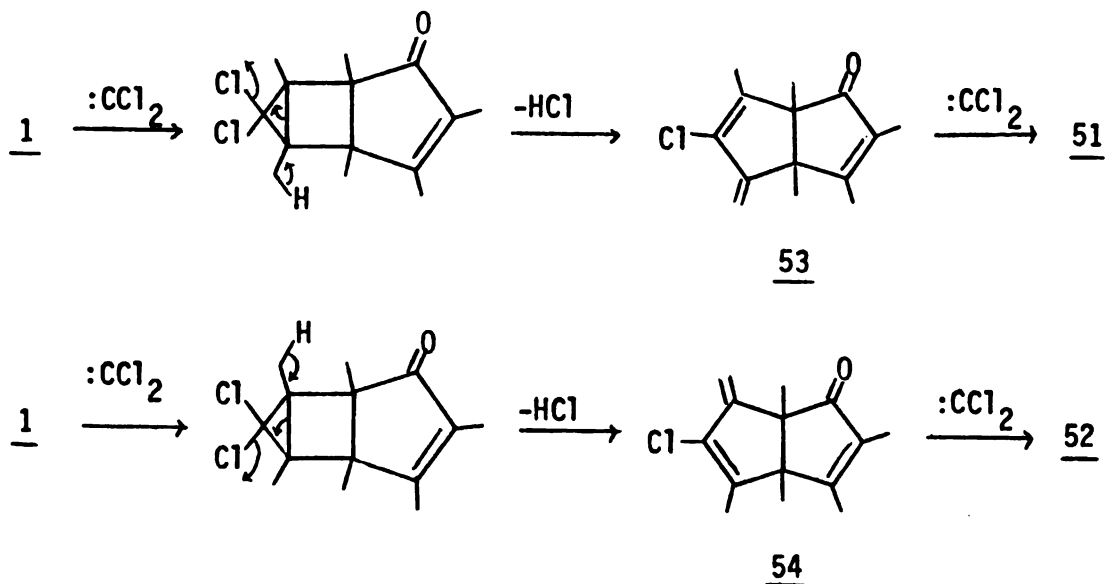


Compounds 51 and 52 were assigned the structures shown. They had similar spectral properties. The molecular formula $C_{15}H_{17}OCl_3$ was confirmed by mass spectra and elemental analyses. NMR signals of 51 showed two mutually coupled vinyl methyls (δ 1.60, 1.90) and two mutually coupled hydrogens (δ 1.92, 2.16, $J = 8\text{ Hz}$); an ir band at 1690 cm^{-1} and

5152

a uv maximum at 242 nm (ϵ 8,700) indicated the presence of a conjugated carbonyl group in a five-membered ring. The distinction between 51 and 52 was based on their europium shift slopes, which showed that in 51 the two hydrogens are remote from the carbonyl group whereas in 52 the methyl adjacent to the chlorine is the one that is furthest from the carbonyl group.

51 and 52 were presumably formed by the following mechanism:

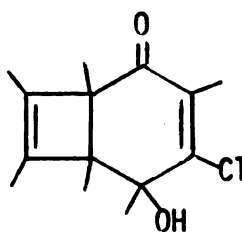


Addition of the dichlorocarbene to the double bond in the four-membered ring followed by elimination of HCl gave 53 and 54. Further attack by dichlorocarbene on the exocyclic double bond gave 51 and 52.

5. Acid-Catalyzed Rearrangement of 4,4-dichloro-1,3,5,6,7,8-hexamethyl-tricyclo(4.2.0.0^{3.5})octa-7-en-2-one (50)

A. Silver Perchlorate Promoted Ring Expansion of 50

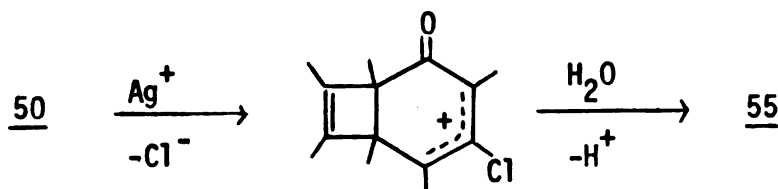
When 50 was treated with an excess of silver perchlorate in aqueous acetone, the dichlorocarbene adduct underwent a ring expansion reaction to give 55. The structure of 55 was assigned as shown based on spectral properties.



55

The molecular formula $C_{14}H_{19}O_2Cl$ was confirmed by a mass spectrum and elemental analysis. The ir band at 1660 cm^{-1} and uv maxima at 237 nm (ϵ 2,700), 248 (4,650) and 285 (1,230) are consistent with a conjugated carbonyl group in a six-membered ring. The presence of a hydroxyl group is clear from the ir band at 3460 cm^{-1} and from the presence of a one-proton peak in the NMR spectrum at δ 2.03. Two mutually coupled vinyl methyls (δ 1.40, 1.62) were also shown by NMR, in addition to singlets for the four remaining methyl groups.

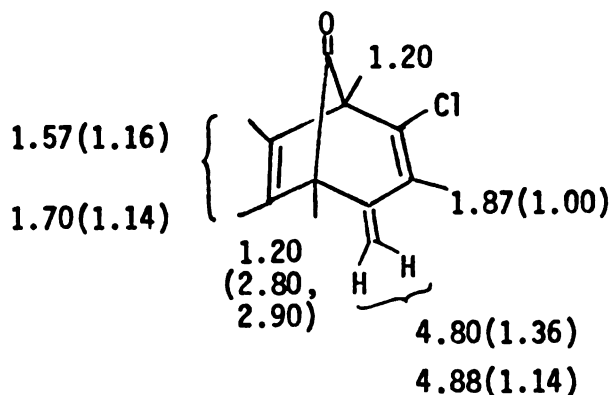
Compound 55 was presumably formed by loss of a chloride ion followed by attack of water on the resulting carbocation.



B. Acid-Catalyzed Rearrangement of 50 in Sulfuric Acid

When a solution of 50 in methylene chloride and methanol was treated with concentrated sulfuric acid at 0°C , two products 56 (10%) and 57 (72%) were formed within 10 minutes.

