This is to certify that the

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1. REGIOSPECIFICITY IN THE DI-π-METHANE REARRANGEMENT

2. THE IONIZATION OF TWO TETRACYCLIC GEM-DIFLUORIDES UNDER STABLE ION CONDITIONS

3. MISCELLANEOUS

presented by

Daryl L. Stein

has been accepted towards fulfillment
of the requirements for

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Harold Hart

Major professor

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PART I

REGIOSPECIFICITY IN THE DI-π-METHANE REARRANGEMENT

PART II

THE IONIZATION OF TWO TETRACYCLIC GEM-DIFLUORIDES UNDER STABLE ION CONDITIONS

PART III

MISCELLANEOUS

By

Daryl L. Stein

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Submitted to
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DOCTOR OF PHILOSOPHY

Department of Chemistry

1978

# ABSTRACT

## PART I

## REGIOSPECIFICITY IN THE DI-π-METHANE REARRANGEMENT

## PART II

## THE IONIZATION OF TWO TETRACYCLIC GEM-DIFLUORIDES UNDER STABLE ION CONDITIONS

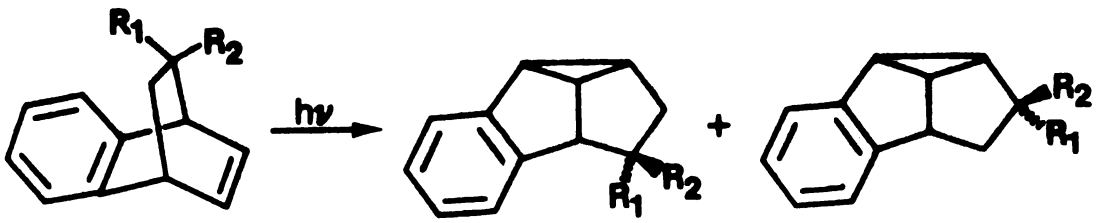
## PART III

## MISCELLANEOUS

By

Daryl L. Stein

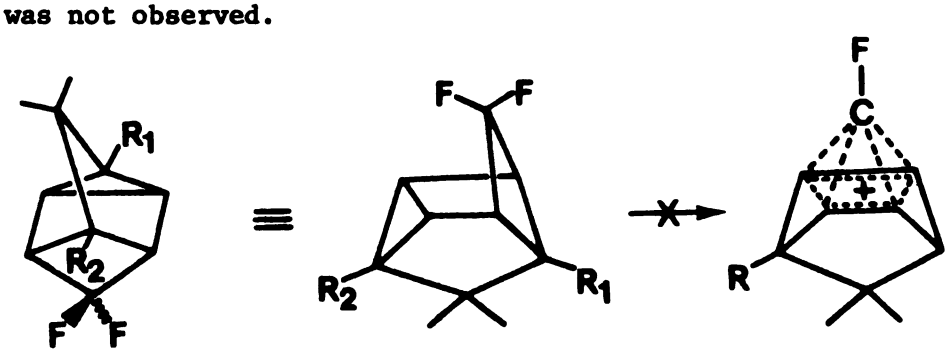
In Part I of this thesis the acetone sensitized di-π-methane rearrangement of 9,9-dimethyl-1,4-dihydro-1,4-ethanonaphthalene 21 was studied. Of the two possible photoproducts, 6,6-dimethyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene 26 is the major (66%) one. The structure of the major isomer was determined by synthesis. This result is in agreement with previous work in which other substituents on the 9 position caused a similar regiospecific rearrangement. In each case the major photoproduct arises from a diradical species in which the unpaired electrons are close to rather than remote from the R groups on the saturated bridge. In addition the quantum yields of formation for the corresponding photoproducts of compounds 21, 7, 10,




| | | | |
|---|---|---|---|
| 21 | $R_1 = R_2 = CH_3$ | 25 | 26 |
| 7 | $R_1 = H_1$, $R_2 = OH$ | 9 | 8 |
| 10 | $R_1 = OH$, $R_2 = H$ | 12 | 11 |
| 13 | $R_1 = H$, $R_2 = CH_3$ | 15 | 14 |
| 16 | $R_1 = CH_3$, $R_2 = H$ | 18 | 17 |

13, and 16 were determined in benzene with various sensitizers. In each case acetone was the most efficient sensitizer. In addition the triplet energy levels for these compounds were found to be between 68 and 72 Kcal/mole.

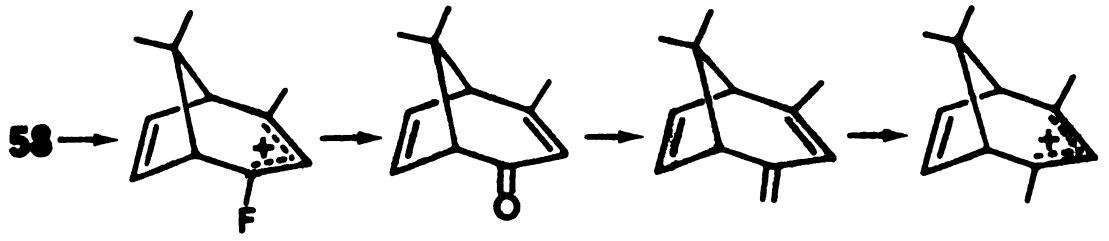
In Part II when either fluorocarbon 58 or 59 was treated with $SbF_5$ at -95° C the corresponding apical substituted fluoro pyramidal ion was not observed.




58 $R_1 = CH_3$, $R_2 = H$ 63

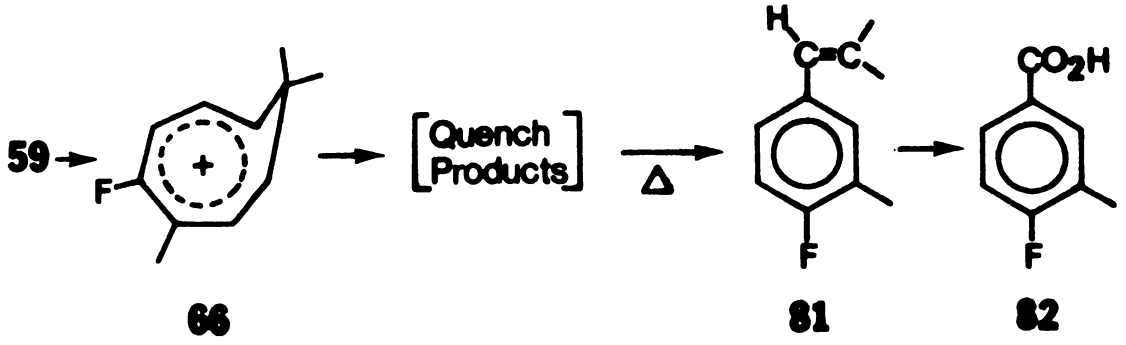
59 $R_1 = H$, $R_2 = CH_3$

Instead 58 ionized to the bicyclic[3.2.1] ion 65. The structure




of 65 was confirmed by quenching in sodium methoxide-methanol to give the corresponding ketone 69. The structure of ketone 69 was proved by treatment with methyllithium to give exo-methylene compound 71 which when treated with $FSO_3H$ at -95° C, gave the symmetric allyl ion 72.

In contrast to 58, fluorocarbon 59 ionized to the homotropylium

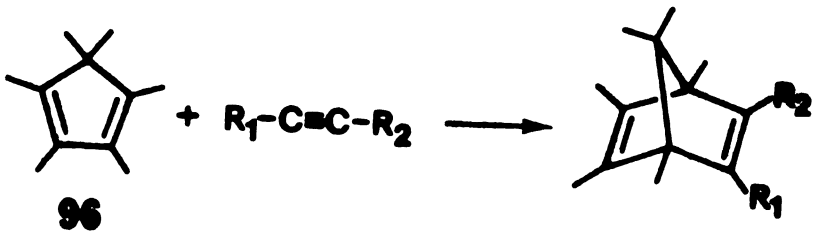



ion 66. A methanol quench at -78° C gave a mixture of methoxyether quench products. Attempted VPC separation of this mixture resulted in ring contraction and loss of methanol to give fluorostyrene 81 as the major product. The structure of 81 was confirmed by converting it to the known fluorotoluic acid 82.

Mechanisms for the formation of ions 65 and 66 are also proposed.

In Part III hexamethylcyclopentadiene 96 was treated with various

dienophiles and subsequent exploratory reactions were performed on the various Diels-Alder adducts.




96

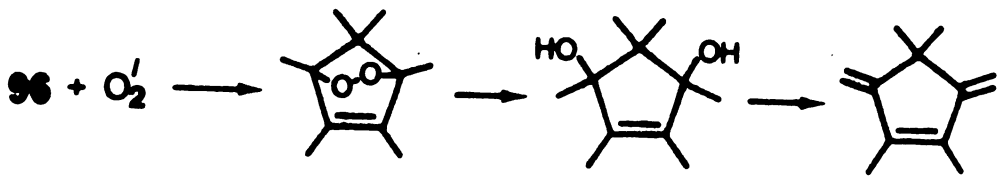
104 $R_1 = R_2 = CO_2CH_3$

105 $R_1 = CH_3$, $R_2 = CO_2H$

108 $R_1 = CH_3$, $R_2 = CO_2CH_3$

113 $R_1 = R_2 = CF_3$

In addition, 96 also undergoes a Diels-Alder reaction with singlet oxygen to form the corresponding endo-peroxide 111. The




111 122 123

structure of 111 was confirmed by reduction of 111 to diol 122 which upon treatment with acid gave the known triene 123.

## ACKNOWLEDGEMENTS

I am indebted to Professor Harold Hart for his guidance and support throughout the course of this study.

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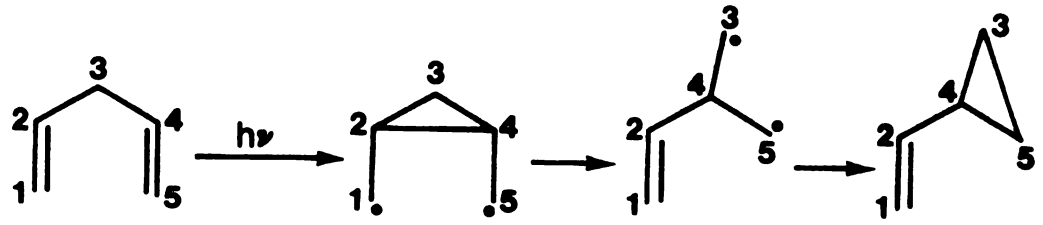
# PART I

# REGIOSPECIFICITY IN THE DI-π-METHANE REARRANGEMENT

# INTRODUCTION

Zimmerman first recognized the importance of the di-$\pi$-methane rearrangement and has extensively characterized it.[1] Basically, this photochemical reaction involves the formation of a vinyl cyclopropane from molecules having two vinyl groups attached to the same methylene carbon (eq 1). The first step of the reaction is usually depicted as initial bonding between C-2 and C-4, which results in a diradical with a cyclopropane ring. Cleavage of either the C-2, C-3 bond or the C-3, C-4 bond of the cyclopropane ring leads to a new diradical which

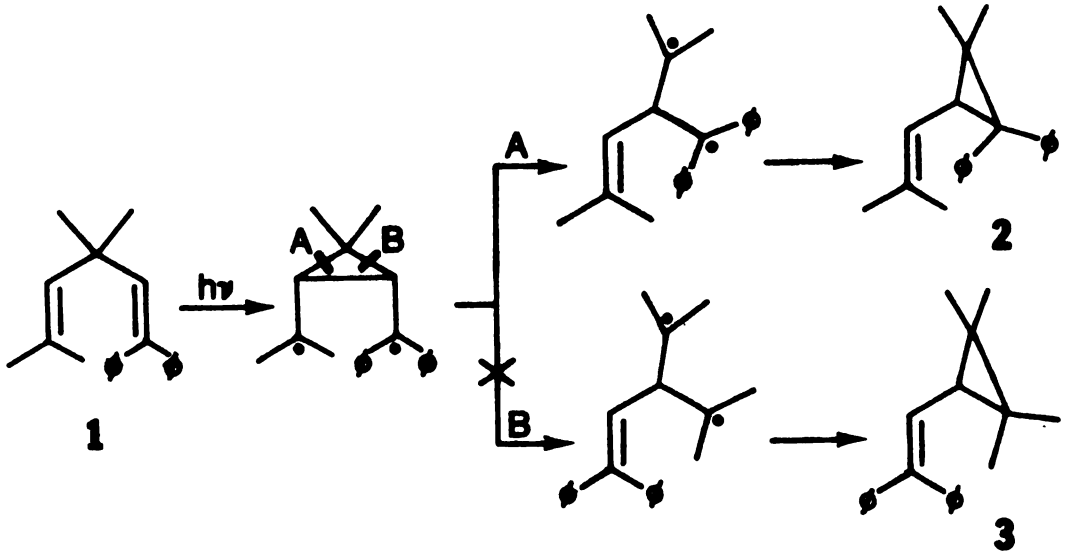



(1)

then closes to the final product. The diradical species are not necessarily discrete intermediates. For example, Zimmerman has suggested on the basis of stereochemical studies that reaction from the singlet excited state may be concerted. In this event, the diradical would simply represent one point along the reaction coordinate. Nevertheless, these qualitative valence bond pictures are useful in describing the gross mechanism and in making predictions when one $\pi$

system will react in preference to another.

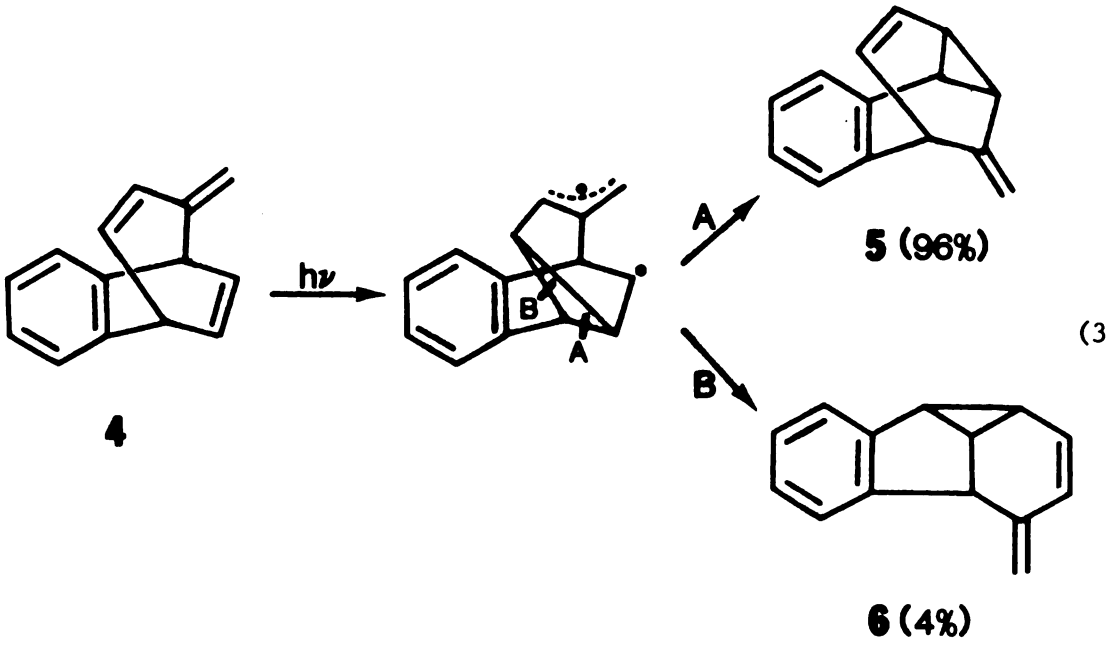
Thus in an unsymmetrical molecule (eq 2), the major product can be predicted by examining which reaction leads to the more stable diradical intermediate.[2] Cleavage of bond A is preferred because the odd electron adjacent to the phenyl groups is stabilized to a greater extent (through resonance) than is the odd electron adjacent to the methyl groups.




(2)

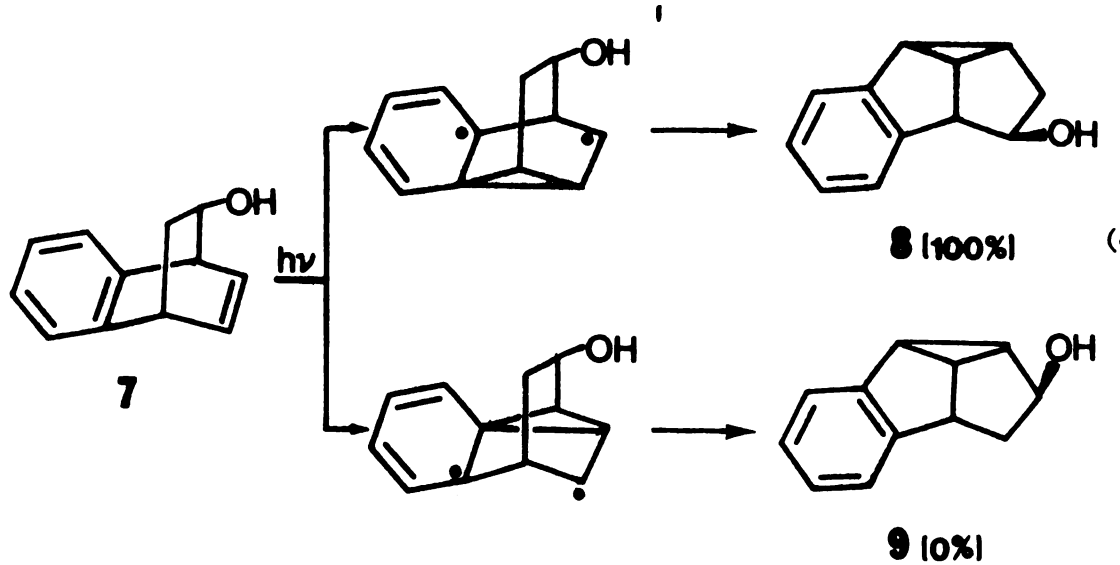
Equation 3 represents another type of regiospecificity in which initial bond formation determines the final product. Although there are formally four di-$\pi$-methane units in the molecule, only two products are observed. Both of these products can be rationalized by an initial bonding which forms an allyl radical. Initial bonding at other positions would form a less stable primary or second diradical species or it would disrupt the aryl ring. Once the allyl radical is formed, the rearrangement then proceeds so as to maintain the odd electron at this position for a long as possible which explains the preponderance of 5 over 6. Since this reaction proceeds via both the singlet and triplet

excited states, multiplicity does not seem to be a controlling factor in determining regiospecificity.




(3)

Although all of the above products can be rationalized by through bond stabilization of radical sites, there are examples of a less well understood through-space control of the di-π-methane reaction. In the reactions represented by eqs 5 and 6, the hydroxyl function is not directly attached to the di-π-methane system, yet somehow it controls the course of the reaction, favoring one diradical intermediate over the other.[4a,b] Proposed explanations for these phenomena are the following: 1) internal hydrogen bonding in which the hydroxyl group stabilizes one of the two possible diradicals, 2) a charge transfer complex involving the lone pairs of oxygen with a radical site, or 3) some type of asymmetric energy transfer from an excited donor molecule to the acceptor molecule.

