ABSTRACT

PART I

A MULTI-STEP CARBONIUM ION REARRANGEMENT IN THE BICYCLO[2.2.2.]OCTYL SYSTEM

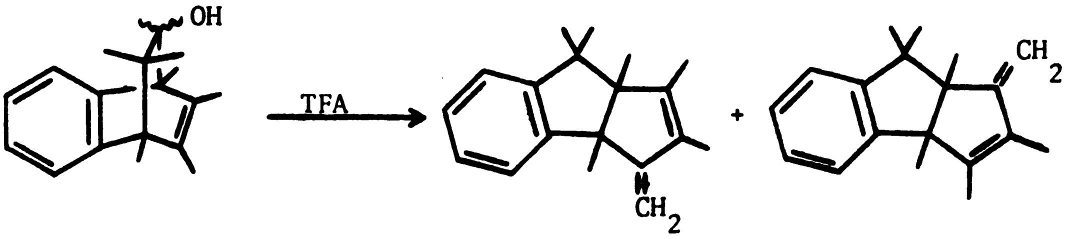
PART II

THE EFFECT OF REMOTE SUBSTITUENTS ON Di-π-METHANE PHOTOISOMERIZATIONS

By

George M. Love

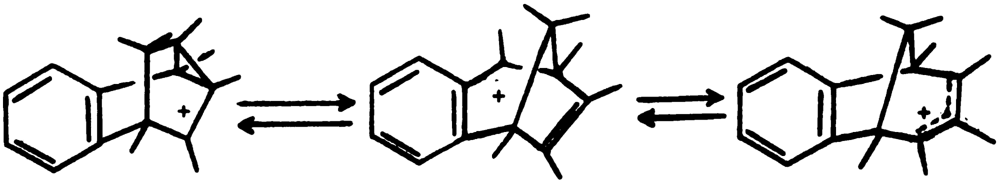
The acid-catalyzed dehydration and concurrent rearrangement of the epimeric alcohols of structure **8** were studied in Part I of this thesis. Dehydration of the alcohols in trifluoroacetic acid (TFA) at room temperature for twenty minutes afforded hydrocarbons **VI** and **VII** in quantitative yield. Treatment of the alcohols at higher temperatures



VI **VII**

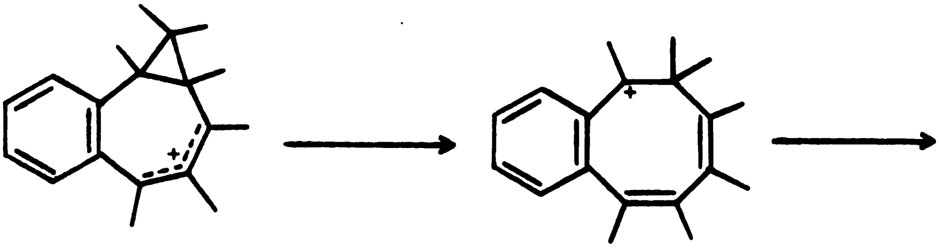
or for longer times led to no further reaction. However, by treating them for shorter times, at lower temperatures, and by using a weaker acid, five intermediate ions could be quenched as their parent olefins (I through V).

These quenching data and appropriate deuterium labeling experiments allowed a fairly complete mechanistic scheme to be postulated. Initial dehydration of the alcohols leads to an equilibrium mixture of ions I^{+}, II^{+}, and III^{+}. Either ion II^{+} or III^{+} may undergo a 1,4-shift of

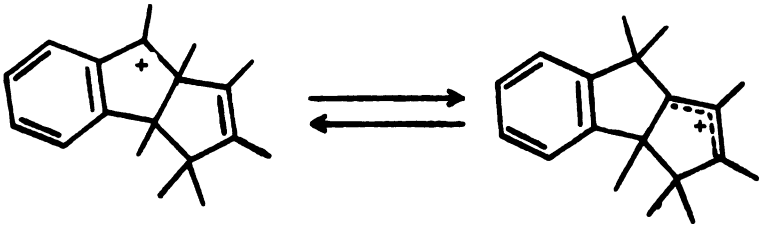


I^{+} II^{+} III^{+}

the one-carbon bridge to afford proposed intermediate ions 13 and 14 which lead to a second equilibrium system of ions IV^{+} and V^{+}. Two

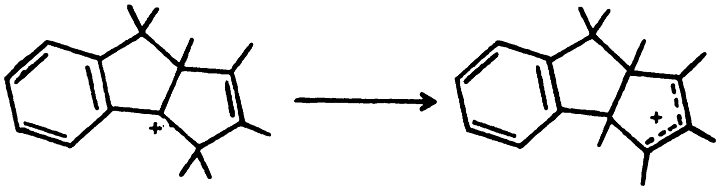


13 14



IV^{+} V^{+}

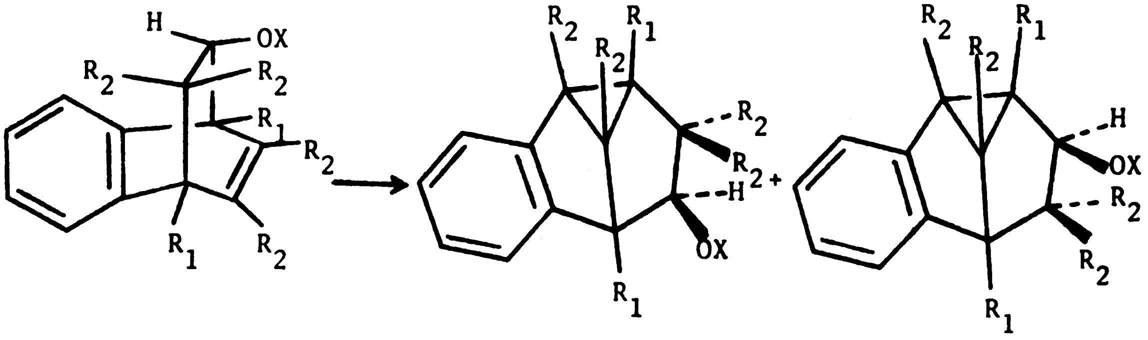
1,2-methyl shifts convert ion V$^+$ *via* intermediate ion 16 to ion 9. Loss of a proton from either end of the allylic moiety of 9 affords the final olefins, VI and VII.



16 9

The structures of olefins I through V are based upon their independent syntheses; those of VI and VII are based upon the spectra of ketones isolated from osmium tetroxide oxidation of the olefins.

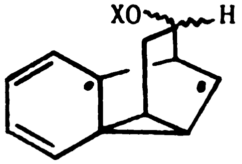
In Part II of this thesis, the acetone-sensitized di-π-methane photoisomerization of several variously substituted *syn* and *anti*-benzobicyclo[2.2.2.]octa-5,7-dien-2-alcohols and acetates was studied. Of the two possible products, labeled A and B, which might arise when the substituent-X was *anti* to the benzene ring, product A always predominated. In one case, 63b, in which there were no methyl



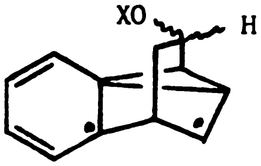
A B

46b, $R_1 = R_2 = CH_3$, X = OH	50b (60%) + 49b (40%)
51b, $R_1 = R_2 = CH_3$, X = OAc	52b (66%) + 53b (33%)
55b, R_1 = H, $R_2 = CH_3$, X = OAc	56b (66%) + 59b (33%)
63b, $R_1 = R_2$ = H, X = OH	64b (100%)

substituents, only A-type product was observed. The products are labeled **A** and **B** to identify them with the benzo-vinyl di-π-methane intermediate, either A-type or B-type, from which they arose.

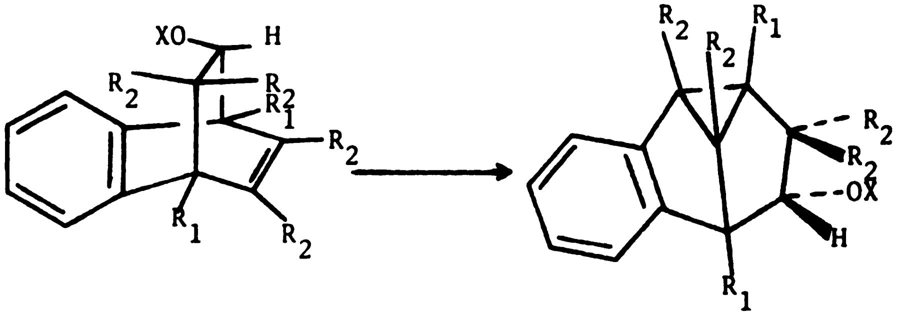


A-type



B-type

Photolysis of the <u>syn</u> isomers afforded only A-type products.



A

46a $R_1 = R_2 = CH_3$, X = OH	**50a**
51a $R_1 = R_2 = CH_3$, X = OAc	**52a**
55a $R_1 = H$, $R_2 = CH_3$, X = OAc	**56a**
63a $R_1 = R_2 = H$, X = OH	**64a**

The results have been interpreted to indicate an unusual stabilization of the A-type intermediates, hypothesized to involve charge-transfer of an oxygen lone pair electron to the carbon unpaired electron directly below it in the A-type intermediate - a triplet intramolecular exciplex.

PART I

A MULTI-STEP CARBONIUM ION REARRANGEMENT IN THE BICYCLO[2.2.2.]OCTYL SYSTEM

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A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1972

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Harold Hart for his enthusiasm, encouragement and guidance throughout the course of this study.

Appreciation is extended to Michigan State University for a Graduate Teaching Assistantship from September,1968 through March, 1969, to the Phillips Petroleum Company for a fellowship from June, 1969 through September, 1969, and to the National Institute of Health and the National Science Foundation for financial support from September, 1969 to the present.

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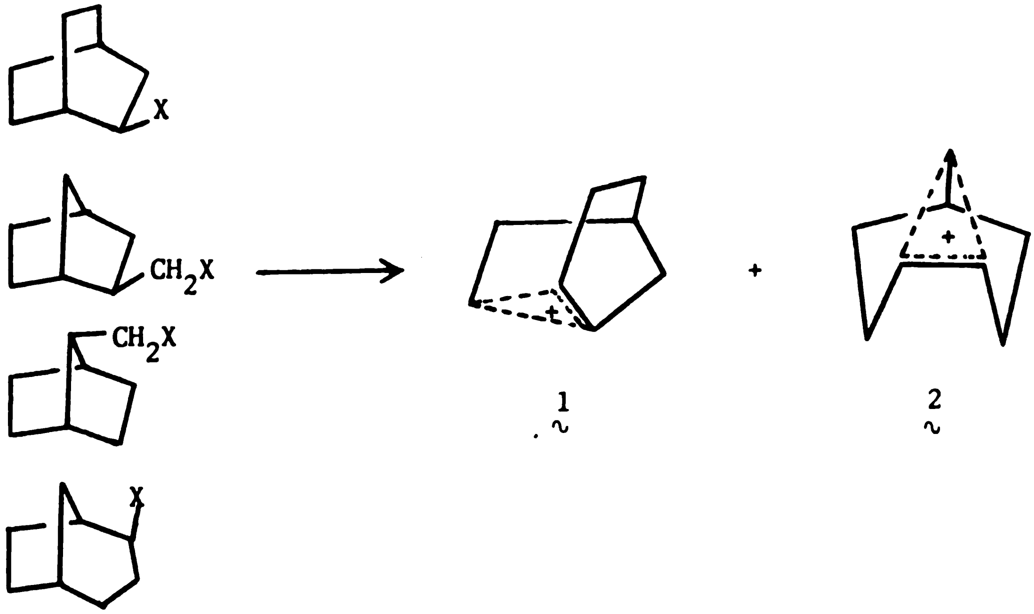
PART I

A MULTI-STEP CARBONIUM ION REARRANGEMENT IN THE BICYCLO[2.2.2.]OCTYL SYSTEM

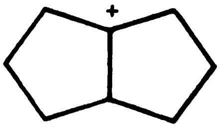
INTRODUCTION

In 1969, Kwart summarized that "in all familiar reactions having a bicyclooctyl cation intermediate, the product compositions distributed between the [2.2.2.], exo[3.2.1.], and endo[3.2.1.] isomers are nearly invariant" (1). This common product distribution led the authors to conclude that the ionization of nearly any bicyclooctyl derivative or precursor led to a mixture of two "non-classical" ions, 1 and 2.



1 2

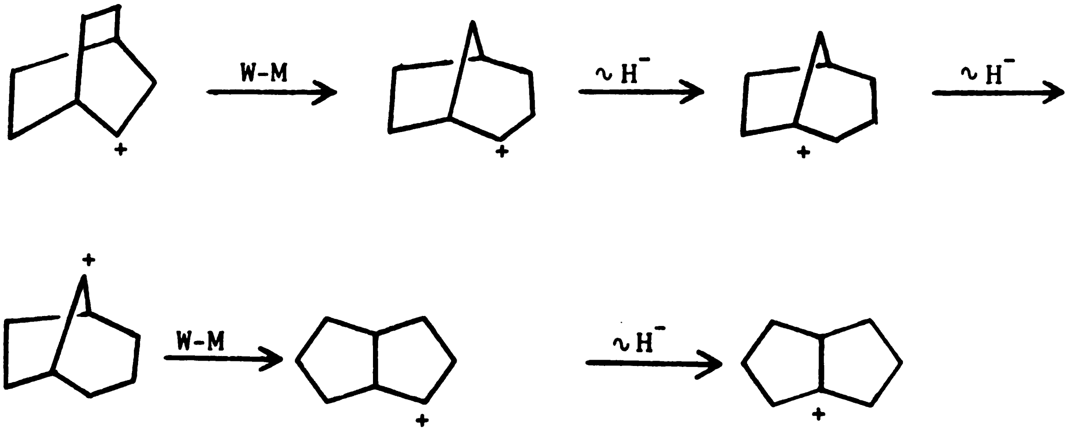
In contrast, just one year later, Olah concluded that "although the carbonium ions in solvolysis reactions of bicyclo[2.2.2.] and [3.2.1.]octyl derivatives have been ascribed non-classical character as in 1 and 2, respectively, we wish to report that, under long-lived ion conditions in superacid media, *all* bicyclooctyl systems rearrange to the more stable tertiary bridgehead bicyclo[3.3.0.]-1-octyl cation, **3**" (2).



3

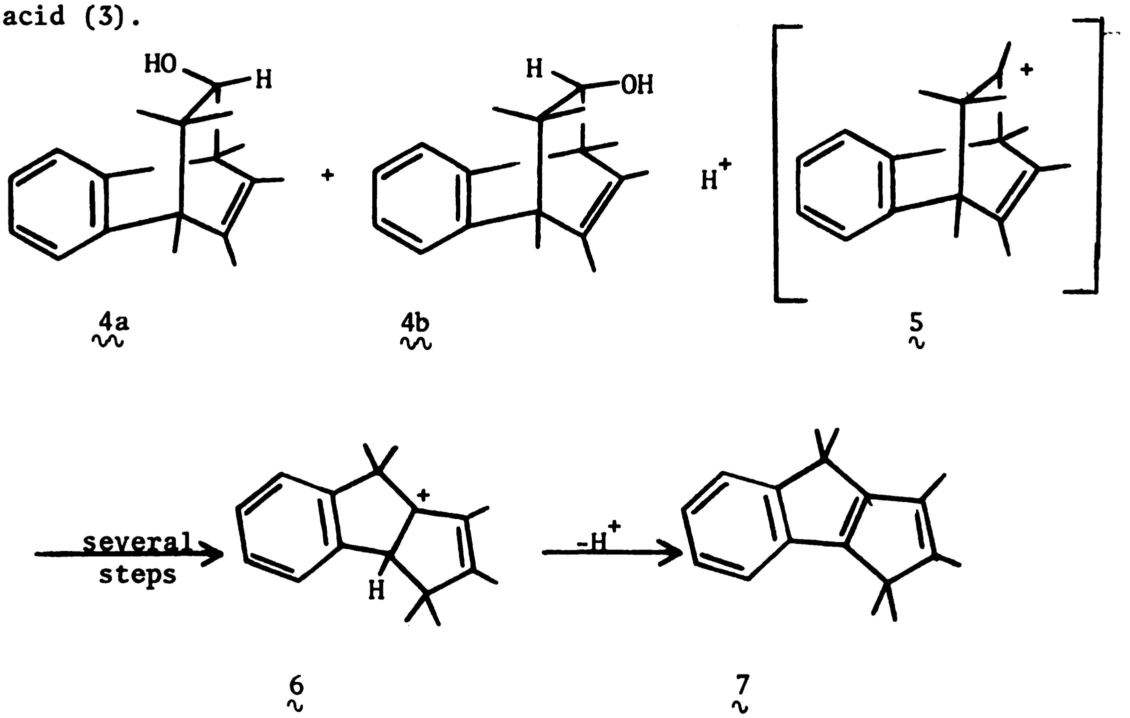
The key word in Kwart's summary is "familiar". He was referring to a large body of solvolysis studies wherein nucleophilic attack by solvent molecules is too fast to allow a true equilibrium to be reached. Olah's work makes it appear that much of what we know about carbonium ion behavior is more a reflection of the interaction of the ions with the solvent than it is a knowledge of the ions themselves.

The cascade of intermediate ions from the [2.2.2.] system to the [3.3.0.] system in Olah's proposed scheme involved two Wagner-Meerwein shifts and three hydride shifts as shown below.



3

In 1967, Gripper Gray and Hart studied a similar bicyclo[2.2.2.] to bicyclo[3.3.0.] rearrangement by examining the dehydration and subsequent rearrangement of the epimeric alcohols **4a** and **4b** in strong acid (3).



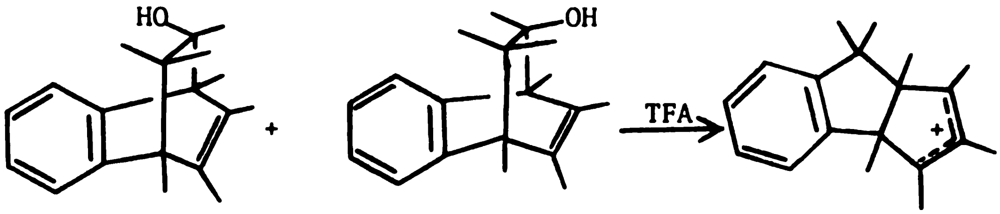
4a **4b** **5**

6 **7**

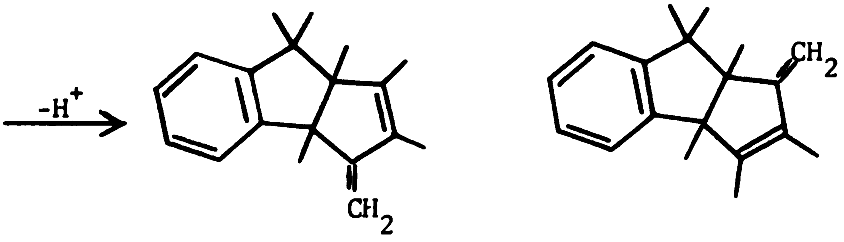
Hydrocarbon **7** was isolated in 65% yield from the reaction. Note that the precursor of **7**, ion **6**, is analogous to Olah's bicyclooctyl ion **3**. Hence, it appears that blocking the system from hydride shifts with methyl groups does not prevent the conversion of the [2.2.2.] system to the [3.3.0.] system. By dehydrating **4a** and **4b** at lower temperatures and for shorter times, Gripper Gray and Hart were able to quench several intermediate ions as the parent olefins, although the yields were not particularly good. In each case the formation of involatile tars prevented the characterization of all products. Nevertheless, they were able to characterize four olefins quenched from the reaction. From these structures, and a deuterium labeling study, the authors were able to propose several mechanistic schemes for the formation of the products isolated. Unfortunately, an unequivocal choice between schemes could not be made, and the structures of the isolated intermediates were based solely on spectral data and therefore open to some question.

Simple dehydration of **4a** or **4b** would afford a secondary ion, **5**. This is shown in brackets since there is no evidence for its formation. Indeed, one would predict that the alcohols would dehydrate with either phenyl or vinyl participation such that ion **5** would never form. However, the presence of a secondary carbon atom in a ring system which contains five tertiary carbon atoms might be expected to direct the multiple rearrangement along a reaction path which would not place a positive charge on the secondary carbon atom. Even if a secondary ion such as **5** were formed, it certainly could not be quenched by loss of a proton since it does not have a beta proton to lose.

For the present study of this type of carbonium ion rearrangement, alcohols **8a** and **8b** were chosen so that all possible intermediate ions would be tertiary and hence able to lose a proton to form a stable alkene. Dehydration of a mixture of **8a** and **8b** in neat trifluoroacetic acid (TFA) for twenty minutes and subsequent quenching afforded a mixture of two hydrocarbons assigned structures **VI** and **VII**, in quantitative yield; both hydrocarbons can arise from the bicyclo[3.3.0.]octyl ion, **9**, by loss of a proton. Treatment of **8a** and **8b** with neat TFA at higher temperatures or for longer times led to no further reaction. Thus the tertiary, allylic ion **9** and derived products **VI** and **VII** represent the thermodynamic sink for the reaction. However, when the reaction was quenched at shorter reaction times or carried out at lower temperatures and with weaker acids, five other olefins, **I** through **V**, were isolated (17). Each olefin was fully characterized. In all experiments,



8a 8b 9



VI VII

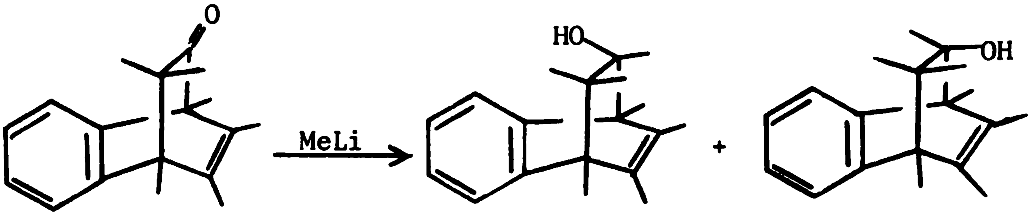
regardless of the dehydration conditions, the mass balance for the overall reaction was nearly quantitative, and all the products were identified.

The isolation and identification of products derived from all quenchable ions in the system, together with a knowledge of the sequence of their formation, allows a fairly complete mechanistic scheme of the carbonium ion cascade to be postulated. This is the topic of Part A of this thesis. This mechanistic scheme has been carefully tested by a deuterium labeling study. Part B describes this study. Part C presents the structural evidence for the olefins described in Parts A and B.

RESULTS AND DISCUSSION

A. The Dehydration and Rearrangement of syn- and anti-1,2,3,3,4,7,8-heptamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diene-2-ols, 8a and 8b, and a Proposed Mechanistic Scheme.

Ketone 10 was prepared by the method of Gripper Gray and Hart (3). Addition of excess methyllithium to 10 quantitatively afforded a mixture of the epimeric alcohols, 8a and 8b in the approximate ratio of two to one. Repeated recrystallization of this mixture from hexane gave the pure _syn_ isomer, 8a, mp 140-142°. The _anti_ alcohol, 8b, was never obtained pure, but preliminary dehydrations of the 8a, 8b epimeric mixture afforded product mixtures identical to those obtained from the dehydration of pure 8a (vide infra). Hence, nearly all the results described here were obtained from dehydrations of the epimeric mixture of 8a and 8b.



10 8a 8b

The alcohols were dehydrated by dissolving them in TFA directly, or by addition of TFA to an ether solution of the alcohols. The reaction mixtures were then quenched by pouring them into ice water and neutralizing the resulting solutions with strong base. The product olefins and unreacted alcohols were then extracted into ether and worked up by conventional techniques. In each case, the mass balance for the overall dehydration/rearrangement reaction was nearly quantitative.

Six of the seven olefins were separated by preparative gas-liquid-phase chromatography (GC) although this could not be done on a single column. The seventh was synthesized and identified in product mixtures by its characteristic nmr spectrum. Integration of GC peak areas proved inadequate for quantitative analysis of the product mixtures because several of the olefins thermally rearranged in the GC column to others which were already present in the mixture. This phenomenon was detected by comparison of the nmr spectral integrations with the GC integrations of an olefin mixture. Hence, the quenching data in Table 1 were obtained from nmr integration of the olefin region (τ 4.5-5.5) of the crude quenched samples. The extent of dehydration in each case was estimated from nmr peak heights of methyl groups known to be characteristic of each of the alcohols. Several approximations were used in the integration of the nmr peaks of the olefin mixtures. Hence, the data in Table 1 are probably no more reliable than ± 10%.

The seven olefinic products of the reaction are numbered with Roman numerals (I through VII) in approximate order of their formation. All other structures are numbered with Arabic numbers.

The initial quenching studies on this system were done in neat TFA at 0°; the results are shown below the dotted line in Table 1. Note that even in thirty seconds dehydration was complete; none of the

Table 1. Products Quenched from the Dehydration of **8a** and **8b**

Quenched Products from TFA/Ether at 0° in Percent

Time	I	II	III	IV	V	VI	VII	%Dehydration
10 min	40	40	20					5
80 min	45	45	10					40
9.5 hrs	15	80	5					100
24 hrs	15	80	5					100

Quenched Products from Neat TFA at 0° in Percent

30 sec	24	16	20	27	13			100
5 min				24	76			100
10 min				25	75			100
30 min				19	42	17	22	100
60 min				8	26	45	25	100
180 min						55	45	100

starting alcohols was present. The freezing point of TFA is -15°; this prevented a substantial lowering of the temperature to slow the reaction to a rate which would allow the use of hand mixing and quenching techniques. Hence, a second, weaker acid was used to monitor the reaction in its early stages. The alcohols were dissolved in ether, and TFA was added. Since TFA completely dissociates in dilute ether solutions, the actual acid is Et_2OH^+, $^-OOCCF_3$, pKa -3.5 (4). The data from this system are shown above the dotted line in Table 1.