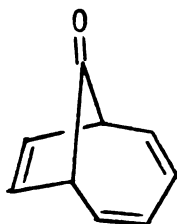
Compound 56 was assigned the structure shown based on spectral properties. The molecular formula $\text{C}_{14}\text{H}_{17}\text{OCl}$ is confirmed by a mass



56

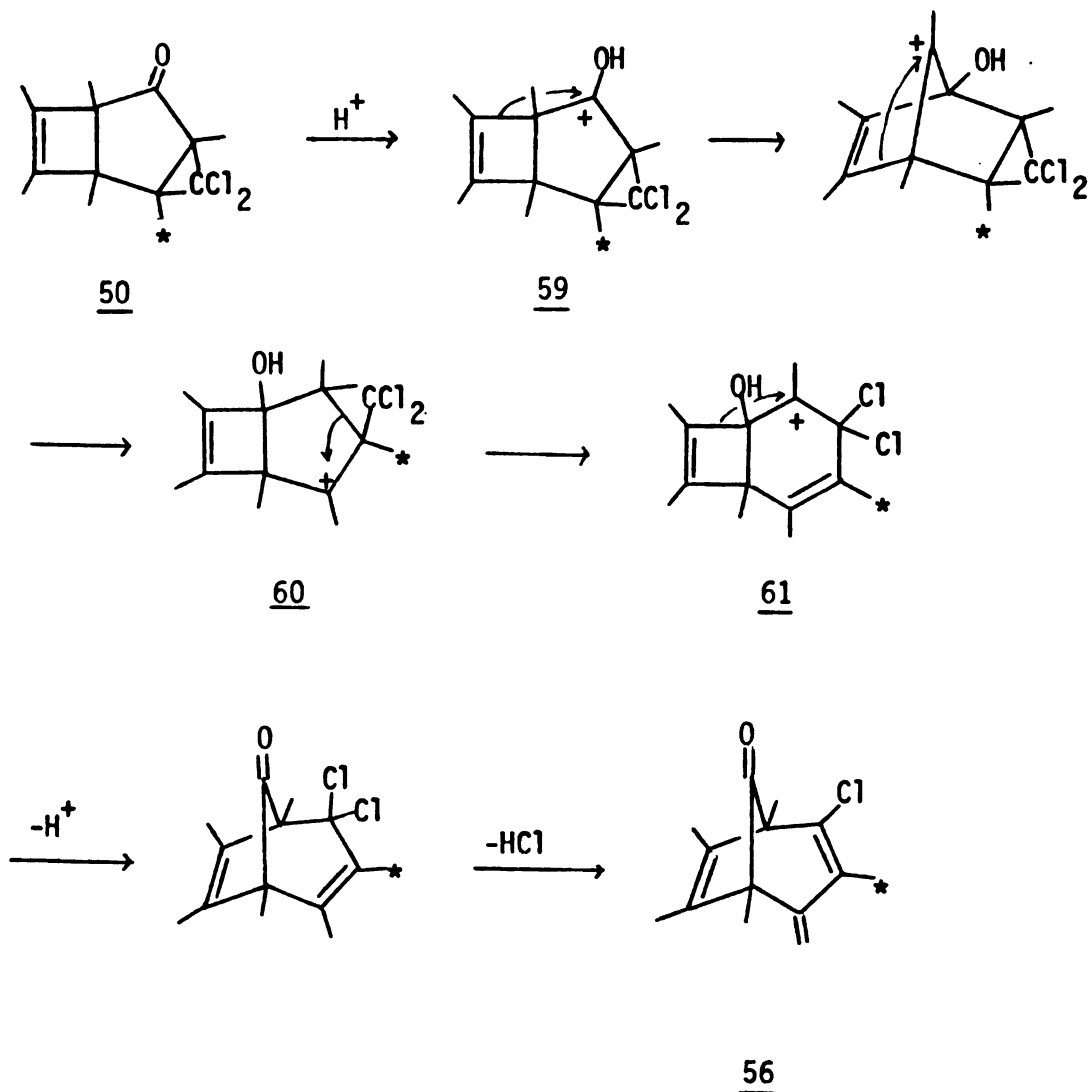
spectrum (parent peak m/e 238). The NMR spectrum showed two mutually coupled vinyl methyls (δ 1.57, 1.70), two vinyl protons (δ 4.80, 4.88),

two aliphatic methyls (δ 1.20) and a singlet vinyl methyl. The europium shift slopes shown on structure clearly indicated that the two aliphatic methyls are close to the carbonyl group whereas the other methyls and methylene group are relatively far away. The uv maxima at 217 nm (ϵ 8,570) and 253 (11,800) indicated a conjugated system. The ir band at 1775 cm^{-1} is indicative of the bridged carbonyl group; compare, for example, with the $\nu_{\text{C=O}}$ of compound 58¹³.

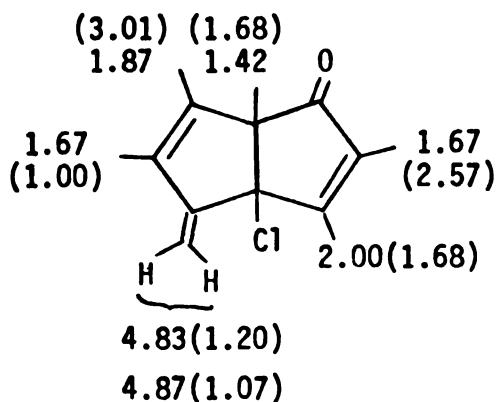
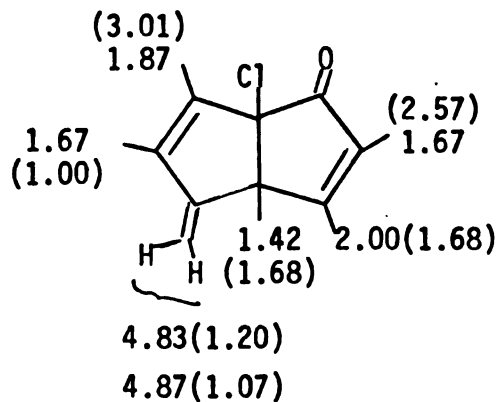
58 $\nu_{\text{C=O}}\ 1780\text{ cm}^{-1}$

A possible route to 56 is shown in Scheme 7. Protonation of the carbonyl oxygen would give 59. The rearrangement of 59 to 60 is a circumambulatory type process similar to the path from 19 to 20 (Scheme 4) in the acid-catalyzed rearrangement of 13. Ring opening would give 61. A 1,2-shift followed by deprotonation and elimination of HCl can lead to 56.

When 50^{*} (derived from dichlorocarbene addition to 1^{*}) was subjected to the same acid conditions, the product 56^{*} lacked the NMR signal at δ 1.87. This result is consistent with the proposed mechanism.