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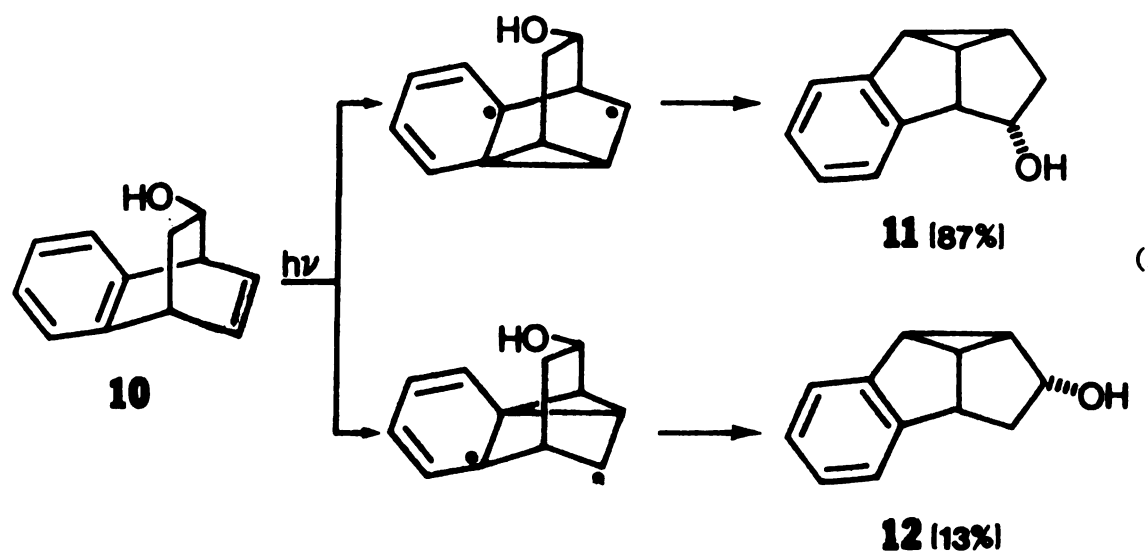
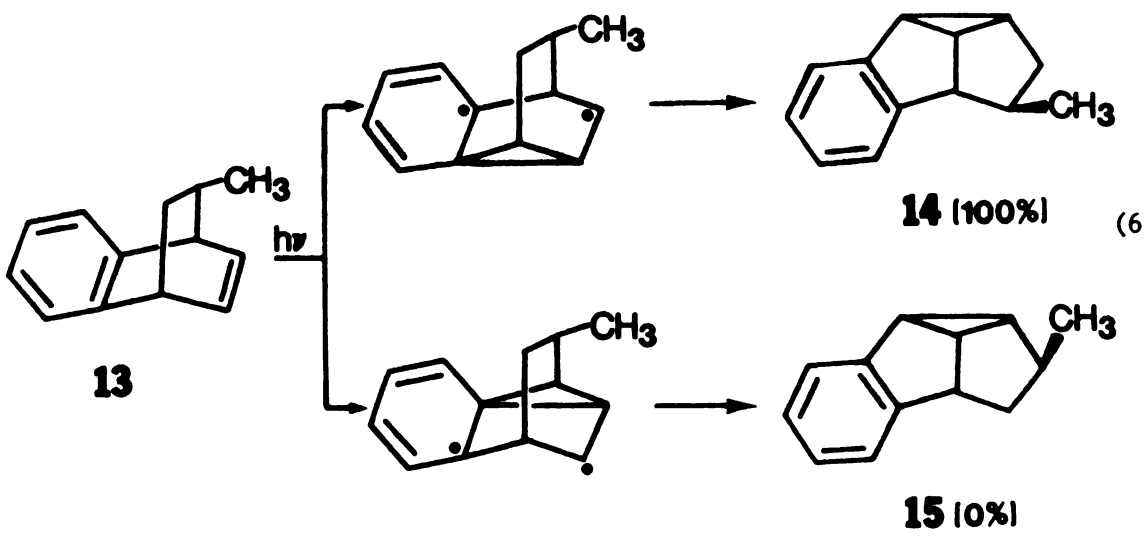



(5)

The observation that the acetates corresponding to 7 and 10 displayed a similar regiospecificity eliminated hydrogen bonding as the exclusive explanation but did not rule out lone pair interaction. However, doubt also was recently cast on this rationalization by the observation that substitution of a methyl group for a hydroxyl as in 13 and

16 does not affect the regiospecificity[5] (eq 6 and 7). Since a methyl group has no unshared electron pairs, there must be another explanation for the observed effect (vide infra).

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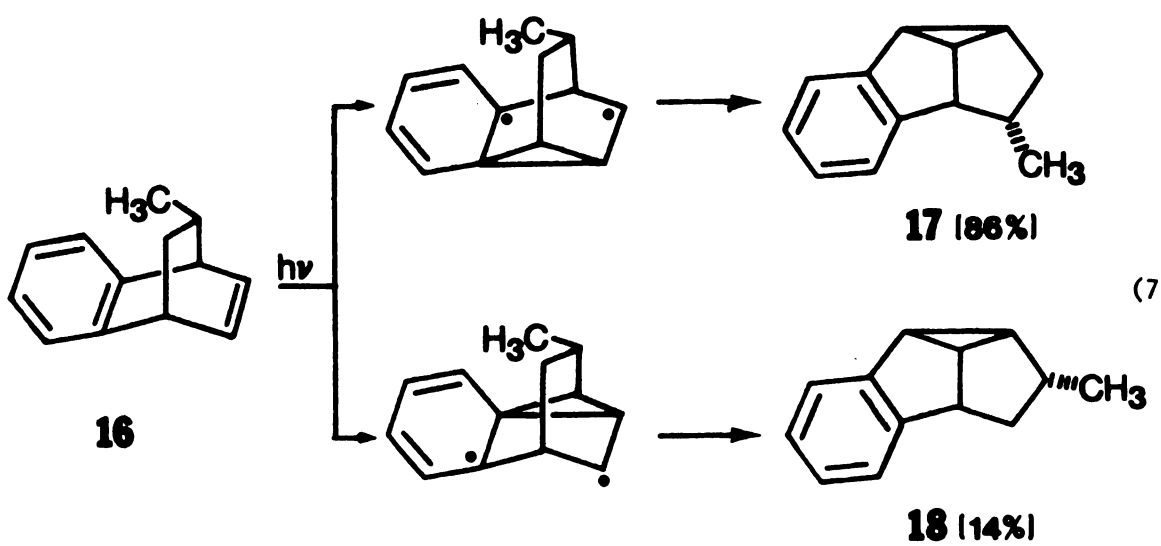


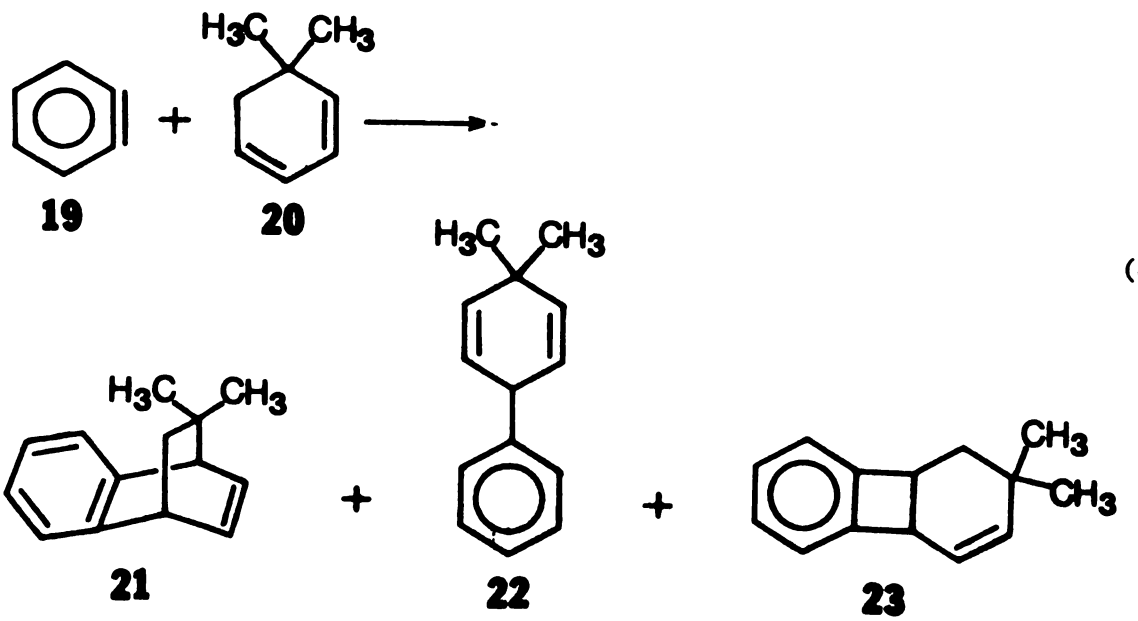

(7)

In order to further understand the factors that control this remote substituent effect of the di-π-methane reaction, several new experiments were carried out. First, in order to determine whether a gem-dimethyl group would exhibit the same regiospecificity as the single methyl group in compounds 13 and 16, the analog 21 was synthesized and irradiated. Second, the quantum yields for the di-π-methane rearrangement of 7, 10, 13, 16, and 21 were determined with various triplet sensitizers in order to ascertain and compare the triplet energy levels of the excited states, and also to better understand the partitioning of the excited state among the various products.

These studies constitute the first part of this thesis.

## RESULTS

The synthesis of 9,9-dimethyl-1,4-dihydro-1,4-ethanonaphthalene (21) was accomplished by adding benzyne to the known[6] 5,5-dimethylcyclohexa-1,3-diene 20 (eq 8). Unfortunately, the reaction mixture contained not only 21 but also 22 and 23, in the ratio of 3:2:1. The




(8)

formation of this mixture was not too surprising, since benzyne is known to react with cyclic olefins to give not only $4\pi + 2\pi$ additions, but also ene reactions and $2\pi + 2\pi$ products.[7]

The separation of 21 from this product mixture, although difficult, could be accomplished by silica gel chromatography, followed by preparative VPC of the 21-enriched fractions in order to remove the last traces of 22 and 23. Compound 22 proved to be an effective quencher of the di-$\pi$-methane rearrangement of 21, and unless it was completely removed

photolysis of 21 was slow.

The structure proof of the products rests on spectral data, and on subsequent chemical transformations (vide infra). The NMR (Nuclear Magnetic Resonance) and IR (Infrared) spectra of 22 were identical with those of an authentic sample.[8]

Comparison of the NMR spectrum of 21 with those of the closely related 13 and 16 was instructive. In compound 16, the methyl group is syn to the aromatic ring, and appears as a shielded doublet at $\delta$ 0.60 ppm. In 13, the methyl group is anti to the ring and appears as a downfield doublet at $\delta$ 0.93 ppm. Compound 21, with methyl groups both syn and anti to the ring, exhibits two singlets, one at $\delta$ 0.60 ppm and the other at $\delta$ 1.03 ppm, consistent with expectation. Furthermore, the aromatic, vinyl, bridgehead and methylene protons for all three compounds have nearly identical chemical shifts. Their mass spectra are also similar, with a base peak at m/e 128, corresponding to bridge cleavage to naphthalene in each case.

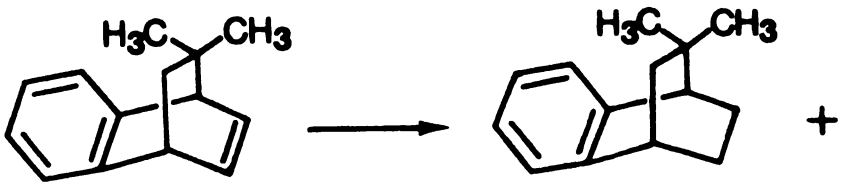
The structural assignment of 23 rests mainly on the premise that benzyne should add to the less hindered double bond (i.e., the double bond which is remote from the gem-dimethyl group). Furthermore the chemical shifts and coupling constants for the vinyl protons [$\delta$ 5.45 ppm (1 H, d, J = 10 Hz) and $\delta$ 5.84 (1 H, dd, J = 10, J = 3 Hz)] are consistent with the assigned structure. The splitting pattern of the vinyl protons would have been different had cycloaddition occurred at the other double bond.

The preparative scale photolysis of 21 was carried out in acetone and was monitored by VPC. In addition to a small amount of starting material, three peaks with an area ratio of 1:1:2 were obtained by

preparative VPC. The products were collected and identified as 24, 25 and 26 (eq 9).

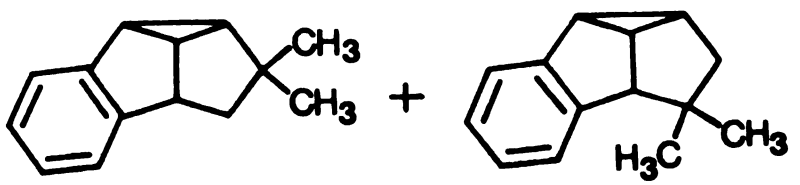
Photoproduct 24 is the result of photoreduction. In addition to literature precedent for such reactions,[9] a similar reaction occurred with 13 and 16.[5] The NMR spectrum of 24 is consistent with its structure, and in its mass spectrum the parent ion was 2 atomic mass units greater than the parent ion of the precursor, 21. The structure of 24 was confirmed by catalytically hydrogenating 21 over Pd/C. The NMR and IR spectra of the hydrogenation product were identical to those of 24 obtained from the photolysis.

Photoproducts 25 and 26 arise from the expected di-π-methane rearrangement of 21. In each case the parent ion in the mass spectrum




21 24

(9)

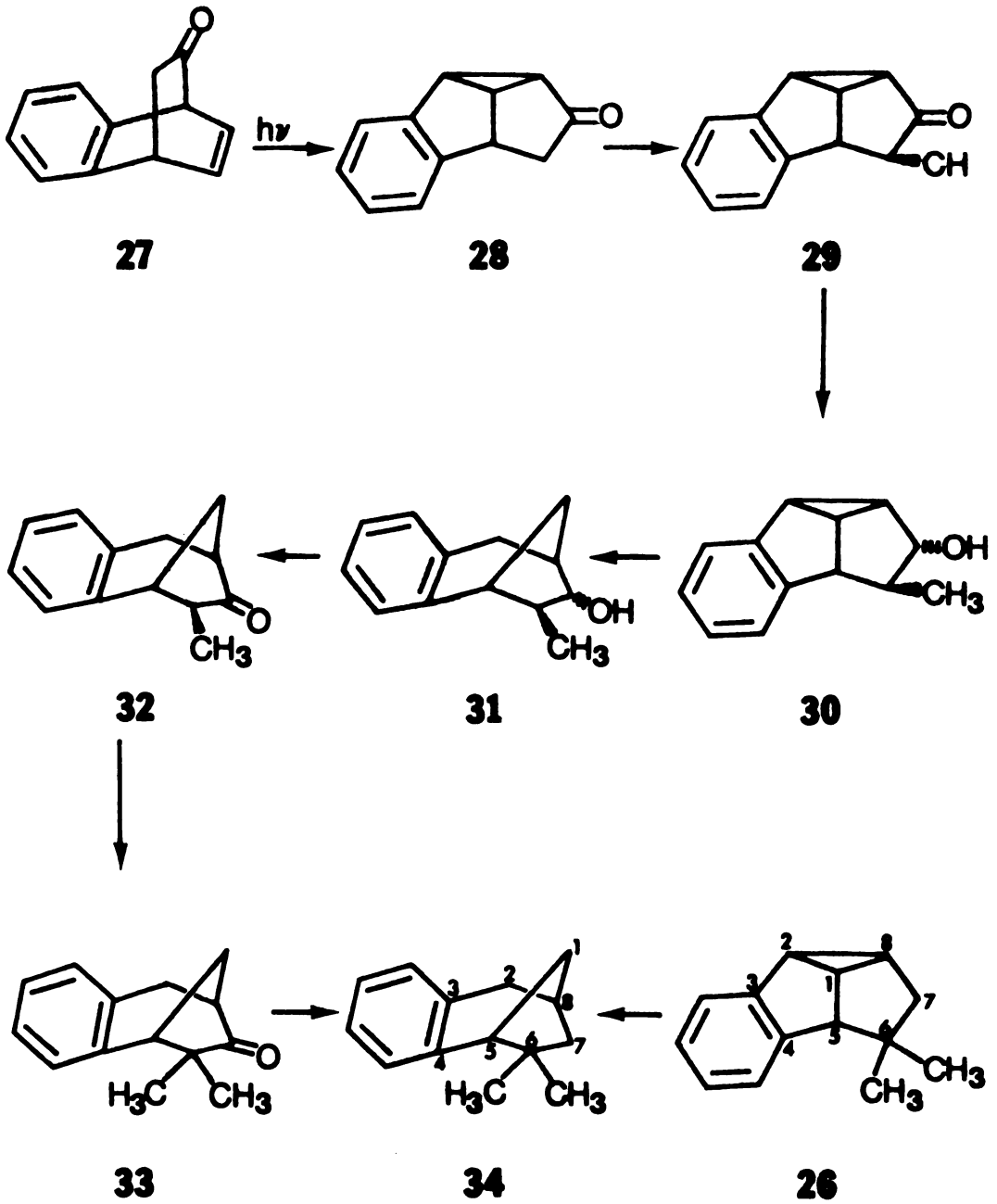



25 26

indicated that these products were isomeric with the starting material. The absence of vinyl protons in the NMR spectra of 25 and 26 indicated the formation of another ring. The two di-π-methane photoproducts can be distinguished by examining the chemical shifts of the gem-dimethyl groups. Examination of models reveals that these photoproducts are cup-shaped. Thus for 25 the syn-methyl group is tucked down toward the phenyl ring, causing it to be shielded by the ring current. This methyl group appears at high field in the NMR spectrum, at δ 0.48 ppm which is in agreement with the chemical shift of the syn-methyl group of 18 which is also at δ 0.48 ppm. The syn-methyl for 26, although it also points toward the phenyl ring, is not nearly as close to it. This methyl group therefore appears at somewhat lower field, at δ 0.76 ppm which is close to the δ 0.74 ppm shift observed for the syn-methyl group of 17. The anti-methyl groups in 25 and 26 appeared at δ 1.12 and 1.19 ppm, respectively which is in good agreement with the chemical shift at δ 1.08 ppm observed for the anti-methyl in 14.

Thus it is clear that the expected di-π-methane rearrangement did, in fact, occur upon sensitized irradiation of 21. However, since proton NMR spectra for the rearrangement products are complex, it was desirable to have a more rigorous criteria than just the chemical shifts of the methyl groups for assigning the product structures. In order to put these assigned structures on more firm ground, the following independent synthetic correlation was carried out (Scheme 1).

Scheme 1




By analogy with previous work,[5] the three-membered ring in 26 was catalytically hydrogenated to give 34. Although a priori any one of the three cyclopropyl bonds could have been cleaved, one would expect either the 1,2 or 2,8 bond to be preferentially hydrogenated since they are activated by the aryl ring. Furthermore, molecular models indicate

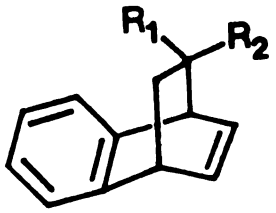
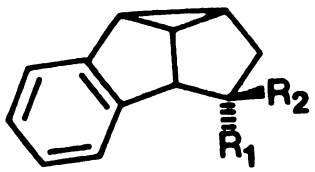
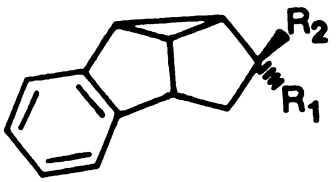
that the 1,2 bond of 26 can lie nearly flat upon a table top (catalytic surface). The geometry of the molecule prevents the 2,8 and 1,8 bonds from approaching the catalyst surface as easily as the 1,2 bond. Consequently 34 (from 1,2 bond cleavage) is expected to be the major hydrogenation product. Analysis of the reaction mixture on an analytical gas chromatograph with an SE-30 column gave only a single peak. The mass spectrum indicated an increase of two mass units. The NMR spectrum indicated 4 aromatic proton signals at δ 6.80 ppm and two methyl group signals at δ 1.10 and δ 0.63 ppm. The remaining proton signals appeared as a complex multiplet. It remained to synthesize 34 by an independent route.