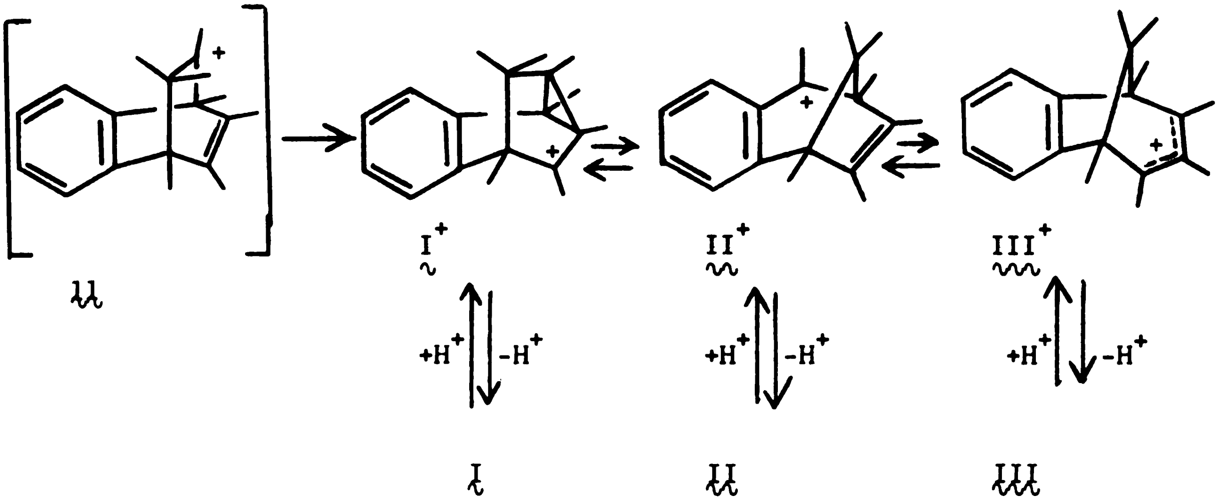
The following equilibria were demonstrated by showing that each of the separate olefins in a short time in acid solution affords a similar mixture. For example, when either pure **I** or **II** or nearly pure **III** was dissolved in TFA/ether solution for one hour at 0° and quenched, a mixture of **I**, **II**, and **III** was obtained.

$$\mathbf{I} \rightleftarrows \mathbf{II} \rightleftarrows \mathbf{III}$$

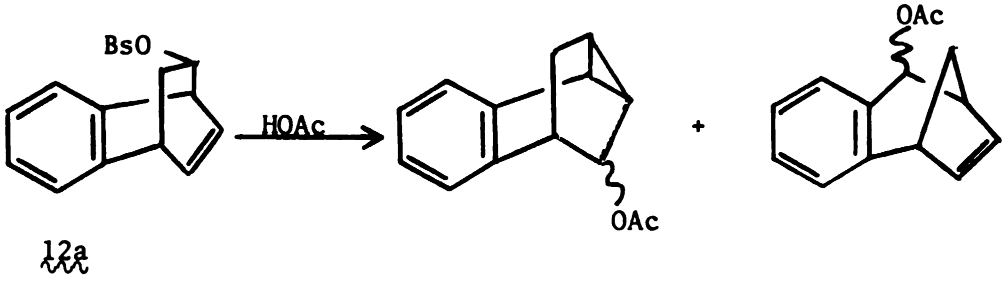
$$\mathbf{IV} \rightleftarrows \mathbf{V}$$

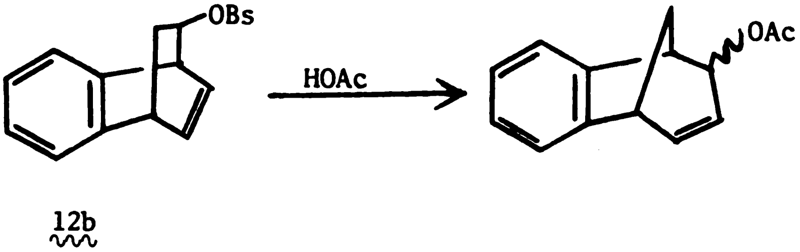
$$\mathbf{VI} \rightleftarrows \mathbf{VII}$$

Examination of Table 1 shows that the first olefins to appear are **I**, **II** and **III**, and that they are apparently in equilibrium with each other. The following scheme is a plausible mechanistic interpretation for their formation and equilibration. No olefin corresponding to the loss of a proton from ion **II** has been isolated. It is therefore possible that the dehydration of **8a** and **8b** is anchimerically assisted by the double bond or the phenyl group (i.e. the direct ionization of **8a** to **I**$^+$ and of **8b** to **III**$^+$). This phenomenon was observed by



Tanida when he studied the solvolysis of the *syn*- and *anti*-p-bromobenzenesulfonates (brosylates) 12a and 12b in acetic acid, as shown below. The evidence in Tanida's case is conclusive; the products of the reaction were controlled by the stereochemistry of the starting materials, and a rate difference was observed (K_{12a}/K_{12b} = 3.8) (5). In the direct

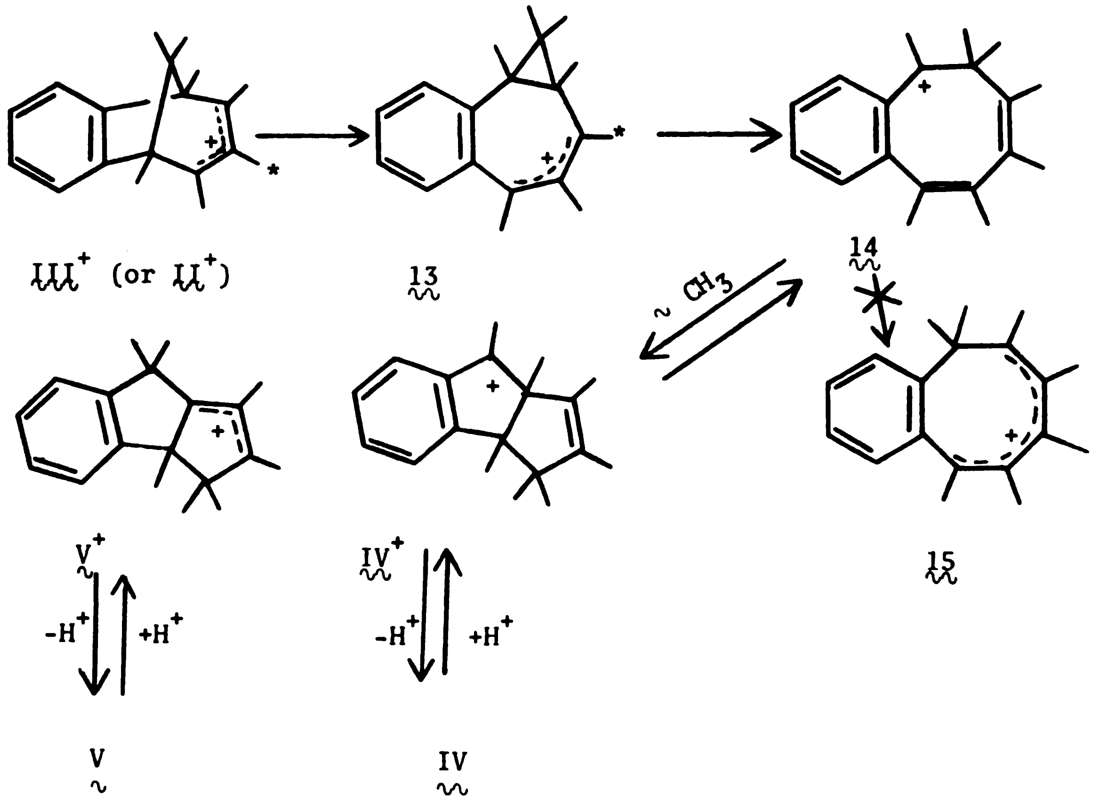




dehydration of **8a** and **8b**, no rate difference was observed. The ratio of **8a** to **8b** is easily measured by integration of characteristic methyl proton peaks of each. This ratio remained nearly constant in both of the low conversion dehydration experiments, and it was the same as that of the starting materials. However, this lack of a rate difference does not require the existence of ion **11**, since it is possible that **8a** and **8b** each ionize <u>at the same rate</u> with participation of the vinyl and phenyl group respectively. Hence, we may not draw any conclusions about the existence of **11** from the data at hand.

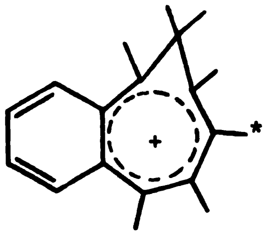
In any case, the first experimentally demonstrated ions are **I**$^{+}$, **II**$^{+}$, and **III**$^{+}$. Since all three ions are present at conversions as low as 5%, it appears that the equilibrium between them is established more quickly than the initial ionization of **8a** and **8b**. This conclusion is supported, if one assumes that **8a** ionizes directly to **I**$^{+}$, by the observation that dehydration of pure **8a** did not alter the ratio of **I**, **II**, and **III** in the product mixture. In the scheme shown, a simple tertiary ion **11** rearranges to **I**$^{+}$, a cyclopropylcarbinyl ion, by donation of an electron pair from the double bond. Ion **I**$^{+}$ rearranges to the benzyl ion **II**$^{+}$ by opening of the lower (as drawn) bond of the cyclopropane ring. Ion **II**$^{+}$ can then rearrange to the allylic ion **III**$^{+}$ by a 1,2-shift of the one carbon bridge. Each of the ions is in equilibrium with its parent olefin, by simple loss of a proton. This scheme receives considerable support from the deuterium labeling experiments (see Part B).

The next step in the proposed scheme requires a stronger acid than the TFA/ether mixture. Indeed, the equilibrium mixture of **I**$^{+}$, **II**$^{+}$, and **III**$^{+}$ did not react further even after refluxing overnight in TFA/ether. In neat TFA at 0°, however, two new olefins **IV** and **V** appear in a matter of seconds. The following scheme is proposed for their formation.



The 1,4-sigmatropic migration which converts ion **III**$^+$ (or ion **II**$^+$) to ion **13** seems to have ample precedent (6), although there is no real evidence in the present case that the process is concerted. However, this process, and the subsequent opening of **13** to **14** are kinetically irreversible, since there is no evidence that the reaction can go back from the **IV**, **V** system which follows ion **13**, to the **I**, **II**, **III**, system which preceeds it. For example, when pure **V** was dissolved in TFA/ether and refluxed overnight, it was recovered quantitatively. When **V** was dissolved in neat TFA at 0° for a short period (5 min), it was recovered together with **IV** and very small amounts of **VI** and **VII**. However, no **I**, **II**, or **III** was detected in such mixtures even when a sensitive flame ionization detector GC was used. Such a method would easily detect one percent of I, II, or III if they were present.

The unusual behavior of ion 13 is further illustrated by a deuterium labeling experiment which will be fully described in Part B. However, one aspect of this experiment will be considered here. The entire dehydration/rearrangement was carried out starting with 8a and 8b containing a CD_3 methyl group at carbon number seven. After the multiple rearrangement to ion 13, this methyl group should be in the position marked with an asterisk in the structure shown for 13. The unusual aspect of this experiment is that this methyl group did not exchange its methyl deuterons in the rearrangement from the I, II, III system to the IV, V system. Ion 13 is drawn as a simple allylic ion; if this structure were correct, one might expect exchange of methyl protons at each terminus of the allylic system, as a consequence of equilibration with the corresponding olefin by proton loss. Since the marked methyl group did not undergo exchange, it appears that ion 13 either has too short a lifetime to do so, or is really much more delocalized than shown. Further delocalization would be possible if ion 13 were to exist in the form of a six pi homoaromatic system as shown below.

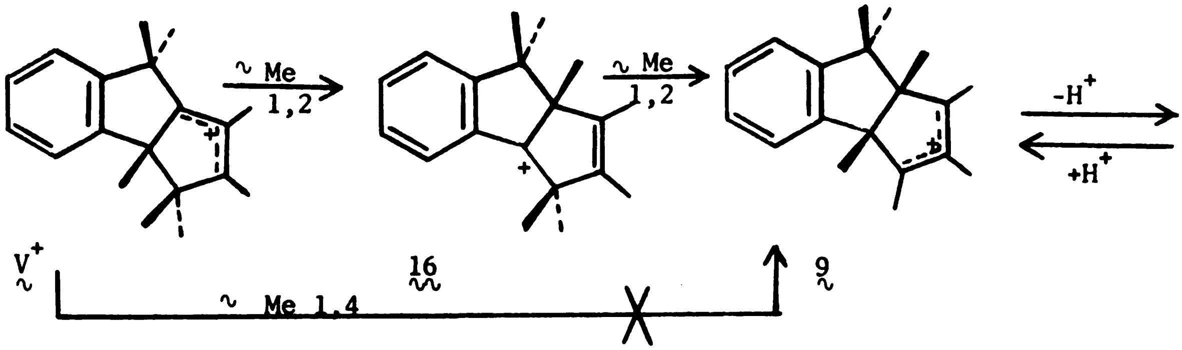


13

Pettit (7) has examined the parent ion of this structure (i.e. the ion without methyl substituents) and concluded that the benzohomotropylium cation "does possess a homoaromatic structure; however, as might be expected, the presence of the benzene ring strongly dampens the extent of the homoallylic interaction". Hence, the actual structure of the heptamethylbenzohomotropylium ion, 13, is merely speculative. It would seem that the added methyl substituents might better stabilize the simply allylic structure shown.

Proceeding,ion 13 can open to ion 14, which has two paths open to it. A 1,2-methyl shift to produce ion 15 would afford an extensively delocalized system. Closure of 15 to a benzo[3.3.0.] system would then give the final ion 9 from which olefins VI and VII are derived. This does not occur, however. In fact, 14 cyclizes to IV^+, which was trapped as olefin IV. Ion IV^+ can also suffer a 1,2-methyl shift to form V^+ which was trapped as the olefin V. This IV^+, V^+ methyl shift is an equilibrium process, as IV and V have been demonstrated to be in equilibrium with each other in the acid mixtures. This process will be further discussed in Part B.

The last step in the proposed scheme is shown below. The rearrangement from V^+ to 9 might involve two sequential 1,2-methyl shifts, and hence



V^+ 16 9

VI + VII

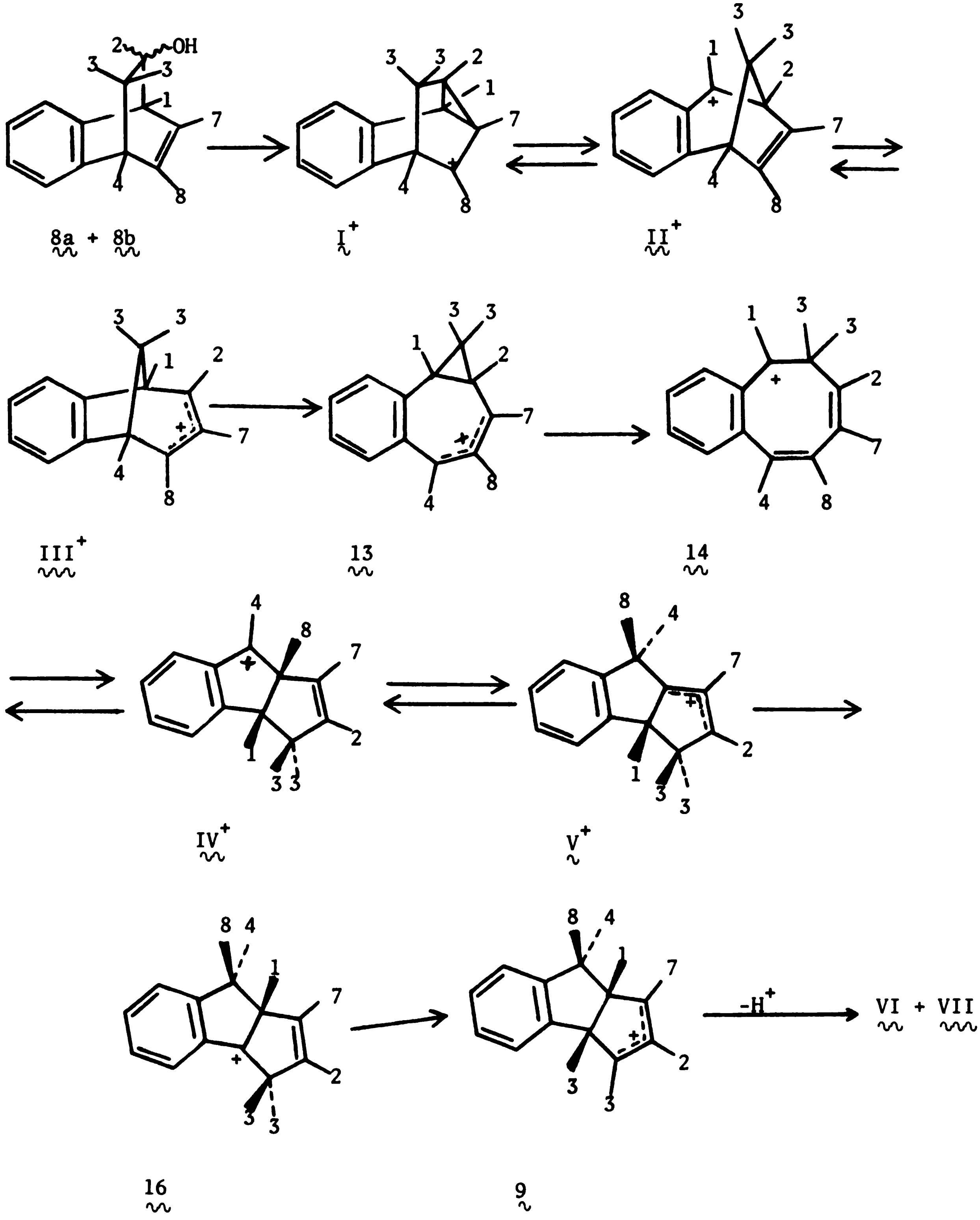
the intermediate ion, 16. Alternatively, ion V^+ could go directly to 9 by a single 1,4-sigmatropic methyl migration. A deuterium labeling study described in Part B showed that the former of these two alternatives is correct. Ion 9 can then lose a proton from either end of the allylic moiety to form the final two products, VI and VII.

B. Deuterium Labeling Studies of the Dehydration and Rearrangement of 8a and 8b.

Several deuterium labeling experiments were carried out to verify the mechanistic scheme proposed in Part A (see the deuterium labeling scheme presented as Figure 1 on the following page). In Figure 1, each methyl group is numbered for identification. It keeps its number through the entire scheme regardless of the number of the carbon atom to which it is attached.

Alcohols 8a and 8b-d_3 were synthesized from ketone 10-d_3, which was prepared by the procedure of Gripper Gray and Hart (3). This procedure incorporated three deuterium atoms on methyl group #7 on the scheme. The dehydration/rearrangement of the labeled alcohols afforded six of the seven olefins by the usual quenching and GC separation techniques (olefin III can not be purified in this manner). Examination of the nmr spectra of these olefins showed that a methyl-d_3 group was present in olefins I, II, IV, and V, but was absent from olefins VI and VII. The chemical shifts of the methyl peaks which were absent from the nmr spectra of I, II, IV, and V are given in the experimental section. It is not essential to enumerate them here, particularly since the nmr assignment of every methyl group in olefins I through VII has not been made. However, it can be noted that the deuterated methyl group in olefins

Figure 1. The Deuterium Labeling Scheme



II and IV was one which showed allylic splitting in the unlabeled olefin.

The results of this experiment require that the mechanistic scheme up to the precursor of VI and VII never involve a carbonium ion center on the carbon atom to which methyl group #7 is attached. This requirement is met by the scheme under consideration for the first three products. However, in ion 13 methyl group #7 is located at one terminus of an allylic ion. Hence, one must presume that ion 13 is either too short lived to exchange, or more delocalized than drawn (i.e. a homotropylium ion). Since olefins VI and VII had exchanged the protons on methyl group #7, the scheme must place a carbonium ion center next to the methyl group #7 at some point after products IV and V are formed. This is done in ion 9, where methyl group #7 is at one end of an allylic ion.

Methyl group #7 shows its unique place in the scheme when the experiment is carried out the other way around. Alcohols 8a and 8b were dehydrated in deuterated TFA (TFA-D) and the products were quenched, separated, and examined. The nmr spectrum of olefin I showed only three methyl peaks, and one of these had the same chemical shift as methyl group #7 (i.e. the one which was deuterated in the previous experiment). Olefin II also showed only three methyl peaks in the nmr, and again one of these was the #7 methyl peak. In both I and II the vinyl proton signals were partially washed out, but not as completely as were the aforementioned methyl signals. Since the vinyl protons in one olefin correspond to methyl protons in the other (see scheme), and the equilibrium between I, II and III is known to be fast, we must presume that the vinyl protons are in some way exchanged back during the quenching process. Olefins IV and V also showed only three methyl peaks in the nmr; in each case, one of them was the #7 methyl group. Olefins VI and VII, however, each had only one methyl peak in its nmr spectrum. This methyl group can not correspond to the #7 methyl group since the #7 methyl group was shown to exchange in the previous experiment.

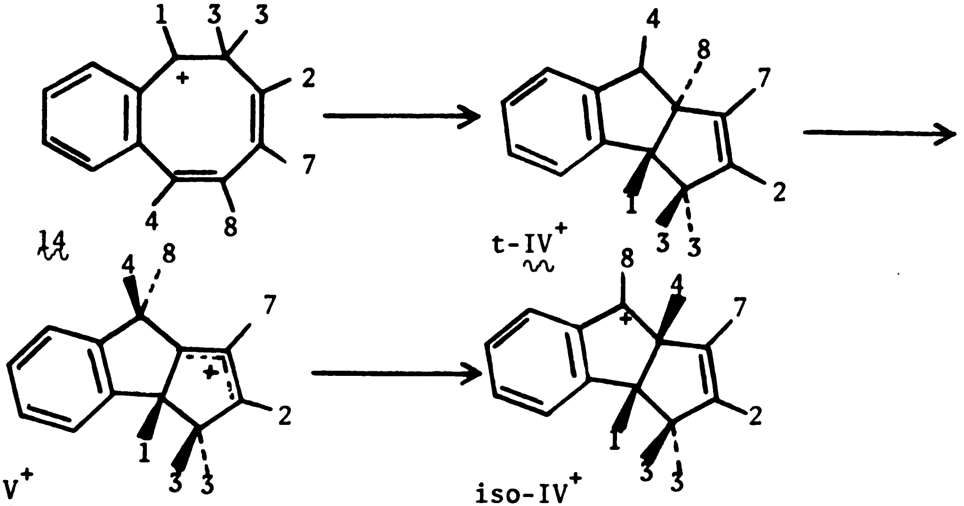
The above results require that the scheme allow the exchange of the protons on four methyl groups in the I, II, III system. Examination of the scheme shows that ion I$^+$ can exchange the protons on methyl group #8; ion II$^+$ can exchange the protons on methyl group #1; and ion III$^+$ can exchange the protons on methyl groups #2 and #8. Since ion III$^+$ has a plane of symmetry, methyl groups #1 and #4 and methyl groups #2 and #8 constitute degenerate pairs. The rapid equilibration of ions I$^+$, II$^+$, and III$^+$ then makes all four of these methyl groups degenerate throughout the entire I, II, III system. Indeed, when the exchange experiment was done in TFA-D/ether, where the reaction does not proceed beyond the equilibration of I$^+$, II$^+$ and III$^+$, and the reaction was quenched just after it had reached 100% dehydration (2 hrs), it was found that in I and II, three of the methyl peaks in each (the fourth was a vinyl group) were approximately half exchanged. The significant point is that the extent of exchange in each methyl group in each compound was the same. Hence, methyl groups #1, #2, #4, and #8 are degenerate to exchange in the system.

The fact that olefins IV and V had exchanged the protons on all but three of their methyl groups reflects the known exchange of their precursors as well as that these three methyl groups can not exchange in ions 13, 14, IV$^+$, or V$^+$. At this point it is easy to deduce that one of these methyl groups is #7, and that the other two must be the geminal pair, both numbered #3. This conclusion is supported by the fact that the protons on two of these methyl groups are exchanged in olefins **VI** and **VII**. Note that in ion **9**, one of the #3 methyl groups and the #7 methyl group are at the ends of the allylic moiety, where they would be expected to exchange.

Since the protons on methyl groups #1, #2, #4, and #8 were all exchanged early in the reaction, they can not be observed later in the scheme and be used as a test for the position of the positive charge. Hence the system was entered at a later point by placing pure undeuterated **V** in TFA-D. In five minutes at 0°, **IV** and **V** appeared to be in equilibrium as the ratio of quenched products was approximately 75% **V** and 25% **IV**, the equilibrium ratio. The nmr spectrum of **V** recovered from this experiment showed the clean loss of one methyl proton singlet. Hence, this exchange must accompany the equilibration of **IV** and **V**. This methyl group must be #4 in the scheme; it can easily exchange in ion **IV**$^+$. Both molecules and ions of structure **IV** and **V** are cup shaped, so one would expect the methyl group on the convex side, #8, to shift back and forth in a 1,2-sigmatropic migration. Since the #8 methyl group is never attached to a positive center, it can not exchange its protons.