Scheme 7

Two possible structures A and B were considered for the major product compound 57, based on its spectral properties. The molecular formula was confirmed by a mass spectrum (parent peak m/e 238). The ir band at 1705 cm^{-1} is consistent with a conjugated carbonyl group in five-membered ring. The uv maximum at 237 nm (ϵ 14,100) also indicates conjugation. The NMR spectrum and europium shift slopes are shown on

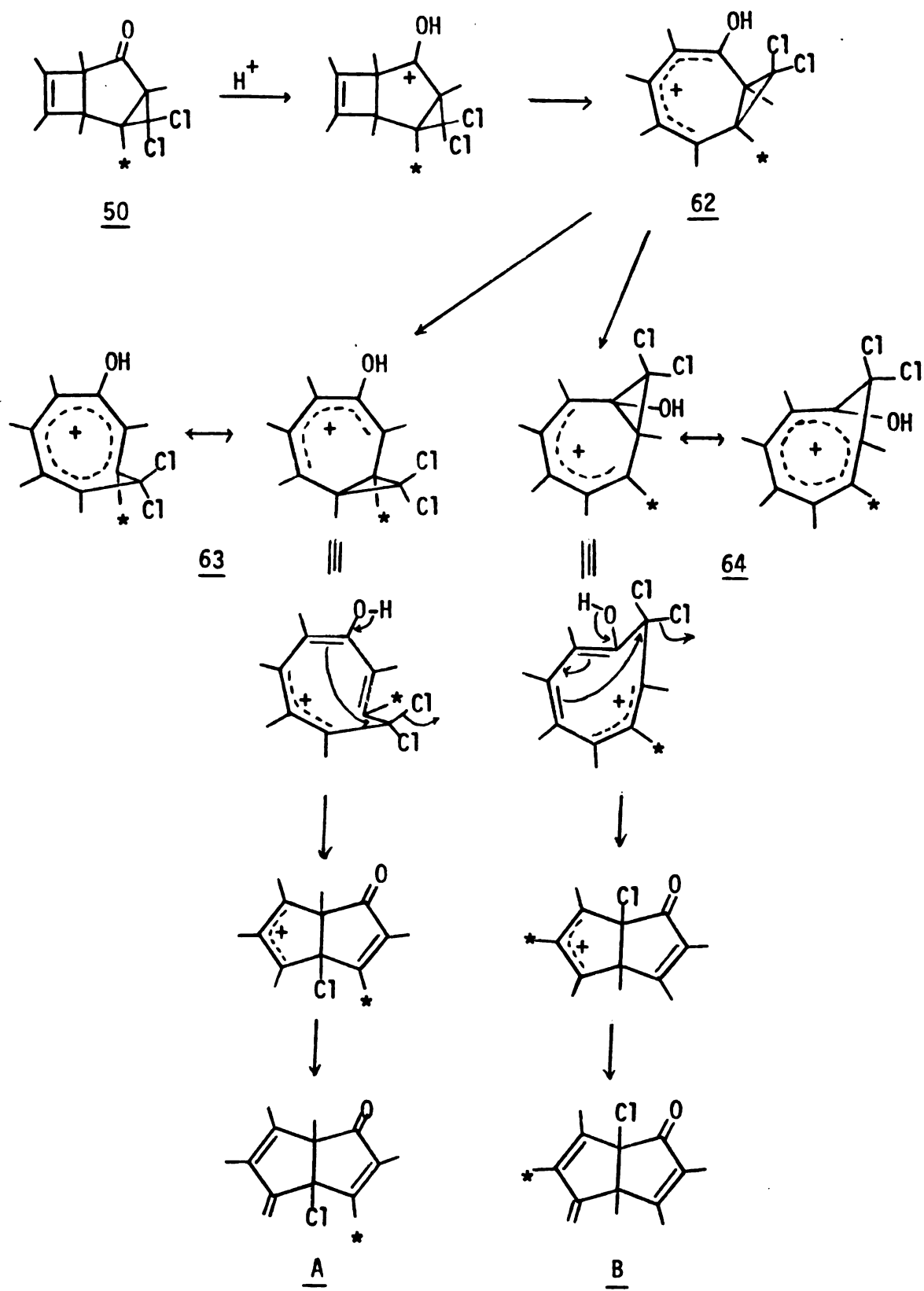
AB

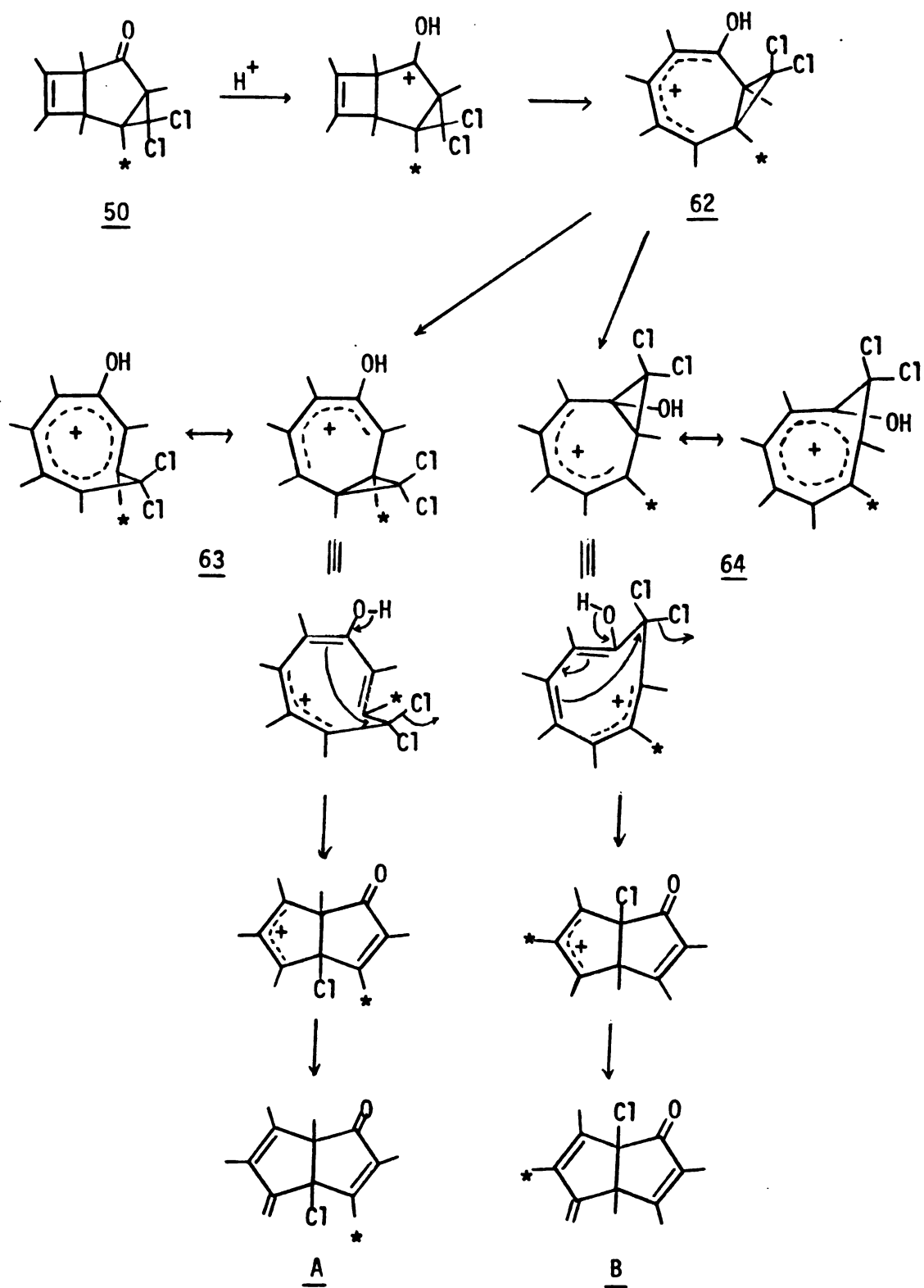
the structures. There are four vinyl methyls (δ 2.00, 1.87 and two at 1.67) each of which shows homoallylic coupling, two vinyl hydrogens (δ 4.83, 4.87) and an aliphatic methyl (δ 1.42).