The bicyclic ketone 27[4b, 10] was photolyzed to the known tricyclic ketone 28 by established procedures.[11] This ketone was then methylated, reduced and hydrogenated according to a procedure developed by P. Lavrik[5] to give alcohol 31. The ketone must be reduced to the alcohol prior to hydrogenolysis because the carbonyl function in 29 activates the 2,8 cyclopropyl bond. Hydrogenation at this stage would exclusively cleave the 2,8 bond.

Alcohol 31 was then oxidized to ketone 32. This ketone, although hindered, was alkylated by using the very reactive base potassium hydride.[13] Wolff-Kishner reduction[12] of the dialkylated ketone 33 gave 34 in low yield. The NMR, IR and mass spectra were identical to that of 34 produced from catalytic hydrogenation of 26. This then proves that the structural assignments of 25 and 26 based on NMR data were correct, and that 26 is the major di-π-methane rearrangement product of 21 which is in agreement with all the other previous work.

The quantum yield for the sensitized formation of the photoproducts of hydrocarbons 13, 16, and 21 as well as alcohols 7 and 10 were determined in degassed benzene solutions using valerophenone actinometry. The conversion to photoproducts proceeded to less than 20% in all cases, while the conversion of valerophenone was less than 3%. Under these conditions the photoreduction reaction was suppressed. As can be seen in Table 1, acetone was in all cases the most effective sensitizer, whereas acetophenone was the poorest. Benzophenone does not sensitize the reactions. Hence the energies for the triplet states of 7, 10, 13, 16, and 21 lie somewhere between 72 and 68 Kcal/mol.

Table 1. Quantum Yields of Formation with Various Sensitizers

| No. | Substrate | Quantum Yields x 10 | | Sensitizer |
|---|---|---|---|---|
| |  |  |  | |
| 21 | $R_1 = R_2 = CH_3$ | 1.3 | 0.67 | A |
| | | 0.70 | 0.34 | B |
| | | 0.25 | 0.12 | C |
| 16 | $R_1 = CH_3$, $R_2 = H$ | 1.5 | 0.28 | A |
| | | 0.87 | 0.19 | B |
| | | 0.3 | - | C |
| 13 | $R_1 = H$, $R_2 = CH_3$ | 1.2 | | A |
| | | 0.83 | | B |
| | | 0.22 | | C |
| 10 | $R_1 = OH$, $R_2 = H$ | 0.64 | | A |
| | | 0.49 | | B |
| | | 0.23 | | C |
| 7 | $R_1 = H$, $R_2 = OH$ | 0.41 | | A |
| | | 0.29 | | B |
| | | 0.1 | | C |

A = Acetone; B = Diethyl Ketone; C = Acetophenone

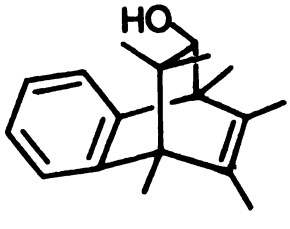
## DISCUSSION

Since the compounds under consideration do not have a stabilizing group directly attached to the di-$\pi$-methane system, it is difficult to understand why there should be any regiospecificity. In general, there are two ways in which this effect might occur. Either the R groups (R = OH, OAc, Me) attached to the bridge carbon are exerting some type of sterically-directed energy transfer (vide infra) or the bridge R group, by some type of long range interaction, preferentially stabilizes one of the two diradical intermediates after energy transfer. Either theory could rationalize the observed regiospecificity but there are certain objections to each.

Steric effects of energy transfer are known in the literature. However there is conflicting evidence as to their importance. Asymmetric induction in racemic acceptors of optically active sensitizers demonstrates the close contact made by the donor and acceptor during energy transfer.[14] In agreement with this observation there is also an example of the photoequilibrium of cis- and trans-stilbenes changing as more hindered ketone sensitizers are used.[15] In addition there are also several examples of hindered ketone and azo quenchers which quench the fluorescence and phosphorescence of various sensitizers at a lower rate than that of unhindered quenchers.[16] In contrast several workers have determined the excited state life times of tert-aryl and alkyl ketones by standard Stern-Volmer quenching experiments without noting any steric effects to

energy transfer.[17] Furthermore, α,α-dimethylvalerophenone 35, a tertiary aryl ketone, underwent Norrish Type-II photoprocesses without any steric effects.

Even though there is conflicting evidence on the importance of steric effects to energy transfer, an argument still could be formulated in which the excited sensitizer due to steric effects preferentially transfers its energy to one side of the molecule. For example, the bridge R group may hinder the approach of the sensitizer on the side of the molecule in which the R group is located. As a result of this steric hindrance the excited sensitizer transfers its energy to some less hindered location, a site on the molecule which is remote from the R group. If this preferential energy transfer in fact happened an explanation for the regiospecificity in these di-π-methane system could be made by postulating that the site of energy transfer favored one diradical intermediate over the other one. However, hindered energy transfer seems unlikely in view of the fact that polymethylated (hindered) alcohols 36 and 37 show nearly the same degree of regio-specificity as do the unhindered alcohols 7 and 10.[4] If steric hindrance to energy transfer was important varying the steric bulk of the acceptor

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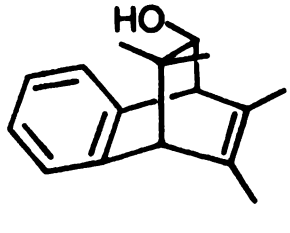


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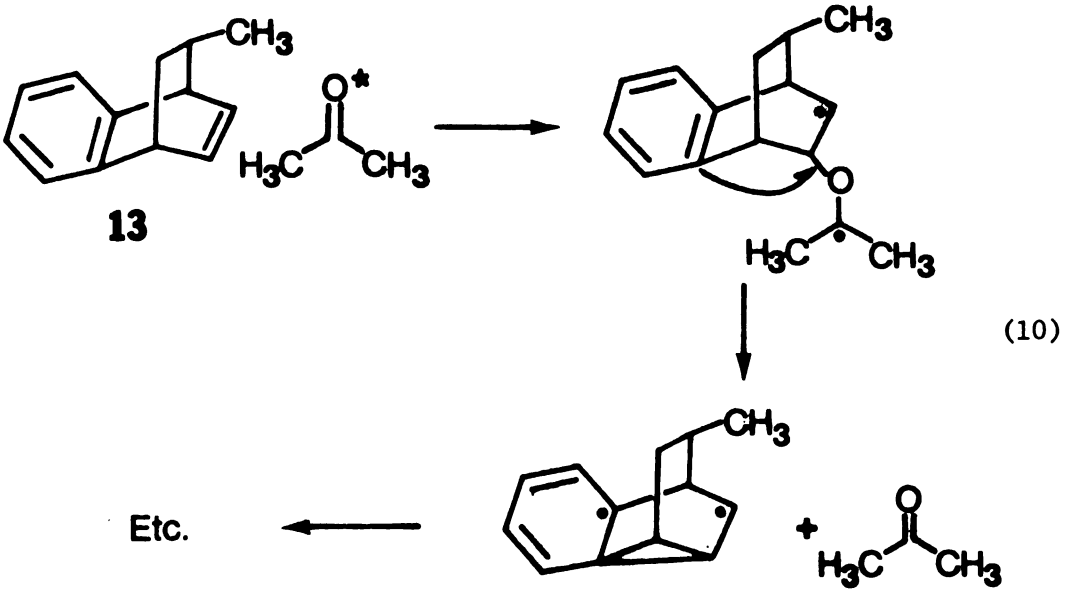
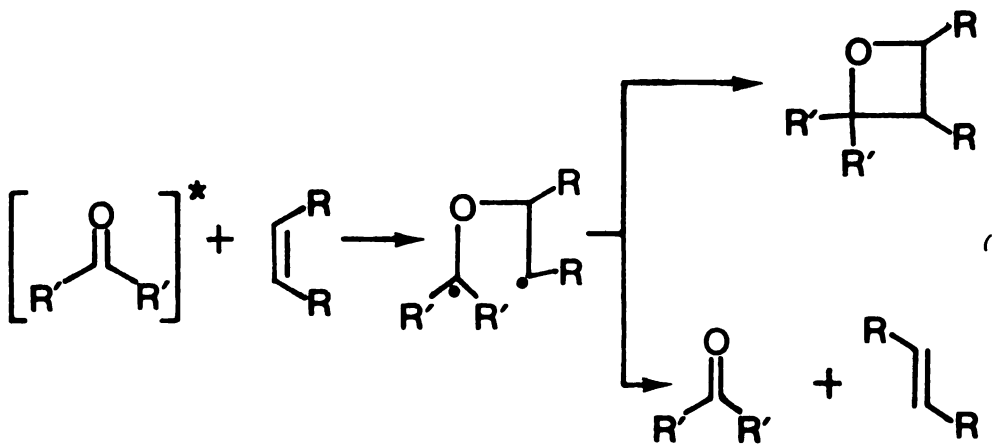
(or sensitizer) should affect the product ratios. The effect, however, was not observed.

Another possible rationalization of the results also based on steric effects, involves a Schenck type mechanism.[19] According to Schenck's scheme (eq 10) an electronically excited sensitizer (in this case acetone) forms a covalent bond with the acceptor. This initiates a rearrangement in which the sensitizer is eventually excised unharmed.



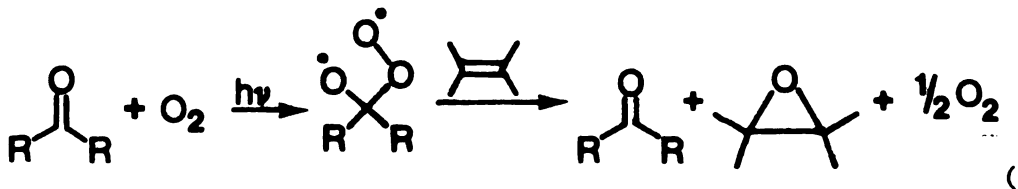

(10)

Although Schenck's original proposals have been disproved, there are some recent studies of reactions where this mechanism may be involved. In the Paterno-Büchi reaction, the photoaddition of an excited state carbonyl compound to an olefin, Yang proposed a biradical intermediate (eq 11) which may either ring close to an oxetane or cleave to regenerate the ground state ketone and isomerized olefin.[20] This latter cleavage process is a Schenck type mechanism. A second example is found in the



(11)

photoepoxidation of olefins (eq 12).[21] Here Bartlett proposed that an electronically excited ketone attacks an oxygen molecule to form a diradical intermediate. This intermediate in turn attacks the olefin which is present, eventually leading to a ground state ketone and an epoxide.

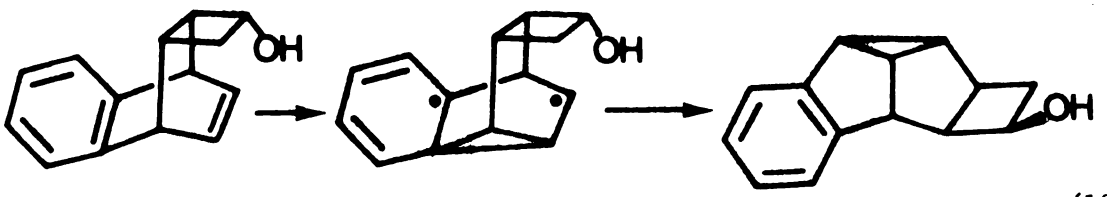


(12)

Despite these two examples there are several objections to a Schenck-type mechanism initiating a di-π-methane rearrangement. The first is the lack of literature precedent. The second objection is evident from examining eq 10. In the first step the excited state acetone molecule attacks the acceptor resulting in bond formation.

In order to explain the regiospecificity of the rearrangement, the attack must occur preferentially on one side of the molecule. For the sake of discussion, attack might be depicted to occur on the least hindered side, the side remote from the bridge R group (methyl).[22] If this hypothesis were correct, attack would consistently occur on the remote side in all cases, in order to rationalize the observed regiospecificity. This would be regardless of the orientation (syn or anti to the aromatic ring) of the bridge R group and regardless of the degree of methyl substitution on the bicyclic ring system. Consequently this explanation does not seem reasonable. A third objection is that different sensitizers with different steric requirements ought to give different isomer ratios of products. However, as is evident in Table 1, the opposite result occurred. Even though the quantum yields vary with different sensitizers, the ratios between major and minor products are invariant. In fact the decrease in quantum yield matches the decrease in triplet energy levels of the sensitizers. This result agrees with the accepted collisional transfer mechanism in which quantum yields decrease when the sensitizers' triplet energy levels fall below that of the acceptor.

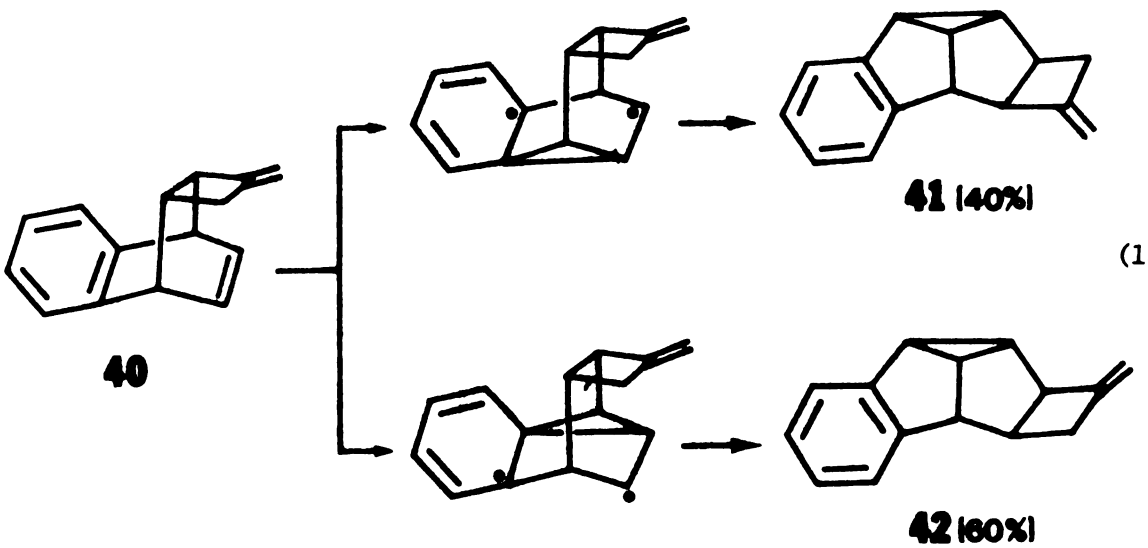
Thus since steric effects on energy transfer are unlikely, the only alternative is that some inherent feature in the bicyclic ring system itself is responsible for the regiospecificity after energy transfer. The interaction of lone pairs in the R groups (R = OH, OAc) may be part of the answer, especially in light of Marata's work[23] (eq 13). Here the bridge R group (R = OH) is two carbon units removed from the di-π-methane system, yet there was only one photoproduct. When the hydroxyl group was replaced by an exo-methylene group the




(13)

38 39 (100%)

regiospecificity was destroyed (eq 14). This suggested that a through space interaction with lone pairs on oxygen was an important effect.

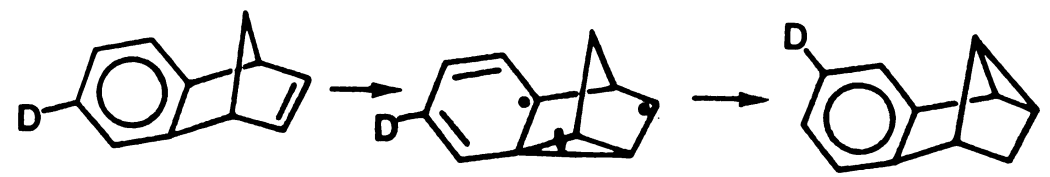



(14)

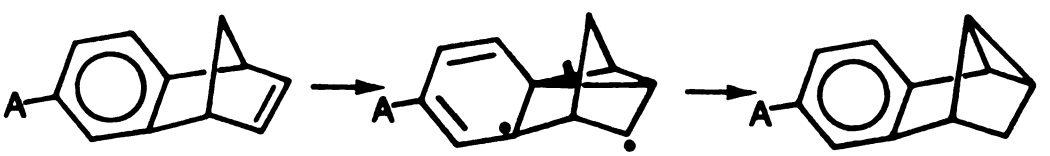
However, lone pair interaction cannot be the only answer since compounds 13, 16, and 21 which have only a methyl group(s) to destroy the symmetry, still react regiospecifically. This fact implies that other effects beside lone pair interactions are important.

The only type of interaction that has not been discussed is an inductive effect by the bridge R group. But even with this hypothesis there are difficulties. First, a methyl group is inductively electron-donating whereas the hydroxyl and acetate groups are inductively electron-withdrawing. It is not obvious how two opposing interactions could favor the same diradical intermediate in the Zimmerman formalism. Second, any inductive effect would have to be operating over two or more carbons but the strength of inductive effects is known to decrease rapidly with distance.

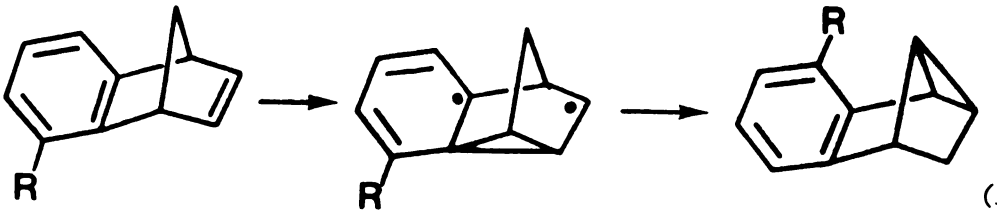
Recent work by Houk on a related system may serve as a model for explaining the observed regiospecificity. In Houk's case (eq 15) an electron donating group in the meta position favored initial meta bridging (meta to the donor group) while a meta acceptor group favored




(15)




initial para bridging. When the R group was in the ortho position (eq 16) initial ortho bridging was favored in all cases whether R was an electron donor or an electron acceptor. The explanation for these effects comes from frontier orbital theory.




(16)

The compounds that Houk studied were approximated by allowing an ethylene unit and the substituted benzene orbitals to interact. Figure 1 shows the resulting HOMO and LUMO orbitals with their coefficients for an ortho substituted aryl ring. In the case of an acceptor substituted benzene, the large coefficient on the lobe ortho

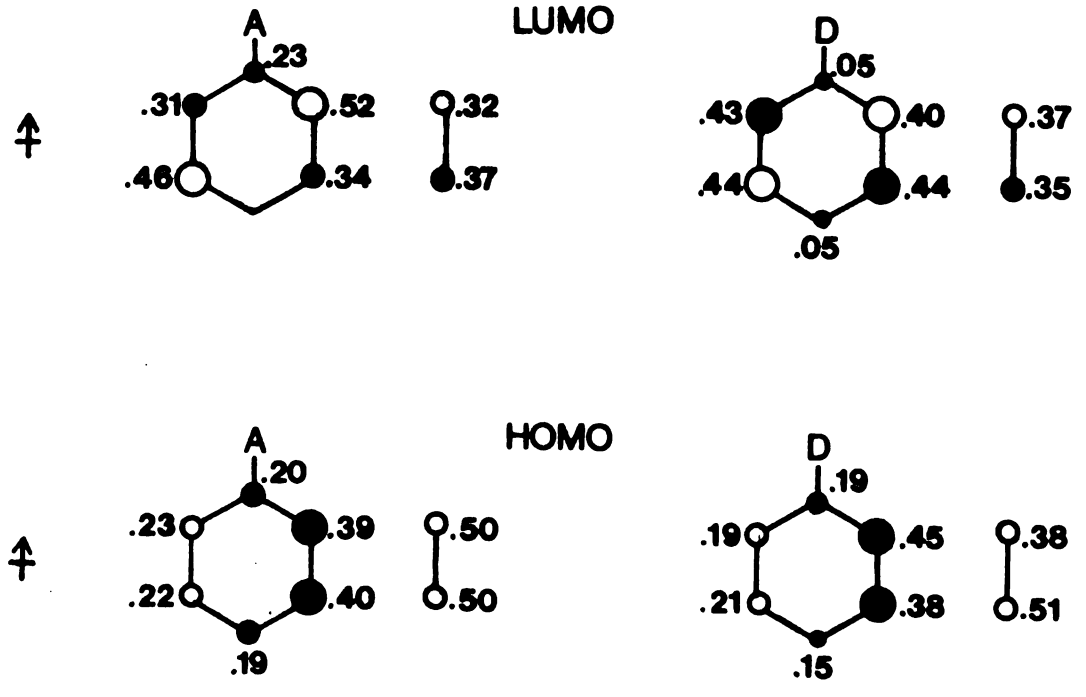



Figure 1. Singly occupied MO's of donor-acceptor substituted benzene after interaction with an ethylene unit.

to the acceptor group in the LUMO favors initial ortho bridging. In the donor substituted case, the large coefficient ortho to the donor group in the HOMO again favors ortho bridging.