When **V** was allowed to react for forty-five minutes at 0° in neat TFA-D, quenched, and separated from the resulting mixture of **IV**, **V**, **VI**, and **VII**, its nmr spectrum revealed the loss of the protons on the #4 methyl group as above, plus the clean loss of the protons on a second methyl group and the partial (ca 50%) loss of the protons from a third methyl group. The loss of the protons from the second methyl group can be explained if it is assumed that ion **IV**$^+$ can and does go back to ion **14**; hence, this second exchanging methyl group is #1 in the scheme.

The partial loss of the protons from a third methyl group is the slowest process which occurs. We know that methyl group #4 is fully exchanged in five minutes at 0°, and that at that time very little exchange is seen in methyl group #1. However, in forty-five minutes at 0°, methyl group #1 is fully exchanged and a third methyl group is partially exchanged. Hence, it appears likely that this partial exchange of the third methyl group accompanies the exchange of methyl group #1 in the ring opening of **IV**$^{+}$ to **14** and subsequent reclosure. If ion **14** were to close to **IV**$^{+}$ with a trans[3.3.0.] system (t-**IV**$^{+}$), methyl groups #4 and #8 would become reversed in the subsequent equilibration of **IV**$^{+}$ and **V**$^{+}$. This process is depicted below. Once this process occurs, of course, methyl group #8 completely exchanges its protons in less than five minutes. Hence, the third "partially exchanged" methyl group is probably a mixture of fully exchanged and completely unexchanged methyl groups. The formation of a trans[3.3.0.] ring junction is not without precedent. Bartlett synthesized the parent hydrocarbon (i.e. trans-bicyclo[3.3.0.]octane) in 1936 and estimated from heat of combustion data that the difference in strain energy between it and its cis isomer was six kcal/mole (8).


14

t-**IV**$^{+}$

iso-**V**$^{+}$

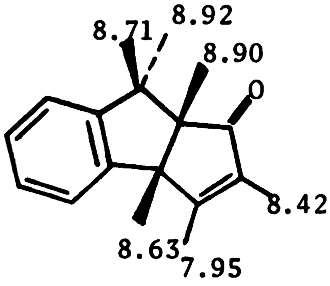
iso-**IV**$^{+}$

The above explanation is given strong support by an examination of olefins **VI** and **VII** from the forty-five minute exchange of **V** just described above. The nmr spectrum of each of these products showed only one full methyl signal, one methyl signal which showed about 20% exchange of the protons on that methyl group, and one methyl signal which showed about 60% exchange of the protons on that methyl group. The full methyl signal must arise from the #3 methyl group at the bridge juncture, as already discussed. The origin of the other two partial methyl signals may be deduced by a process of elimination. We know that methyl groups #4 and #2 (#2 is a vinyl in olefin **V**, but must exchange in the fast **IV**$^+$, **V**$^+$ equilibration) are fully exchanged in five minutes before the system goes on to ion **9**. We also know that ion **9** can exchange one of the #3 methyl groups and the #7 methyl group, since these are at the termini of the protonated allylic moiety of ion **9**. The other #3 methyl group is the full signal. Hence, the partial methyl signals can only arise from methyl groups #1 and #8.

The extent of exchange in these two methyl groups reflects the irreversibility of the formation of the **VI**, **VII** system (i.e. ion **9**) from the **IV**$^+$, **V**$^+$ system. The olefin **V** examined in the forty-five minute experiment had clearly been present in the reaction mixture as part of the **IV**$^+$, **V**$^+$ system for the full forty-five minutes. However the **VI** and **VII** quenched from the same experiment had been time averaged; some had rearranged from the **IV**$^+$, **V**$^+$ system immediately, and some had remained in the **IV**$^+$, **V**$^+$ system long enough to exchange as much as the olefin **V**. Hence, one would expect that the exchange in methyl groups #1 and #8 would be greater in **V** than in products **VI** and **VII**. The methyl group which was only 30% exchanged in olefins **VI** and **VII** must be methyl group #8; in olefin **V** it was exchanged approximately 50%. The methyl group which was 60% exchanged in **VI** or **VII** must be methyl group #1; in olefin **V** it was fully exchanged.

The last problem which was examined by deuterium labeling was that of the precise nature of the methyl shift or shifts of ion V^+ to go to the final ion, 9. Two possibilities are evident: 1) a direct suprafacial 1,4-migration of one of the #3 methyl groups in ion V^+ to form ion 9, or 2) two sequential 1,2-shifts as shown on the scheme. As previously discussed, the final products in the rearrangement, VI and VII, are fully deuterated in five of the six methyl groups if the entire dehydration/rearrangement is done in TFA-D. The one undeuterated methyl group must be one of the #3 methyl groups--the one that moved in the shift or shifts from V^+ to ion 9.

The structure proof (see Part C) of VI and VII is based on the oxidation of VI and VII to two ketones and an aldehyde. Fortuitously, these oxidation products complex with the europium shift reagent; this allows the complete nmr assignment of all the methyl groups in the molecules. The major ketone isolated from this oxidation is shown below with its nmr assignments. If the #3 methyl group had shifted in a

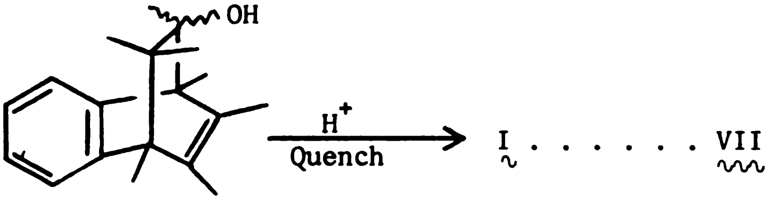


1,4-sigmatropic manner, it would appear at τ 8.90 in the above ketone. However, two sequential 1,2-sigmatropic shifts would leave the #1 methyl at τ 8.90 and the undeuterated #3 methyl group at τ 8.63 in the above ketone. When dienes VI and VII, which were fully deuterated in all but one methyl group, were oxidized, and the above ketone was isolated, the nmr spectrum of the ketone showed only one methyl signal, at τ 8.63.

Hence, the methyl groups must move by two 1,2-shifts; that is, a 1,2-shift of methyl group #1 to give intermediate ion **16**, followed by a second 1,2-shift of methyl group #3 to give the substitution pattern shown on the scheme.

C. Structure Determination of Olefins **I** Through **VII**: The Products of the Dehydration and Rearrangement of **8a** and **8b**.

An analysis of all the products of a given reaction is, if possible, the first step in any mechanistic study. The acid-catalyzed dehydration and subsequent rearrangement of the epimeric alcohols of structure **8** afforded seven isomeric olefins when quenched under various conditions. These have been arbitrarily numbered with Roman numbers **I** through **VII** in the approximate order of their formation in the reaction.



8

Table 2 lists the nmr spectrum of each of these olefins as well as the electronic spectra of all but **III**, which has never been isolated in an analytically pure form. All methyl group signals in Table 2 appear as sharp singlets with the exception of those labeled with an asterisk; these show a small (< 1 Hz) splitting typical of adjacent methyl groups on a carbon-carbon double bond, but are not clearly resolved. In addition to the methyl and vinyl proton signals shown in Table 2, all seven olefins also had four aromatic protons in their nmr spectra.

The electronic spectra in Table 2 were not particularly useful for structure elucidation because of the unusually long wavelength

Table 2. The Nmr and Electronic Spectra of I Through VII

The Nmr Spectra of I Through VII, in Tau Units

	I	II	III	IV	V	VI	VII
3H	9.80	9.38	9.18	9.00	9.24	9.07	9.08
3H	9.18	9.04	9.03	8.93	8.85	8.92	8.97
3H	8.88	8.88	8.73	8.88	8.66	8.82	8.77
3H	8.77	8.80	8.67	8.80	8.54	8.77	8.73
3H	8.67	8.60	8.33*	8.55*	8.48	8.35*	8.33*
3H	8.52	8.60	8.23*	8.44*	8.17	8.32*	8.20*
1H	5.47	4.06	5.17	5.15	5.41	5.37	5.35
1H	5.35	4.42	5.03	4.60	5.25	5.13	5.34

The Electronic Spectra of I Through VII, Absorptions in Nanometers, $\log_{10}\varepsilon$ in Parentheses

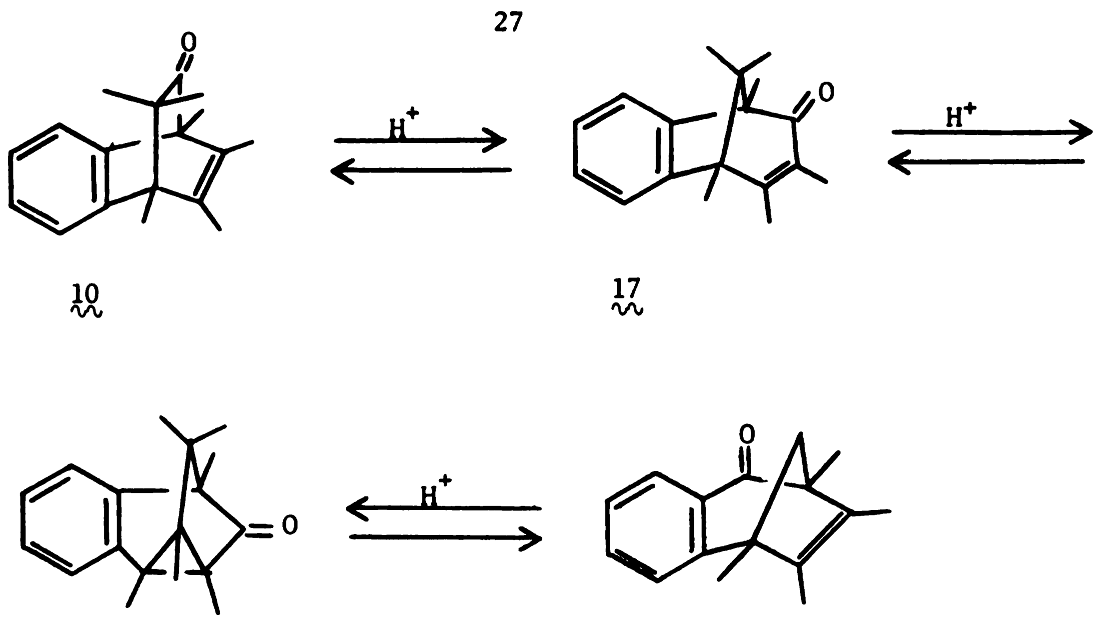
I	II	III	IV	V	VI	VII
236 (3.69)	260 (2.70)		253 (3.83)	240 (3.32)	250 (5.05)	248 (5.02)
266 (3.05)	270 (2.84)		261 (3.72)	252 (3.33)	263 (4.97)	272 (4.08)
276 (2.76)	278 (2.90)		280 (3.15)	272 (3.06)	272 (4.43)	
			289 (3.31)	299 (2.98)		
			299 (3.25)			

absorptions. Once the structures were known (vide infra) it appears that these long wavelength absorptions are due to interactions between the double bond (or bonds) and the aromatic ring present in each olefin.

The infrared spectra of olefins I through VII all show absorptions characteristic of double bonds, but these are not particularly informative since the presence of double bonds in I through VII is evident from the vinyl proton signals in the nmr spectrum of each. The mass spectra of I, II, IV, V, VI, and VII are all very similar; each has a parent peak at m/e 252, and a base peak at m/e 237 (P-15).

Although the spectral data allow one to generalize certain features of the structures of olefins I through VII, it does not appear that any of the structures can be definitively elucidated by spectral methods alone. Hence, resort was made to the more traditional methods of independent synthesis and chemical degradation.

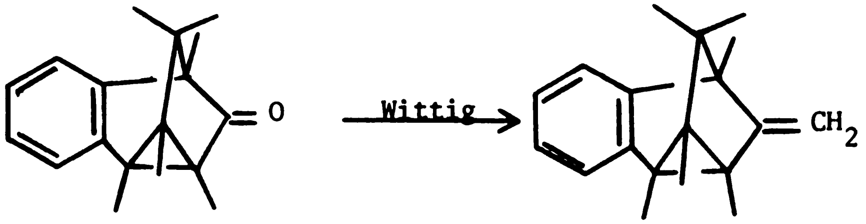
Ketone 10, the precursor of alcohols 8a and 8b, has recently been shown to be in equilibrium with ketones 17, 18, and 19 in strong acid (9). Since the methylene Wittig product of any one of these ketones would be isomeric with olefins I through VII, this mixture seemed to be a good place to start the synthesis of the unknown olefins. Initially, ketones 10 and 17 were separately added to a Wittig ylid; each failed to reac under the most strenuous Corey conditions (10). Hence, the entire equilibrium mixture of 7% 10, 28% 17, 6% 18 and 59% 19 was added to a Wittig ylid. The reaction was monitored by removing aliquots and examining them by GC. The first aliquot removed showed the complete



10 17

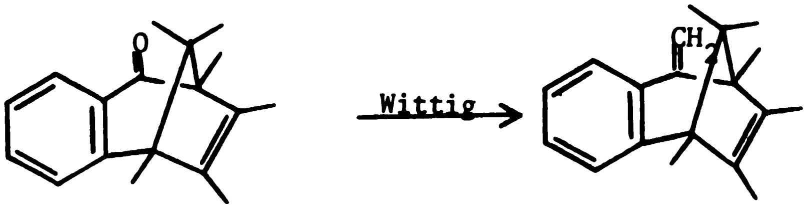
18 19

loss of ketone 18 and the formation of an olefin, which upon GC collection and examination had an nmr spectrum identical to that of olefin I. Hence, olefin I is 7-methylene-1,4,5,6,8,8-hexamethyl-2,3-benzotricyclo-[3.2.1.$0^{4,6}$]oct-2-ene. Subsequently, ketone 19 slowly reacted (the



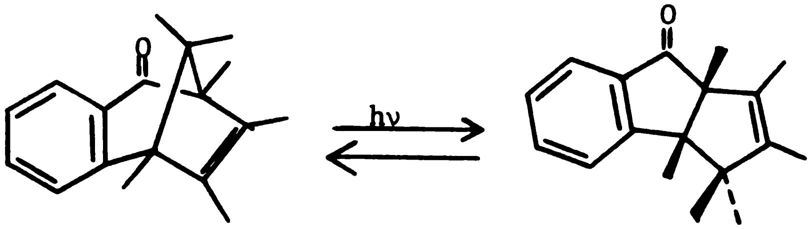
18 I

reaction was not allowed to go to completion) to form a second olefin, which, upon GC collection and examination had an nmr spectrum identical to that of olefin II. Olefin II must therefore be 2-methylene-1,5,6,7,8,8-hexamethyl-3,4-benzobicyclo[3.2.1.]octa-3,6-diene.

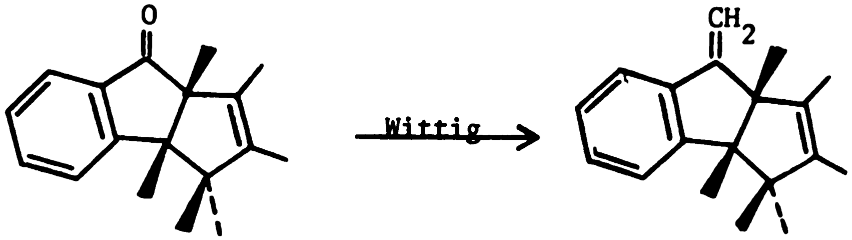


19 II

Ketone 19 has also been shown to be in photoequilibrium with its 1,3-acyl shift isomer 20 (9). Addition of ketone 20 to a methylene Wittig ylid afforded an olefinic product which had an identical nmr spectrum to that of olefin IV. Hence, olefin IV must be 8-methylene-1,2,3,4,4,5-hexamethyl-6,7-benzobicyclo[3.3.0.]octa-2,6-diene.

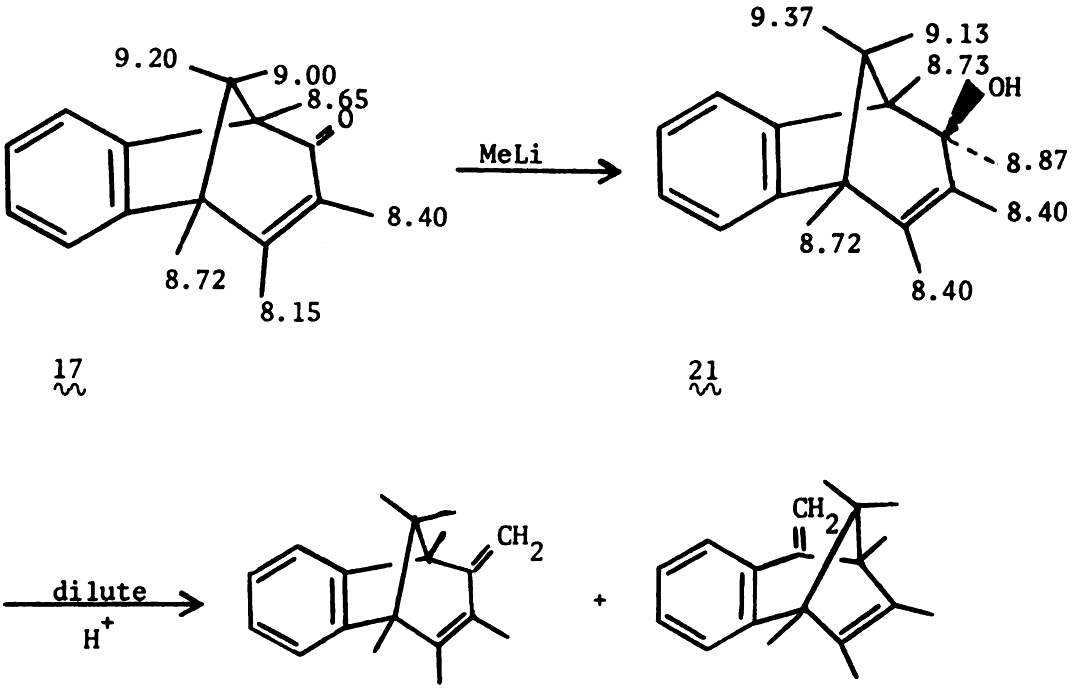


19 20



20 IV

Olefin III has never been isolated in an analytically pure form. Injection of a mixture of I, II, and III into a GC column affords only two peaks. Collection of the compounds giving rise to these two peaks and examination of them by nmr shows them to be I and II only; III apparently quantitatively rearranges to II on the column. Thin layer chromatography was ineffective in the separation of the I, II, III mixture. However, III has been synthesized in 85% yield by the following route from ketone 17. The nmr methyl assignments shown for alcohol 21 were made by inspection facilitated by comparison with the known assignments of ketone 17. The addition of methyllithium to 17 afforded only one alcohol in quantitative yield; alcohol 21 would be expected since the geminal methyl groups in the one carbon bridge of 17 would block nucleophilic attack of the methyllithium from the top side of the carbonyl group, whereas attack from the underside of 17 would



17

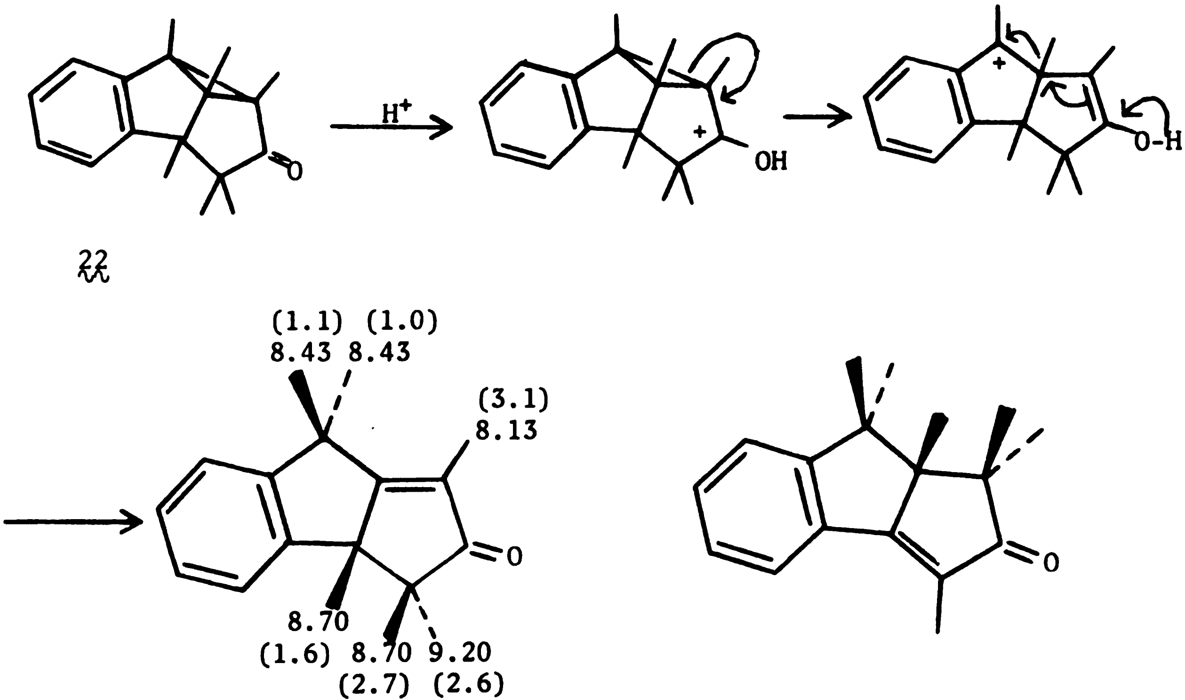
21

III, 85%

II, 15%

not be so hindered. Alcohol 21 was then dehydrated by treatment at room temperature for six minutes in five ml of ether which contained just six drops of TFA. Examination of the resulting product mixture after quenching revealed that only II and III were present in the ratio of approximately one to five respectively. This mixture was then seventeen times richer in III than the equilibrium mixture of I, II, and III which arose from the dehydration of 8a and 8b by a 30% solution of TFA in ether. Hence, we may conclude that III arises from the dehydration of **21**, and not by an equilibration which takes place in the very dilute acid. On the basis of this evidence, then, **III** is 2-methylene-1,3,4,5,8,8-hexamethyl-6,7-benzobicyclo[3.2.1.]octa-3,6-diene.

The synthetic precursor of olefin **V**, ketone **23** has recently been prepared by Keith Bodrero of these laboratories by the acid catalyzed rearrangement of ketone **22** (11). The structure of ketone **23** is based on the following evidence. Ketone **23** has a carbonyl absorption in the infrared at 1703 cm^{-1}, and a broad absorption from 240 to 250 nm in the ultraviolet. The latter indicates the presence of an α,β-unsaturated ketone, and the former fixes this moiety in a five-membered ring (12). All the nmr methyl group signals shown with the structure of **23** are sharp singlets. From this evidence we may postulate that ketone **23** must have either structure **23** or **24** since they are the only isomers which have an α,β-unsaturated ketone moiety in a five-membered ring, and would



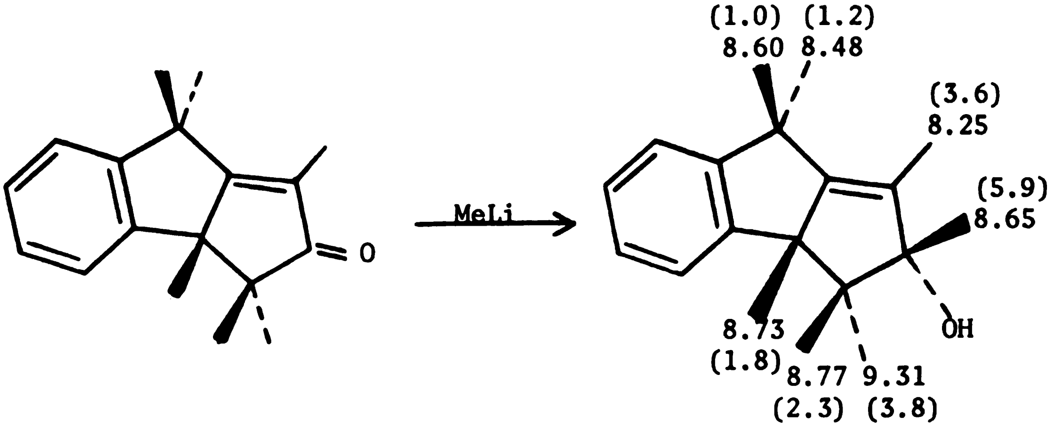
22

23

24

not be expected to show allylic splitting in their nmr spectra. The differentiation between structures 23 and 24 is based on the fact that structure 23 is mechanistically available from ketone 22 (as shown), and the fact that compound 23 displays a high-field methyl signal at τ 9.20 in its nmr spectrum. The cup-shaped nature of 23 can easily force one of the methyl groups at C-4 over the aromatic ring, where it would be expected to be shielded by the pi electrons of the aromatic ring. None of the methyl groups in structure 24 could be in such a magnetic environment.