The conjugation of the exocyclic double bond with one of the double bonds in the ring was confirmed by a deuterium exchange experiment. When 57 was treated with deuterio-trifluoroacetic acid at room temperature, the NMR signals at δ 4.83, 4.87 and 1.87 disappeared in 10 min, and a europium shifted spectrum showed that the signal at δ 1.67 (Eu-shift slope 1.00) had sharpened to a singlet. This phenomenon is consistent with both structures A and B.

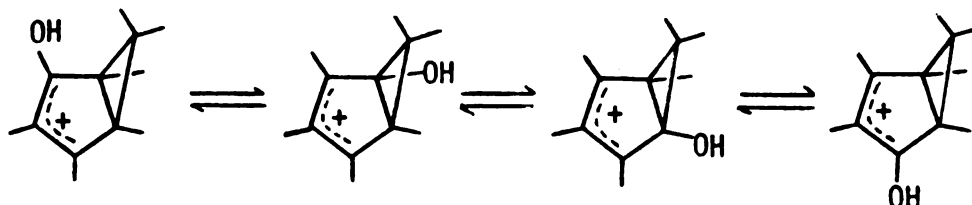
An attempt to deuterate compound 57 in $\text{CH}_3\text{ONa}/\text{MeOD}$ solution failed due to the instability of 57 under basic conditions.

Possible routes to A and B are shown in Scheme 8. Protonation of 50 followed by ring opening could give cation 62. A [1,6] sigmatropic shift of 62 could lead to either 63 or 64. Elimination of HCl accompanied by ring closure followed by deprotonation could lead to A or B.

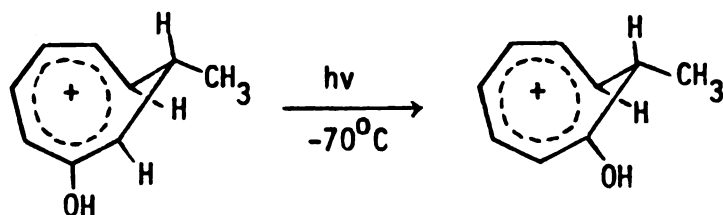
Scheme 8



The rearrangement of 62 to 63 or 64 is similar to the well established¹⁴ degenerate rearrangement of the bicyclo(3.1.0)hex-3-en-2-yl cation which was first reported by Swatton and Hart¹⁵.



However, the degenerate rearrangement of the homotropylium cation, though symmetry allowed, has not been detected thermally¹⁶. A photo-induced rearrangement of the 2-hydroxyhomotropylium cation 65¹⁷ has been reported recently by Childs and Rogerson.



65

The difference in energetics between the rearrangements of the homotropylium cation and the bicyclo(3.1.0)hexenyl cation have been rationalized in terms of stabilization of the ground-state of homotropylium cations through aromaticity¹⁸. Although the proposed mechanism in Scheme 7 is still doubtful, it does provide a good explanation for the

formation of A or B.

Structure A or B could be tested by labeling experiments. However, the product 57^{*} derived from 50^{*} showed no deuterium labeling. One rationale is that the deuterons of the CD₃ group were exchanged during the workup steps. Thus structure A, which would have the deuterated methyl group in an enolizable position, is more favored to be the structure of compound 57.

EXPERIMENTAL

1. General Procedures

Except where otherwise noted, all NMR spectra were measured in CDCl_3 or CCl_4 solutions using TMS as an internal standard. The 60 MHz spectra were recorded on a Varian T-60 spectrometer. The small numbers placed next to protons in the structures in the results and discussion section are the NMR chemical shifts of those protons. The numbers beside the chemical shifts in parentheses are the normalized europium shift numbers. These were obtained by adding small increments of tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione)Eu(III) to the CDCl_3 or CCl_4 solution of the compound being investigated. After each addition the NMR spectrum was scanned and the new frequency of each absorption was recorded. The shift for each absorption is the difference between the frequency of the shifted absorption and the original one. The normalized shift numbers are ratios obtained by dividing the shift of each signal in the spectrum by the shift of the least shifted signal.

Infrared spectra were taken on a Perkin Elmer 237 grating spectrophotometer and were calibrated against a polystyrene film. Ultraviolet spectra were obtained with a Unicam SP-800 in methanol unless otherwise noted. Mass spectra were obtained from a Hitachi-Perkin Elmer RMU-6 operated by Mrs. Ralph Guile. Melting points were determined with a Thomas-Hoover Melting Point Apparatus and are uncorrected. Varian

Aerograph gas chromatographs were used. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

2. Epoxidation of Hexamethylbicyclo(3.2.0)hepta-3,6-dien-2-one (1)
with Alkaline Hydrogen Peroxide

To a solution containing 2.0 g (10.5 mmol) of 1 and 3.6 g (31.5 mmol) of 30% aqueous hydrogen peroxide in 10 ml of methanol was added, at 0°C, 1 ml (6 mmol) of 6N aqueous sodium hydroxide. After being stirred at room temperature overnight, the reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with saturated salt solution and dried (MgSO₄). Evaporation of the solvent left 2.01 g (9.76 mmol, 93%) of a colorless oil considered to be hexamethylbicyclo(3.2.0)hepta-3,4-epoxy-6-en-2-one (13), which on standing at room temperature for 1 hr gave colorless crystals, mp 40-41°C; NMR (CCl₄) δ 1.02 (s, 3H), 1.12 (s, 3H), 1.27 (s, 3H), 1.34 (s, 3H), 1.43 (q, 3H, J = 1 Hz), 1.58 (q, 3H, J = 1 Hz); ir (neat) 3000 (s), 2900 (m), 1720 (s), 1455 (s), 1380 (s), 1315 (w), 1280 (w), 1250 (w), 1175 (m), 1110 (m), 1070 (m), 1060 (m), 1050 (m), 1020 (s), 860 (s), 740 (w) cm⁻¹; uv (MeOH) $\lambda_{\max}$ 215 nm (ϵ 1,950), 237 (1,340), 315 (320); mass spectrum (70 ev) m/e (rel intensity) 206 (33), 178 (8), 164 (9), 163 (8), 149 (15), 136 (53), 135 (100), 121 (32), 119 (35), 107 (20), 105 (26), 93 (16), 91 (23), 79 (12).