Applying Houk's theory to the compounds under investigation could provide an explanation for the observed regiospecificity, especially for 13 and 16 which have no lone pairs. Although no calculations were done a qualitative description may be useful. The problem essentially is to explain why initial bridging occurs at the site remote from the bridge R group (Fig 2). This is most easily done by considering the


Figure 2. Two possible diradical intermediates.

compounds studied as a pair of substituted benzenes and olefins (Fig 3). R' and R" represent the points where the aromatic ring and olefin unit

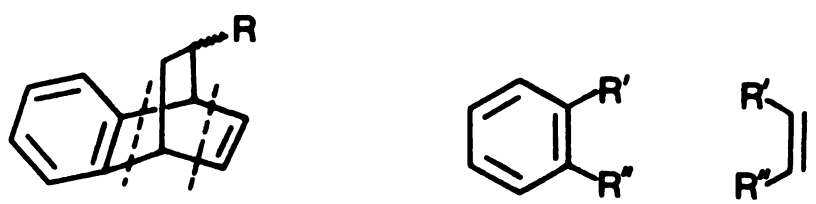



Figure 3. The di-π-methane system as a substituted benzene and ethylene.

are attached to the remainder of the bicyclic ring system. R' is the point of attachment nearer the bridge R group (R = OH, OAc, $CH_3$) while R" is the point of attachment farther from the bridge R group. If R' is either slightly more negative or positive than R" due to its proximity to the bridge R group, the HOMO and LUMO orbitals may be polarized in a similar manner as in Figure 1. Although the coefficients of the various lobes probably will not be the same as in Figure 1, there is still the possibility of a larger coefficient ortho to R' in either the HOMO or LUMO (depending on whether R' is an electron donor or acceptor) in analogy to the ortho substituted molecules (Fig 1). Thus initial bridging would be favored ortho to R', that is, away from the bridge R group. An alternate way to describe this bridging is to say that the unpaired electrons of the diradical intermediate are on the same side of the molecule as the bridge R group (which was how the di-π-methane rearrangement was described in all previous work).

So instead of a through space stabilization of a formal diradical intermediate, the bridge R groups by a through bond inductive effect favor initial ortho bridging (diradical A, Fig 2) which then leads to the observed products. Thus this proposal rationalizes the observed regiospecificity in these systems. In order to test this proposal, however, frontier orbital calculations would have to be employed.

# EXPERIMENTAL

## A. General

NMR spectra were measured on a Varian model T-60 with TMS (tetramethylsilane) as an internal standard. Infrared spectra were recorded on either a Perkin Elmer 167 or a Unicam SP-200 grating spectrophotometer, calibrated with a polystyrene film. Mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6 at 70 ev operated by Mrs. Ralph Guile. Elemental analyses were performed at Spang Microanalytical Laboratories, Ann Arbor, MI. All preparative VPC (vapor phase chromatography) separations were carried out with a Varian-Aerograph Model 90-P chromatograph. All analytical VPC separations were carried out with a Varian-Aerograph Series 1400 chromatograph with a flame ionization detector. Integrations of analytical VPC traces were accomplished with a Disc Instruments, Inc., Disc Integrator. The following VPC columns were used: A) 5 ft x .125 in. column of 20% FFAP (Analabs, Inc.) on 80/100 mesh Chromasorb W, B) 10 ft x .25 in. column of 20% FFAP on 80/100 mesh Chromasorb W, C) 5 ft x .125 in. column of 5% SE-30 on 60/80 mesh Chromasorb G, D) 10 ft x .125 in. column of 10% FFAP on 80/100 mesh Chromasorb W, E) 10 ft x .25 in. column of 20% SE-30 on 80/100 mesh Chromasorb W.

B. Quantum Yields

Quantum yields were determined with valerophenone actinometry[25] and a standard merry-go-round apparatus fitted with a Hanovia 450 W mercury lamp in a water cooled quartz immersion well. The 300-313 nm band was isolated with Pyrex and a 1-cm path of .002 M potassium chromate in 5% aqueous potassium carbonate. The conversion of valerophenone was limited to less than 3% while the conversion of the substrates was limited to less than 20%.

C. Materials (for quantum yield studies)

Thiophene-free benzene was stirred over reagent grade sulfuric acid for three days. After the benzene was washed with water and was dried over magnesium sulfate, it was distilled from phosphorus pentoxide through a 40-cm vacuum-jacketed column packed with glass helices. Spectrograde acetone (Mallinckrodt) was used without further purification. Diethyl ketone, valerophenone (Aldrich), and acetophenone were passed through alumina and twice distilled under reduced pressure through a 10-cm vacuum-jacketed vigreux column. Benzophenone was recrystallized 3 times from ethanol. Compounds 7, 10, 13, 16, and 21 were twice collected with VPC using column B. Analytical VPC of the collected materials, using column D, gave a single peak in all cases.

D. Procedure (for quantum yield studies)

The materials to be photolyzed were weighed out in volumetric flasks. An internal standard (for valerophenone, 13, 16, and 21, pentadecane; for 7 and 10, docosane) and sensitizer were added and the contents diluted to the mark with benzene. The solutions were transferred with a 9-in. pipet into separate, constricted, 13 x 100 mm Pyrex test tubes. The samples were degassed by 3 freeze-pump-thaw cycles and sealed under vacuum at < .005 Torr.

E. Preparation of 9,9-dimethyl-1,4-dihydro-1,4-ethanonaphthalene (21)

To 70 mL of 1,2-dichloroethane was added 3.24 g (30 mmol) of 5,5-dimethylcyclohexa-1,3-diene, 5.87 g (32 mmol) of benzenediazonium-2-carboxylate·HCl[26] and 4.64 g (80 mmol) of propylene oxide. The magnetically stirred solution was then refluxed for 2 h. After the mixture was cooled, and solvent removed, the dark red oil was eluted through a short alumina column with pentane. The colorless oil thus obtained (3.9 g, 71%) gave three peaks with VPC using column A at 130° C, in an area ratio of 3:2:1.

Chromatography with silica gel (Woelm, > 230 mesh) using hexane as the eluent followed by preparative VPC with column B at 140° C, (He flow rate 50 mL/min) of the 21-enriched fractions yielded pure 21 as the major product: NMR ($CCl_4$) $\delta$ 6.83 (s, 4, aromatic), 6.38-5.93 (m, 2, olefinic), 3.76-3.54 (m, 1, bridgehead), 3.30-3.15 (m, 1, bridgehead), 1.12 (m, 2, $CH_2$), 1.30 (s, 3, anti-$CH_3$), 0.60 (s, 3, syn-$CH_3$); IR (neat) 3050 (m), 3020 (m), 2950 (s), 2865 (s), 1600 (w), 1470 (m), 1457 (m),

1382 (m), 1361 (m), 1343 (m), several weak bands from 1240 to 760, 750 (s), 720 (s), 680 $cm^{-1}$ (s); UV (cyclohexane) $\lambda_{max}$ 226 nm ($\epsilon$ = 1700), 252 (450), 257 (540), 264 (660), 271 (630); mass spectrum, m/e (rel intensity) 184 (1), 128 (100).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.08; H, 8.78.

The second component (22) collected with column E at 135° C (He flow rate 50 mL/min) had spectral data identical to known[8] 1-phenyl-4,4-dimethylcyclohexa-2,5-diene: NMR ($CCl_4$) $\delta$ 7.03 (s, 4, aromatic), 6.48 (s, 4, olefinic), 3.73 (s, 1, benzyl), 1.13 (s, 3, $CH_3$), 1.08 (s, 3, $CH_3$); IR (neat) 3060 (w), 3020 (m), 2950 (s), 2860 (m), 1600 (w), 1490 (m), 1465 (m), 1450 (m), 1370 (w), 1355 (m), weak absorptions from 1170 to 910, 853 (s), 785 (m), 760 (m), 740 (m), 730 (s), 695 $cm^{-1}$ (s); mass spectrum m/e (rel intensity) 184 (42), 169 (100).

The third component (23) collected with column E at 135° C (He flow rate 50 mL/min) had the following spectral data: NMR ($CCl_4$) $\delta$ 6.90 (bs, 4, aromatic), 5.84 (dd, 1, J = 10 Hz, J = 3 Hz, olefinic), 5.45 (d, 1, J = 10 Hz, olefinic), 3.78 (m, 2, bridgehead), 1.70 (m, 2, $CH_2$), 1.02 (s, 3, $CH_3$), 0.78 (s, 3, $CH_3$); IR (neat) 3064 (m), 3016 (s), 2956 (s), 2920 (s), 2865 (s), 1600 (w), 1489 (w), 1468 (m), 1453 (s), 1395 (w), 1373 (m), 1360 (m), many weak bands from 1280 to 780, 748 (m, sh), 740 (s), 720 (s), 697 $cm^{-1}$ (m); UV (cyclohexane) $\lambda_{max}$ 223 nm ($\epsilon$ = 1600), 247 (1600), 252 (2100), 266 (2300), 272 (1900); mass spectrum m/e (rel intensity) 184 (22), 128 (100).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.03; H, 8.93.

F. Preparation of 9,9-dimethyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (24)

To 10 mL of methanol was added 105 mg of 21 and 10 mg 10% Pd-C. The mixture was stirred under one atmosphere of $H_2$ until one equivalent had been consumed. After the solution was filtered and the solvent was removed, preparative TLC (alumina with hexane eluent) of the residue yielded 56 mg of product (24): NMR ($CCl_4$) δ 6.90 (s, 4, aromatic), 2.88 (m, 1, bridgehead), 2.38 (m, 1, bridgehead), 2.13-1.30 (m, 6), 1.16 (s, 3, anti-$CH_3$), 0.56 (s, 3, syn-$CH_3$); IR (neat) 3070 (m), 3040 (m), 3020 (m), 2940 (s), 2860 (s), 1485 (s), 1460 (m), 1382 (m), 1364 (m), several weak bands from 1330 to 1250, 1183 (m), 1168 (m), 1130 (m), 1120 (m), 1100 (m), 1042 (w), 1025 (m), 932 (w), 910 (w), 750 $cm^{-1}$ (s); mass spectrum m/e (rel intensity) 186 (13), 130 (100).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.17; H, 9.82.

G. Preparation of 7,7-dimethyl-2,3-benzobicyclo[3.2.1]octen-6-one (33)

In 3 mL of dry THF was dissolved 140 mg (0.81 mmol) of anti-7-methyl-2,3-benzobicyclo[3.2.1]octen-6-one (32).[5] The solution was slowly injected under nitrogen at room temperature into 4 mL of THF containing 200 mg of 27.6% KH. The magnetically-stirred mixture slowly evolved hydrogen for approximately 0.5 h. Upon the addition of 570 mg (4.0 mmol) methyl iodide, a white precipitate immediately formed. After the mixture was stirred an additional 0.5 h, the reaction was carefully quenched with water. The solution was extracted with ether, and dried

over magnesium sulfate. Evaporation of the solvent and TLC of the resultant oil (silica gel with 10% ether/hexane eluent) gave 112 mg, 69%, of product (33): NMR ($CCl_4$) δ 7.07-6.66 (m, 4, aromatic), 3.28-1.73 (m, 6, aliphatic), 1.13 (s, 3, anti-$CH_3$), 0.59 (s, 3, syn-$CH_3$); IR (neat) 2950 (s), 1725 (s), 1495 (m), 1480 (m), 1420 (m), 1385 (m), 1365 (w), 1345 (w), 1290 (m), 1160 (m), 1085 (m), 1020 (m), 970 (w), 895 (w), 885 (w), 850 (w), 775 (s).

H. Preparation of 7,7-dimethyl-2,3-benzobicyclo[3.2.1]octane (34)

To 2 mL of triethylene glycol was added 112 mg (0.56 mmol) 33, 100 mg KOH and 64 mg anhydrous hydrazine. The mixture was heated at 200° C for 5 H. The solution was cooled, poured into 6N HCl and extracted with ether. After the ether extract was dried over magnesium sulfate and the solvent removed, TLC (alumina with hexane eluent) yielded 16 mg of product (34): NMR ($CCl_4$) δ 6.97-6.63 (m, 4, aromatic), 3.23-1.16 (m, 8, aliphatic), 1.10 (s, 3, anti-$CH_3$), 0.63 (s, 3, syn-$CH_3$); IR (neat) 2960 (s), 1500 (m), 1480 (m), 1468 (s), 1426 (m), 1398 (m), 1376 (m), many weak bands from 1340 to 840, 832 (m), 776 (s), 758 (s), 734 $cm^{-1}$ (s); mass spectrum m/e (rel intesity) 186 (16), 129 (100).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.24; H, 9.73.

I. Hydrogenation of 6,6-dimethyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (26).

Catalytic hydrogenation of 60 mg of 26 in methanol with 10% Pd-C yielded, after 1 equivalent of hydrogen was absorbed, 40 mg of product. Analytical VPC with column C at 125° C indicated only one peak.[27] The spectral data were identical to that of 34.

J. Preparative photolysis of 9,9-dimethyl-1,4-dihydro-1,4-ethano-naphthalene (21).

Compound 21 (224 mg) was dissolved in 140 mL of spectrograde acetone and the solution was purged with nitrogen. Photolysis with a 450 W Hanovia mercury lamp with a Pyrex filter was monitored using analytical VPC with column D. After most of the starting material was consumed, the photolysis was stopped and the solvent removed. Preparative VPC with column B at 155° C (He flow rate of 50 mL/min) gave in addition to a trace of starting material 21.4 mg of 24, 25.6 mg of 25, and 51.7 mg of 26.

Compound 24 had the same spectral characteristics as an independently prepared sample (vide supra).

Compound 25 had the following spectral data: NMR ($CCl_4$) δ 7.03-6.33 (m, 4, aromatic), 3.60-3.33 (m, 1), 3.02-2.67 (m, 1), 2.33-1.95 (m, 2), 1.67-1.33 (m, 2), 1.12 (s, 3, anti-$CH_3$), 0.48 (s, 3, syn-$CH_3$); IR (neat) 3070 (m), 3040 (m), 3020 (m), 2950 (s), 2920 (s), 2860 (s), 1585 (s), 1520 (s), 1382 (m), 1362 (m), 1330 (m), several weak bands from 1312 to 1220, 1183 (m), 1164 (m), 1130 (m), 1120 (m), 1100 (m), several weak

bands from 1035 to 900, 750 $cm^{-1}$ (s); mass spectrum m/e (rel intensity) 184 (41), 128 (100).

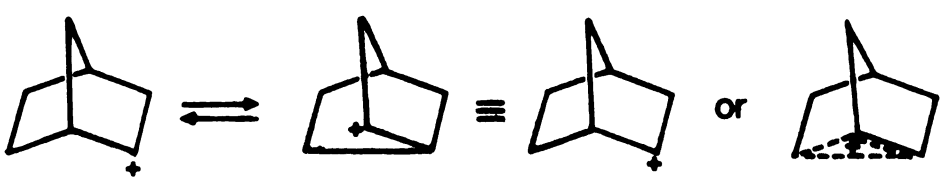
Compound 26 had the following spectral data: NMR ($CCl_4$) $\delta$ 7.03 (m, 4, aromatic), 2.93-2.70 (m, 2), 2.36-1.50 (m, 4), 1.19 (s, 3, anti-$CH_3$), 0.76 (s, 3, syn-$CH_3$); IR (neat) 3040 (m), 3020 (m), 2950 (s), 2860 (m), 1470 (m), 1380 (m), 1360 (m), 1290 (m), several weak bands from 1370 to 875, 780 (m), 755 (m), 740 (s), 725 $cm^{-1}$ (m); mass spectra m/e (rel intensity) 184 (36), 128 (100).

# PART II

## THE IONIZATION OF TWO TETRACYCLIC GEM-DIFLUORIDES UNDER STABLE ION CONDITIONS

# INTRODUCTION

The study of carbocations is one of the most intensely investigated fields in organic chemistry. This is not only because such species are intermediates in numerous organic reactions but also because they are a subject of considerable theoretical interest. One area of interest and controversy deals with the existence of nonclassical carbonium ions.[28] The crux of this problem is illustrated in Figure 4. Here the 2-norbornyl cation 43 may be viewed either as a set of rapidly equilibrating localized (classical) secondary cations or it may be viewed as a static delocalized (non-classical) two-electron, three-center cation in which the charge is distributed through the σ-bonds.

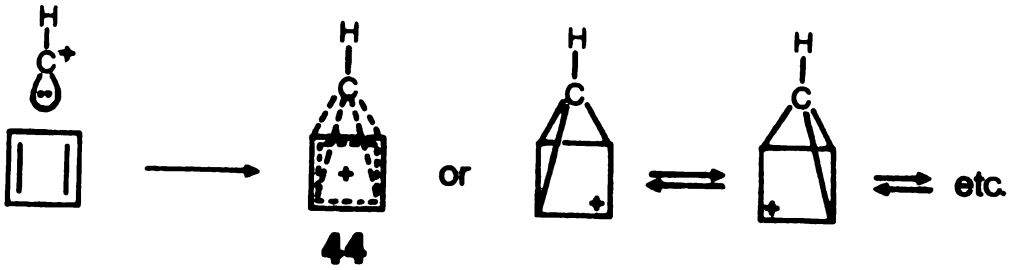



43

Figure 4. The 2-norbornyl cation represented as an equilibrating pair of classical ions and as a nonclassical ion.

In addition to the 2-norbornyl cation, many other types of nonclassical ions have been suggested. For example, in 1972 based on Extended Hückel Calculations, Stohrer and Hoffmann proposed that the pyramidal

structure 44 may be a true energy minimum for the $(CH)_5^+$cation.[29] Formally this pyramidal cation may be viewed as a positively charged methine carbon bonding to the face of a cyclobutadiene molecule. The alternate view, of course, is that the cation is actually a set of rapidly equilibrating classical ions. Since then a number of




44

Figure 5. The pyramidal nonclassical $(CH)_5^+$ ion.

examples of pyramidal ions, 45,[30] 46,[31] 47,[32] 48,[33] 49,[34] 50,[35] 51,[36] 52,[36] have appeared in the literature (Figure 6). Evidence for the existence of these ions is as follows: 1) deuterium label is scrambled equally among the basal carbons, 2) the NMR (Nuclear Magnetic Resonance) spectra of these ions indicate a symmetric structure, 3) the apical carbons appear at an unusually high field in the carbon-13 NMR spectra; for ions 45, 47A, 51 and 52 their resonances occur above TMS (tetramethylsilane). This latter observation is in agreement with Stohrer and Hoffmann's prediction that the apical carbon possesses little if any positive charge. It further suggests that these ions indeed have a nonclassical structure since it is difficult to rationalize this high field NMR resonance with a set of equilibrating classical ions.