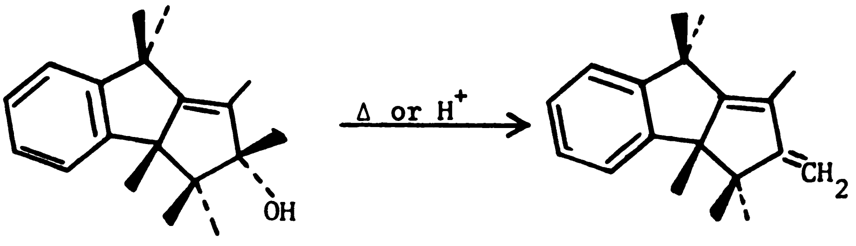
Addition of methyllithium to 23 afforded a single tertiary alcohol, 25, as shown below. The stereospecificity of this addition is presumably a consequence of the cup shape of 23; methyllithium can only attack the carbonyl group from the least sterically hindered convex side of the molecule.



23

25

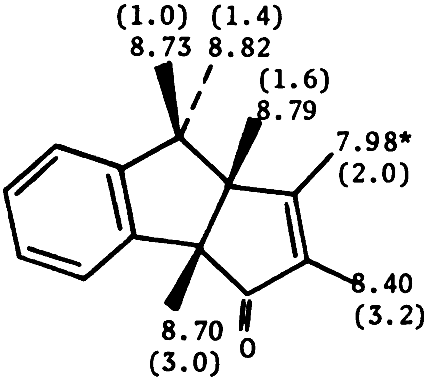
Injection of 25 into a GC column at 180° afforded a single peak. Collection of this compound and examination of its spectrum showed it to be identical to that of olefin V. Furthermore, 25 was smoothly dehydrated to V in one minute at 0° in an ether solution containing thirty volume percent of TFA. Hence, olefin V is 3-methylene-2,4,4,5,8,8-hexamethyl-6,7-benzobicyclo[3.3.0.]octa-1,6-diene.



25

V

Olefins VI and VII were characterized together by the OsO_4 oxidation of their exocyclic double bonds by the procedure of Zimmerman (13). This reaction afforded the mixture of products 26-28 shown below.



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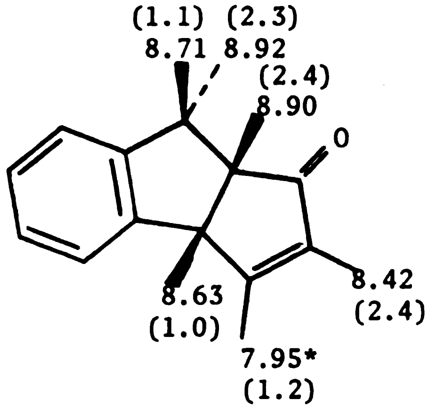
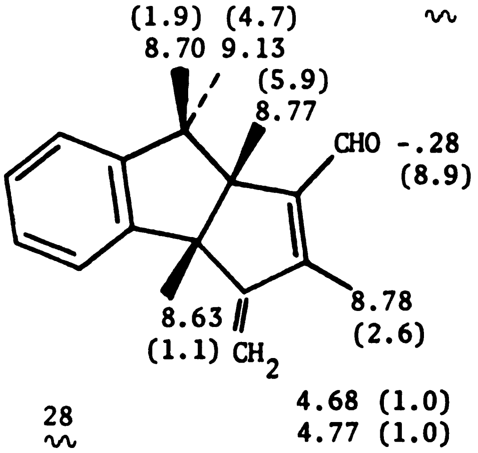


27



28

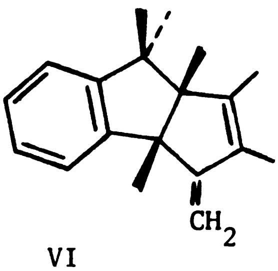
This mixture also contained some unoxidized **VI** and **VII** in the equilibrium ratio of two to one, even if the starting diene was pure, GC-collected **VI**. Hence, **VI** and **VII** can interconvert in OsO_4, and had to be characterized together.

The structures of **26** and **27** seem secure. Both have carbonyl absorptions at 1695 cm^{-1}, and both have base-exchangable methyl groups which appear at low-field in the nmr and show allylic ($J < 1$ Hz) splitting. These are indicated by asterisks in the structures. The base-exchangable methyl groups prove the presence of an α,β-unsaturated ketone moiety, and the carbonyl absorptions at 1695 cm^{-1} force it into a five-membered ring (12). Hence **26** and **27** are the only isomeric possibilities. The absolute differentiation between them is based upon the europium shift numbers. In structure **26** there are two methyl groups near the ketone moiety where the shift reagent complexes; and, indeed, only two methyl groups in the nmr spectrum shown with structure **26** have substantially higher shift numbers than the rest of the methyl groups in the molecule. Alternatively, structure **27** has three methyl groups near the carbonyl group, and in this case three methyl signals of the nmr spectrum shown with structure **27** have higher shift numbers.

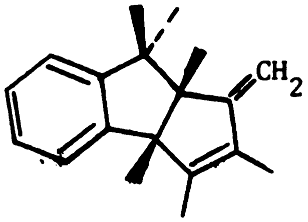
The structure of **28**, an unexpected product of the oxidation reaction, is not as firm as that of **26** or **27**. For example, there is no certain evidence of ring size. However, it seems reasonable that it could be structure **28**. The C=C-C=C-CHO moiety is indicated by the ultraviolet maximum at 293 nm (3 x 5 nm for the 3 alkyls, plus 5 nm for the exocyclic double bond, plus 270 nm base affords 290 nm), and by the infrared absorption at 1665 cm^{-1} (expected 1660-1680 cm^{-1}) (12).

The aldehyde moiety is indicated by the one proton singlet at τ -0.28 in the nmr spectrum of **28**.

The differentiation between **VI** and **VII** is based upon the nmr spectra of the dienes themselves, since there is no way to tell which ketone arises from which olefin in the OsO_4 oxidation. The nmr spectrum of olefin **VII** has vinyl singlets at τ 5.35 and τ 5.34 which are so close together that they are nearly not resolved by a Varian A-60. The spectrum of **VI** has vinyl singlets at τ 5.13 and τ 5.37. Examination of a model of either **VI** or **VII** shows that they are cup-shaped, and that in **VI**, it is possible for one of the vinyl protons to be in the de-shielding (edge) region of the aromatic ring. This is not possible in **VII**. Hence, if we assume that τ 5.35 (or 5.37) is the "normal" chemical shift for these vinyl protons, **VI** appears to have the unusual low-field vinyl peak at τ 5.13, and is therefore the structure shown. Olefin **VI** is then



VI



VII

4-methylene-1,2,3,5,8,8-hexamethyl-6,7-benzobicyclo[3.3.0.]octa-2,5-diene, and olefin **VII** is 4-methylene-1,2,3,5,6,6-hexamethyl-7,8-benzobicyclo-[3.3.0.]octa-2,7-diene.

EXPERIMENTAL

A. General Procedures

All nmr spectra were measured in CCl_4 solutions using TMS as an internal standard with either a Varian A-60 or T-60 spectrometer. All chemical shifts are recorded in units of τ(tau). The small numbers beside the methyl groups in structures in the discussion section are the nmr chemical shifts of those methyl protons; other types of protons are treated similarly. The numbers beside the chemical shifts in parentheses are the normalized europium shift numbers. These were obtained by adding very small increments of tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) Eu(III) (14) to a CCl_4 solution of the compound being investigated. The relative mole ratio of shift reagent to substrate after the final addition was approximately 1:10. The relative shifts in chemical shift of the various protons were then "normalized" so that the least shifted protons have a shift number of 1.0. Hence, a methyl group whose protons have a shift number of 2.4 is shifted 2.4 times as much by the reagent as the least shifted protons in the molecule (15).

Infrared spectra were recorded on a Unicam SP-200 spectrophotometer; ultraviolet spectra were measured in 95% ethanol solutions using a Unicam SP-800 spectrophotometer. Mass spectral data were obtained from a Hitachi-Perkin Elmer RMU-6 operated by Mrs. Ralph Guile.

Preliminary studies of this problem were investigated by Mr. John C. Bernhardt of these laboratories. Several of the experimental procedures to follow were devised by him; these are followed by his initials, J.C.B. (17).

B. Synthesis of *syn* and *anti*-1,2,3,3,4,7,8-heptamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-dien-2-ols, **8a** and **8b** (J.C.B.).

A solution of 22.7 g of 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo-[2.2.2.]octa-5,7-dien-2-one (3) in 200 ml of ether was added dropwise to a solution of methyllithium (85 ml, 1.75 M, excess) in ether and refluxed for 18 hours. Sufficient water was then added to hydrolyze the excess methyllithium and to dissolve the lithium hydroxide which formed. The aqueous layer was then discarded, and the ether layer was washed with water (3 X 80 ml). It was then dried with anhydrous $MgSO_4$ and evaporated under reduced pressure to afford 22.4 g (93.5%) of a yellow-white solid, mp 104-112°. The nmr spectrum of this sample showed it to be a mixture of the *syn* and *anti* epimers **8a** and **8b** in the approximate ratio of two to one. Repeated recrystallization of this mixture from hexane afforded the pure *syn* isomer, **8a**, mp 140-42°; λ_{max}^{EtOH} 220 nm ($\log_{10}\varepsilon = 3.43$), 257 (2.59), 264 (2.68), and 271 (2.62); nmr (CCl_4) τ 2.90 (s, 4H), 8.30 (s, 6H), 8.40 (s, 3H), 8.45 (s, 3H), 9.00 (s, 3H), 9.08 (s, 3H), 9.55 (s, 3H), and 9.83 (broad, 1H, removed on shaking with D_2O); $\lambda_{max}^{CCl_4}$ 3610 cm^{-1}, 2960, and 1460. The nmr spectrum of the *anti* alcohol, **8b**, was deduced by subtraction of the spectrum of pure **8a** from that of the mixture of **8a** and **8b**: τ 2.96 (s, 4H), 8.24 (s, 6H), 8.40 (s, 3H), 8.45 (s, 3H), 9.12 (s, 3H), 9.28 (s, 3H), and 9.63 (s, 3H).

Anal. Calcd: C, 84.39; H, 9.69

Found: C, 84.52; H, 9.79

C. Synthesis of 1,2,3,3,4,7-hexamethyl-8-methyl-d_3-5,6-benzobicyclo[2.2.2.]octa-5,7-dien-2-ols, **8a**-d_3 and **8b**-d_3 (J.C.B.).

1,3,3,4,7-pentamethyl-8-methyl-d_3-5,6-benzobicyclo[2.2.2.]octa-5,7-dien-2-one (3) was added to methyllithium and worked-up as described in Part B. The nmr spectrum of **8a**-d_3 was identical to that of **8a** except that the singlet at τ 8.30 in **8a**-d_3 integrated for only 3H. Similarly, the nmr spectrum of the mixture of **8a**-d_3 and **8b**-d_3 resembled that of the mixture of **8a** and **8b** except that the previously mentioned singlet at τ 8.30 integrated for 3H, and the singlet at T 8.24 integrated for 3H.

D. Quenching Studies, General

The compound to be investigated (50 mg) was dissolved in either neat TFA or a solution of 30 vol% TFA in ether (3 ml). After the requisite time had elapsed, the reaction was quenched by pouring it into ice water and neutralizing the solution with strong NaOH to a phenolphthalein end-point. The aqueous solution was then extracted with ether (50 ml), and the aqueous layer was discarded. The ether layer was washed with water (3 x 20 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. In every case, the yield was nearly quantitative. The nmr spectrum of the sample was then examined to determine the product ratios by integration of the appropriate vinyl signal peaks (see Table 2, Part C for the complete nmr spectra of **I** through **VII**). In cases where vinyl proton peaks overlapped, simple algebra was used to calculate the product ratios. For example, the nmr spectrum of **VI** displays one proton vinyl singlet at τ 5.13 and 5.37, and the nmr spectrum of **VII** displays a broad two proton singlet at τ 5.35. Analysis of the nmr spectrum of the mixture of **VI** and **VII** from the 180 minute neat TFA dehydration of **8a** and **8b** (these data from Table 1, Part A) shows a singlet at τ 5.13 of relative area 21 and a singlet at τ 5.35 of relative area 56. Analysis of the entire spectrum shows methyl, vinyl, and aromatic proton signals which may *all* be assigned to either **VI** or **VII**. Hence, the τ 5.13 peak accounts for one proton of **VI** (area 21) and the τ 5.35 peak accounts for one proton of **VI** and two protons of **VII** (area 56). One proton of **VII** is then (56-21)/2 = 17.5, and the mixture is 21/(17.5 + 21) = 55% **VI**. The percentage of **VII** is then 17.5/(17.5 + 21) = 45%. In cases where dehydration was not complete, the percentage of dehydration was estimated by comparison of the peak heights of methyl proton signals characteristic of **8a** and **8b** and of the olefinic products **I**, **II**, and **III**. These signals were too close together for electronic integration using the nmr spectrometer. All the quenching data in Table 1, Part A, and the equilibria studies were determined in this manner.

E. Separation of Products **I** through **VII** (J.C.B.).

The crude product mixtures from the quenching experiments could be separated by preparative GC using two columns. Column A was a 10' X 1/4" 14% OV-25 on Chromosorb W, column B was a 10' X 1/4" 20% FFAP on Chromosorb W; both were held at 200° with a He flow of 100 ml/minute for these measurements. The chart below gives the retention time of the olefins in minutes on the two columns. Note that **I** and **IV** could not be separated with column A, and **VI** and **VII** could not be separated with column B. Olefin **III** could not be separated by gas chromatography, since it thermally rearranged to **II** (see Part C). Samples of pure olefins were prepared from preparative GC separation and collection in this manner.

Compound	Column A	Column B
I	72	60
II	67.5	46.5
III	-	-
IV	72	54
V	33.5	22.6
VI	51	37.5
VII	58.5	37.5

F. Dehydrations Using Alcohols **8a**-d_3 and **8b**-d_3 (J.C.B.).

A mixture of the epimeric alcohols, **8a**-d_3 and **8b**-d_3, was dehydrated in TFA and quenched at various times as outlined in Section D. The mixtures of olefins obtained were separated by GC (see Section E) to afford pure samples of **I**, **II**, **IV**, **V**, **VI**, and **VII**. The nmr spectra of **VI** and **VII** were identical to those of samples of **VI** and **VII** which had been separated from the dehydration of unlabeled alcohols (see Table 2, Part C for the complete nmr spectra of **I** through **VII**). The nmr spectra of **I**, **II**, **IV**, and **V**, however, each showed the loss of one (3H) methyl singlet when compared to the spectra of the unlabeled olefins. The chemical shift of the methyl proton singlets which were missing were as follows: **I**, τ 8.77; **II**, 8.63*; **IV**, 8.44*; **V**, 8.17.((An asterisk indicates that this methyl singlet had shown allylic splitting in the unlabeled compound.)

G. The Dehydration of **8a** and **8b** in TFA-D.

A mixture of the epimeric alcohols **8a** and **8b** was dehydrated in TFA-D and TFA-D/ether and quenched as outlined in Section D. The resulting mixtures of olefins were separated by GC using the methods of Section E to afford pure samples of **I**, **II**, **IV**, **V**, and **VII** (see Table 2, Part C for the complete nmr spectra of **I** through **VII**). Examination of the nmr spectrum of olefin **I** from this dehydration showed that the methyl proton singlets at τ 8.88, 8.67 and 8.52 were absent, and the vinyl proton singlets at τ 5.47 and 5.35 were diminished in area. The nmr spectrum of **II** showed the methyl proton signals at τ 8.88, 8.80, and 8.60 were absent, and the vinyl proton signals at τ 5.06 and 4.42 were reduced in area. The nmr spectrum of **IV** showed that the methyl proton singlets at τ 8.88, 8.80, and 8.55 were absent, and the vinyl proton singlets at τ 5.15 and 4.60 were reduced in area. The nmr spectrum of **V** showed the methyl proton singlets at τ 8.85, 8.54 and 8.48 were absent, and the vinyl proton singlets at τ 5.41 and 5.25 were diminished in area. The nmr spectrum of **VI** showed only one 3-proton singlet at τ 8.82, plus vinyl signals at τ 5.37 and 5.13 which integrated for less than 1H each, plus aromatic protons. The nmr spectrum of **VII** showed only one 3-proton singlet at τ 8.73 plus a partial broad (2H) vinyl signal at τ 5.34, plus aromatic protons.

H. The Equilibration of **IV** and **V** in TFA-D.

A GC collected sample of **V** (53 mg) was dissolved in neat TFA-D (3 ml) at 0° and quenched after five minutes to afford a mixture of **IV** (25%) and **V** (75%), separated by GC on column A. The nmr spectrum of the sample of **IV** collected was identical to that of a sample from the rearrangement in TFA except that the methyl proton signal at τ 8.88 was absent. The nmr spectrum of olefin **V** collected from this same experiment showed the loss of the methyl proton singlet at τ 8.47.

A second GC collected sample of **V** (275 mg) was dissolved in neat TFA-D (10 ml) at 0° and quenched after 45 minutes to afford a mixture of **IV** (10%), **V** (30%), **VI** (40%), and **VII** (20%), separated on column A. The nmr spectrum of **IV** from this experiment showed the loss of the methyl proton singlets at τ 8.88 and 8.55, plus a partial (ca 50%) loss of the methyl proton singlet at τ 8.80. The nmr spectrum of **V** showed the loss of the methyl proton singlets at τ 8.47 and 8.85, and a partial loss of the methyl proton singlet at τ 8.53. The nmr spectrum of olefin **VI** showed the loss of methyl proton signals at τ 9.07, 8.35, and 8.32, plus a 30% loss of the methyl proton signal at τ 8.78 and a 60% loss of the signal at τ 8.93. The nmr spectrum of **VII** showed the loss of methyl proton signals at τ 9.08, 8.33, and 8.20, plus a 30% loss of the methyl proton singlet at τ 8.73, and a 60% loss of the methyl proton singlet at τ 8.97.

I. The Synthesis of 1,5,6,7,8,8-hexamethyl-3,4-benzobicyclo[3.2.1.]-octa-3,6-diene-2-one, **19**, 1,3,4,5,8,8-hexamethyl-6,7-benzobicyclo[3.2.1.]octa-3,6-diene-2-one, **17**, and 1,2,5,7,8,8-hexamethyl-3,4-benzotricyclo[3.2.1.0.^{2,7}]oct-3-ene-6-one, **18** (9).

A 500 mg sample of ketone **10** (3) was refluxed for 3 hours in neat TFA and quenched using the procedure outlined in Section D to afford

480 mg of a pale yellow oil. Injection of an acetone solution of this oil into a 5' X 1/4' 20% FFAP GC column at 200° using a flow of 100 ml He/min afforded three peaks with the following retention times in minutes and areas: 7.5 min, 52%; 9.0, 41%; and 13.0, 7%. The entire reaction mixture was preparatively injected into the GC column and the material corresponding to each peak was collected and examined.

The material corresponding to the 7.0 min peak has been identified as ketone **19**. The nmr spectrum of **19** showed 2 aromatic multiplets centered at τ 2.07 (1H), and τ 2.77 (3H), as well as methyl proton singlets at τ 8.53 (6H, europium numbers 1.0 and 1.6, assigned to methyl groups on C5 and C6 respectively), 8.73 (3H, 3.5, methyl at C1), 8.88 (3H, 1.6, methyl at C4), 8.97 (3H, 1.3, methyl at C8 <u>anti</u> to benzene ring), and 9.25 (3H, 2.1, methyl at C8 <u>syn</u> to benzene ring). The ir spectrum (CCl_4 soln) showed strong absorptions at 3000, 1687, 1600, 1300, 990, and 885 cm^{-1}. The mass spectrum of **19** showed a parent peak of m/e 254 and a base peak of m/e 239.

<u>Anal</u>. Calcd: C, 84.99; H, 8.72

Found: C, 85.16; H, 8.63

The material corresponding to the 9.0 min peak has been identified as a mixture of 90% ketone **17** and 10% ketone **10**. These were separated by preparative TLC. The nmr spectrum of **17** showed an aromatic singlet at τ 2.98 (4H), 2 allylic methyl proton signals as poorly resolved quartets ($J < 1$ Hz) at τ 8.15 (3H, 1.2, methyl at C4) and 8.40 (3H, 2.9, methyl at C3), and methyl proton singlets at τ 8.65 (3H, 3.1, methyl at C1), 8.72 (3H, 1.0, methyl at C5), 9.00 (3H, 1.7, methyl at C8 <u>anti</u> to benzene ring), and 9.20 (3H, 1.1, methyl at C8 <u>syn</u> to benzene ring). The ir spectrum of **17** (CCl_4 soln) showed strong absorptions at 300, 1667, 1390, 1260, and 885 cm^{-1}. The mass spectrum showed a parent peak of m/e 254 and a base peak of m/e 239.

Anal. Calcd: C, 84.99; H, 8.72

Found: C, 84.72; H, 8.64

The material corresponding to the 13 min peak has been identified as ketone **18**. The nmr spectrum of **18** showed an aromatic multiplet centered at τ 2.90 (4H) and methyl proton singlets at τ 8.48 (3H, 1.2, methyl at C2), 8.78 (6H, 1.0 and 2.5, methyl groups at C1 and C5 respectively), 8.87 (3H, 2.5, methyl at C7), 9.03 (3H, 1.7, methyl at C8 *anti* to benzene ring), and 9.62 (3H, 1.0, methyl at C8 *syn* to benzene ring). The ir spectrum of **18** (CCl_4 soln) showed strong absorptions at 2995, 1720, 1400, 1000, and 880 cm^{-1}. The mass spectrum of **18** showed a parent peak of m/e 254 and a base peak of m/e 239.

Anal. Calcd: C, 84.99; H, 8.72

Found: C, 85.10; H, 8.75

J. The Synthesis of Olefins **I** and **II**.

Into a 100-ml flask was placed 560 mg (11.7 mmole) of 50% NaH in mineral oil and a magnetic stirring bar. The flask was sealed with a septum, and continuously flushed with nitrogen, which was flushed in and vented through needles placed in the septum. The contents of the flask were magnetically stirred, and warmed in an oil bath. Dimethylsulfoxide (DMSO) (5 ml) was injected, and the temperature was raised to 80° until the evolution of hydrogen stopped (about 45 min). The DMSO-Na solution was allowed to cool to room temperature, and a solution of 4.16 g (11.7 mmole) of triphenylmethylphosphonium bromide in 10 ml of DMSO was injected. This was followed by the injection of a DMSO solution (5 ml) containing a total of 1 g of a mixture of ketones **10**, **17**, **18**, and **19** (9). Ketones **10** and **17** were known not to react under these Wittig conditions. The mixture immediately darkened to a deep brown, but did not go through any color which could be described as red. The mixture was stirred for 4 hours at room temperature, and a 500 µl aliquot was withdrawn, hydrolyzed in 5 ml of water, and extracted into 500 µl of CCl_4. Five µl of this CCl_4 solution was then injected into a 5' X 3/8" 20% FFAP GC column at 200°. A small amount of product corresponding in area to the ketone **18** initially present appeared at retention time 7.5 minutes, along with ketone **19** at **11** minutes, and ketones **10** and **17** at 14 minutes. (These were never GC-resolvable, but were inert under these conditions.) Ketone **18** had a retention time of 17 minutes on this GC column, but did not appear at all in this aliquot; it had apparently been converted quantitatively to the product with a retention time of 7.5 minutes. The reaction mixture was allowed to stir for 4 days at room temperature, and a second aliquot was withdrawn and prepared for GC injection in the same manner. The GC trace of this aliquot showed a new peak at retention time 6.5 minutes, the Wittig product of **18** at 7.5 minutes, a smaller peak for ketone **19** at 11 minutes, and the peak for the other two ketones at 14 minutes. It appeared that ketone **19** had been transformed to the 6.6-minute product in about 25% conversion.

The reaction mixture was then hydrolyzed in 70 ml of ice water and extracted with CCl_4 (3 X 20 ml). The CCl_4 layer was washed with water (3 X 20 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to afford a colorless semi-crystalline product. This was dissolved in 3 ml of acetone and cooled. Approximately 1 g of nearly white crystals of triphenylphosphine oxide precipitated (identified by mp and nmr), and these were filtered from the solution. The mixture was then preparatively injected into the GC column used to monitor the reaction, and each peak was collected and examined by nmr. The 6.5 minute peak had an nmr spectrum identical to that of olefin **II**. The 7.5 minute peak had an nmr spectrum identical to that of olefin **I**. The 11 minute peak had an nmr spectrum identical to that of ketone **19**. The 14 minute peak had an nmr spectrum identical to that of the mixture of ketones **10** and **17** initially present.

K. The Synthesis of Olefin **III**.

To an ether solution (5 ml) of TLC-purified ketone **17** (30 mg) was slowly added 1 ml (excess) of a 1.7 molar solution of methyllithium in ether. The solution was magnetically stirred for 30 minutes at room temperature, and the excess methyllithium was hydrolyzed by the dropwise addition of 1 ml of water. The mixture was then extracted with ether (40 ml) and the ether layer was washed with water (4 X 20 ml). The ether layer was then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to afford 32 mg of a pale yellow oil, which is identified as 1,2,3,4,5,8,8-heptamethyl-6,7-benzobicyclo[3.2.1.]oct-2-ene-4-anti-ol, **21**. The nmr spectrum of **21** is shown beside the structure of **21** in Part C of the text. The infrared spectrum of **21** (CCl_4) showed no absorption in the region from 1600 to 2000 cm^{-1}, but did show a ν_{OH} at 3660 cm^{-1}.