Anal. Calcd. for C₁₃H₁₈O₂: C, 75.69; H, 8.80.

Found: C, 75.49; H, 8.82.

3. Preparation of 4-Trideuterohexamethylbicyclo{3.2.0}hepta-3,6-dien-2-one (1^{*})

A solution of 500 mg of 1 in 10 ml of CH₃OD containing 100 mg of NaOCH₃ was allowed to stir at room temperature overnight. The reaction mixture was then poured into ice-water and extracted with ether. The ether layer was washed with water and dried (MgSO₄). Removal of the solvent gave quantitative yield of 1^{*}.

4. Epoxidation of 1^{*}

The procedure and workup were as described for the epoxidation of 1. The product 13^{*} had an NMR spectrum identical with that of 13 except that the signal at δ 1.34 was absent.

5. Epoxidation of Hexamethylbicyclo{3.2.0}hepta-3,4-epoxy-6-en-2-one (13) with m-Chloroperbenzoic Acid

To a solution of 206 mg (1.0 mmol) of 13 in 2 ml of methylene chloride was added, at 0°C, a solution of 250 mg (1.23 mmol) of m-chloroperbenzoic acid in 3 ml of methylene chloride. The mixture was stirred at 0°C for 5 hr. After the solvent was evaporated under reduced pressure, petroleum ether (bp 30-60°) was added to the residue. The precipitated m-chlorobenzoic acid was removed by filtration. The filtrate was washed successively with aqueous sodium bicarbonate, saturated salt solution and dried (MgSO₄). Evaporation of the solvent left 200 mg of a colorless oil. The crude material was considered to be a mixture of two stereoisomeric diepoxides hexamethylbicyclo{3.2.0}-hepta-3,4;6,7-diepoxy-2-one (15 and 14) in a 9:1 ratio shown by the

NMR spectrum. Preparative vpc (6'x0.25 in column, 15% SE-30 on chromo-sorb W, AW-DMCS 60/80, 165°C, 60 ml/min) gave 14 (ret time 4 min), which on standing at room temperature for hours gave white crystals, mp 86-87°C. NMR (CCl₄) δ 0.90 (s, 3H), 1.04 (s, 3H), 1.18 (s, 3H), 1.37 (s, 3H), 1.38 (s, 3H), 1.45 (s, 3H); ir (neat) 2970 (m), 2940 (m), 2880 (w), 1740 (s), 1450 (m), 1375 (m), 1265 (w), 1175 (w), 1160 (m), 1110 (w), 1085 (w), 1065 (w), 1050 (m), 850 (w), 820 (w), 760 (w) cm⁻¹; uv (MeOH) λ_{max} 215 nm (ε 1,110), 310 (60); mass spectrum (70 ev) m/e (rel intensity) 222(1), 164 (8), 151 (36), 149 (8), 137 (22), 136 (9), 125 (11), 124 (100), 123 (30), 109 (41), 91 (10), 81 (11).

Anal. Calcd. for C₁₃H₁₈O₃: C, 70.24; H, 8.16.

Found: C, 70.22; H, 8.16.

15 (ret time 4.5 min): NMR (CCl₄) δ 0.94 (s, 3H), 1.12 (s, 3H), 1.28 (s, 3H), 1.32 (s, 3H), 1.34 (s, 3H), 1.37 (s, 3H); ir (neat) 2975 (m), 2940 (m), 2880 (w), 1740 (s), 1470 (m), 1450 (m), 1385 (m), 1375 (m), 1310 (w), 1255 (w), 1215 (m), 1185 (w), 1105 (m), 1080 (m), 1010 (m), 890 (w), 845 (m), 720 (w) cm⁻¹; uv (MeOH) λ_{max} 218 nm (ε 830), 308 (50); mass spectrum (70 ev) m/e (rel intensity) 222(2), 164 (10), 151 (39), 149 (10), 137 (23), 136 (10), 125 (11), 124 (100), 123 (33), 109 (42), 91 (11), 81 (12).

Anal. Calcd. for C₁₃H₁₈O₃: C, 70.24; H, 8.16.

Found: C, 70.22, H, 8.16.

6. Epoxidation of 13^{*} with m-Chloroperbenzoic Acid

The procedure and workup were as described for the epoxidation of 13. The product 15^{*} had an NMR spectrum identical with that of 15

except that the signal at δ 1.34 was absent. The product 14^{*} had an NMR spectrum identical with that of 14 except that the signal at δ 1.45 was absent.

7. Epoxidation of Hexamethylbicyclo[3.2.0]hepta-6,7-epoxy-3-en-2-one (10) with Alkaline Hydrogen Peroxide

To a solution containing 103 mg (0.5 mmol) of 10 and 170 mg (1.5 mmol) of 30% aqueous hydrogen peroxide in 0.5 ml of methanol was added, at 0°C, 0.1 ml (0.6 mmol) of 6N aqueous sodium hydroxide. After being stirred at room temperature overnight, the reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with saturated salt solution and dried (MgSO₄). Evaporation of the solvent gave a quantitative yield of the diepoxide 14 as the only product.

8. Epoxidation of 10 with m-Chloroperbenzoic Acid

To a solution of 103 mg (0.5 mmol) of 10 in 1 ml of methylene chloride was added, at 0°C, a solution of 500 mg (2.5 mmol) of m-chloroperbenzoic acid in 3 ml of methylene chloride. The mixture was stirred at room temperature for 72 hr. The solvent was evaporated and petroleum ether (bp 30-60°C) was added to the residue. The m-chlorobenzoic acid was removed by filtration. Evaporation of the solvent from the filtrate gave a quantitative yield of the diepoxide 14 as the only product.