The work of Hart and Kuzuya provides additional insight into the

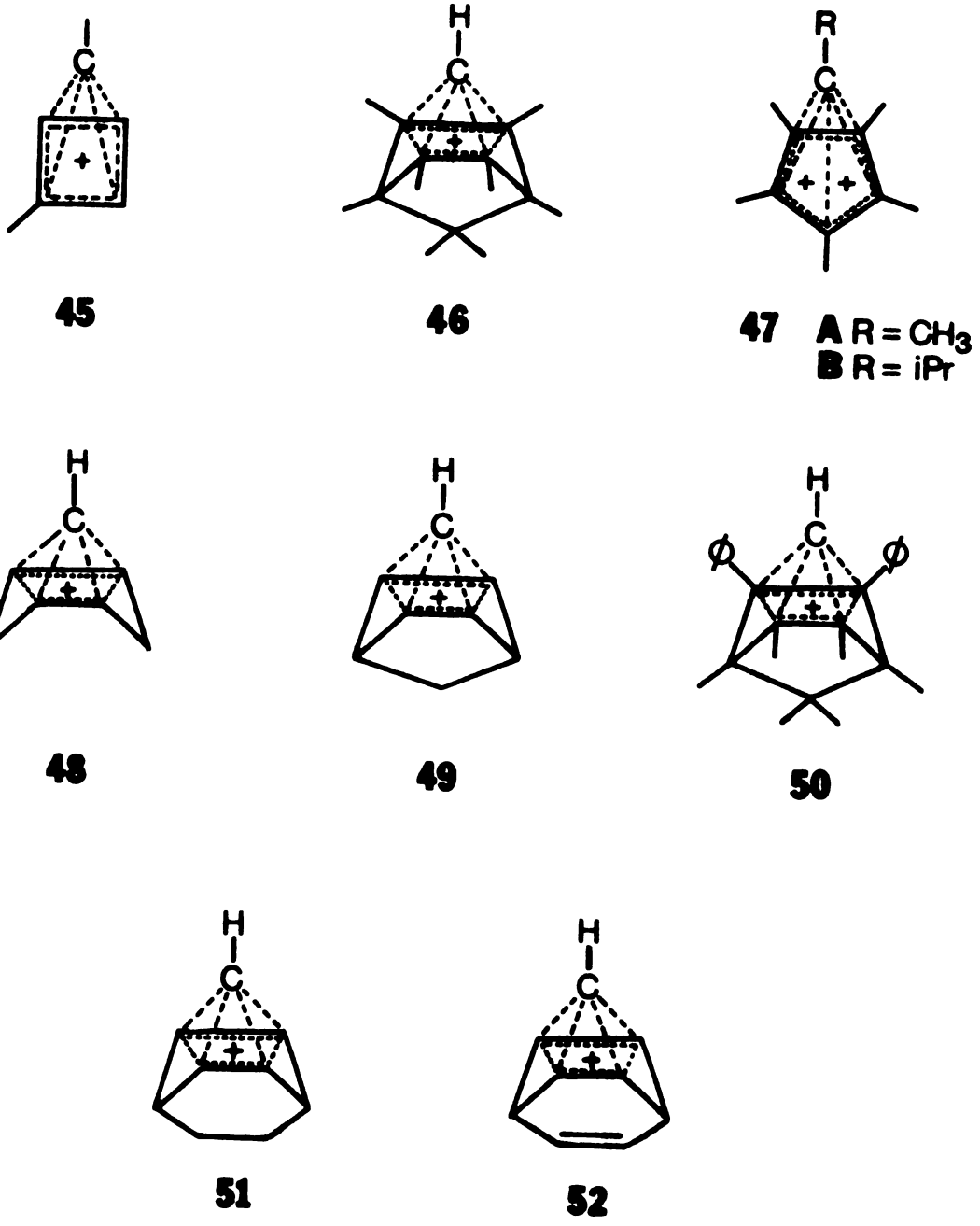
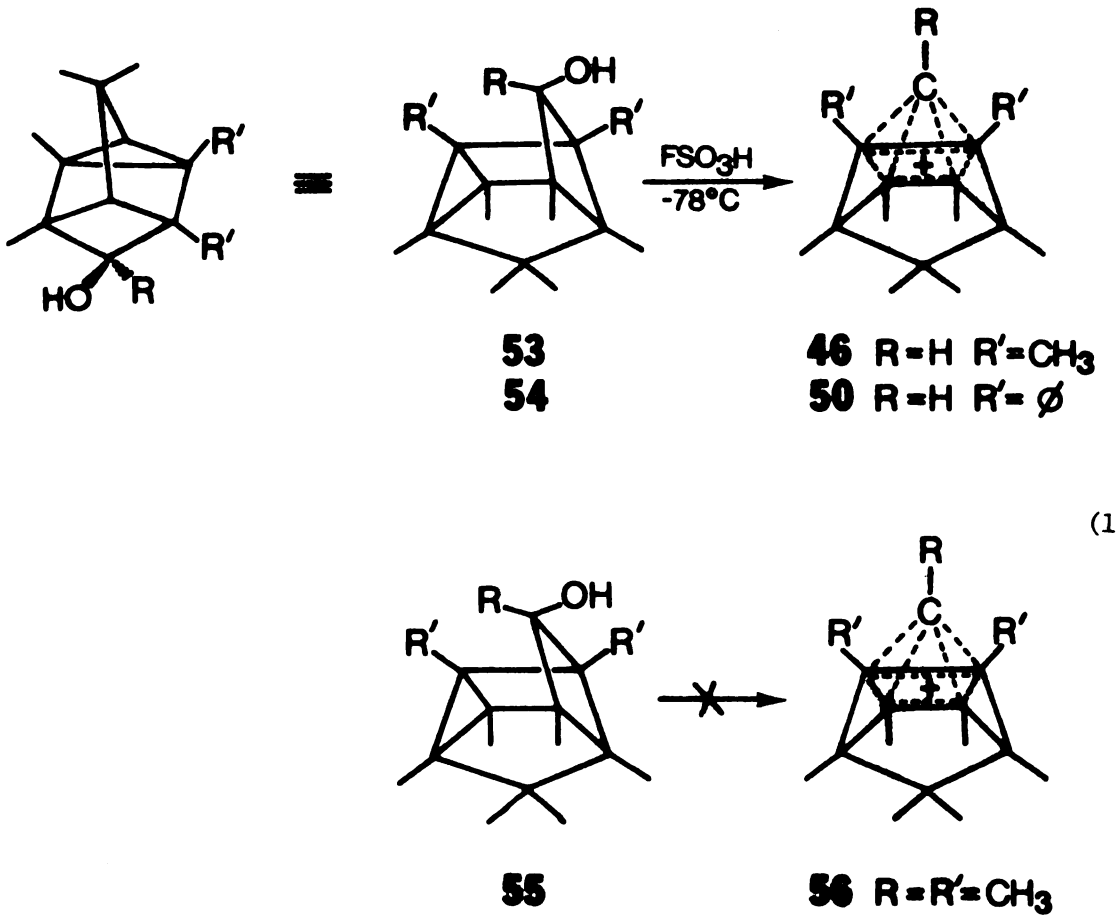



Figure 6. Examples of known pyramidal cations.

factors which govern the stability of pyramidal ions.[35, 37] Ion 46, which was prepared by treating alcohol 53 with strong acid (eq 17), is a reasonably stable carbonium ion which can be warmed to -40° C before irreversible rearrangements occur. A priori one would predict that methyl or phenyl substituents would stabilize this ion by dissipating the positive charge. However, the opposite result occurred. Ion 50 is stable only below -100° C and ion 56 proved impossible to prepare, even at -130° C. Studies of a model indicate that the phenyl groups in 50, are twisted out of the basal plane due to steric crowding. Consequently any stabilizing resonance interaction with the basal carbons is hindered and the ion is destabilized by the inductive effect of the phenyl groups.

The inability of ion 56 to form is somewhat more puzzling since ions 45 and 47A do possess apical methyl groups. One possible explanation is that upon ionization of alcohol 55 the methyl group by electron release lessens the demand for cyclopropyl participation (delocalization) and other rearrangements then become feasible. Another possibility is that since the apical carbon may in fact be slightly negative, methyl substitution at this position may actually be destabilizing. Since ion 45 is not polymethyl substituted and since ion 47A is doubly charged, perhaps these ions can better tolerate apical methyl substitution than ion 56 because the apical position, in these two cases, feels a greater effective positive charge from the basal carbons. The fact that the substitution of an apical methyl group for a more electron donating isopropyl group in ion 47B destabilized the system supports this hypothesis.[32d] If there is indeed a slight negative charge at the apical position, perhaps in contrast to an electron donor, an electron



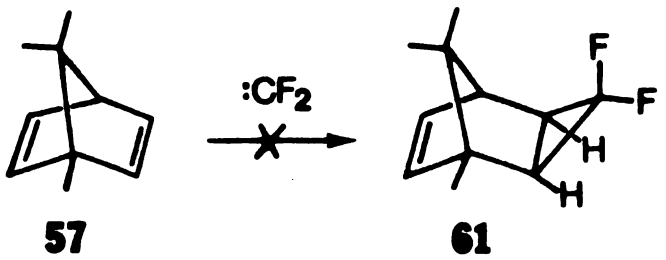

withdrawing substituent like fluorine would stabilize the ion. Not only would this be the first example of a pyramidal cation with an apical fluorine but it would also provide an explanation for the instability of cation 56.

The problem then is to prepare suitable pyramidal ion precursors which can be ionized under stable ion conditions.

Recently Jefford discovered that when the 7-position of the

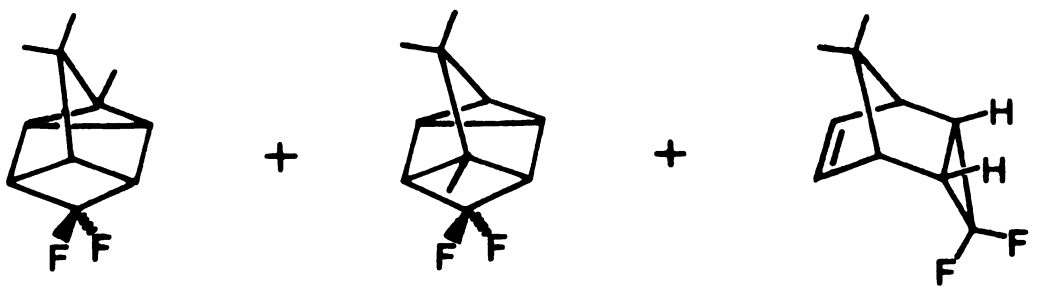
norbornadiene skeleton is blocked by di-alkyl substitution the normal exo-1,2 addition of a carbene to the double bond is sterically hindered. As a result of this steric hindrance, the carbene is forced to attack in an unusual endo-1,4 manner (eq 18).[38] Compounds 58 and 59, which are the products of 1,4 endo attack by difluorocarbene on bornadiene 57, are potential precursors to a fluoro substituted pyramidal carbonium ion (eq 19). A priori there are three possible reactions which could occur after the abstraction of a fluorine by $SbF_5$ from 58 (or 59). One possibility is that nonclassical delocalization with the cyclopropyl group would lead directly to the tris-homocyclopropenyl cation 62. Another possibility is that a fully delocalized pyramidal cation 63 would be formed, or finally, as in the case of alcohol 55, the molecule could rearrange to form a non-pyramidal cation.

In addition to being synthetically available there are several other reasons for selecting these compounds for study. First, both 58 and 59 are expected to form the same pyramidal ion. Second, since a pyramidal ion like 63 has the same skeleton as the ions studied by Hart and Kuzuya, further insight may be gained into the charge distribution and other factors that govern the stability of this ring system.

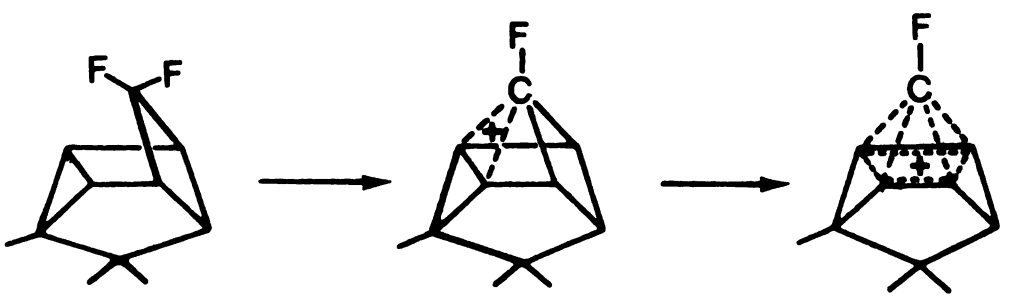



57 61


(18)




58 (35%) 59 (61%) 60 (4%)




58 (or 59) 62 63

(19)

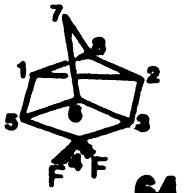
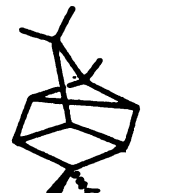
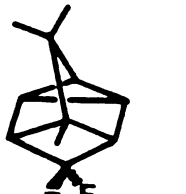
# RESULTS

Compounds 58 and 59 were synthesized by the method outlined by Jefford.[38] The mixture could be separated by VPC (vapor phase chromatography) with column A. The proton NMR spectra of these compounds agree with those published by Jefford.[38] In Table 2 the carbon-13 chemical shifts of 58 and 59 are compared with those of 64, the adduct of difluorocarbene to norbornadiene. In 59 the chemical shift and carbon-fluorine coupling constants for the difluoro substituted carbon agree with those found in adduct 64. Furthermore the chemical shifts of the 1,2 positions in 59 are in fairly close agreement with the chemical shifts of the 1,2 positions in adduct 64. Unfortunately the difluoro substituted carbon in 58 was not observed because its signal is inherently weak due to the lack of Nuclear Overhauser Enhancement and the fluorine coupling. For compounds 59 and 64 the difluoro carbon signal was barely observable. However the adjacent carbons 3 and 5 in 58 have nearly the same chemical shifts and fluorine carbon coupling constants as the corresponding 3 and 5 carbons in adduct 64. The remaining carbon positions in both 58 and 59 are affected by the $\alpha$ and $\beta$ deshielding effects of the methyl groups and have different chemical shifts from the corresponding positions in the adduct 64.

The carbonium ions were generated by adding under a nitrogen atmosphere at $-95^{\circ}$ C (acetone slush) a solution of $SbF_5$ in $FSO_2Cl$ to an

Table 2

Carbon-13 Chemical Shifts of Compounds 58, 59, 64

| Compound | Carbon Number 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | C7 Me | C6 Me | C8 Me |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  64 | 12.91[a] | 12.91 | 49.10 | 128.1 | 49.19 | 33.18 | 31.77 | 25.16 | | | |
| | | | (20) | (300) | (20) | | | | | | |
| | | | | (272) | | | | | | | |
|  58 | 21.9[b,c] | 21.9 | 48.8 | - | 48.8 | 46.9 | 43.2 | 44.8 | 19.4 | | 10.2 |
| | (5.6) | (5.6) | (20.2) | | (20.2) | (11.0) | (4.9) | (6.3) | | | (3.5) |
| | | | | | | (1.9) | | | | | |
|  59 | 9.4 | 9.4 | 59.5 | 128.3 | 59.5 | 47.0 | 47.0 | 38.4 | 19.6 | 14.8 | |
| | (11.1) | (11.1) | (18.8) | (294.9) | (18.8) | (m) | (m) | (3.2) | | (6.1) | |
| | | | | (280.2) | | | | | | | |

[a]Ref. 38b. [b]Carbon-13 shifts are in parts per million from TMS, in deutero acetone solvent.
[c]Coupling constants ($J_{C-F}$), in Hertz, are in parentheses.

NMR tube containing either 58 or 59 frozen at -130° C (pentane slush). After addition of the acid solution, the NMR tube was then warmed to -95° C in order to complete ionization. A clear red-orange solution resulted in each case. The NMR spectra were recorded between -85° C to -95° C. This procedure generally afforded clean ion solutions with minimal decomposition.

It is obvious from the carbon-13 spectra (Table 3) of ions 65 and 66 that the same ion was not formed from 58 and 59. Furthermore since both the pyramidal ion 63 and the tricyclopropenyl ion 62 have a plane of symmetry and only 8 peaks are expected in their carbon-13 spectra neither 65 nor 66 can be either of these ions since they both have 11 peaks in their spectra. A mixture of 58 or 59 ionized to give a mixture whose spectrum was a composite of the spectra for 65 and 66. Thus, it is clear that 58 and 59 ionize in different ways to give two different ions.

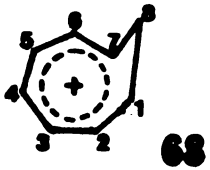
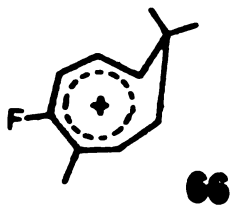
The structures of the ions were assigned from their spectral data and from an analysis of their quenching products. The evidence for each structure will be discussed separately. Later, the reasons for the different ionization behavior of 58 and 59 will be discussed.

## A. The Structure of Ion 65

For ion 65 it is obvious from the carbon-13 chemical shifts that the positive charge resides primarily on two carbons. This deshielding is reminiscent of an allyl type ion where the charge is primarily on the terminal carbons. However, the exact ring structure of ion 65 was not obvious from the carbon-13 spectrum. Furthermore as can be seen in

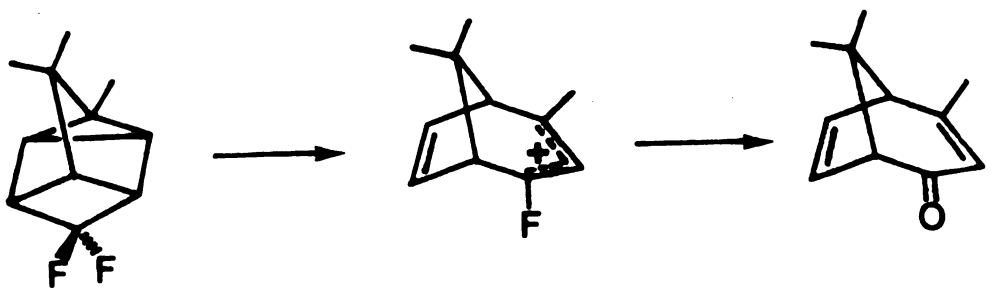
Table 3

Carbon-13 Spectra of Fluorocarbonium Ions 65 and 66 Compared with Those of Model Ions

| Compound | Carbon Number 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 3C Me | 4C Me | 8$C_s$ Me | 8$C_a$ Me |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  67 | 50.5[a] | 212.5 | 136.1 | 212.5 | 50.5 | 19.4 | 19.4 | 40.4 | | | | |
|  65 | 64.6[b,c] | 218.1 | 121.6 | 240.9 | 71.8 | 138.8 | 144.2 | 90.0 | | 34.0 | 27.9 | 20.8 |
| | (5.4) | (372.4) | (14.8) | (36.7) | | | (6.0) | (5.0) | | | | |
|  68 | 122.2[d] | 153.7 | 145.2 | 144.7 | 145.2 | 153.7 | 122.2 | 49.0 | | | | |
|  66 | 92.4 | 164.7 | 138.8 | 174.6 | 124.8 | 162.0 | 95.2 | 47.1 | 19.0 | | 11.7 | 28.6 |
| | | (14.9) | (25.0) | (282.3) | (36.7) | (20.7) | | | (8.3) | | | |

[a]Ref. 39. [b]Chemical shifts are in parts per million, from TMS in external capillary. [c]Coupling constants ($J_{C-F}$), in Hertz, are in parentheses. [d]Ref. 40.

Figure 7 the proton NMR spectrum was surprisingly complex and essentially uninterpretable. The clue to this ring structure was obtained by quenching the ion solution in either a saturated solution of aqueous sodium bicarbonate at 0° C or in a solution of sodium methoxide and methanol at -78° C (eq 20). In either case ketone 69 was obtained.