Alcohol **21** was dehydrated by dissolving it in ether (5 ml) and adding 6 drops of TFA to the solution. The solution was stirred at room temperature for 6 minutes, then quenched by the procedure outlined in Section D. Examination of the nmr spectrum of the resulting product revealed that it contained only olefins **II** and **III**. Integration of the τ 4.42 vinyl proton singlet from **II** and the τ 5.03 vinyl proton from **III** showed that the ratio of **II** to **III** was 1:17.

L. The Synthesis of Olefin **IV**.

A Wittig ylid (11.7 mmole) was prepared exactly as described in Section J. Ketone **20** which had been GC-collected (100 mg) was then injected into the solution of ylid, and the resulting mixture turned deep red. It was then warmed to 60°; after two hours an aliquot was withdrawn, worked-up, and examined by GC as outlined in Section J. The GC trace showed that the ketone **20** peak at retention time 16 minutes was reduced in area to approximately one fifth of the area of a similar aliquot which had been removed just after the addition of **20** to the ylid solution. A second peak corresponding in area to the loss of the 16-minute peak appeared at retention time 8 minutes. The reaction mixture was then worked-up using the procedure outlined in Section I, and the product responsible for the 8-minute peak was preparatively GC-collected to afford a sample which had an identical nmr spectrum to that of olefin **IV**.

M. The Synthesis of Olefin **V**.

To an ether solution (20 ml) of GC-collected ketone **23** (35 mg) (16) was slowly added 4 ml (excess) of a 1.7 molar solution of methyllithium in ether. The solution was magnetically stirred for 30 minutes at room temperature, and the excess methyllithium was hydrolyzed by the dropwise addition of 1 ml of water. An additional 40 ml of ether was then added, and the resulting mixture was washed with water (4 X 20 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to afford a pale yellow oil which was identified as 2,3,4,4,5,8,8-heptamethyl-6,7-benzobicyclo[3.3.0.]octa-1,6-dien-3-*syn*-ol, 25. The nmr spectrum of 25 is shown with the structure of 25 in Part C of the text. The infrared spectrum of 25 showed ν_{OH} at 3650 cm^{-1}.

Anal. Calcd: C, 84.39; H, 9.69

Found: C, 84.52; H, 9.79

Injection of a 20% acetone solution of 25 into a 5' X 3/8" 20% FFAP GC column at 180° afforded a single peak, which had the same retention time on this column as olefin V. Collection of 10 mg of this compound afforded an nmr sample which gave spectrum which was identical to that of olefin V.

To a solution of 20 mg of 25 in 5 ml of ether was added 1.5 ml of TFA. The solution was allowed to stand at room temperature for one minute and then quenched as outlined in Section D. The nmr spectrum of the resulting sample was identical to that of olefin V.

N. The OsO_4 Oxidation of VI and VII.

To a solution of OsO_4 (761 mg, 3.0 mmole) in 30 ml of ether, was slowly added an ether solution (20 ml) of VI and VII (ratio 2:1, 800 mg total, 3.17 mmole). The resulting solution was then stirred magnetically for five hours at room temperature. During this time, the solution turned black and precipitated a black gum. The ether was evaporated under reduced pressure at room temperature, and a solution of 3 g of $NaHSO_3$ in 50 ml of 50% aqueous ethanol was added. The resulting suspension was refluxed for two hours, cooled and filtered. The filtrate was evaporated to half volume at reduced pressure and extracted with $CHCl_3$ (4 X 20 ml). The $CHCl_3$ layers were then combined, washed with water (3 X 20 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to afford 700 mg of a yellow oil.

Injection of an acetone solution of this oil into a 5' X 3/8" 20% FFAP GC column at 230° afforded five peaks with the following retention times and approximate areas: 2.5 min (25%), 3.5 min (15%), 8 min (18%), 10 min (6%), and 12 min (36%). Each of these peaks was collected and examined.

The 2.5 and 3.5 minute peaks corresponded to unreacted **VI** and **VII** respectively (by nmr). The 8 minute peak was due to 1,3,4,5,8,8-hexamethyl-6,7-benzobicyclo[3.3.0.]octa-3,6-dien-2-one, **27**. The spectral data for **27** are given in Part C of the text. When **27** was refluxed overnight in a 6 molar solution of NaOMe in MeOD, worked-up, and examined by nmr, it showed no splitting in the τ 8.42 peak, and a complete loss of the low-field τ 7.95 peak.

Anal. Calcd: C, 84.99; H, 8.72

Found: C, 85.04; H, 8.60

The 10 minute peak was identified as due to 1,3,4,5,6,6-hexamethyl-7,8-benzobicyclo[3.3.0.]octa-3,7-dien-2-one, **26**. The spectral data for **26** are given in Part C of the text. When **26** was refluxed overnight in a 6 molar solution of NaOMe in MeOD, worked-up, and examined by nmr, it showed no splitting in the τ 8.40 peak, and a complete loss of the low-field τ 7.98 peak.

Anal. Calcd: C, 84.99; H, 8.72

Found: C, 84.98; H, 8.60

The 12 minute peak has been tentatively identified as 4-methylene-1,3,5,8,8-pentamethyl-6,7-benzobicyclo[3.3.0.]octa-2,6-dien-2-carboxaldehyde, **28**. The spectral data for **28** are given in Part C of the text.

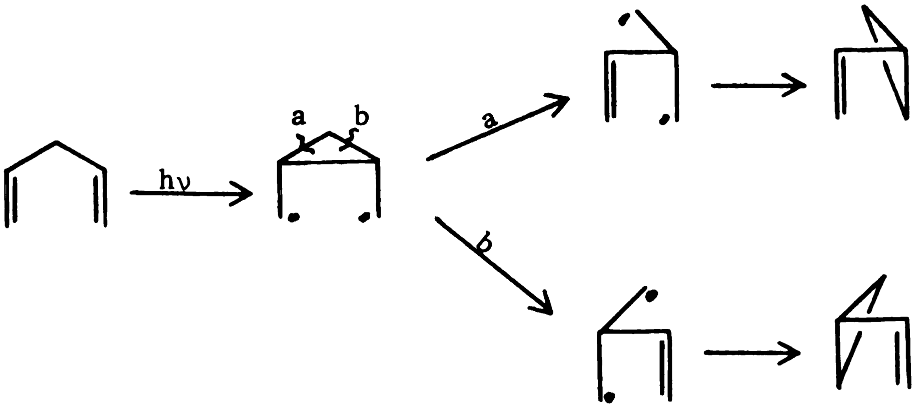
PART II

THE EFFECT OF REMOTE SUBSTITUENTS ON Di-π-METHANE PHOTOISOMERIZATIONS

INTRODUCTION

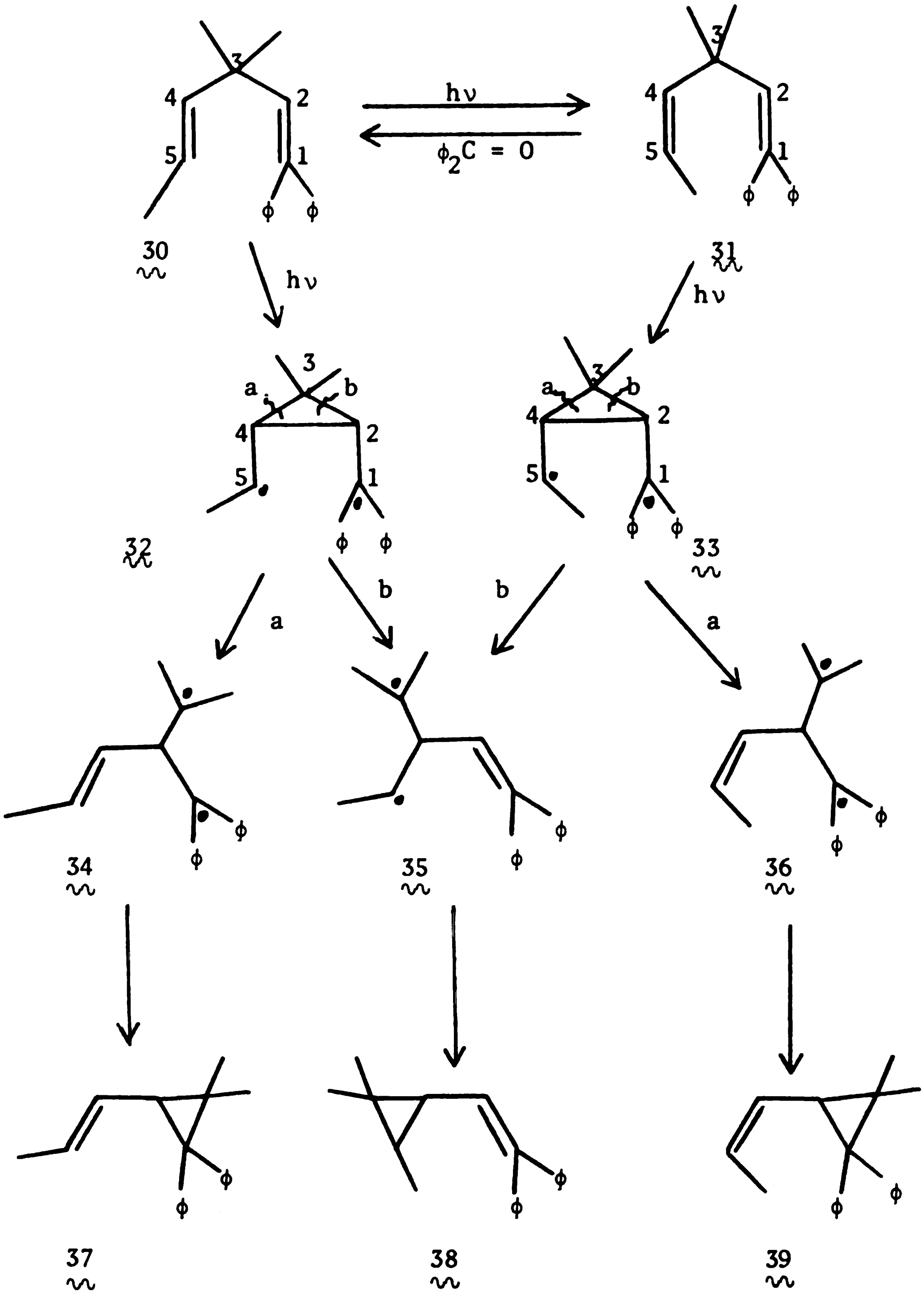
The di-π-methane photorearrangement, the generality of which was first recognized by Zimmerman in 1967, involves "an excited state transformation in which a divinylmethyl moiety is converted into a vinylcyclopropane" (18). The reaction was then further generalized by Givens in 1969 when he noted that a carbon-oxygen π bond can participate in the same manner as a carbon-carbon double bond (19). Dauben termed this the oxa-di-π-methane rearrangement (20).

A schematic representation of the rearrangement is given below.



In this generalized representation, dots are used to indicate atoms with a free valence; no multiplicity is inferred. In fact, di-π-methane rearrangements have been observed to occur from both singlet and triplet excited states. Note also that fission of either bond a or bond b in the cyclopropane intermediate (or transition state) leads to the same product. However, real systems are often not degenerate to such bond fission.

Zimmerman's study of the irradiation of **30** and **31**, shown below, constitutes an example of a di-π-methane rearrangement which occurs from a singlet excited state. Initially **30** and **31** were separately



irradiated in solutions containing benzophenone as a sensitizer. No vinylcyclopropanes were produced, but the cis-trans equilibration of **30** and **31** was observed. Hence, the triplet excited states of **30** and **31** do not undergo the di-π-methane rearrangement. However, direct irradiation of **30** afforded **37** only; similarly direct irradiation of **31** afforded **39** only. Under these conditions, no cis-trans isomerization of reactants or products was observed. Interestingly, no **38** was formed in either reaction.

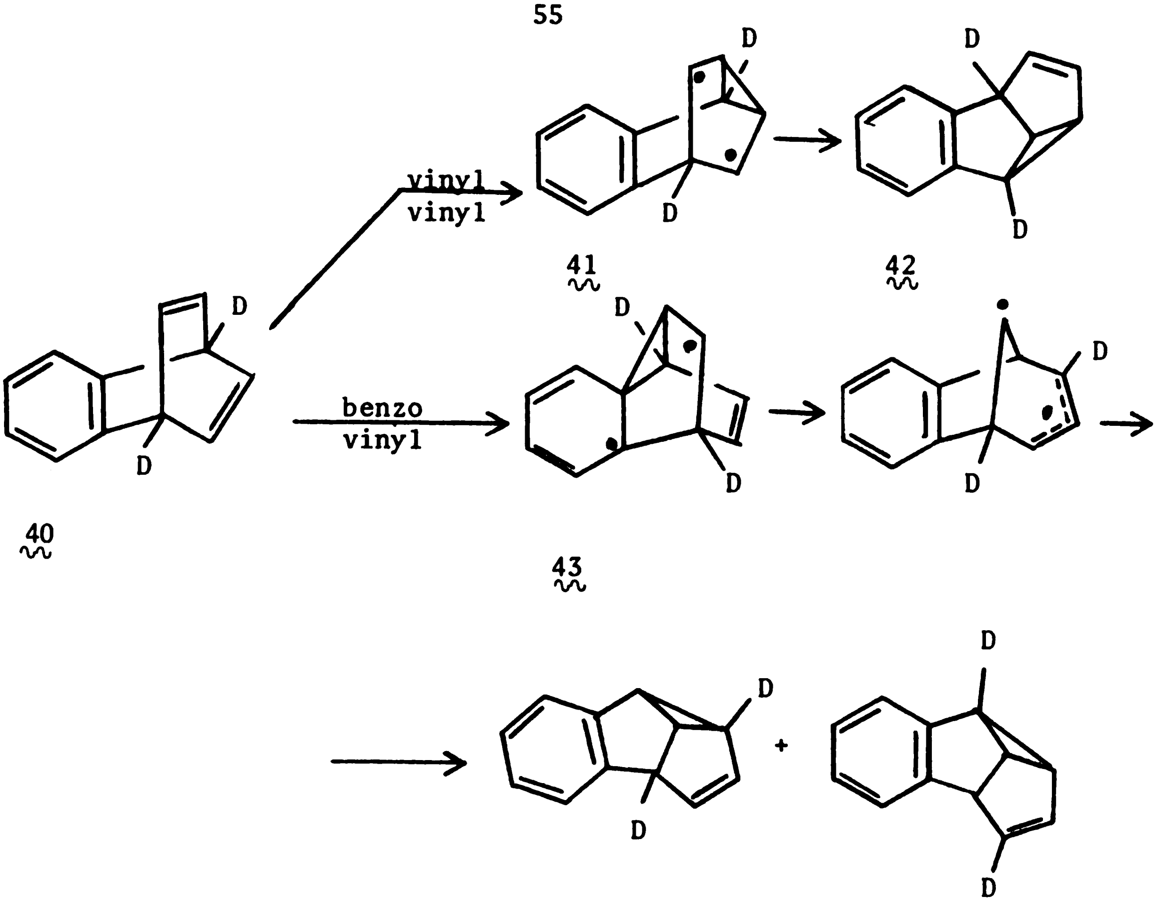
This selectivity in the opening of the cyclopropane intermediates (or transition states) **32** and **33** by the fission of only bond **a** in each case, indicates that the reaction proceeds by the route which allows maximum odd-electron delocalization. Thus, opening bond **b** in either **32** or **33** affords **35**, a species which places the free valences on a tertiary and a secondary carbon. Hence, **35** would be expected to be a higher energy species than either **34** or **36**, which afford the observed products. In each of these, the free valences are located on a tertiary and a diphenylmethyl carbon atom (21).

It has been proposed that the di-π-methane rearrangement, especially from the singlet state, may be concerted (22). Hence, "intermediates or transition states" such as **32**-**36** may not be discrete species. For example, **32** and **33** cannot be long lived, as they could interconvert through rotation around the C4, C5 bond; this is not observed. Thus, we must consider the scheme of **32**-**36** only as a working model of the system.

This example was the first acyclic system which Zimmerman had studied in which cis-trans isomerization could be directly observed. However, he had previously postulated that cis-trans isomerization was probable in excited triplet acyclic systems since he had empirically observed that unstrained monocyclic and acyclic systems undergo the di-π-methane rearrangement exclusively from a singlet excited state, whereas the more constrained bicyclic systems only undergo the arrangement from a triplet excited state (22). The theoretical justification for this observation was that bicyclic or constrained triplets were unable to dissipate their excitation energy by rotation around double bonds and thus undergo the di-π-methane rearrangement. Alternatively, acyclic systems such as 30 or 31 do not have this constraint. However, recently Goldschmidt and Kende examined the photochemistry of a bicyclic system which contained an exocyclic double bond and found that it underwent the di-π-methane rearrangement *faster* from the triplet than from the singlet state (23). Since the molecule had an exocyclic double bond - i.e. a "free rotor" - it appears that Zimmerman's empirical observation may require modification.

Many bicyclic systems undergo the di-π-methane rearrangement; a summary of them is beyond the scope of this thesis. An illustrative example is Zimmerman's study of the photosensitized rearrangement of benzobarrelene 40, shown on the next page (24).

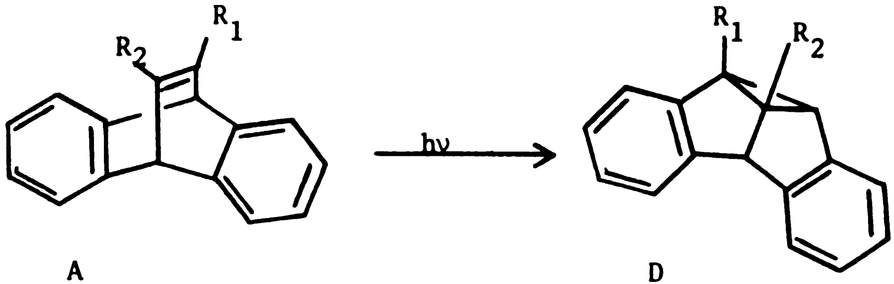
Compound 40 has two different di-π-methane moieties, one consisting of a vinyl bond, a π bond of the aromatic ring, and a bridgehead carbon, and the other consisting of the two vinyl bonds and a bridgehead carbon. Hence the rearrangement could take place by initial vinyl-vinyl bridging to afford intermediate 41, or by initial benzo-vinyl bridging to afford intermediate 43. Zimmerman was able to differentiate between these two possibilities by deuterium labeling as shown. In fact, the



40 41 42 43 44 45

acetone-sensitized photolysis of 40 afforded only 42 plus benzocyclooctatetraene, a secondary product. Direct photolysis of 40 gave only benzocyclooctatetraene by a process assumed to arise from a singlet state. Hence the di-π-methane rearrangement of 40 proceeds only from the excited triplet state, and only <u>via</u> vinyl-vinyl bonding.

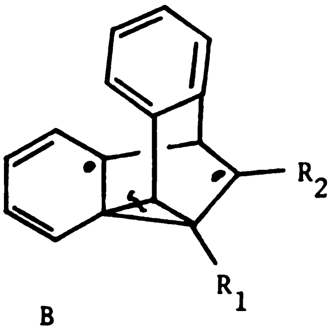
However, di-π-methane rearrangements which do occur by initial benzo-vinyl bridging have also been observed. An example of such a process is Ciganek's sensitized photolyses of variously substituted dibenzobarrelenes of the general structure A. Photolysis of the symmetrical members of this series ($R_1 = R_2$) afforded the general product D (25). Such molecules must initially pass through benzo-vinyl



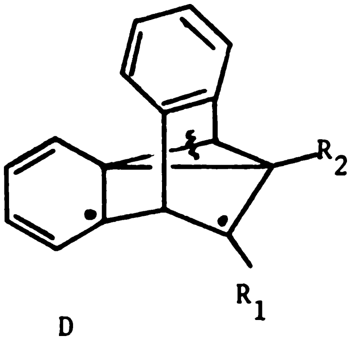
A

D

intermediates **B** and/or **C** as shown below. Note that intermediates **B** and



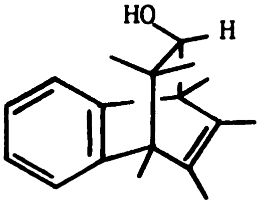
B



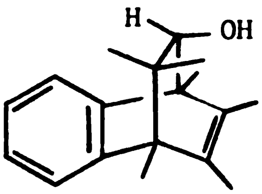
D

C must break the bond shown to afford the observed product. This is reasonable since it brings about rearomatization of the benzo moiety. In one experiment, Ciganek photolyzed the unsymmetrical dibenzobarrelene with R_1 = H and R_2 = CO_2CH_3. Since this molecule is unsymmetrical to the rearrangement, intermediates **B** and **C** are no longer degenerate; each would lead to a different product. In fact, only one product was isolated, **D**, R_1 = H, R_2 = CO_2Me. This indicates that the reaction proceeded through only one of the two possible intermediates, **B**. Since R_2, the carbomethoxy group, is substituted on the carbon which bears one of the odd electrons in **B** and the carbomethoxy group is known to be radical stabilizing, it appears that triplet di-π-methane intermediates are sensitive to such influences.

Ciganek broke the degeneracy of the two possible benzo-vinyl di-π-methane intermediates by substituting one of the carbon atoms in the vinyl bridge which is part of the initial reacting system. The explanation of stabilization of intermediate **B** by substitution of carbomethoxy at R_2 seems adequate. However, in 1969, Hart and Murray (26) examined the photosensitized di-π-methane rearrangement of the unsymmetrical alcohols **46a** and **46b** and also observed a directive effect.



46a

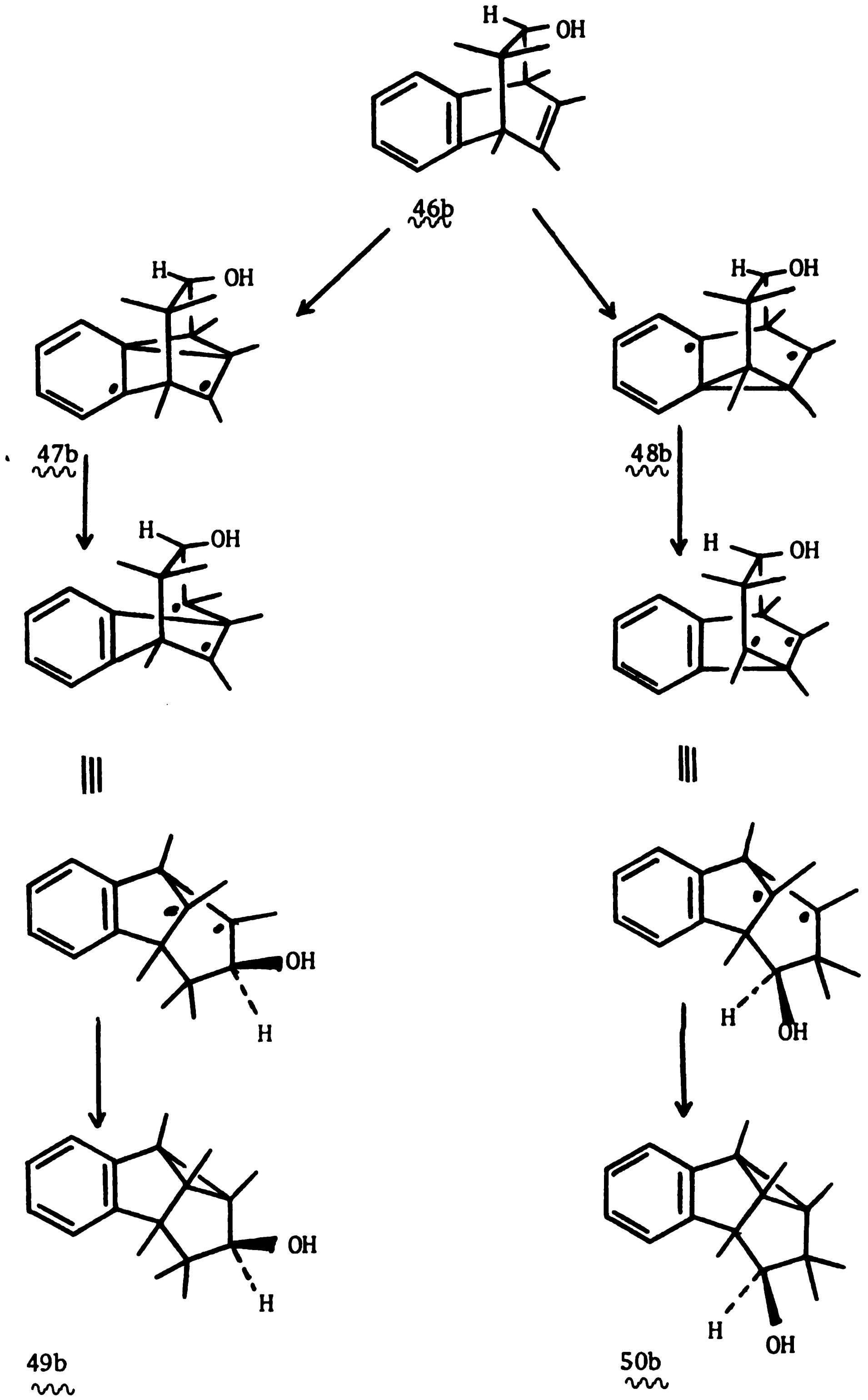


46b

Note that these are unsymmetrical to the rearrangement in a saturated bridge, which formally plays no part in the rearrangement. Hence, no direct free valence stabilization is possible.