9. Acid-Catalyzed Rearrangement of Hexamethylbicyclo(3.2.0)hepta-3,4-epoxy-6-en-2-one (13)

A solution of 200 mg (0.97 mmol) of 13 in 3 ml of ice-cold trifluoroacetic acid was stirred at 0°C for one hour. The reaction was quenched by adding the mixture dropwise to a precooled saturated sodium carbonate solution at 0°C. The mixture was extracted with methylene chloride. The combined methylene chloride layers were washed successively with aqueous sodium bicarbonate, saturated aqueous sodium chloride and dried (MgSO₄). Evaporation of the solvent left 220 mg of light brown crystals. An NMR spectrum of the crude material showed it to be 95% pure. The crude product was recrystallized from methylene chloride to give 198 mg (0.62 mmol, 64%) of white crystals which were considered to be a 10:9 mixture of two isomeric compounds 16 and 17. The mixture had the following properties: mp 140-150°C; NMR (CCl₄) δ 1.20 (s, 12 H), 1.67 (s, 6H); NMR (acetone-d₆): δ 1.12 (s, 3H), 1.15 (s, 2.7H), 1.20 (s, 2.7H), 1.33 (s, 3H), 1.70 (s, 5.7H); ¹⁹F NMR (acetone-d₆) two singlets at δ 84.4, 85.9 (upfield from CCl₃F) in a ratio of 10:9; ir (KBr) 3400(s), 3000 (m), 1755 (s), 1470 (m), 1450 (m), 1430 (m), 1400 (m), 1255 (m), 1220 (s), 1190 (s), 1115 (s), 1080 (s), 1060 (s), 980 (w), 930 (m), 750 (m) cm⁻¹; uv (MeOH) 214 nm (ε 1,030), 232 (590); mass spectrum (70 ev) m/e (rel intensity) 320 (3), 206 (13), 165 (14), 164 (100), 163 (18), 149 (49), 147 (10), 137 (23), 136 (26), 135 (15), 121 (12), 119 (11), 105 (14), 91 (15), 77 (13), 69 (11).

Anal. Calcd. for C₁₅H₁₉O₄F₃: C, 56.24; H, 5.97

Found: C, 56.28; H, 5.55

10. Acid-Catalyzed Rearrangement of 13*

The procedure and workup were as described for the acid-catalyzed rearrangement of 13. The product mixture 16* and 17* had an NMR spectrum (CCl_4) identical with that of 16 and 17 except that the signal at δ 1.20 was reduced by one-quarter in area.

11. Hydrolysis of 16 and 17

A solution of 46 mg of a 10:9 mixture of 16 and 17 in 2 ml of 7% solution of K_2CO_3 in aqueous methanol (2:5 v./v.) was stirred at room temperature for 4 hr. The reaction mixture was then poured into water and extracted with ether. Removal of the solvent from the combined ether layer left white crystals which were identified as 16 and 17 by NMR and ir spectra.

12. Photolysis of Hexamethylbicyclo(3.2.0)hepta-3,4-epoxy-6-en-2-one (13)

A solution of 75 mg (0.36 mmol) of 13 in 25 ml of anhydrous ether in a pyrex test tube sealed with a septum was deoxygenated with a nitrogen stream for 15 min. This solution was irradiated through a pyrex filter with a 450W Hanovia lamp. The photolysis was followed by analytical vpc (5'x0.125 in column, 5% FFAP on chromosorb w, AW-DMCS 80/100, 145° , 60 ml/min). As the reaction proceeded, the peak corresponding to 13 (ret time 3.9 min) decreased in area. Three peaks corresponding to 33 (ret time 3.7 min), 12 (20.6 min) and 34 (27 min) appeared along with several other small peaks. The reaction was complete in 18 hr. An NMR spectrum (CCl_4) of the crude reaction mixture

10. Acid-Catalyzed Rearrangement of 13^{*}

The procedure and workup were as described for the acid-catalyzed rearrangement of 13. The product mixture 16^{*} and 17^{*} had an NMR spectrum (CCl₄) identical with that of 16 and 17 except that the signal at δ 1.20 was reduced by one-quarter in area.

11. Hydrolysis of 16 and 17

A solution of 46 mg of a 10:9 mixture of 16 and 17 in 2 ml of 7% solution of K₂CO₃ in aqueous methanol (2:5 v./v.) was stirred at room temperature for 4 hr. The reaction mixture was then poured into water and extracted with ether. Removal of the solvent from the combined ether layer left white crystals which were identified as 16 and 17 by NMR and ir spectra.

12. Photolysis of Hexamethylbicyclo(3.2.0)hepta-3,4-epoxy-6-en-2-one (13)

A solution of 75 mg (0.36 mmol) of 13 in 25 ml of anhydrous ether in a pyrex test tube sealed with a septum was deoxygenated with a nitrogen stream for 15 min. This solution was irradiated through a pyrex filter with a 450W Hanovia lamp. The photolysis was followed by analytical vpc (5'x0.125 in column, 5% FFAP on chromosorb w, AW-DMCS 80/100, 145⁰, 60 ml/min). As the reaction proceeded, the peak corresponding to 13 (ret time 3.9 min) decreased in area. Three peaks corresponding to 33 (ret time 3.7 min), 12 (20.6 min) and 34 (27 min) appeared along with several other small peaks. The reaction was complete in 18 hr. An NMR spectrum (CCl₄) of the crude reaction mixture

showed four peaks in the region of δ 1.00-1.26 corresponding to 35 (70%): 1.00 (s, 6H), 1.03 (s, 3H), 1.08 (s, 3H), 1.26 (s, 6H); europium shift reagent resolved signals of 35 to six equal singlets with relative slopes (in the order of the above signals): 1.74, 2.11, 1.06, 2.15, 1.00, 1.34; and there were three peaks in the region of δ 1.97-2.12 corresponding to 12 (8%) and 34 (5%). An ir spectrum of the crude reaction mixture showed bands at 3500 (w), 3000 (s), 2960 (s), 2900 (m), 1760 (s), 1640 (w), 1450 (s), 1380 (s), 1170 (s), 1080 (m), 1065 (m), 865 (w), 835 (w), 780 (m) cm^{-1} . The mixture was subjected to preparative vpe (5'x0.25 in column, 10% FFAP on chromosorb w, 80/100). Three major components 33, 12 and 34 were collected. Compound 33 (60%) was identified as 1-acetyl-pentamethylcyclopentadiene by comparing its spectral data with those of an authentic sample: NMR (CCl_4) δ 1.10 (s, 3H), 1.45 (s, 3H), 1.65 (q, 6H, $J = 1$ Hz), 1.80 (q, 6H, $J = 1$ Hz); ir (neat) 2950 (w), 1695 (s), 1650 (w), 1450 (s), 1355 (s), 1200 (s), 1090 (s), 1070 (m), 970 (m), 875 (w), 765 (w) cm^{-1} ; uv (MeOH) λ_{max} 217 nm (ϵ 4,800), 255 (6, 400); mass spectrum (70 ev) m/e (rel intensity) 178 (51), 163 (7), 136 (100), 135 (63), 121 (72), 120 (20), 119 (42), 107 (21), 105 (32), 93 (17), 91 (27). Compound 34 was identified as pentamethylphenyl acetate by comparing its spectral data with those of an authentic sample: NMR (CCl_4) δ 1.97 (s, 6H), 2.12 (s, 9H), 2.20 (s, 3H); ir (KBr) 2950 (m), 1740 (s), 1460 (m), 1380 (m), 1230 (s), 1090 (m) cm^{-1} ; uv (MeOH) λ_{max} 227 nm (ϵ 3,000); mass spectrum (70 ev) m/e (rel intensity) 206 (17), 165 (13), 164 (100), 163 (11), 149 (63), 105 (12), 91 (13). Compound 12 was identified as pentamethylphenol by comparing its NMR data with those of an authentic sample:

2.12 (s); mp 127-128⁰C.

13. Photolysis of 13^{*}

The procedure and workup were as described for the photolysis of 13. The crude product mixture had an NMR spectrum identical with that of photolysis of 13 except that the signal at δ 1.26 was reduced in area to half (europium shifted spectrum showed that the signal with shift slope 1.34 was absent) and the signal at δ 2.20 was absent. 33^{*} had an NMR spectrum identical with that of 33 except that the signal at δ 1.45 was reduced 50% in area.

14. Addition of Dichlorocarbene to Hexamethylbicyclo(3.2.0)hepta-3,6-dien-2-one (1)

To a solution of 3.8 g (20 mmol) of hexamethylbicyclo(3.2.0)-hepta-3,6-dien-2-one in 80 ml of CHCl_3 containing 500 mg of triethylbenzylammonium chloride at 0⁰C was added dropwise with stirring 54 ml of 50% aqueous NaOH solution, and the mixture was stirred at room temperature for 72 hr. The reaction mixture was then diluted with 400 ml of water and extracted with CH_2Cl_2 . The combined CH_2Cl_2 layer was washed successively with water, saturated NaCl solution and dried (MgSO_4). After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (EM60, finer than 230 mesh) using methylene chloride as eluent. The first fraction gave 3.2 g of light yellow crystals, which were recrystallized from petroleum ether (bp 30-60⁰) to give 2.5 g (9 mmol, 45%) of 50 as white crystals, mp 91-92⁰C; NMR (CCl_4) δ 1.05 (s, 3H), 1.22 (s, 3H), 1.28 (s, 3H), 1.30

(s, 3H), 1.43 (q, 3H, $J = 1$ Hz), 1.65 (q, 3H, $J = 1$ Hz); The six signals were shifted by europium shift reagent to give the following slopes: 3.18, 2.23, 1.29, 1.46, 1.70, 1.00. Ir (KBr) 3000 (m), 1715 (s), 1645 (m), 1445 (m), 1385 (m), 1295 (m), 1160 (m), 1095 (w), 1065 (w), 1015 (s), 905 (w), 895 (m), 815 (m), 765 (w) cm^{-1} ; uv (MeOH) λ_{max} 230 nm (ϵ 2,210), 305 (440); mass spectrum (70 ev) m/e (rel intensity) 274 (0.8), 272 (0.8), 239 (24), 237 (72), 221 (10), 173 (18), 158 (15), 139 (65), 137 (100), 135 (95), 120 (22), 119 (37), 107 (24), 105 (22), 93 (20), 91 (28).

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{OCl}_2$: C, 61.54; H, 6.64.

Found: C, 61.54; H, 6.53.

The second fraction gave 300 mg of light yellow crystals which were recrystallized from petroleum ether (bp 30-60 $^{\circ}$) to give 240 mg (0.75 mmol, 3.8%) of 51 as white crystals, mp 112-113 $^{\circ}$ C; NMR (CCl_4) δ 1.18 (s, 3H), 1.33 (s, 3H), 1.60 (q, 3H, $J = 1$ Hz), 1.70 (s, 3H), 1.90 (q, 3H, $J = 1$ Hz), 1.92 (d, 1H, $J = 8$ Hz), 2.16 (d, 1H, $J = 8$ Hz); ir (KBr) 3000 (m), 2950 (w), 1690 (s), 1640 (s), 1450 (s), 1390 (s), 1325 (m), 1260 (w), 1235 (w), 1080 (w), 1050 (w), 960 (m), 775 (m), 755 (w), 700 (w) cm^{-1} ; uv (MeOH) λ_{max} 242 nm (ϵ 8,700), 332 (270); mass spectrum (70 ev) m/e (rel intensity) 322 (2), 320 (6), 318 (6), 224 (18), 222 (54), 207 (15), 187 (100), 159 (32), 127 (13), 128 (15), 115 (9), 105 (7), 91 (11).

Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{OCl}_3$: C, 56.36; H, 5.36.

Found: C, 56.33; H, 5.32.

The third fraction gave 275 mg of light yellow crystals, which were recrystallized from petroleum ether (bp 30-60 $^{\circ}$) to obtain 210 mg

(0.66 mmol, 3.3%) of 52 as white crystals, mp 144⁰C; NMR (CCl₄) δ 1.00 (s, 3H), 1.08 (s, 3H), 1.57 (d, 1H, J = 8 Hz), 1.69 (q, 3H, J = 1 Hz), 1.93 (s, 3H), 1.95 (q, 3H, J = 1 Hz), 1.97 (d, 1H, J = 8 Hz); ir (KBr) 3000 (w), 2950 (w), 1700 (s), 1650 (m), 1450 (s), 1385 (s), 1330 (m), 1275 (w), 1235 (w), 1085 (m), 1020 (s), 965 (m), 880 (w), 810 (w), 775 (s), 735 (w) cm⁻¹; uv (MeOH) λ_{max} 244 nm (ϵ 6,230); mass spectrum (70 ev) m/e (rel intensity) 322 (2), 320 (6), 318 (6), 287 (11), 285 (65), 283 (100), 268 (11), 255 (6), 247 (8), 235 (9), 219 (21), 205 (9), 185 (22), 153 (14), 128 (16), 115 (17).

Anal. Calcd. for C₁₅H₁₇OC₃Cl₃: C, 56.36; H, 5.36.

Found: C, 56.29; H, 5.25.