58 65 69 (20)

The methanol quench gave a cleaner reaction mixture (by NMR) and a higher yield of ketone 69.

Some care was taken to prove the structure of 69 since it provides chemical evidence for the structure of ion 65. The structure proof rests on spectral data and subsequent chemical transformations.

The IR (infrared) spectrum of 69 had a carbonyl absorption at 1670 $cm^{-1}$ which is in agreement with the 1680 $cm^{-1}$ absorption for the known parent ketone 70. Also the mass spectrum of 69 gave the expected m/e 162 value for parent ion.

The carbon-13 NMR spectrum assignments of 69 (Table 4) were made by comparing them with the chemical shifts of the parent ketone 70[41] and by off resonance decoupling. Similarly, the corresponding proton NMR spectrum assignments (Table 4) were made by comparison with chemical shifts of the parent ketone 70, by the spin multiplicities of the peaks and by a europium shift study (Figure 8).

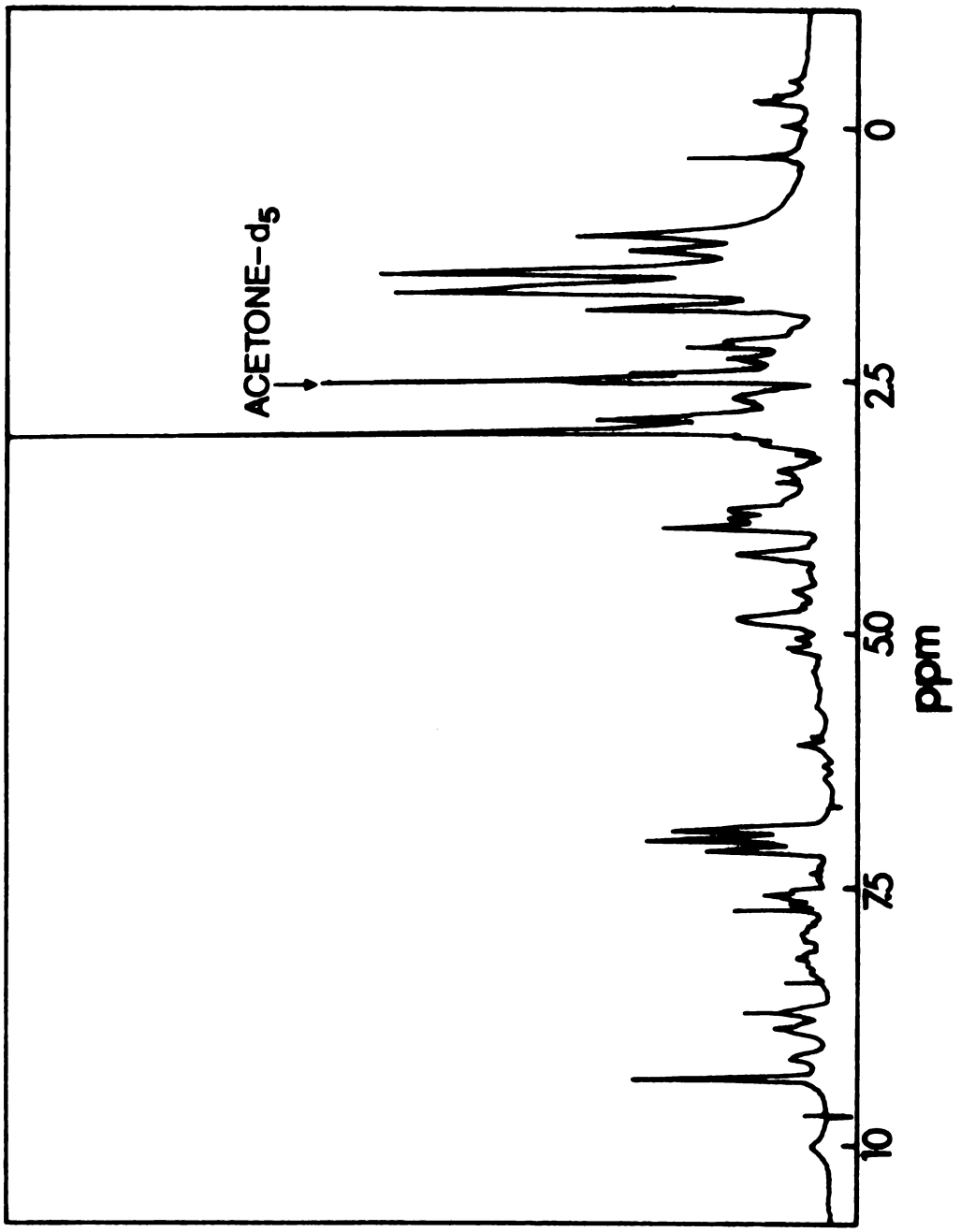
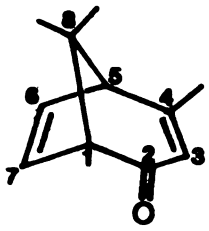
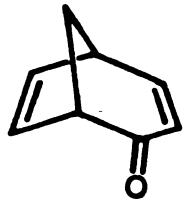



Figure 7. Proton NMR spectrum of ion 65.

Table 4

Proton and Carbon-13 Data for Ketone 69 and Model Compound 70

| Compound | | Carbon Numbers 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 4($CH_3$) | $8_s$($CH_3$) | $8_a$($CH_3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | δH | 2.68[a,b] | | 5.13 | | 2.47 | 6.42 | 5.88 | | 1.88 | 1.20 | 1.20 |
| | | (m) | | (q,1.5) | | (m) | (d,d) (5.5,3.1) | (d,d) (5.5,3.3) | | (d,1.5) | (s) | (s) |
| **69** | δ $C^{13}$ | 66.9[c] | 198.8 | 120.5 | 164.6 | 58.9 | 143.0 | 132.9 | 59.5 | 27.01 | 23.6 | 21.5 |
|  | δH | 3.25[d] | | 5.41 | 7.32 | 3.25 | 6.66 | 6.15 | 2.54 | | | |
| | | (m) | | (d,10.0) | (d,d) (10.0,6.0) | (d,d) (6.0,3.0) | (d,d) (3.0,3.0) | (d,d) (7.0,3.0) | (m) | | | |
| **70** | δ $C^{13}$ | 57.1[e] | 198.8 | 123.6 | 154.9 | 42.1 | 143.3 | 131.8 | 52.0 | | | |

[a]Chemical in parts per million, referenced to TMS. [b]Multiplicities and coupling constants (J) in Hertz are in parentheses.
[c]Chemical shifts are parts per million, referenced to TMS in deuterochloroform. [d]Ref. 41[a,c] [e]Ref. 41[b]

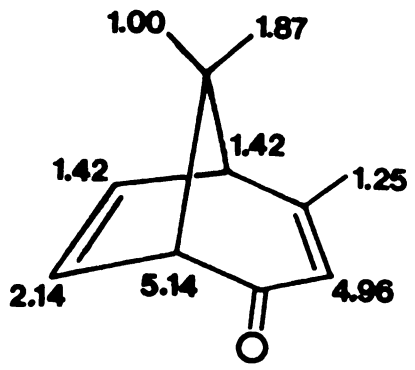


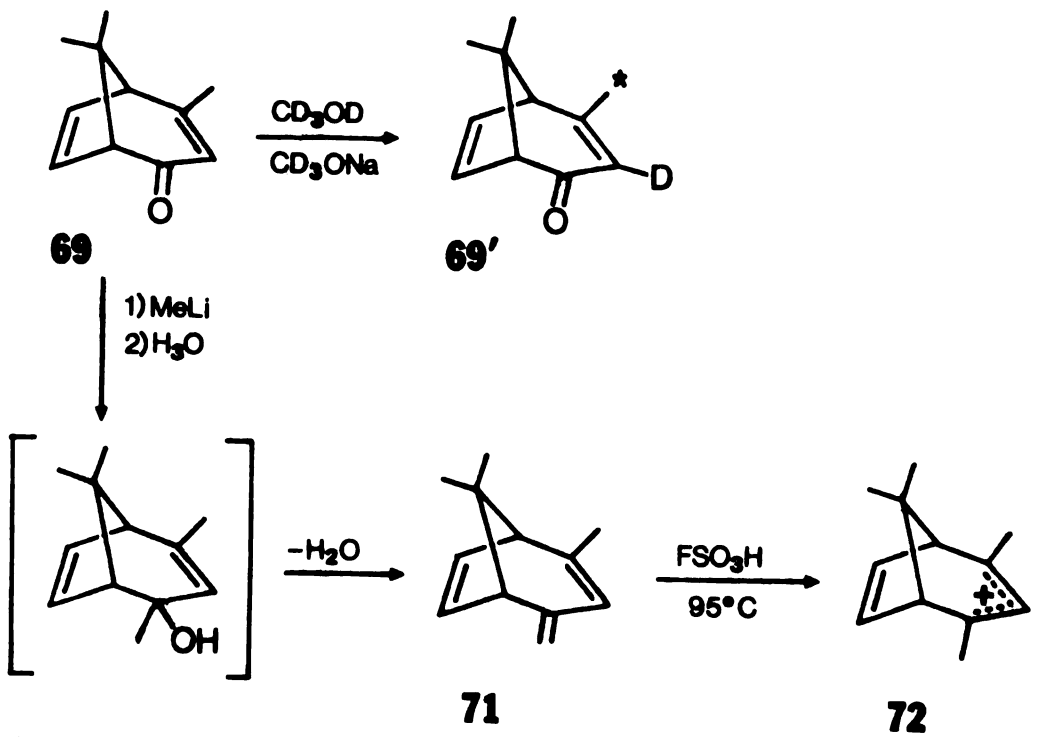

Figure 8. Europium shift slopes for the protons in ketone 69.

Comparison of the assigned chemical shifts of 69 with those of 70 shows that there is reasonably good agreement between the two systems. However, in the proton NMR spectrum the chemical shift differences between the bridgehead protons H-1 and H-5 in the two systems are rather large. The chemical shifts of these protons for ketone 69 are 0.57 and 0.78 ppm higher field than those for the corresponding protons in 70. Since other bicyclic[3.2.1] ketones[42] show bridgehead proton chemical shifts which are approximately the same as those for 70, the high field absorptions found for ketone 69 are indeed puzzling. Perhaps these high field bridgehead absorptions are the results of shielding by the C-8 methyl groups.

These chemical shift differences made it desirable to perform some chemical transformations on 69 in order to put its structure on firmer ground.

These chemical transformations are outlined in Scheme 2. In the NMR spectrum the proton absorption at $\delta$ 5.13 and the methyl group

Scheme 2



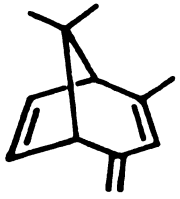
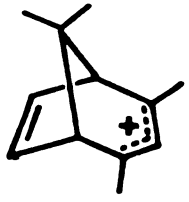

absorption at δ 1.88 disappeared upon base-catalyzed deuterium exchange. This clearly indicates that these protons are attached to the α,β-unsaturated carbonyl fragment of the molecule. Further proof for the structure of 69 was obtained by adding methyllithium to 69 followed by elimination of water to give the exo-methylene compound 71.

Evidence for the structure of 71 is found in the absence of a carbonyl absorption in the IR, in the mass spectrum with an expected m/e 160 value for the parent ion, and in two new olefinic proton NMR signals at δ 4.60 and δ 4.40

The chemical shift assignments for olefin 71 were made by comparison with the proton shifts of ketone 69.

Table 5

Proton NMR Spectra of 71 and the Corresponding Carbonium Ion 72

| Compound | 1 | 2 | 3 | 4 | 5 | 6 | 7 | $8_s$ | $8_a$ | Exo-methylene | |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  71 | 2.43[a,b] (m) | | 5.28 (q,2.0) | 1.73 (d,2.0) | 2.10 (m) | 5.92 (m) | 5.50 (m) | 1.07 (s) | 0.95 (s) | 4.40 (d,2.0) | 4.60 (d,2.0) |
|  72 | 3.97[c] (s) | 2.89 (s) | 7.17 (s) | 2.89 (s) | 3.97 (s) | 6.94 (s) | 6.94 (s) | 1.49 (s) | 1.26 (s) | | |

[a]Chemical shift in parts per million, referenced to TMS in $CS_2$. [b]Multiplicities and coupling constants (J) in Hertz are in parentheses. [c]Referenced to $HCDCl_2$ (5.32 ppm) which is present in $CD_2Cl_2$.

When 71 was added to fluorosulfonic acid at -95° C ion 72 was formed. The symmetry of ion 72 is clearly indicated by the proton NMR spectra, which contained only six signals. The chemical shifts for the allyl methyl groups, δ 2.88 ppm and the allylic methine proton, δ 7.17 ppm, are comparable to those of other allyl systems.[43]

These results clearly establish the structure of 69, the quench product of ion 65, and consequently provide additional chemical support for the ring structure assigned to 65. Once the ring structure for 65 was established the assignment of the corresponding carbon-13 chemical shifts is fairly straightforward (Table 3). That C-2 (δ 218.1) held a fluorine substituent was clear from the C-F coupling. To C-4, the other terminus of the allyl system, was assigned the δ 240.9 peak. The shifts of C-2 and C-4 also compare favorably with those of other cyclic allyl cation systems.[43] Furthermore, that more of the charge is located on C-4 than on C-2 (δ 240.9 vs δ 2.18.1) is consistent with the methyl group being somewhat more effective than the fluorine in stabilizing the positive charge. An off resonance decoupling experiment did not further split either of these peaks showing that these carbons have no protons.

By examining the magnitude of the long range fluorine-carbon coupling constants the chemical shifts for the other positions could be assigned.[44] Due to its proximity to fluorine, C-3 was assigned the peak at δ 121.6 ($^2J_{C-F}$ = 14.8 Hz), because its fluorine-carbon coupling constant is larger than that of the other peaks in the olefinic region of the spectrum. The chemical shift for C-3 is approximately 15 ppm higher (upfield) than for the corresponding center carbons of

other allyl ions.[43] This is probably the result of the β-shielding effect of fluorine.[45a, 46]

With similar reasoning (vide supra) C-7, which is in closer proximity to fluorine than C-6, was assigned the split δ 144.2 peak ($^3J_{C-F}$ = 6.0 Hz) whereas the unsplit δ 138.8 peak was assigned to the more remote C-6 position. Off resonance proton decoupling did not further split the δ 90.0 ($^3J_{C-F}$ = 5.0 Hz) peak so this absorption corresponds to C-8. Since the δ 64.6 ($^2J_{C-F}$ = 5.4 Hz) peak is split by fluorine this absorption was assigned to C-1 whereas the unsplit δ 71.8 peak was assigned to the more remote C-5. The absorption at δ 34.0 is typical for a methyl group on the terminus of an allyl system and is therefore the C-4 $CH_3$. Since syn-C-8 $CH_3$ is over the allyl ion system it corresponds to the lower field δ 27.9 peak, while the anti-C-8 $CH_3$ which points over the π system corresponds to the δ 20.8 peak.

## B. The Structure of Ion 66

The clue to the homotropylium structure for 66 came mainly from the high field proton NMR peak of the endo methyl group at δ -0.10 and the peak from the exo-methyl group at δ 2.43 (Table 6). The high field endo group absorption along with the large endo-exo chemical shift difference is characteristic of the homotropylium system,[38a, f] and has traditionally been used as evidence for a ring current. This is evident in the parent homotropylium ion 68 where the endo-proton resonance occurs at δ -0.73 ppm while the exo-proton resonance is much farther down field at δ 5.13. Additional support for a homotropylium structure is found

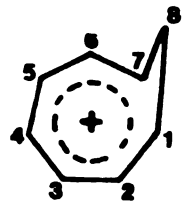
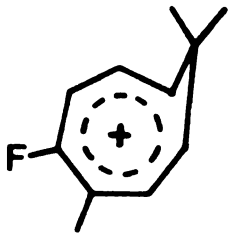
in the spectrum of the 8,8-dimethyl homotropylium ion.[47] Here the endo-methyl group shift is at δ -0.48 ppm while the exo-methyl group shift is at δ 2.36 ppm in close agreement with the shifts observed for 66.

Furthermore, it is evident from the carbon-13 spectrum of 66 (Table 2) that the charge in this ion is much more delocalized than the charge in the allyl ion 65. The most deshielded carbon in 66 is the one bearing the fluorine with a chemical shift of δ 174.6, which is 43.5 to 66.3 ppm higher field than the charge-bearing allyl carbons (δ 218.8 and δ 240.9) of 65. Another indication of the charge delocalization in 66 can be seen by noting that the fluorine substituted carbon in 66 is only 10.8 to 13.5 ppm more deshielded than the corresponding carbons in fluorobenzene,[44] (δ 163.8) and 2-fluoropropene (δ 161.1).[48] Thus both the proton and carbon-13 spectra indicate an extensively delocalized system, like the homotropylium ion, for cation 66.

The problem then is to locate the positions of the methyl and fluoro substituents on the ring. This was accomplished by examining the proton NMR spectrum (Table 6). Since there are two proton absorptions at δ 5.01 and δ 4.80, these two peaks probably correspond to the H-1 and H-7 positions on the homotropylium ring. Therefore the fluorine and methyl group can only be on either the H-2, H-3, H-4, H-5, or the H-6 positions. Since the methyl group is split by fluorine (the methyl doublet does not collapse when the other proton frequencies are decoupled), the methyl group is probably adjacent to the fluorine. With these restrictions there are only four possible isomers for the homotropylium ion. A further restriction is placed on the system by

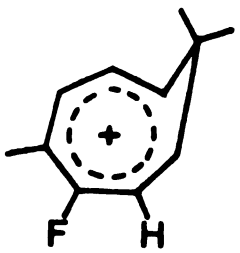
Table 6

The Proton NMR Spectrum of Ion 66 Compared with That of a Model Ion

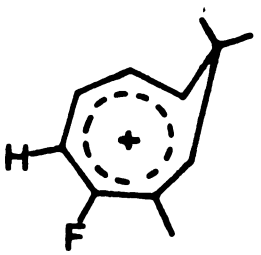
| | Proton Number | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 en | 8 ex |
|  68 | 6.48[a,b] | 8.39 | 8.45 | 8.27 | 8.45 | 8.39 | 6.48 | -0.73 | 5.13 |
| | (7.4, 7.2) (9.8) | (8.6, 7.4) | (8.6, 10.1) | (10.1) | | | | | (7.2, 9.8) |
|  66 | 4.80[c] | 8.45 | 2.80 | | 8.00 | 8.45 | 5.01 | -0.10 | 2.43 |
| | (d, d) (4.3, 7.7) | (m) | (d, 5.0) | | (d, d) (10.2, 18.4) | (m) | (d, d) (4.3, 7.7) | (s) | (s) |

[a]Ref. 49a. [b]Chemical shifts are in parts per million with the coupling constants, in Hertz, in parentheses. [c]Referenced to acetone-$d_5$ (δ 2.49 ppm) which is present in acetone-$d_6$ in an external capillary.

noting that the δ 8.00 peak is a doublet of doublets. The larger coupling constant J = 18.6 Hz is probably due to hydrogen-fluorine splitting. Support for this hypothesis comes from the fact that the largest J value for the parent homotropylium system is only 10.1 Hz (Table 6). Therefore if the δ 8.00 peak is indeed split by a fluorine and an adjacent proton, only structures 66, 73, and 74 are possible. However, once the δ 8.00 ppm peak is assigned to a proton adjacent to the fluorine, it becomes very difficult to rationalize the observed coupling constants and chemical shifts with either ion 73 or 74.