Photolysis of the <u>anti</u> isomer, **46b** afforded both products of benzo-vinyl bonding, **50b** and **49b** in the ratio of three to two respectively. This process is shown in detail in Figure 2 on the next page. Since the saturated bridge in **46b** is unsymmetrical to the rearrangement, the two benzo-vinyl intermediates, **47b** and **48b** are different. Each may lead to a different product. <u>A priori</u> one would expect them to be of equal energy; hence one would predict an equal distribution of **49b** and **50b** in the products. Note that C2, the carbon bearing the alcohol function does not enter the reaction directly. However, the observed three to two product ratio of **50b** to **49b** indicates

Figure 2. The di-π-methane rearrangement of **46b**.

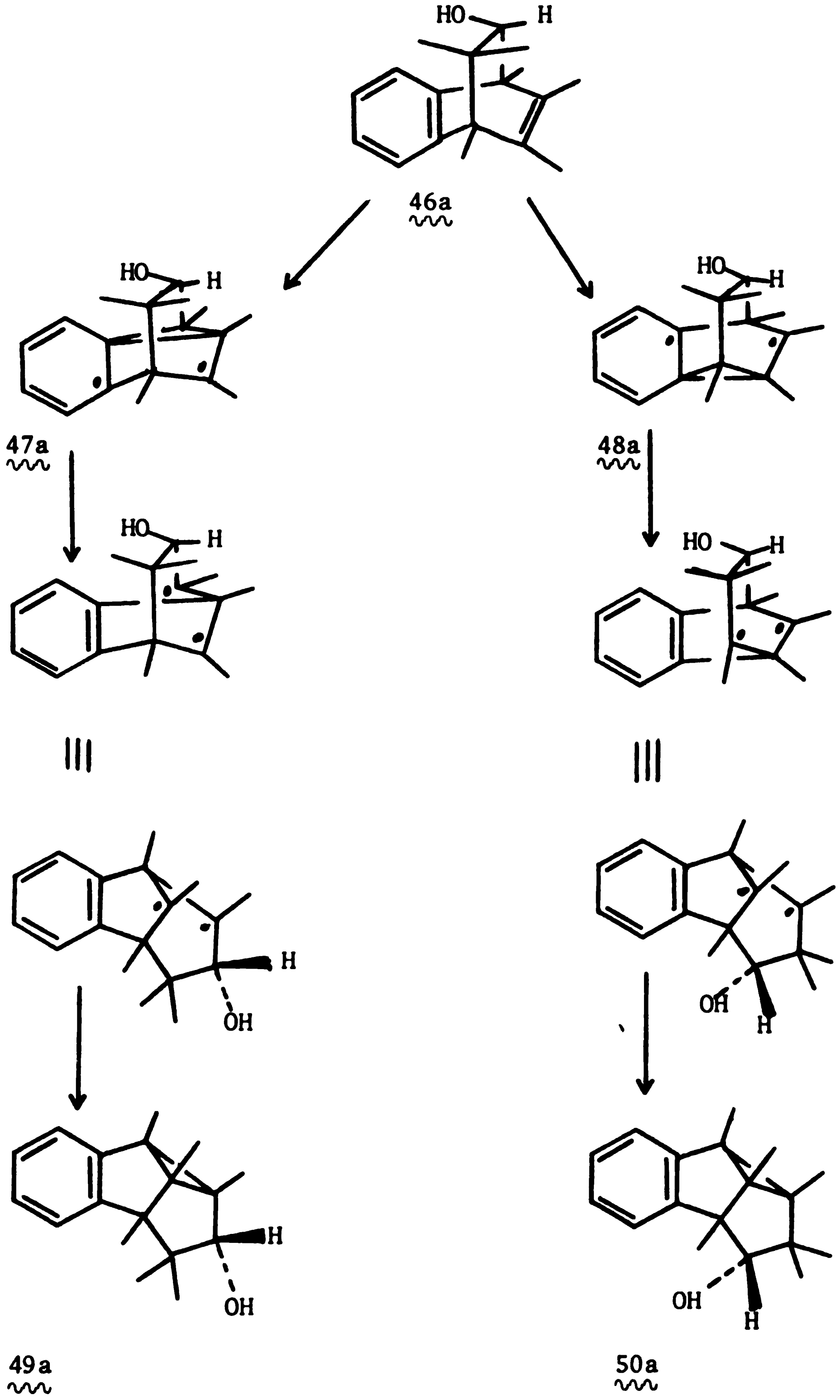


that it must in some way do so. Such an effect must be either electronic through space, or steric.

This effect is far more striking in the sensitized photolysis of the *syn* isomer, **46a**, which is depicted in Figure 3 on the next page. Only one of the two possible products, **50a**, was observed to form. Hence, we must conclude that the benzo-vinyl intermediate **48a** is substantially lower in energy than **47a**. Hart and Murray suggested that this apparent stabilization of **48a** could arise from either charge transfer or hydrogen bonding interaction of the hydroxyl moiety with the cyclohexadienyl triplet free valence located directly beneath it. The possibility of a hydrogen bonded interaction in intermediate **48a** seemed especially attractive since the ground state molecule, **46a**, showed an unusual infrared absorption at 3580 cm^{-1} (3) which was assigned to an intramolecular hydrogen-bonded OH stretch. Such intramolecular hydroxyl proton interactions with aromatic and other π-electron systems have been observed in other systems (26).

The purpose of this thesis was to examine the unusual effect with the hope of learning more about the precise nature of the stabilization of triplet excited states by groups not bonded directly to the sites of odd electron density.

Figure 3. The di-π-methane rearrangement of 46a

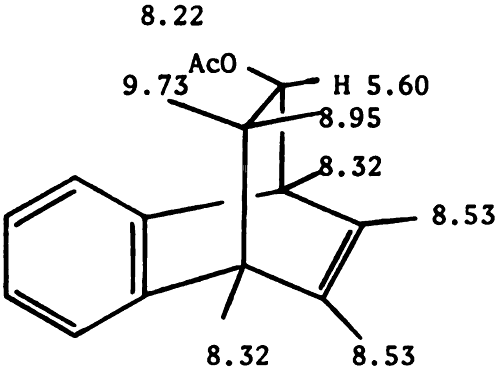


RESULTS AND DISCUSSION

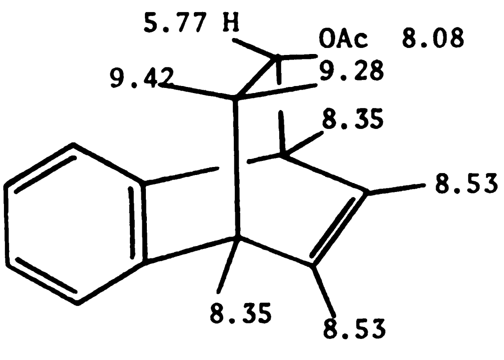
A. The Photolysis of the *syn*- and *anti*-2-acetoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diens, 51a and 51b.

One of the proposals of Hart and Murray for the selective formation of bridged intermediate 48a rather than 47a in the photolysis of 46a was that in 48a the hydroxyl group was ideally positioned to hydrogen bond with, and thus stabilize the unpaired electron at C6.

This hypothesis was tested by synthesizing and photolyzing the corresponding acetates, 51a and 51b. Alcohol 46a was obtained by fractional crystallization of an epimeric mixture of 46a and 46b (3). Treatment of 46a with acetyl chloride and hydrolytic work-up afforded 51a in quantitative yield. Photolysis of 51a in acetone solution gave

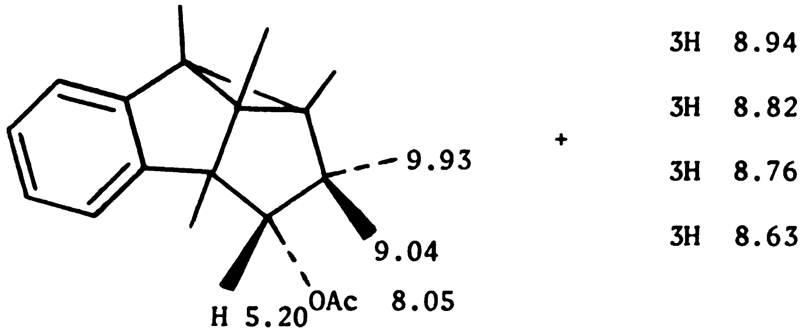


51a



51b

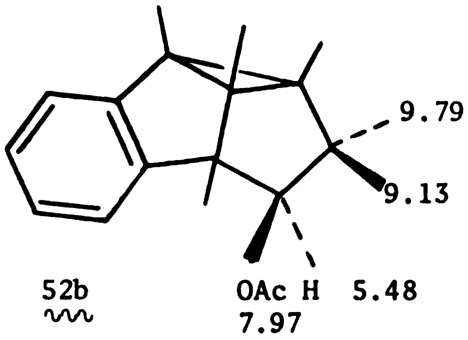
a single photoproduct which is assigned the structure 52a, 4-syn-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, since lithium aluminum hydride (LAH) reduction of the acetate afforded the known alcohol, 50a (26).



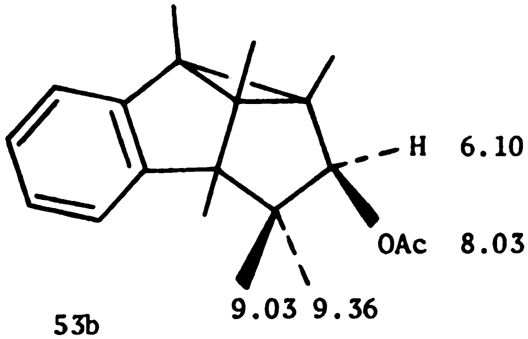
52a

Acetate 51b was not prepared pure; instead a mixture of 51a and 51b was synthesized from a mixture of the epimeric alcohols 46a and 46b and photolyzed in acetone solution. Three photoproducts were observed by GC monitoring. These were separated by preparative GC and identified as 52a, (nmr, ir) which arose from the 51a present in the mixture, 52b, and 53b. The ratio of 52b to 53b was two to one. Esters 52b, 4-anti-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, and 53b, 3-anti-acetoxy-1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo-[3.3.0.0^{2,8}]oct-6-ene were identified by their LAH reduction to the corresponding known alcohols 50b and 49b respectively (26).

Hence, it appears that the directing effect of an acetate group is approximately the same as that of a hydroxyl group. This result eliminates the hydrogen-bonding explanation for the regiospecificity (28) of the reaction.



52b

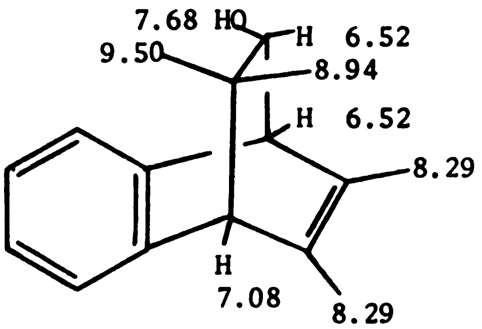


53b

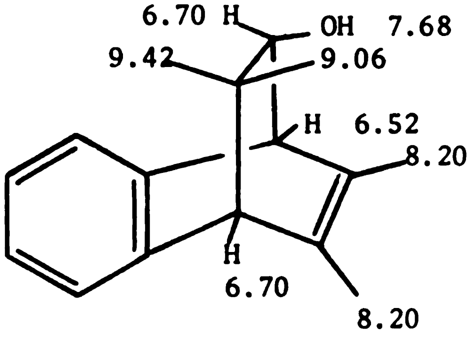
3H	8.95	3H	9.00
3H	8.85	3H	8.84
3H	8.77	3H	8.77
3H	8.62	3H	8.51

B. The Photolysis of the 2-syn and anti Alcohols and Acetates of 3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diene (54 and 55).

In order to test the generality of the directive effect a second set of syn and anti acetates and alcohols were photolyzed. Alcohols 54a and 54b were synthesized by the method of Kakihana (29). The nmr assignments shown below, due to Kakihana, were made from the spectrum of a mixture of both alcohols. The mixture of epimeric alcohols

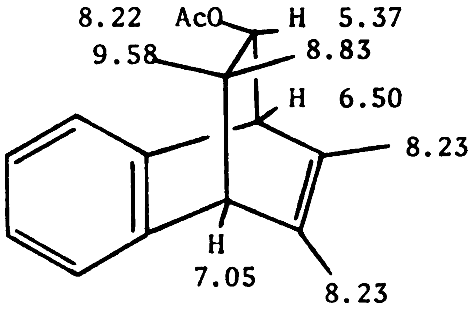


54a

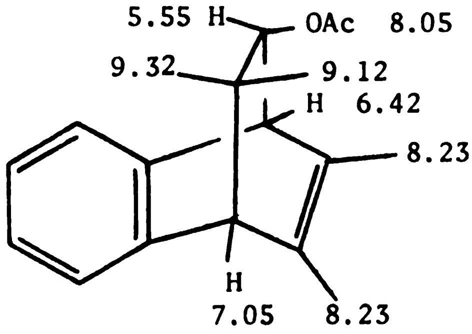


54b

was then converted to acetates 55a and 55b by treatment with acetyl chloride. The acetates were separated by preparative GC. The



55a

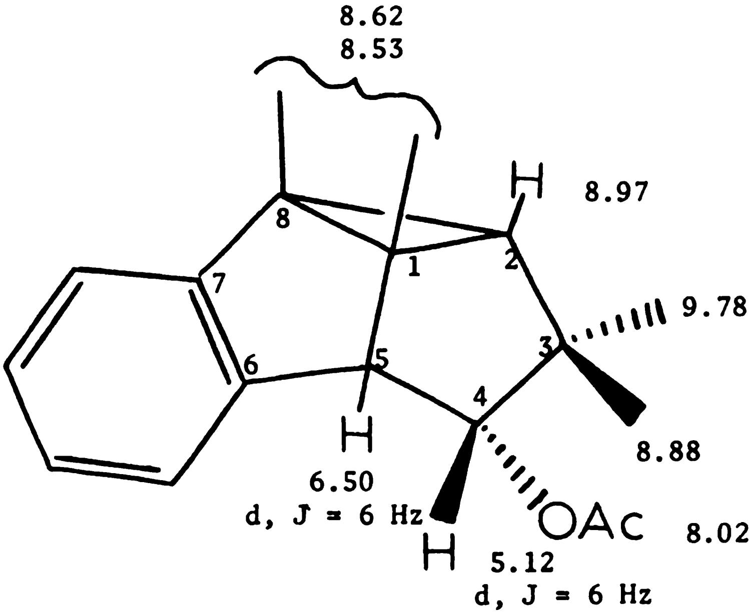


55b

configurations assigned above are based primarily on the chemical shifts of the acetyl methyl singlets. The *syn* isomer, 55a, displayed an acetyl methyl proton singlet at higher field (τ 8.22) than that of the *anti* isomer, 55b (τ 8.05). This is expected because the *syn* methyl group is situated in the shielding region of the aromatic ring.

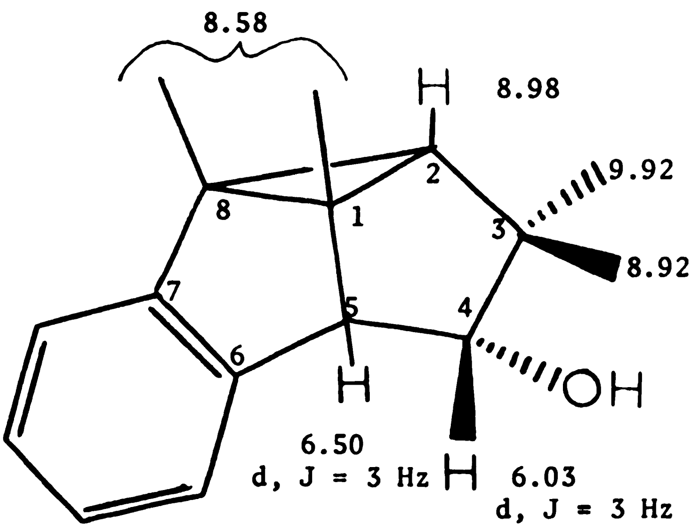
Separate samples of 55a and 55b were reduced back to alcohols 54a and 54b with LAH. This confirmed the structural assignments of 55a and 55b. Photolysis of either 54a or 54b in acetone solution afforded only 2,3-dimethylnaphthalene. Although this elimination of (presumably) isobutyraldehyde had been observed thermally (on a GC column) for 54a and 54b, and for 46a and 46b as well, the photochemical elimination was somewhat surprising. However, since it gave no insight into the di-π-methane rearrangement, it was not further investigated.

The acetates, 55a and 55b, proved more interesting photochemically. Photolysis of the syn acetate 55a in acetone solution, monitored by GC, showed the formation of two photoproducts in the ratio of five to one. After the reaction had proceeded to 82% conversions, the photolysis was stopped and the products were separated by preparative GC. The minor photoproduct was 2,3-dimethylnaphthalene (nmr, ir). The major photoproduct is assigned the structure 4-syn-acetoxy, 1,3,3,8-tetramethyl-6,7-benzobicyclo[3.3.0.0^{2,8}]oct-6-ene, 56a, on



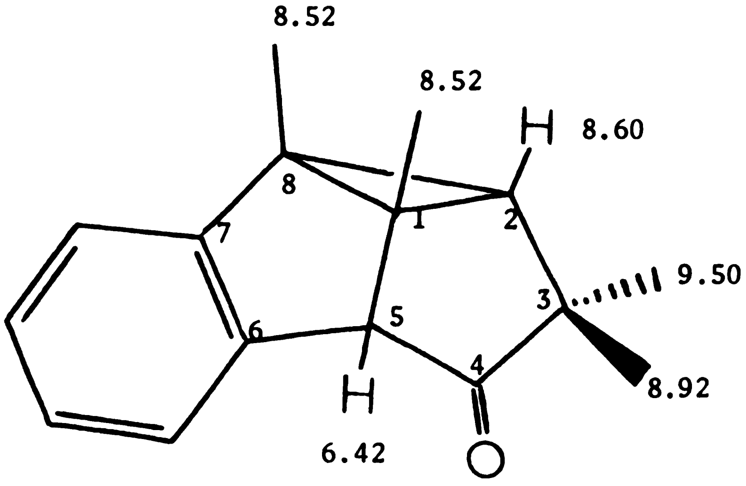
56a

the basis of its nmr spectrum as well as the following chemical transformations. Acetate 56a was reduced with LAH to afford 1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-4-syn-ol, 57a, as shown below. Alcohol 57a, was subsequently oxidized with Jones



57a

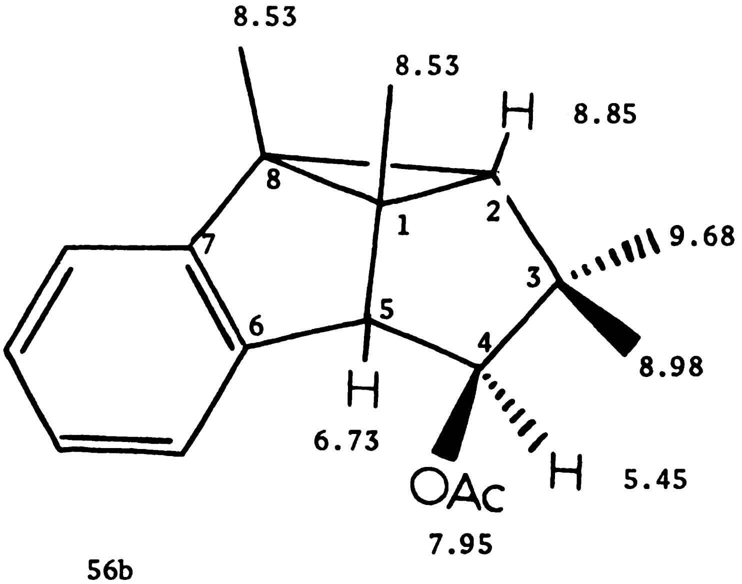
reagent to ketone 58, 1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-ene-4-one. Reduction of 58 with LAH afforded 57a only. This is consistant with the assigned stereochemistry of 57a; LAH would be



58

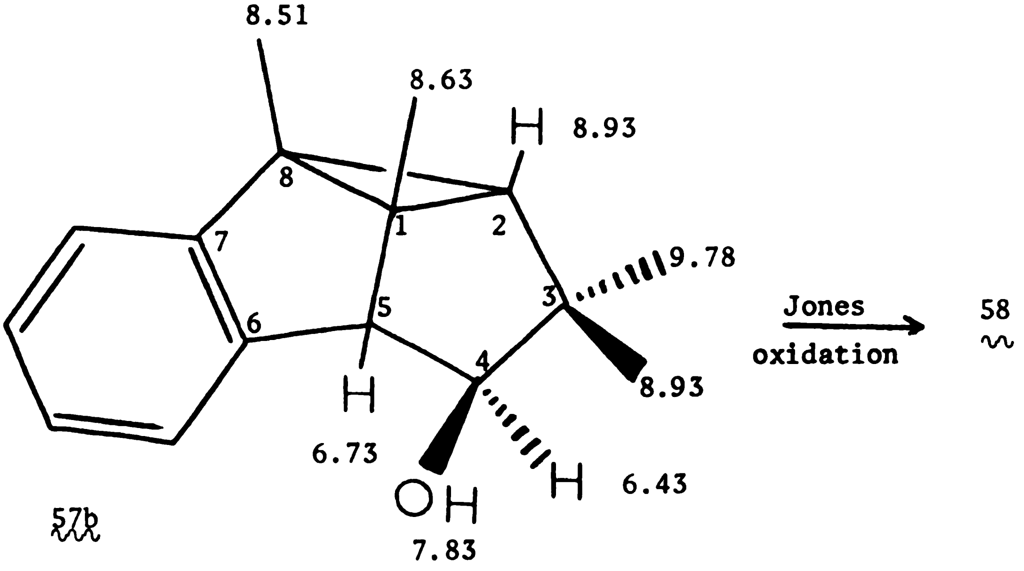
expected to attack the carbonyl carbon of 58 from the least hindered convex side of the molecule to afford 57a. The configurations of C4 in 56a and in 57a is also supported by the observed 6 Hz splitting between the C4 anti proton and the C5 proton. Examination of a model of either molecule reveals a dihedral angle between these protons of approximately 25°. If the C4 protons were syn to the aromatic ring, the dihedral angle would be approximately 90°. The Karplus equation predicts a 6 Hz splitting for a 25° angle and a near zero splitting for a 90° angle (30).

Photolysis of the anti acetate, 55b, in acetone solution, monitored with GC, showed the formation of three photoproducts in the ratio of 6:2:1. These products were then separated by preparative GC. The product formed in smallest yield was identified as 2,3-dimethylnaphthalene (nmr, ir). The major photoproduct was 4-anti-acetoxy-1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene 56b, identified on the basis of



56b

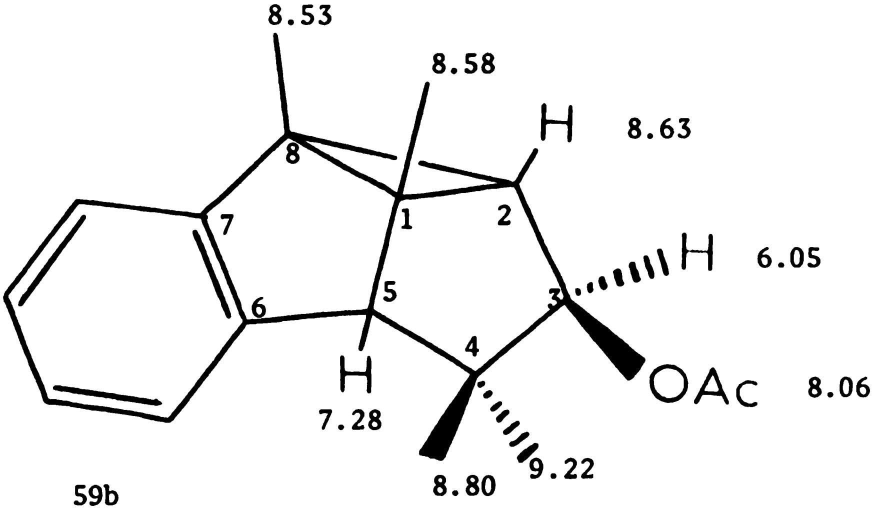
its nmr spectrum as well as upon its LAH reduction to 1,3,8,8-tetramethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene-4-*syn*-ol, 57b, and the



57b

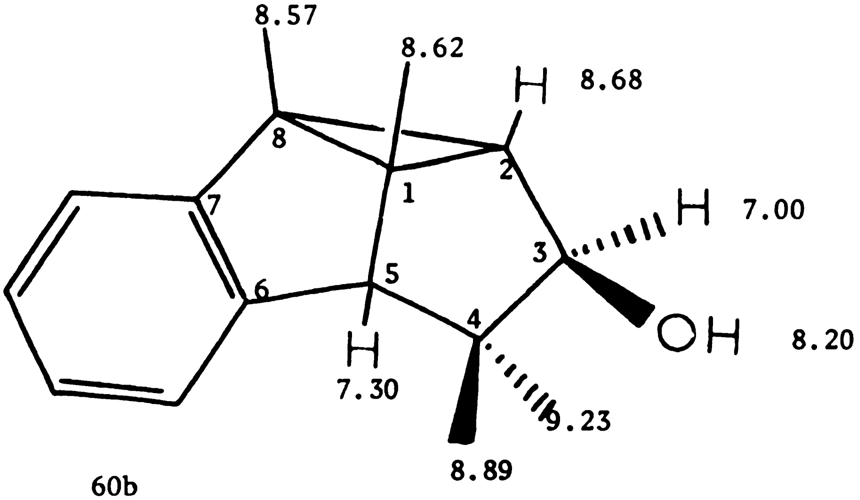
subsequent oxidation of 57b to the known (vide supra) ketone, 58. As predicted from models and the Karplus equation, there was no splitting between the C4 and C5 protons in 56b or 57b.