15. Addition of Dichlorocarbene to 4-Trideuterohexamethylbicyclo-(3.2.0)hepta-3,6-dien-2-one (1^{*})

The procedure and workup were as described for the addition of dichlorocarbene to 1. The product 50^{*} had an NMR spectrum identical with that of 50 except that the singlet at δ 1.28 disappeared; 51^{*} was identical with that of 51 except that the quartet at δ 1.90 disappeared and the quartet at δ 1.60 collapsed to a singlet; 52^{*} was identical with that of 52 except that the quartet at δ 1.95 disappeared and the quartet at δ 1.69 collapsed to a singlet.

16. Silver Perchlorate Promoted Ring Expansion of 50

To a solution of 273 mg (1 mmol) of 50 in 1 ml of 90% aqueous acetone was added a solution of 1.04 g (5 mmol) of silver perchlorate in 20 ml of 90% aqueous acetone. The mixture was stirred at room

temperature for 24 hr. After the silver chloride precipitate was removed by filtration, 10 ml of water was added. The solution was extracted with ether and the combined ether layers were washed with water and dried (MgSO_4). Evaporation of the solvent left 248 mg of a light yellow oil which was shown by NMR to consist of 40% of unreacted 50 and 60% of a product considered to be 4-chloro-5-hydroxy-1,3,5,6,7,8-hexamethylbicyclo[4.2.0]octa-3,7-dien-2-one (55). The mixture was chromatographed on a thin layer silica gel plate using CH_2Cl_2 as eluent to obtain 90 mg of 55 as light yellow solids. It was further purified by preparative vpc (6'x0.25 in column, 15% SE-30 on chromosorb w, 60/80, 210° , 60 ml/min) to give white solids. NMR (CCl_4) δ 1.06 (s, 3H), 1.20 (s, 3H), 1.23 (s, 3H), 1.40 (q, 3H, $J = 1$ Hz), 1.62 (q, 3H, $J = 1$ Hz), 1.80 (s, 3H), 2.03 (broad singlet, 1H); ir (KBr) 3460 (s), 2980 (m), 2940 (m), 1660 (s), 1610 (m), 1440 (m), 1380 (m), 1300 (s), 1190 (m), 1170 (m), 1060 (m), 965 (m), 930 (m), 800 (w), 750 (m) cm^{-1} ; uv (MeOH) λ_{max} 237 nm (ϵ 2,700), 248 (4,650), 285 (1,230); mass spectrum (70ev) m/e (rel intensity) 256 (34), 254 (100), 241 (13), 239 (34), 219 (67), 211 (27), 204 (29), 203 (68), 175 (45), 173 (44), 147 (33), 135 (28), 133 (28), 119 (29), 105 (33), 91 (51), 83 (49).

Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_2\text{Cl}$: C, 66.00; H, 7.52.

Found: C, 66.01; H, 7.44.

17. Acid-Catalyzed Rearrangement of 50 in Sulfuric Acid

To a solution of 273 mg (1 mmol) of 50 in 1 ml of CH_2Cl_2 and 5 ml of MeOH was added dropwise, at 0°C , 3 ml of concentrated sulfuric acid. The mixture was stirred at 0°C for 10 minutes. The reaction was then

quenched by adding 20 ml of water and the mixture was extracted with methylene chloride. The combined methylene chloride layers were washed successively with saturated NaHCO_3 solution, water, saturated NaCl solution and dried (MgSO_4). Evaporation of the solvent left 245 mg of a yellow-brown oil. The crude mixture was chromatographed on silica gel (EM 60, finer than 230 mesh) using methylene chloride as solvent. The first fraction gave 23.5 mg (0.1 mmol, 10%) of 56. NMR (CCl_4) δ 1.20 (s, 6H), 1.57 (q, 3H, $J = 1\text{ Hz}$), 1.70 (q, 3H, $J = 1\text{ Hz}$), 1.87 (s, 3H), 4.80 (s, 1H), 4.88 (s, 1H); ir (neat) 2980 (m), 2940 (m), 1775 (s), 1610 (w), 1450 (m), 1380 (m), 985 (m), 885 (m) cm^{-1} ; uv (MeOH) λ_{max} 253 nm (ϵ 11,800), 217 (8,570); mass spectrum (70 ev) m/e (rel intensity) 238 (15), 236 (40), 223 (12), 221 (32), 208 (24), 201 (15), 195 (13), 193 (36), 173 (100), 158 (40), 157 (24), 154 (22), 143 (21), 141 (19), 128 (21), 119 (28), 115 (20), 91 (23). Due to the compound's thermal instability, no attempt was made to obtain its elemental analysis.

The second fraction gave 170 mg (0.72 mmol, 72%) of 57. NMR (CCl_4) δ 1.42 (s, 3H), 1.67 (q, 6H, $J = 1\text{ Hz}$), 1.87 (q, 3H, $J = 1\text{ Hz}$), 2.00 (q, 3H, $J = 1\text{ Hz}$), 4.83 (s, 1H), 4.87 (s, 1H); ir (neat) 3000 (m), 2950 (m), 1705 (s), 1640 (s), 1450 (s), 1385 (s), 1325 (m), 1020 (m), 915 (s), 900 (m), 855 (m), 765 (m), 720 (s) cm^{-1} ; uv (MeOH) λ_{max} 237 nm (ϵ 14,100), 260 (shoulder, 7,880), 339 (980); mass spectrum (70 ev) m/e (rel intensity) 238 (26), 236 (76), 223 (10), 221 (30), 202 (35), 201 (84), 187 (54), 186 (21), 185 (20), 173 (100), 159 (30), 158 (35), 157 (21), 143 (22), 142 (15), 141 (18), 128 (22), 119 (19), 115 (18), 105 (14), 91 (22). Due to the compound's thermal instability,

no attempt was made to obtain its elemental analysis.

18. Acid-Catalyzed Rearrangement of 50*

The procedure and workup were as described for the acid-catalyzed rearrangement of 50. The product 56* had an NMR spectrum identical with that of 56 except that the singlet at δ 1.87 was absent; 57* was identical with that 57 and showed no deuterium labeling.

19. Treatment of 57 in Trifluoroacetic Acid-d₁

A solution of 15 mg of 57 in 0.5 ml of trifluoroacetic acid-d₁ was stirred at room temperature for 10 min. The mixture was then poured into D₂O. After workup, the product showed identical NMR spectrum with that of 57 except that the signals at δ 1.87, 4.83 and 4.87 were disappeared. Europium-shifted spectrum showed that the signal at δ 1.67 (with Eu-shift slope 1.00) sharpened to a singlet.

20. Treatment of 57 in CH₃ONa/CH₃OD solution

A solution of 15 mg of 57 in 1 ml of CH₃OD and 10 mg of CH₃ONa was stirred at room temperature for 0.5 hr, then poured into ice-water and extracted with methylene chloride. NMR spectrum showed that 57 had been converted into a different compound due to its instability under basic condition.

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