73



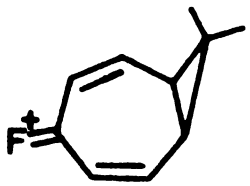

74

Structures 73 and 74 were conclusively eliminated by the following decoupling results. When the frequencies at H-1 or H-7 were irradiated the δ 8.00 doublet of doublets peak does not collapse. Conversely decoupling at δ 8.00 does not collapse either the H-1 or the H-7 peaks. Therefore since the δ 8.00 proton can not be coupled to either of these protons structure 73 is eliminated. When the 2 proton multiplet at δ 8.45 was irradiated both H-1 and H-7 collapsed to doublets (J = 4.3 Hz) which implies <u>both</u> of these protons are coupled to other ring protons which is inconsistent with structure 74. These decoupling results are however consistent with structure 66. The fact that H-1 and H-7 collapse only to doublets upon irradiation at δ 8.45 indicates that either H-1 and H-7 are coupled to each other or H-1 and H-7 are coupled to the fluorine.

Coupling between the H-1 and H-7 protons of ion 66 is somewhat unusual since there is considerable experimental and theoretical evidence,[50, 28a, f] that the parent ion 68 exists in an open form (68A) as opposed to closed form (68B). Therefore if coupling does occur between H-1 and H-7 in ion 66, a canonical structure like 66A may be an important resonance contributor (vide infra).

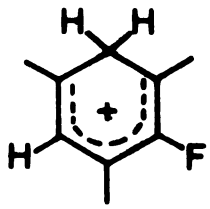
68A

68B

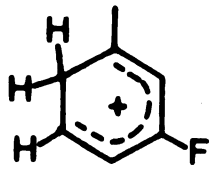


66A

However the possibility of long range (5 bonds) fluorine, proton coupling for H-1 and H-7 can not be completely discounted in view of the fact that the methylene protons in para protonated fluorobenzene (refer to Figure 9) have a long range (5 bonds) coupling of 12 Hz with the fluorine.[51] Additionally in protonated fluoromesitylene 75




75




76

and in 76 the long range (4 bonds) couplings between the fluorine and meta ring protons are 4 and 5.5 Hz, respectively.[52]

Once the structure for 66 was deduced, the remaining carbon-13 shifts could be assigned in the following way (Table 3). The peak at δ 138.8 was assigned to C-3, whereas the peak at δ 124.8 was assigned to C-5. There are two reasons for making these assignments. The first reason is that in other carbonium ions,[46] the fluorine shields the ortho position. Thus in para protonated fluorobenzene 77 (Figure 9) the carbons ortho to the fluorine are actually at a higher

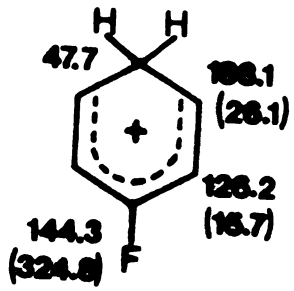



Figure 9. Carbon-13 chemical shifts of protonated fluorobenzene, 77, with carbon-fluorine coupling constants in parentheses.

field than the meta carbons. A similar chemical shift pattern is proposed for 66. The second reason is that off-resonance decoupling does not further split the δ 138.2 peak which is consistent with the 3 position being methyl substituted. The 13.4 ppm shift difference between C-3 and C-5 positions can then be rationalized on the basis of the well known deshielding effect of a α-methyl group.[44, 53] Although it is difficult to distinguish between the chemical shifts for the C-2 and C-6 positions the δ 164.7 peak probably corresponds to C-2 because of an expected deshielding β-effect from the methyl group. Therefore the δ 162.0 peak was assigned to C-6. Similarly the higher field δ 92.4 peak was assigned to C-1 since this position is expected to be more shielded than C-7 (δ 95.2) due to the shielding γ-effect

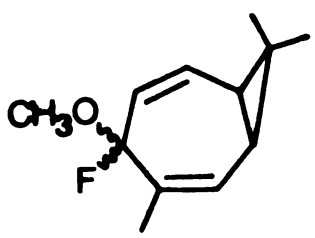
from the methyl substituent.

The fact that the peaks at C-7 and C-1 are 27 ppm and 29.8 ppm higher field than for the corresponding peaks in the parent ion 68 may either be another indication of partial bonding (66A) between these positions which would be expected to shift these carbon peaks to higher field in the NMR spectrum or it may be due to the charge delocalization by the methyl and fluorine substituents.

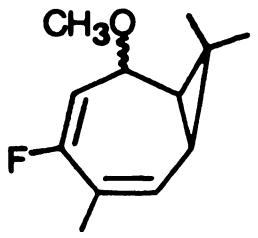
Position C-8 corresponds to the peak at δ 47.1 since it remains a singlet in off-resonance decoupling. The peak at δ 28.6 is assigned to the exo-C-8 methyl group while high field δ 11.7 peak is assigned the endo-C-8 methyl. The peak at δ 19.0 should be from the C-3 methyl group since it is split by fluorine.

When ion 66 was carefully quenched in a sodium methoxide-methanol solution at -78° C a methoxyether could be isolated after preparative TLC chromatography with 50% ether/hexane eluent. Similar quenching of ion 66 in saturated aqueous sodium bicarbonate at 0° C yielded an intractable mixture.

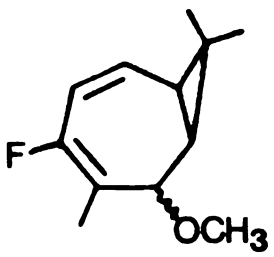
The absence of hydroxyl and carbonyl absorptions in the IR spectrum along with a sharp 3-proton singlet at δ 3.13 in the NMR spectrum is evidence for methoxyether formation. Unfortunately both the proton and carbon-13 NMR spectra had more peaks than can adequately be accounted for by a single compound. However, since an acceptable carbon, hydrogen analysis was obtained, the quench product must be a mixture of isomers. Assuming the methoxide ion would attack only the most positive carbons in 66, *a priori* three sets of epimers 78, 79, and 80 are possible. However the major isomer has not yet been identified due to the complexity of the proton NMR spectrum.




78



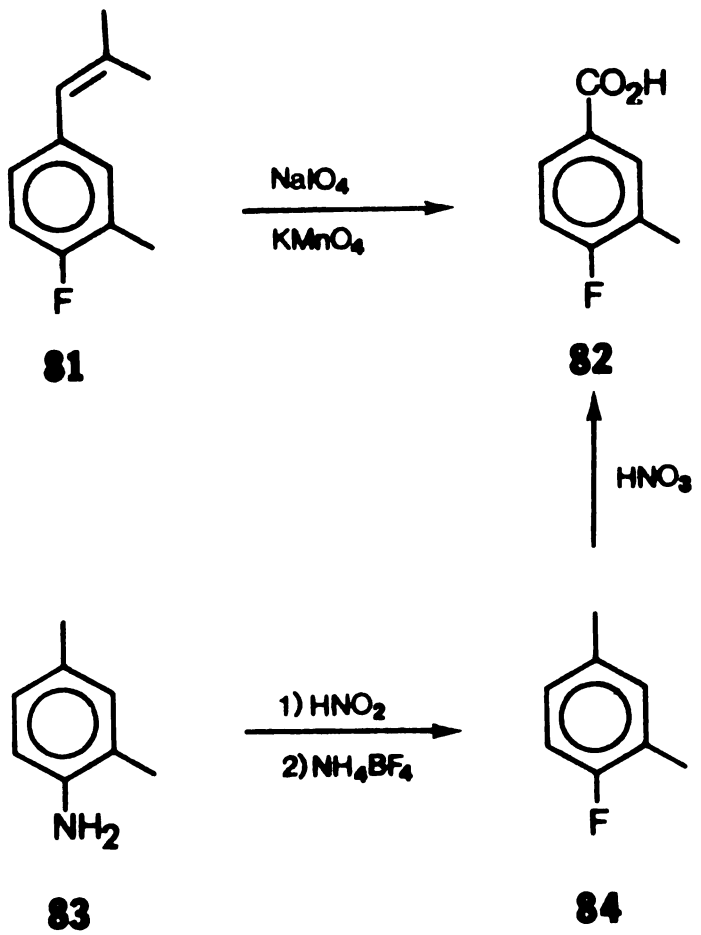

79




80

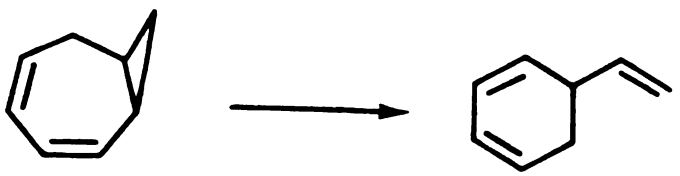
Attempted VPC separation of the quench products with column C resulted in ring contraction and loss of methanol to give fluorostyrene 81 along with two minor products (not identified) in a 6:1:1 ratio. The proposed structure for 81 is based on spectral data and subsequent chemical transformations (Scheme 3). In the proton NMR the two vinyl methyl doublets at δ 1.83 (J = 1.6 Hz) and δ 1.88 (J = 1.6 Hz) collapse to singlets upon irradiation of the proton at δ 6.20. This result is consistent with methyl groups on an ethylene fragment being split by a vinyl proton. The 3 proton doublet at δ 2.27 ppm (J = 2.1 Hz) has a chemical shift typical for an aromatic methyl group. Since the doublet does not collapse upon irradiation of the other proton positions, this methyl group is probably split by an adjacent fluorine. Unfortunately even in a 180 MHz NMR spectrum the three aromatic protons appear as a complex multiplet centered at δ 6.98 with overlapping peaks. So it is not possible by NMR to determine exactly the position of the ethylene substituent on the aromatic ring. The chemical structure proof for 81 is outlined in Scheme 3. Periodate oxidation converted 81 to the corresponding

Scheme 3




fluorotoluic acid 82.[53] Several fluorotoluic acids are known and were prepared by oxidation of the corresponding fluoroxylenes.[54] The oxidation of 2,4-dimethylfluorobenzene 84 gave the known carboxylic acid 82 which had NMR and IR spectra identical to the carboxylic acid obtained from periodate oxidation.

Furthermore since the thermal rearrangement of bicyclo[5.1.0]octa-2,4-diene 85 to 1-vinyl-cyclohexa-2,4-diene 86 is a known reaction,[55] there is at least some chemical support for the proposal that either 78, 79, or 80 is indeed the quench product(s) of ion 66 which thermally

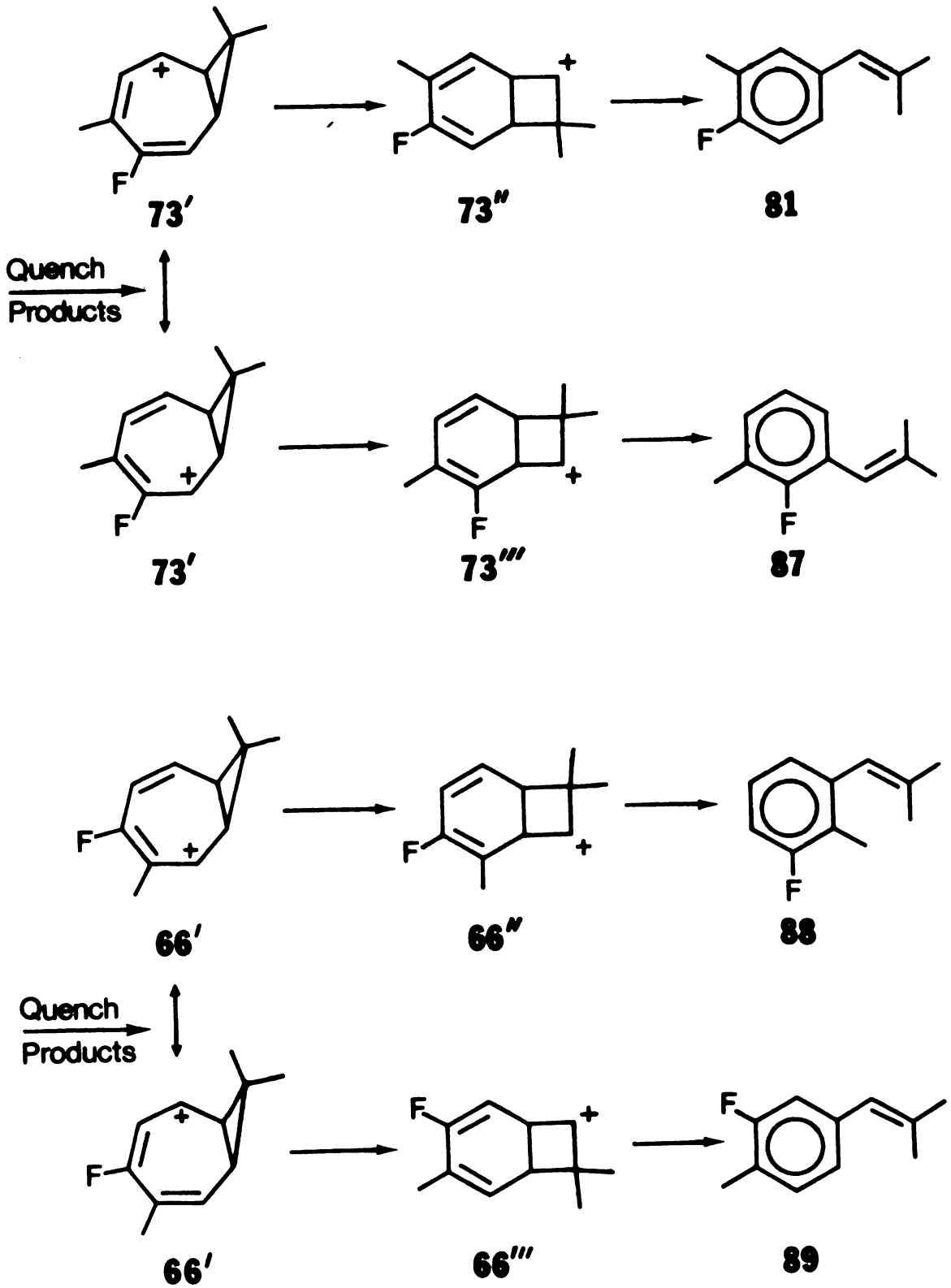


85 86 (21)

rearranges to 81.

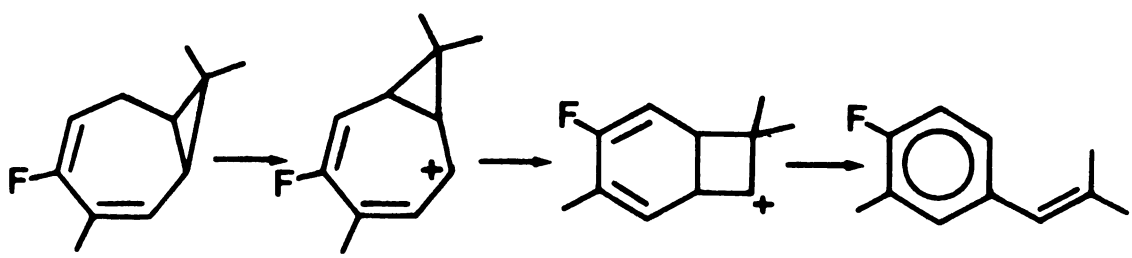
Unfortunately the results for the pyrolysis of the quench product(s) do not give any additional clues about its structure. The reason for this is illustrated in Scheme 4. During the pyrolysis and rearrangement a molecule of methanol is lost which is depicted as a two step process which involves the loss of a methoxy group followed by the loss of a proton. Thus the quench product(s) of ion 66 should lose the methoxy group to give the corresponding carbonium ion 66'. Even though a free carbonium ion never may be formed during the pyrolysis, the intermediates of the pyrolitic rearrangement will be depicted, for the sake of simplicity, as carrying a formal positive charge. Ion 66' could then undergo ring expansion in one of two directions to give either ion 66" or 66'". These ions after ring opening and proton loss, would yield the corresponding fluorostyrenes 88 and 89. However, neither 88 nor 89 was the observed pyrolysis product. The observed pyrolysis product, 81, could be obtained via this mechanism by invoking ion 73'. Ion 73', in analogy with the formation of ion 66', could be obtained from the quench product(s) of ion 73.

Scheme 4


F
73′
73″
81
Quench
Products
F
73′
73‴
87
F
66′
66″
88
Quench
Products
F
66′
66‴
89

However, the NMR evidence clearly favors ion 66 as the ion from which the quench products are derived and not ion 73. In other words, the most likely sequence of reactions is fluorocarbon 59 → ion 66 → quench product(s) → pyrolysis ion 66' → fluorostyrene 81, and not the other sequence, fluorocarbon 59 → ion 73 → quench product(s) → pyrolysis ion 73' → fluorostyrene 81.

In order to obtain fluorostyrene 81 via the pyrolysis of ion 66', the mechanism outlined in Scheme 4 has to be modified. One way to modify this mechanism is to invoke an additional rearrangement step in which the cyclopropyl ring shifts before ring expansion.




66′ 73′ 81

It is obvious that there are now two possibilities: 1) the general mechanism outlined in Scheme 4 is incorrect, or 2) the pyrolysis of the quench product(s) entails extensive rearrangement. In either event it is difficult to draw conclusions about the structure of the quench product(s) from the structure of the pyrolysis product 81.

## DISCUSSION

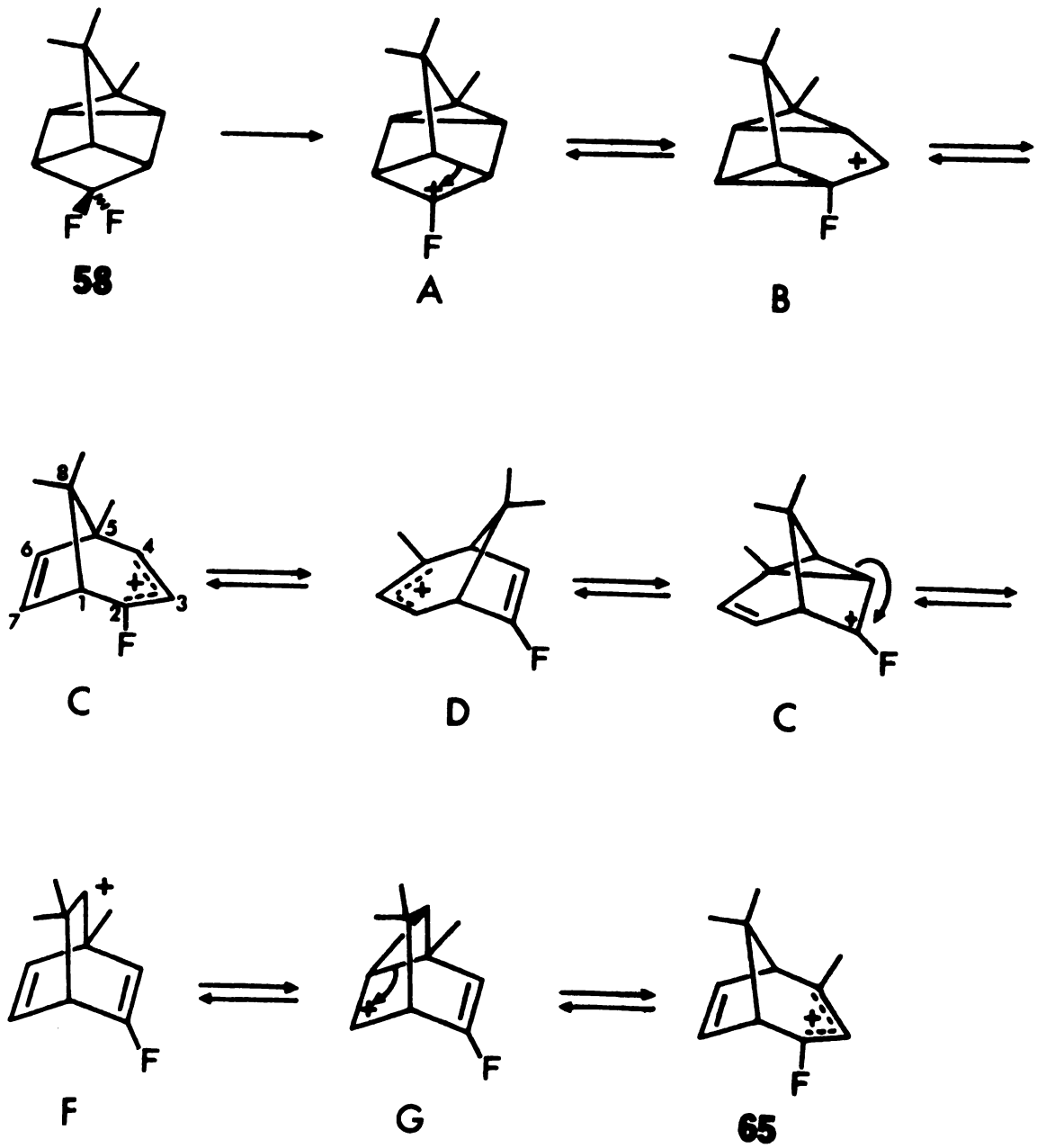
These carbocations are of interest not only because ion 65 is a relatively rare example of a fluoro substituted allyl ion[56] and ion 66 is the first example of a fluorine substituted homotropylium ion but also because there are several intriguing questions concerning the ionizations and rearrangements of the precursor fluorocarbons 58 and 59. The first question is, what are the mechanisms of their rearrangements? The second question is, why do these compounds ionize to different types of carbonium ions? The third question is, why is the pyramidal ion not formed? First, mechanisms for the ionization of 58 and 59 will be discussed. Later, some reasons why the pyramidal ion is not formed will be suggested.