The remaining product of this photolysis was identified as 3-anti-acetoxy-1,4,4,8-tetramethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene, 59b, on the basis of its nmr spectrum and the following chemical



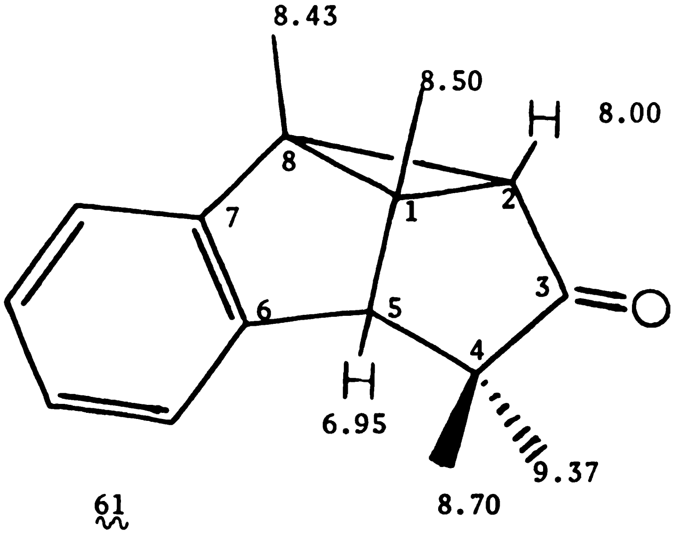
59b

transformations. Reduction of **59b** with LAH afforded 1,4,4,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-3-anti-ol, **60b**, as shown below.



60b

Subsequent oxidation of **60b** with Jones reagent gave 1,4,4,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-3-one, **61**. The configuration



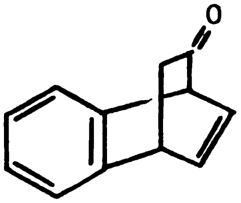
61

at C3 in 59b and 60b is based on the fact that there is no observed splitting between the protons at C3 and C2. Examination of a model of either molecule reveals that the dihedral angle between a C3 syn proton and the C2 proton is about 95°. The Karplus equation predicts little or no splitting for such a dihedral angle. If the protons at C3 were anti, the dihedral angle would be very small, and a substantial splitting would have been expected.

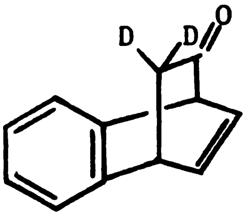
The photochemical results obtained with the tetramethyl acetates 55a and 55b are consistent with those observed in Part A for the hexamethyl acetates 51a and 51b, and indicate that whatever factor is responsible for the regiospecificity of the di-π-methane photoisomerization appears general.

C. The Photolysis of syn and anti-5,6-benzobicyclo[2.2.2.]octa-5,7-dien-2-ols, 63a and 63b.

In order to further test the directive effect of the OH or OAc groups on the di-π-methane rearrangement, as well as eliminate the possibility that the methyl substituents might in some way be responsible for the effect, the rearrangement was examined using precursors without methyl groups. Ketone 62 was prepared by electrolysis

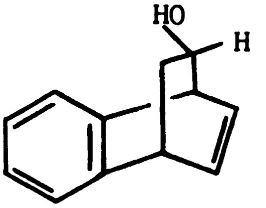


62

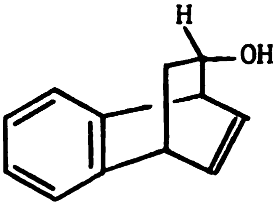


62-d_2

(31) of the corresponding 7,8-diacid. Its spectral properties were identical to those reported by Zimmerman (24). Ketone **62** could be deuterated in the α methylene positions by exchange with sodium methoxide in methanol-d. This was done to simplify the nmr spectra of all compounds subsequently prepared from **62**. Reduction of **62** and **62**-d_2 with LAH afforded a mixture of epimeric alcohols **63a** and **63b** as shown below.



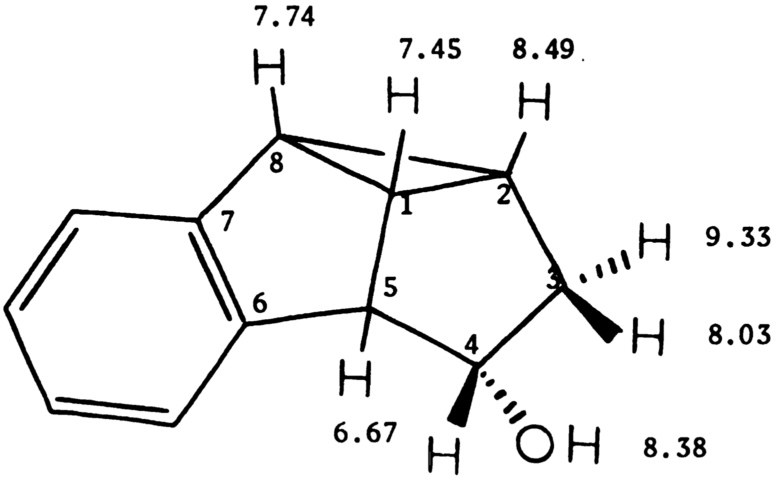
63a



63b

The mixture of **63a** and **63b** was separated by preparative GC, although the formation of naphthalene on the GC column precluded obtaining analytically pure samples of either alcohol. Hence the alcohols were characterized by Jones oxidation back to the known ketone, **62**. The spectral properties of **63a** and **63b** are given in the experimental section. The configurational assignments of **63a** and **63b** are based on the chemical shifts of their acetates. A small sample of each alcohol was treated with acetyl chloride to make the acetates. The acetyl methyl protons of the **63a**-acetate had a chemical shift of τ 8.22, whereas that of the **63b**-acetate was τ 8.07. These values compare quite well with those of **51a** and **b** (τ 8.22 and 8.08) and those of **55a** and **b** (τ 8.22 and 8.05).

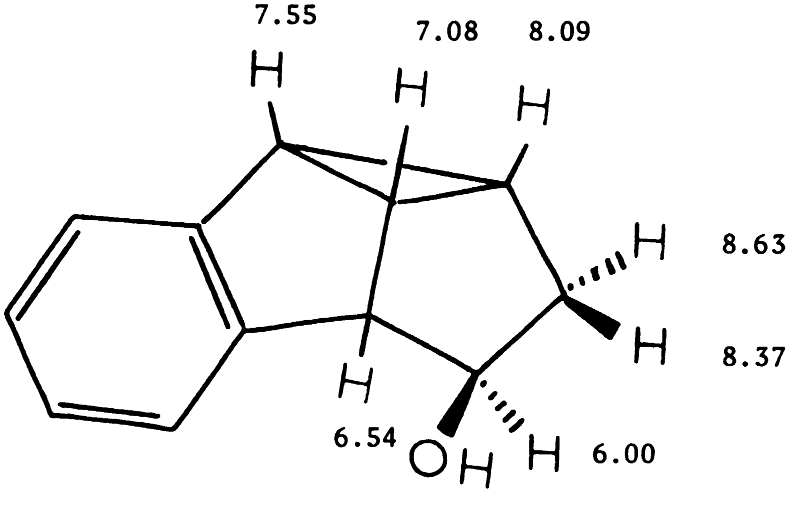
Photolysis of the syn alcohol, 63a in acetone solutions, monitored by GC, showed the formation of two photoproducts in the ratio of one to seven. The photoproducts were separated by preparative GC, although the formation of naphthalene from the unreacted 62a present again precluded the preparation of analytically pure samples. The minor photoproduct has not been identified. The major product was identified from its 100 MHz nmr spectrum as 6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene-4-syn-ol, 64a.



64a

The only unsplit proton in the nmr spectrum of 64a was that of the OH group. Decoupling by irradiation at τ 5.65 simplified the splitting patterns at τ 6.67, 8.03 and 9.33. Irradiation at τ 6.67 simplified the signals at τ 5.65 and τ 7.45 only. The signals at τ 9.33 and τ 8.03 were absent from the spectrum of 64a-d_2 (prepared from 63a-d_2). This spectrum also showed simplification of the τ 5.65 signal to a doublet (J_{45} = 6 Hz) and of the τ 8.49 signal to a triplet due to J_{12} and J_{28}. The observed J_{45} splitting of 6 Hz is the basis for the assignment of the configuration at C4; see Section B for a pertinent discussion.

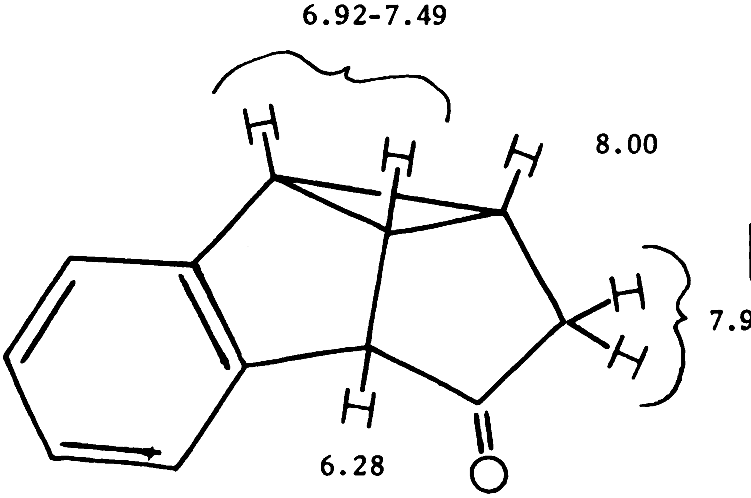
Photolysis of the anti isomer, 63b in acetone solution, monitored by GC, showed the formation of a single photoproduct which was identified as 6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-4-anti-ol, 64b, from its 100 MHz nmr spectrum. As with 64a, the only unsplit proton signal in the nmr spectrum of 64b was that of the OH. Irradiation of the signal at τ 6.00 simplified the splitting at τ 8.63 and removed a very small perturbation at τ 6.54 to make it a sharp doublet of doublets due to J_{15} and J_{35}. This result shows that J_{45} is too small to be fully resolved by a Varian HA-100 spectrometer, and fixes the configuration at C4 (see Part B for a discussion of this). The unusual J_{35} splitting was 2.5 Hz; examination of a model of 64b revealed that the protons responsible for the signals at τ 8.37 and τ 6.54 are geometrically fixed in the classic "W" configuration which is known to exhibit an appreciable splitting through four sigma bonds (32).



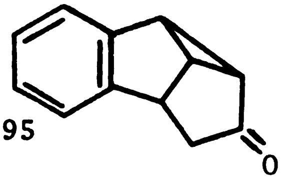
64b

Irradiation at τ 6.54 sharpened the doublet at τ 6.00 a little and simplified the signals at τ 7.08 and τ 8.37. Alcohol 64b-d$_2$ (prepared from 63b-d$_2$) did not exhibit signals at τ 8.37 or 8.63 and displayed simplified signals at τ 8.09, 6.54, and 6.00.

Jones oxidation of either 64a or 64b afforded a single ketone, 6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-4-one, 65. The nmr spectrum of 65



65



66

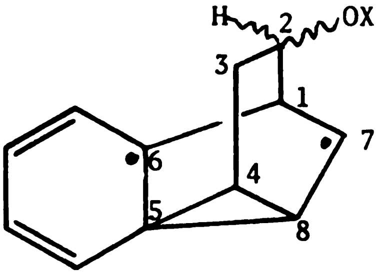
was measured with a 60 MHz instrument, and the C1 and C8 protons seem to form a second-order pattern. The broad two-proton doublet at τ 7.95 was clearly absent from the spectrum of 65-d$_2$, so both C3 protons are in nearly equivalent magnetic environments. The nmr spectrum of 65-d$_2$ also revealed that the τ 6.28 signal was simplified from a doublet of doublets in 65 to a simple doublet in 65-d$_2$. Hence, this molecule has the same long range "W" splitting as does 64b. Ketone 66 is known, and can be eliminated as a structural possibility for 65 (33).

Reduction of 65 with LAH afforded a single alcohol, 64a. Hence it appears that even without methyl substituents on the molecule, the aluminum hydride moiety can only approach from the least hindered, convex side of the molecule. This experiment further confirms the configurational assignments of 64a and 64b.

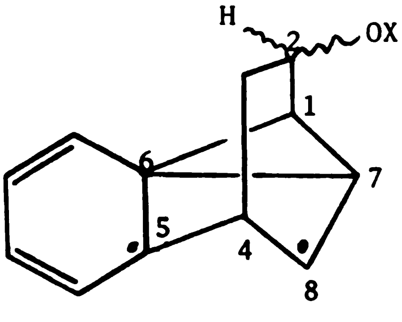
The results of the photolysis of 63a and 63b are that *both* the *syn* and *anti* alcohols afford only one of two possible di-π-methane products upon triplet excitation. Thus the hydroxyl substituent, regardless of its geometry in 63, causes the di-π-methane rearrangement to be regiospecific. The reaction mechanism is discussed in the following section.

D. Conclusions

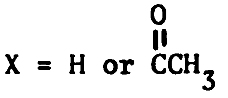
The results of Sections A, B, and C, may be summarized by examining the two benzo-vinyl intermediates A and B which afforded the observed products. In intermediates of type A the unpaired electron density is



A



B



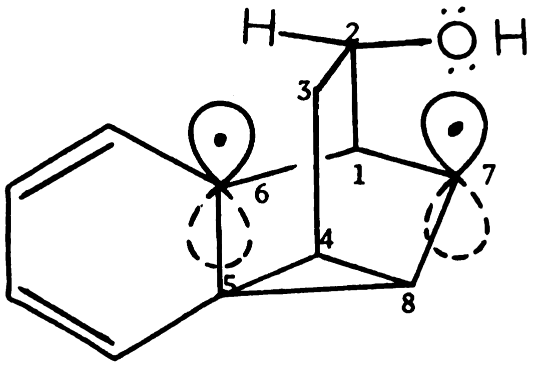
$X = H \text{ or } \overset{O}{\overset{\|}{C}}CH_3$

centered at C6 and C7, directly under and within interacting distance of the alcohol or acetoxy function at C2, whereas in intermediates of type B, the unpaired electron density is centered at C5 and C8, away from those groups. The chart below details the di-π-methane products of the photolyses in terms of the intermediate A or B which afforded that product.

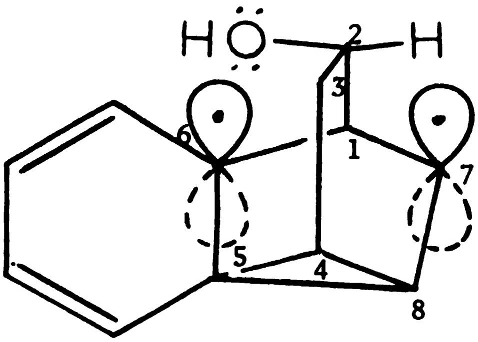
Substituent at C2	Configuration at C2	Compound	%A	%B
hydroxyl	syn	46a	100	0
hydroxyl	anti	46b	60	40
acetoxy	syn	51a	100	0
acetoxy	anti	51b	66	33
acetoxy	syn	55a	100	0
acetoxy	anti	55b	66	33
hydroxyl	syn	63a	86-100	<14
hydroxyl	anti	63b	100	0

Two general trends in the data are evident: (1) intermediate A is favored in all cases, regardless of the configuration at C2; (2) in cases where the hydroxyl or acetoxy group at C2 is <u>syn</u> to the aromatic ring, the products arise solely from intermediate A. In one case (63a and 63b), the A-type intermediate is favored regardless of the stereochemistry of the substituent.

Since the acetoxy and hydroxy function can direct the reaction in a similar manner, we may conclude that either the oxygen atom directly bonded to C2 or, in the case of the acetoxy group, perhaps the carbonyl oxygen, is interacting in some manner with the unpaired electrons in intermediate A to direct the reaction preferentially through that intermediate. This possible interaction can be seen in both the *syn*- and *anti*-**A** intermediates. In the *anti* **A**-type intermediate, the oxygen



anti-**A**



syn-**A**

atom attached to C2 is positioned directly over the carbon p orbital containing the unpaired electron at C7. In the *syn*-**A** intermediate, the oxygen atom is in a position favorable for interaction with the extended π system of the pentadienyl radical. In **B**-type intermediates, the geometry is unfavorable for such interaction.

Let us now examine the results of only the *anti* alcohols and acetates. Both the alcohol and the acetate with six methyl substituents, **46b** and **51b**, as well as the acetate with four methyl substituents, **55b**, formed products predominantly from a type **A** intermediate, but products from a type **B** intermediate were observed. However alcohol **63b** formed a product from a type **A** intermediate only. The key difference is that **63b** has no methyl substituents at C7 and C8 where an unpaired electron is located in a type **A** or type **B** intermediate whereas **46b**, **51b** and **55b** have methyl groups at both positions. Hence, the unpaired electron at C7 (or C8) in the intermediates arising from **63b** are on a secondary carbon, whereas in all the other cases examined, C7 and C8 were tertiary. As secondary radicals are less stable, and therefore more electron-demanding, than tertiary radicals we may assume that the di-π-methane intermediates arising from **63b** are less stable than those with methyl substituents. Hence, they are more susceptible to stabilization by a proximate oxygen atom. Conversely, the triplet intermediates with methyl substituents at C7 and C8 have sufficient inherent stabilization to allow intermediate **B** to compete.

Examination of the products of the photolyses of the *syn* alcohols and acetates is less revealing; all isomerize exclusively through a type **A** intermediate. Alcohol **63a** could possibly be an exception, but since the minor product of its photolysis is unknown, little can be said about it. In all cases studied, the substitution at C5 and C6 were identical - cyclohexadienyl - hence, the *syn* alcohols and acetates should exhibit the same behavior. We may only conclude that since all the *syn* cases studied isomerized only through a type **A** intermediate, the stabilization by the proximate oxygen over C6 must be substantial.

The precise nature of this proposed stabilizing interaction is still speculative. Hart and Murray's suggestion of a charge transfer interaction is attractive, but there is at present no definitive evidence for it. In principle this would imply that the proximate oxygen atom was partially donating one of its non-bonded electrons to the unpaired electron at either C6 or C7 to allow the electron to delocalize over a larger region. A full electron transfer of this nature would result in a carbanion center at C6 or C7 and a radical cationic center on oxygen. This seems unlikely. However a partial transfer would result in a partial net transfer of negative charge from oxygen to carbon. Since the charge transfer complex we are describing is in a triplet excited state, we have, by definition, a triplet *intramolecular* exciplex. Such excited state intramolecular complexes have recently been observed in the singlet state (34), so their existence in the triplet state is likely since triplet lifetimes are several orders of magnitude longer.

Alternate explanations for the observed effects seem less satisfactory. Clearly the functionality at C2 can be the only directive influence on the reaction since it is the only element dissymmetric to the reaction in **63a** and **63b**. Furthermore, the influence must be through space, since any inductive effect of the functionality at C2 would be equal in both the *syn* and the *anti* epimers, and in several cases the *syn* and *anti* forms do not react similarly. Hence we must look for other through-space effects.

One such possibility would be that the oxygen atom interacts with the unpaired electron at C6 or C7 and allows it to change its spin state. This would then be a net intersystem crossing induced by an oxygen atom, which is not normally considered a heavy atom. Such a scheme would imply a photostationary state of type **A** and **B** intermediates in which the type **A** intermediates could intersystem cross and go on to products, whereas the type **B** intermediates would eventually either go on to products or revert back to the ground state of the starting material. Such an effect could easily afford the observed product ratio.

A second through-space effect could be an asymmetric energy transfer of triplet energy from the acetone sensitizer to the molecule.

This would afford only one type of intermediate initially. Such a scheme was proposed by Schenck in 1948, but has yet to be demonstrated (35). This mechanism would require that the functionality at C2 direct the excited acetone molecule to transfer its triplet energy asymmetrically to the substrate. Such a directive effect could be either steric or polar.

While this work was in progress, a related study was reported by Paquette and Meisinger. They examined the acetone-sensitized photolysis of the N-methyl amide, 67, and each of its four monomethyl derivatives (with methyls at the bridgehead or vinyl positions) (36). The results of all five of these di-π-methane rearrangements are presented in Figure 4 on the next page. Above each column of photoproducts is the intermediate type from which these products arose. These have been labeled A and B in a similar manner: in intermediate A, the unpaired electrons are under the heteroatom; in intermediate B the unpaired electrons are remote from the heteroatom. In this case, however, the heteroatom is nitrogen instead of oxygen, and it is not positioned directly over C6 or C7 where the unpaired electrons are centered.

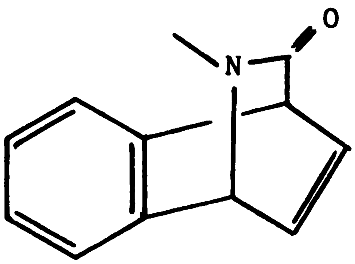


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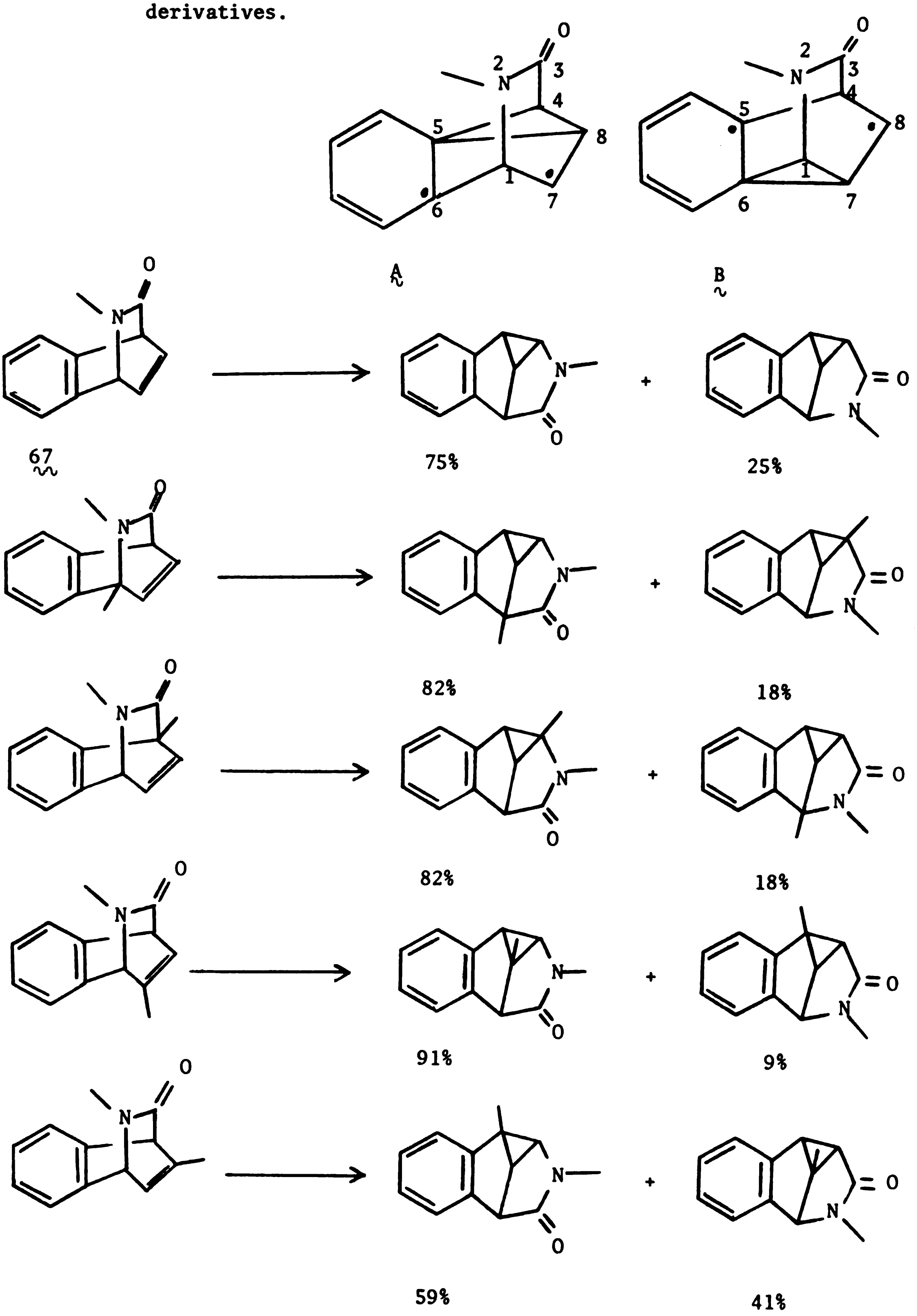
Figure 4. The di-π-methane rearrangement of **67** and its monomethyl derivatives.



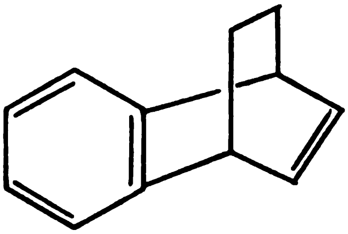
However, examination of Figure 4 reveals that a similar regiospecific effect is observed; in all cases, products from the type **A** intermediate predominate. Both nitrogen and oxygen have lone pair electrons which could interact with unpaired electrons to partially stabilize them (vide infra). Hence, interaction of the lone pair electrons of nitrogen in **67** with the unpaired electrons at C6 and/or C7 would stabilize the type **A** intermediate and rationalize the observed product ratios.

It should be noted, however, that Paquette and Meisinger propose a different explanation for the general tendency for **67** and its methyl derivatives to form intermediates of type **A**. They suggest that because the unpaired electrons in the type **A** intermediate are in conjugation with the carbonyl function at C3 through the cyclopropyl ring, they are better stabilized than they are in intermediate **B**, which offers no such stabilization.

Paquette and Meisinger's explanation does adequately rationalize their results, but it is meaningless when applied to the molecules examined by Hart and Murray or described in this thesis, since they have no carbonyl carbon. However, the concept of unpaired electron stabilization by heteroatom lone pair electrons seems to rationalize both cases.

By photolyzing all four monomethyl derivatives of **67**, Paquette and Meisinger clearly demonstrate the directive effect of methyl substituents at C7 and C8. Note in Figure 4 that methyl groups at C1 and C4 do not substantially alter the product ratios. A similar lack of effect was noted in Section B of this thesis when methyl substituents were removed from C1 and C4. However a methyl group at C7 clearly directs the reaction through intermediate B to a greater extent. Hence, the assumption of methyl group stabilization of unpaired electron density seems justified.

Clearly the proposed intramolecular triplet exciplex can not be assumed simply from product ratio studies of a single type of reaction. In principle, such a species could be observed spectroscopically by examining the absorption or emission spectra of the triplet intermediates generated from flash photolysis. However such experiments are very difficult. Perhaps a more fruitful method would be a careful kinetic study of the reactions described in this thesis. If, for example, 63a and 63b were found to photoisomerize faster than the dihydrobenzobarrelene 66, one would have a strong case for a proposed stabilization of an intermediate species. A non-kinetic test of these conclusions would be the sensitized photolysis and product examination of a methyl substituted dihydrobenzobarrelene such as 67. If this photolysis afforded an uneven product distribution of di-π-methane products, the exciplex theory proposed in this thesis would be very difficult to accept since the methyl group has no lone pair electrons to share.



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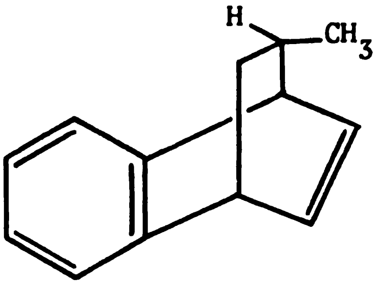

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In conclusion, the results presented here seem best explained by some sort of through-space interaction of the substituents with the reaction site - perhaps an intramolecular exciplex. This may seem a rather esoteric theory. However, like any other theory, it can be transformed into fact or fiction by further work.

EXPERIMENTAL

A. Synthesis of *syn*-2-acetoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diene, **51a**.

Two grams of 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diene-2-*syn*-ol, **46a** (3), was refluxed with 10 ml of acetyl chloride for 15 minutes. The excess acetyl chloride was distilled under reduced pressure, and the crude mixture was dissolved in 20 ml of ether. The ether solution was washed with saturated $NaHCO_3$ solution (3 X 10 ml) and water (3 X 10 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to afford off-white crystals of **51a**, which were recrystallized from pentane to afford an analytical sample, mp 85-86°. The nmr spectrum of **51a** is given in Section A of the text. The ir spectrum of **51a** (neat smear) showed absorptions at 3000, 1720, 1380, 1250, 1230, and 1030 cm^{-1}. The uv spectrum of 51a showed λ_{max}^{EtOH} 272 nm ($\varepsilon = 852$), 264 nm ($\varepsilon = 1070$), 257 nm ($\varepsilon = 852$), and 209 nm ($\varepsilon = 18{,}800$).

Anal. Calcd: C, 80.54; H, 8.73

Found: C, 80.47; H, 8.78

B. Synthesis of *anti*-2-acetoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diene, **51b**, mixed with **51a**.

An epimeric mixture of **46a** and **46b** (3) was fractionally crystallized from pentane to remove as much of the *syn* isomer, **46a**, as possible. The remaining pentane solution of **46a** and **46b** was then evaporated under reduced pressure, and acetylated with acetyl chloride as in Section A. The nmr spectrum of **51b** given in Section A of the text was determined by subtraction of the signals known to arise from **51a** from the nmr spectrum obtained of this mixture. Integration of this mixture indicated that it contained ca 40% **51a** and 60% **51b**.

C. Photolysis of *syn*-2-acetoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diene, **51a**.

A solution of 782 mg of **51a** in 15 ml of spectral grade acetone was placed in a pyrex test tube and sealed with a septum. The solution was de-oxygenated by bubbling nitrogen through it for 30 minutes and then affixed to a water cooled lamp well which contained a 450 watt Hanovia type L lamp. Monitoring the photolysis by GC (5' X 1/4" SE-30 column; 150°; 100 ml/min He) indicated the formation of a single photoproduct. After 9 hours of irradiation, the GC trace integration indicated 92% conversion. The photolysis solution was evaporated under reduced pressure and the residue was dissolved in pentane. The photoproduct, *syn*-4-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene, **52a**, crystallized from the solution as colorless crystals mp 93-94°. The nmr spectrum of **52a** is given in Section A of the test; the acetoxy function was evident from the ir absorption (neat smear) of 1725 cm^{-1}. Photoacetate **52a** was characterized as in D, below.

Anal. Calcd: C, 80.54; H, 8.73

Found: C, 80.44; H, 8.84

D. Lithium Aluminum Hydride Reduction of *syn*-4-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene, **52a**.

An ether solution of **52a** (20 mg in 5 ml) was slowly added to a stirred suspension of 500 mg of LAH in 20 ml of anhydrous ether at room temperature. Thirty minutes after the addition, 2 ml of water was added dropwise, followed after a short interval by the addition of ca 1 g of anhydrous $MgSO_4$. The alumina and $MgSO_4$ were then filtered from the solution and the ether was evaporated under reduced pressure to afford a colorless oil which had identical nmr and ir spectra to those of 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene-4-*syn*-ol, **50a** (26).

E. Photolysis of a Mixture of *syn* and *anti*-2-acetoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diens, **51a** and **51b**.

One gram of the epimeric mixture of **51b** and **51a** from Section B was dissolved in acetone (15 ml) and prepared for photolysis as described in Section C. The reaction was monitored by GC using a 5' X 1/4" 20% SE-30 column at 150° which would not resolve **51a** and **51b**, and which resolved only one photoproduct peak. When integration of the **51a**, **51b** peak and the photoproduct peak indicated a 92% conversion, the reaction was stopped and the acetone was evaporated under reduced pressure. The entire product mixture was then separated by preparative GC using a 10' X 3/8" 20% FFAP column at 200° which resolved six peaks; the first three were due to decomposition products of the unreacted **51a** and **51b** since injection of the starting mixture of **51a** and **51b** afforded the same three peaks. The products which gave rise to the fourth, fifth and sixth peaks (area ratio 2:2:1) were collected and examined. The compound corresponding to the fourth peak had an identical nmr spectrum to that of 52a. The compound corresponding to the fifth peak, anti-4-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene, **52b**, showed an ir (CCl_4 soln) absorption at 1725 cm^{-1}; its nmr spectrum is given in the text, Section A. It was characterized as in Section F which follows. The compound corresponding to the sixth peak, anti-3-acetoxy-1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene, **53b**, showed an ir (CCl_4 soln) absorption at 1725 cm^{-1}; it's nmr spectrum is also given in Section A of the text. It was characterized as in Section G which follows.

F. Lithium Aluminum Hydride Reduction of anti-4-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene, 52b.

The entire GC collected sample of **52b** from the photolysis in Section E was reduced with LAH and worked-up by the same procedure described in Section D. The nmr and ir spectra of this product were identical to those of the known alcohol, **50b** (26).

G. Lithium Aluminum Hydride Reduction of anti-3-acetoxy-1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-ene, 53b.

The entire GC collected sample of **53b** from the photolysis in Section E was reduced with LAH and worked-up by the same procedure described in Section D. The nmr and ir spectra of this product was identical to those of the known alcohol, **49b** (26).

H. Synthesis of *syn* and *anti*-2-acetoxy-3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-dienes, **55a** and **55b**.

Six grams of an epimeric mixture of alcohols **54a** and **54b** (29) was refluxed for 15 minutes in a large excess of acetyl chloride (25 ml). The acetyl chloride was evaporated under reduced pressure and the crude product mixture was dissolved in 50 ml of ether. The ether solution was washed with saturated $NaHCO_3$ solution (3 X 20 ml) and water (3 X 20 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to afford a brown oil which displayed an nmr spectrum of both *syn* and *anti*-2-acetoxy-3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-dienes, **55a** and **55b**. Separation was accomplished with preparative GC using a 10' X 3/8" 20% FFAP column at 200°. The nmr spectrum the *syn* isomer, **55a**, is included in the text of Section B. The ir spectrum of **55a** ($CHCl_3$ soln) showed absorptions at 2930, 1705, 1375 and 1255 cm^{-1}. The uv spectrum showed λ_{max}^{EtOH} 288 nm (s, ε = 575), 279 nm (s, ε = 1,300), 272 nm (ε = 1,900), 265 nm (ε = 1,900), 260 nm (ε = 1,750), 226 nm (ε = 38,000) and 207 nm (ε = 36,000).

Anal. Calcd: C, 80.00; H, 8.15

Found: C, 80.38; H, 8.29

The nmr spectrum of the *anti* isomer, **55b**, is included in the text of Section B. The ir spectrum of **55b** ($CHCl_3$ soln) showed absorptions at 2940, 1710, 1375, and 1250 cm^{-1}. The uv spectrum showed λ_{max}^{EtOH} 288 nm (s, ε = 270), 273 nm (ε = 1,300), 266 nm (ε = 1,400), 260 nm (s, ε = 1,100), 223 nm (ε = 28,000), 208 nm (ε = 52,000). The mass spectrum of **55b** had a parent peak at m/e 270 and a base peak at m/e 156.

Anal. Calcd: C, 80.00; H, 8.15

Found: C, 80.08; H, 8.23

I. Photolysis of *syn*-2-acetoxy-3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2.]octa-5,7-diene, **55a**.

A 595 mg sample of **55a** which had been GC collected as in Section H was dissolved in acetone (15 ml) and prepared for photolysis as in Section C. The reaction was monitored by GC using a 10' X 3/8" 20% FFAP column at 200°, which indicated the formation of two photoproducts in the ratio of 5:1. After 59 hours of irradiation, the reaction had proceeded to 82% conversion. The acetone was evaporated under reduced pressure, and the residue was preparatively injected into the above column to separate the major photoproduct, *syn*-4-acetoxy-1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, **56a**, from the minor photoproduct, 2,3-dimethylnaphthalene, and the unreacted **55a** present. The 2,3-dimethylnaphthalene was identified by its nmr spectrum. The nmr spectrum of the major photoproduct, **56a**, is given in Section B of the text. Photoacetate **56a** showed ir absorptions (CCl_4 soln) at 2950, 1725, 1375, and 1240 cm^{-1}. Its mass spectrum showed a parent peak at m/e 270 and a base peak of m/e 156. Photoacetate **56a** was further characterized as in Sections J and K, below.

Anal. Calcd: C, 80.00; H, 8.15

Found: C, 80.00;;H, 8.16

J. Lithium Aluminum Hydride Reduction of *syn*-4-acetoxy-1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, **56a**.

The entire GC collected sample of **56a** from the photolysis described in Section I was reduced with LAH and worked up as described in Section D. The nmr spectrum of the product, 1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-4-*syn*-ol, **57a**, is given in the text of Section B. The ir spectrum of **57a** showed (CCl$_4$ soln) absorptions at 3600, 3500, 2950, 1480, 1390, and 1080 cm^{-1}. Alcohol **57a** was further characterized by its oxidation as in K, below.

K. Jones Oxidation of 1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-ene-4-*syn*-ol, **57a**.

The entire sample of **57a** from Section J was dissolved in 5 ml of acetone and chilled to 0°. Jones reagent (37) was added dropwise until the solution remained pink for 2 minutes. Fifty ml of water was then added, and the solution was extracted with ether (3 X 15 ml). The ether solution was dried over anhydrous MgSO$_4$ and evaporated under reduced pressure to afford a colorless oil which displayed the nmr spectrum given in Section B of the text for 1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-4-one, **58**. The sample was then preparatively injected into a GC column (5' X 1/4" SE-30, 150°) and collected to purify it for analysis. Ketone **58** showed strong infrared absorptions (neat smear) at 2950, 1730 and 1470 cm^{-1}. Its uv spectrum showed λ_{max}^{EtOH} 287 nm (ε = 9,600), 239 nm (s, ε = 11,000), and 210 nm (ε = 12,000). Its mass spectrum showed a parent peak of m/e 226 and a base peak of m/e 156.

Anal. Calcd: C, 84.96; H, 7.96

Found: C, 84.79; H, 8.00

L. Photolysis of *anti*-2-acetoxy-3,3,7,8-tetramethyl-5,6-benzobicyclo-[2.2.2.]octa-5,7-diene, 55b.

A 612 mg sample of 55b which had been GC collected as in Section H was dissolved in acetone (15 ml) and prepared for photolysis as in Section C. The photolysis was monitored by GC using a 10' X 3/8" 20% FFAP column at 200°, which indicated the formation of three photoproducts in the ratio of 6:2:1. After the irradiation had proceeded to 80% conversion (25 hr), the photolysis was stopped, and the acetone was evaporated under reduced pressure. The reaction mixture was then separated by preparative GC using the column described above. The photoproduct formed in smallest yield was identified by its nmr spectrum as 2,3-dimethylnaphthalene. The nmr spectrum of the major photoproduct, *anti*-4-acetoxy-1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, 56b is given in Section B of the text. Photoacetate 56b showed absorptions (CCl_4 soln) at 2950, 1725, 1375, 1240, and 1035 cm^{-1} in its infrared spectrum. Its mass spectrum showed a parent peak of m/e 270 and a base peak of m/e 156.

Anal. Calcd: C, 80.00; H, 8.15

Found: C, 80.07; H, 8.24

The nmr spectrum of the minor photoproduct, *anti*-3-acetoxy-1,4,4,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, 59b, is given in Section B of the text. Photoacetate 59b showed infrared absorptions (CCl_4 soln) at 2950, 1730, 1375, 1250 and 1040 cm^{-1}. Its mass spectrum showed a parent peak of m/e 270 and a base peak of m/e 156.

Anal. Calcd: C, 80.00; H, 8.15

Found: C, 80.18; H, 8.19

M. Lithium Aluminum Hydride Reduction of *anti*-4-acetoxy-1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, **56b**.

The entire GC collected sample of **56b** from the photolysis described in Section L was reduced with LAH and worked up as described in Section D. The nmr spectrum of the product, 1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-*anti*-4-ol, **57b**, is given in Section B of the text. The ir spectrum of 57b (CCl_4 soln) showed absorptions at 3650, 3500, 2950, 1485, 1390, and 1050 cm^{-1}. Alcohol **57b** was further characterized as in Section N, below.

N. Jones Oxidation of 1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-ene-*anti*-4-ol, **57b**.

The entire sample of alcohol **57b** from Section M was oxidized with Jones reagent as described in Section K. The product of this oxidation had identical nmr and ir spectra to those of ketone **58**. See Section K for the spectra of ketone **58**.

O. Lithium Aluminum Hydride Reduction *anti*-3-acetoxy-1,4,4,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene, **59b**.

The entire GC collected sample of **59b** from the photolysis described in Section L was reduced with LAH and worked up as described in Section D. The nmr spectrum of the product, 1,4,4,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-*anti*-3-ol, **60b**, is given in Section B of the text. The ir spectrum of **60b** (CCl_4 soln) showed absorptions at

3650, 3500, 2950, 1485, 1390 and 1075 cm^{-1}. Alcohol 60b was further characterized in P, below.

P. Jones Oxidation of 1,4,4,8-tetramethyl-6,7-benzotricyclo$[3.3.0.0^{2,8}]$-oct-6-ene-*anti*-3-ol, 60b.

The entire sample of 60b from Section O was oxidized with Jones reagent and purified as described in Section K to afford 1,4,4,8-tetramethyl-6,7-benzotricyclo$[3.3.0.0^{2,8}]$oct-6-ene-3-one, 61. The nmr spectrum of ketone 61 is given in Section B of the text. The ir spectrum of ketone 61 (CCl_4 soln) showed absorptions at 2920, 1715, 1465, 1380, 1100, and 1060 cm^{-1}. Its uv spectrum showed λ_{max}^{EtOH} 300 nm (ε = 2,400), 289 nm (ε = 2,600), 278 nm (ε = 6,900), 270 nm (s,ε = 10,000), 261 nm (s,ε = 13,000), 251 nm (s,ε = 17,000) and 208 nm (ε = 100,000). The mass spectrum of 61 showed a parent peak of m/e 226 and a base peak of m/e 156.

Anal. Calcd: C, 84.96; H, 7.96
Found: C, 85.00; H, 8.04

Q. Synthesis of 5,6-benzobicyclo[2.2.2.]octa-5,7-diene-2-one, 62 and 62-d_2.

Twenty grams of 1,2,3,4-tetrahydro-9-oxo-1,4-ethanonaphthalene-2,3-dicarboxylic acid (77 mmole) (38) was dissolved in a solution containing 150 ml of pyridine, 2 ml of triethylamine, and 12 ml of water. The solution was placed in a rectangular glass jar which contained two Pt electrodes (5 X 7.5 cm) separated by 4.5 cm, a water cooling coil, and a nitrogen bubbler. A constant unfiltered DC potential of 110 volts r.m.s. was placed on the electrodes; the initial current was 490 ma. After 15 hrs of electrolysis, the current had fallen to 200 ma, and the solution had turned black. The solvents were evaporated under reduced pressure to afford 25 g of a black tar. This was extracted with hot ether (10 X 50 ml), and the ethereal solution was washed with 30% aqueous acetic acid (6 X 50 ml) and water (10 X 50 ml). The ether solution was then dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to afford 5.5 g (32 mmole, 42%) of a brown oil which had an identical nmr spectrum to that of **62** reported by Zimmerman (24). The oil was crystallized from ethanol/water and recrystallized from hexane to afford white needles mp 53-55° (reported 55.5-57°). Ketone **62**-d_2 was prepared by stirring a sample of ketone **62** for 6 hours in an excess of a 5 M solution of $NaOCH_3$ in CH_3OD. Normal hydrolytic work-up afforded **62**-d_2 which displayed an identical nmr spectrum to that of **62** except that the 2H multiplet centered at τ 8.07 was absent.

R. Synthesis of syn and anti-5,6-benzobicyclo[2.2.2.]octa-5,7-diene-2-ols, **63a**, **63b**, **63a**-d_2, and **63b**-d_2.

One gram of **62** (or **62**-d_2) was reduced with LAH using the procedure outlined in Section D. Injection of the product mixture into a GC column (5' X 1/4" 30% SE-30 at 150°) afforded 2 peaks in the ratio of 3:2. The compounds corresponding to these peaks have been identified as **63a** and **63b** respectively. The nmr spectrum of **63a** consisted of an aromatic singlet (4H) at τ 2.95, a broad multiplet (2H) at τ 3.67, a broad multiplet (2H) at τ 6.15, a broad multiplet (1H) at τ 7.93, a singlet (1H) at τ 8.63, and a broad multiplet (1H) at τ 9.10. The nmr spectrum of **63a**-d_2 was identical to that of **63a** except that the one proton signal at τ 7.93 and 8.63 were absent, and the one proton signal at τ 9.10 in 63a-d_2 was a singlet. The ir spectrum of 63a (CCl_4 soln) showed absorptions at 3600, 3100, 2950, 1400, 1250, and 1060 cm^{-1}. A small sample of 63a was refluxed with acetyl chloride and worked-up as described in Section H. The nmr spectrum of the resulting acetate showed a sharp 3 proton singlet at τ 8.22. Alcohol 63a was further characterized as in Section S.

The nmr spectrum of 63b consisted of an aromatic singlet (4H) at τ 2.95, a broad multiplet (2H) at τ 3.42, a broad multiplet (2H) at τ 6.05, a broad multiplet (1H) at τ 8.00, a singlet (1H) at τ 8.07, and a multiplet at τ 8.75. The nmr spectrum of 63b-d_2 was identical to that of 63b except that the one proton signal at τ 8.00 and 8.07 were absent, and the one proton signal at τ 8.75 in 63b-d_2 was a singlet. The ir spectrum of 63b (CCl_4 soln) showed absorptions at 3600, 3100, 2950, 1400, 1250, and 1050 cm^{-1}. A small sample of 63b was refluxed with acetyl chloride and worked-up as described in Section H. The nmr spectrum of the resulting acetate showed a sharp 3 proton singlet at τ 8.07.

S. Jones Oxidation of 5,6-benzobicyclo[2.2.2.]octa-5,7-diene-*syn*- and *anti*-2-ols, 63a and 63b.

Fifty mg of the epimeric mixture of 63a and 63b synthesized in Section R was oxidized with Jones reagent and worked-up using the procedure described in Section K. The nmr spectrum of the product was identical to that of ketone 62.

T. Photolysis of 5,6-benzobicyclo[2.2.2.]octa-5,7-diene-syn-2-ol, **63a** (**63a**-d_2).

A 123 mg GC collected sample of **63a** was dissolved in 3 ml of acctone and sealed in a pyrex test tube with a septum. The solution was deoxygenated by bubbling nitrogen through it for 30 minutes. An initial GC aliquot was withdrawn and injected into a 5' X 1/4" 20% FFAP column at 185°. It showed two peaks, with R_t 3.5 and 21 minutes. The solution was then irradiated for 85 hours in a Rayonet Photochemical Reactor fitted with 300 nm tubes. The GC trace of an aliquot then showed the 3.5 min and the 21 min peaks plus photoproduct peaks at 18 minutes and 27 minutes, the latter in the ratio of 1:7 respectively. The entire photolysis mixture was separated by preparative GC. The compound corresponding to the 3.5 minute peak was identified as naphthalene from its nmr spectrum. The minor photoproduct corresponding to the 18 minute peak was not identified. The compound corresponding to the 21 minute peak was identified as unreacted **63a** from its nmr spectrum. The compound corresponding to the 27 minute peak has been identified as 6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-*syn*-4-ol, **64a** (or **64a**-d_2) from its 100 MHz nmr spectrum which is given in Section C of the text. The ir spectrum of **64a** (CCl_4 soln) showed absorptions at 3590, 3490, 3050, 2950, 1480 and 1400 cm^{-1}. Alcohol **64a** was further characterized as in Section U, below.

U. Jones Oxidation of 6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-syn-4-ol, **64a** (**64a**-d_2).

The entire GC collected sample of **64a** was oxidized with Jones reagent and worked-up as described in Section K. The nmr spectrum of the product, 6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-4-one, **65**, is given in Section C of the text. The ir spectrum of **65** (CCl_4 soln) showed absorptions at 2980, 3080, 1738, 1480, and 1265 cm^{-1}. Its uv spectrum showed λ_{max}^{EtOH} 285 nm (ε = 12,000), 235 nm (s, ε = 33,000) and 209 nm (ε = 175,000). The mass spectrum of **65** showed a base peak of m/e 128 and a parent peak of m/e 170 (172 for **65**-d_2).

Anal. Calcd: C, 84.68; H, 5.92

Found: C, 84.75; H, 6.02

V. Photolysis of 5,6-benzobicyclo[2.2.2.]octa-5,7-diene-*anti*-2-ol, **63b** (**63b**-d_2).

A 97 mg sample of GC collected **63b** was prepared for photolysis, irradiated, and monitored by GC as described in Section T. A single photoproduct peak at 34 minutes was observed. Collection of the compound corresponding to the peak afforded 6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-ene-*anti*-4-ol, **64b** (or **64b**-d_2). The 100 MHz nmr spectrum of **64b** is described in Section C of the text. The ir spectrum of **64b** (CCl_4 soln) showed absorptions at 3590, 3400, 3050, 2950, and 1480 cm^{-1}. Alcohol **64b** was further characterized as in Section W, below.

W. Jones Oxidation of 6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-*anti*-4-ol, **64b** (**64b**-d_2).

The entire GC collected sample of **64b** was oxidized with Jones reagent and worked-up as described in Section K. The product of this oxidation had identical nmr and ir spectra to those described in Section U for ketone **65**.

X. Lithium Aluminum Hydride Reduction of 6,7-benzotricyclo[3.3.0.$0^{2,8}$]-oct-6-ene-4-one, **65**.

A 50 mg sample of ketone **65** was reduced with LAH and worked-up using the procedure outlined in Section D. The product of this reduction had identical nmr and ir spectra to those reported for alcohol **64a** in Section T.

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