### A. Mechanism for the ionization of Fluorocarbon 58

Outlined in Scheme 5 is a proposed mechanism for the ionization of 58 to cation 65. The Lewis acid $SbF_5$ first pulls off a fluoride ion from 58 to form fluorocation A. Cation A then ring contracts via a 1,2 carbon shift to form the cyclopropylcarbinyl cation B which ring opens to cation C. The steps leading from ions A to C are analogous to the steps in the ionization mechanism proposed for alcohol 55 which also forms an allyl cation with a bicyclic[3.2.1] ring system.[57] However it is not obvious how the methyl group at the C-5

position in ion C shifts to the C-4 position in the observed ion 65. A straight forward 1,2 methyl shift (from C-5 to C-4) is unlikely since this would place a positive charge at the bridgehead position. One possible way around this difficulty is to have a 1,2 bridge shift to form ion D. Since ion D has a methyl substituted allyl system

Scheme 5



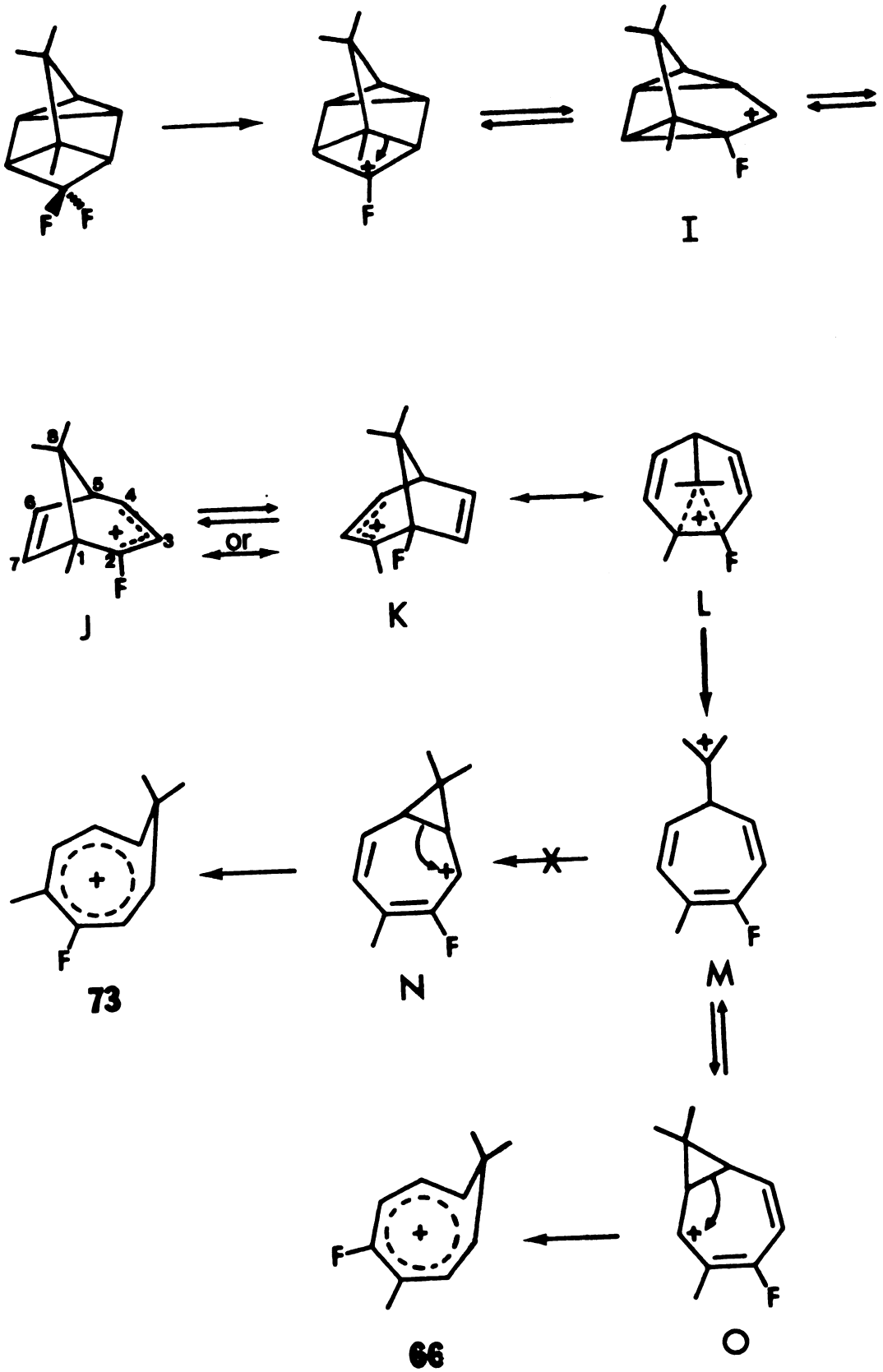
as opposed to the fluorine substituted one in ion C, ion D is probably the more stable species (recall that more charge is located on methyl substituted C-4 than on fluorine substituted C-2 in ion 65. The greater stability of ion D thus provides a driving force for the 1,2 bridge shift. Once ion D is formed it can, via a series of cyclopropylcarbonyl rearrangements, proceed to ion 65. It is interesting to note that the steps from ion D to ion 65, constitute one cycle in a process known as circumambulation.[57] The net effect of circumambulation is that C-1, C-8, and C-5 positions remain fixed in space while the C-2, C-3, C-4, C-6, and C-7 positions "rotate" around them. In principle, ion 65 could be a composite of five rapidly equilibrating ions. There is, however, no NMR evidence for such rapid equilibration. Once ion 65 is formed further rearrangement probably ceases because the two stabilizing groups are at the termini of the allyl system. Ion 65 is in effect an energy sink for the bicyclic[3.2.1] system.

If there is any type of degenerate rearrangement in this system, it is "unseen" by NMR. One way to test for this possibility is to incorporate a label into the system which would be scrambled if the ion was rearranging.

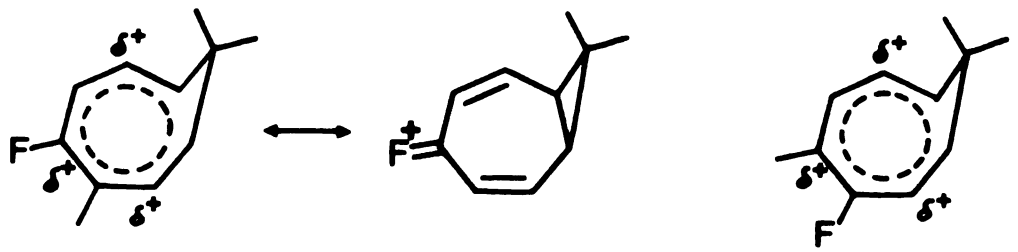
## B. Mechanism for the Ionization of Fluorocarbon 59

Scheme 6 depicts a proposed mechanism for the formation of ion 66. The first three steps of the mechanism are similar to the mechanism for

Scheme 6



fluorocarbon 58 (Scheme 5). It is after the formation of ion J where these reaction paths diverge. A 1,2 bridge shift in ion J would produce ion K. However ion K is not expected to be any more stable than ion J because of the destabilizing inductive effect on the allyl system by the adjacent fluorine. In fact none of the other possible isomers in the bicyclic[3.2.1] system in which the methyl and fluorine substituents are adjacent to each other seem to possess any special stability like that found for ion 65 (Scheme 5). Therefore ions J and K, which are in either rapid equilibrium or are canonical structures of ion L, have little driving force to rearrange further along the bicyclic[3.2.1] pathway, This allows other reactions to become competitive. Ion L (or J, or K) can now ring open to ion M. There are two ways in which ion M could reclose. However closure to ion 66 is the preferred course because ion 66 has two stabilizing influences as opposed to only one for ion 73. In both 66 and 73 the methyl group may stabilize charge by its inductive effect. However since resonance places the

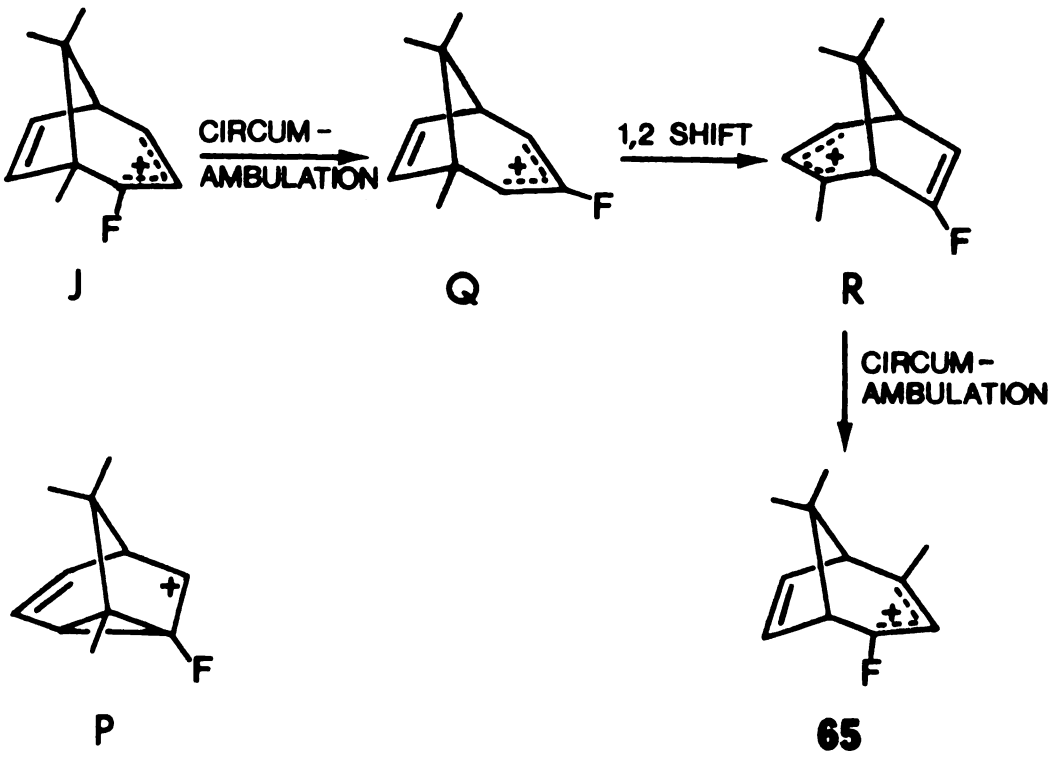



66 66A 73

charge on the C-2, C-4, and C-6 positions in the homotropylium system, ion 66 has an extra canonical form, 66A, in which fluorine stabilizes charge by back bonding. This implies that 66 is the more stable of the two ions which is in agreement with the experimental results.

It is also noteworthy that in principle ion J could also, via a series of circumambulations and 1,2 bridge shifts, rearrange to ion 65 as outlined in Scheme 7. It is not obvious why this type rearrangement does not occur. One possibility is that one of the ions produced in going from ion J to ion Q via circumambulation is ion P. Ion P is expected to be especially unstable since the positive charge is placed adjacent to the fluorine substituted carbon. Therefore any

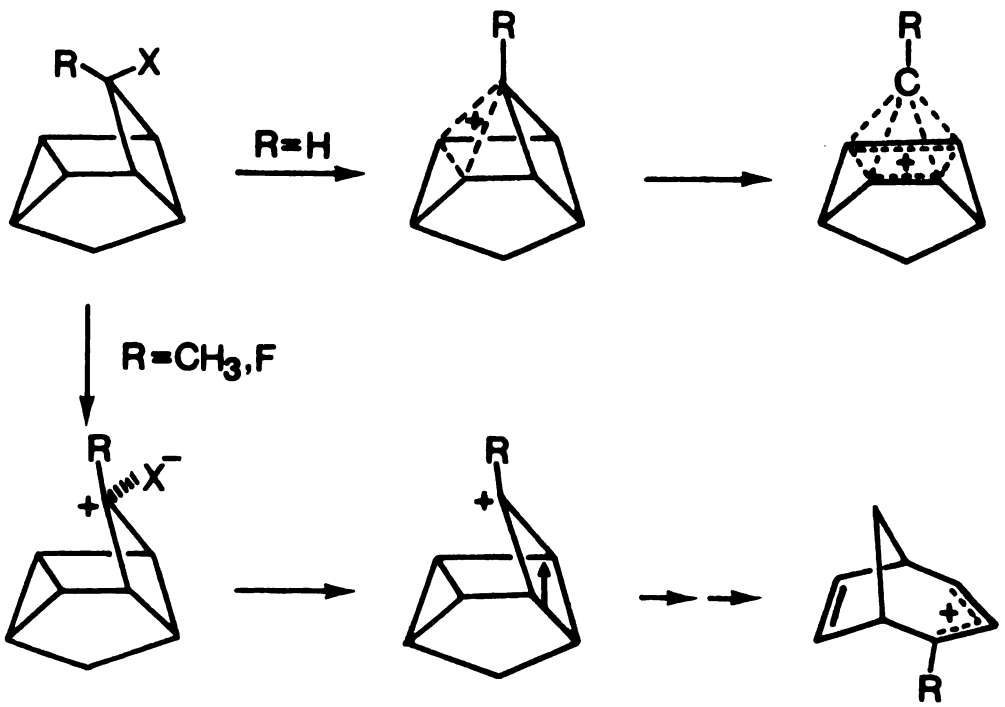
Scheme 7



circumambulatory process that "separates" the fluorine and methyl substituents on ion J (or K) is unlikely. A second possibility is that since any rearrangement from ion J to ion 65 entails many steps there are simply more opportunities for intervening side reactions.

These results indicate the subtle effects that influence the course of these ion rearrangements. But an explanation is still necessary to understand why the pyramidal ion is not formed. Scheme 8 which depicts the tetracyclic skeleton under consideration suggests one possible explanation. When the R group is a hydrogen, there is

Scheme 8




a demand for stabilization by the incipient carbonium ion. The cyclopropyl part of the molecule is able to meet this demand by non-classical delocalization of the charge into the cyclopropyl ring. As a result of this initial delocalization of charge, the ion then

proceeds to the fully delocalized pyramidal ion. However when the R group is a fluorine or a methyl, there is less demand for non-classical delocalization because the R group is now able to stabilize the charge. As a result, the initial charge is now more localized and other rearrangements, like 1,2 carbon shifts, become competitive with pyramidal ion formation.

# EXPERIMENTAL

## A. General

In addition to the equipment described in Part I of the thesis the following instruments were also used. The carbon-13 NMR spectra were recorded with a Varian Model CFT-20 instrument. The probe temperature was calibrated with a Doric Trendicator 400 type T/$^{o}$C temperature meter. Proton NMR spectra were recorded on a Brucker WH180 instrument. The following VPC columns were used: A) 10 ft x .375 in. column of 20% carbowax 20-M on 80/100 mesh chromasorb W, B) 10 ft x .125 in. column of 10% FFAP on 80/100 mesh chromasorb W, C) 5 ft x .375 in. column of 20% carbowax 20-M on 80/100 mesh chromasorb W.

## B. Preparation of bornadiene (57)

Compound 57 was distilled from a solution of 2,6-dichlorobornane[58a] and potassium octyloxide in octyl alcohol by the method by Willcott.[58c] The product can be conveniently separated from the co-distilled octyl alcohol by chromatography with basic alumina (Baker) and pentane eluent. A 2 g sample of crude product on a 10 x 1.5 cm column of alumina was completely eluted by the second 20 mL fraction as indicated by analytical VPC at 90$^{o}$ C with column B.

C. Preparation of 4,4-difluoro-6,7,7-trimethyltetracyclo-[3.3.0.$0^{2,8}0^{3,6}$]octane (59) and 4,4-difluoro-7,7,8-trimethyl-tetracyclo[3.3.0.$0^{2,8}0^{3,6}$]octane (58).

These compounds were essentially prepared by the method of Jefford.[38, 59] The reaction could be followed by withdrawing a small aliquot and adding it to 1 mL of ether. The ether solution was then analyzed by VPC at 90° C with column B.

Products 58 and 59 were separated by preparative VPC at 120° C using column A with a helium flow rate of 50 mL/min and retention times of 40 and 50 min, respectively.

Compound 59 is a white solid mp 44-45° C whereas 58 is a colorless liquid.

D. Preparation of 2-fluoro-4,8,8-trimethylbicyclo[3.2.1]octa-2,6-dienylium ion (65) and 4-fluoro-3,8,8-trimethylcyclooctatrienylium ion (66).

Carbon-13 Spectra

The following procedure is typical for preparing carbonium ions 65 and 66. Into a 8 mm NMR tube was added 259 mg (1.39 mmol) of 58. The tube was flushed with nitrogen and placed in a Dewar containing a pentane-liquid nitrogen slush. The Dewar was then placed in a nitrogen filled glove bag. To compound 58 was then added via a disposable pipet 1.5 mL of a 3.0 M acid solution (0.45 mmol $SbF_5$ in 1.6 mL $FSO_2Cl$) which was cooled in a Dewar of acetone-liquid nitrogen slush in a 15 mL graduated distilling tube. After the acid solution

was added, the NMR tube and its contents were transferred to the Dewar of acetone slush. The mixture was then stirred occasionally with a supermixer in order to dissolve the frozen starting material. After approximately 1 h a clear dark red-orange solution of 65 was obtained.

Next a glass insert containing deutero-acetone and TMS was frozen in liquid nitrogen and added in the glove bag to the cold acid solution. The spectrum was then recorded at -85° to -90° C.

Proton Spectra.

The following procedure is typical for proton NMR spectra. Into a 5 mm NMR tube fitted with Teflon spacers was added 76.8 mg of 59. The 5 mm tube was inserted into a 10 mm NMR tube containing acetone-$d_6$ (99.5%) and the tubes were frozen in pentane-liquid nitrogen slush. To 59 was added via disposable pipet approximately 0.5 mL of a 3.5 M acid solution (0.5 mL $SbF_5$ to 1.5 mL $FSO_2Cl$) which was cooled in acetone slush. After the addition of the acid solution the NMR tubes were then transferred to the acetone slush. The tubes were occasionally shaken with the supermixer in order to dissolve the frozen starting material. The spectrum was recorded at -85° C. The proton signal from the 0.5% acetone-$d_5$ present (2.49 ppm) was used as an external reference.

Quenching Procedure

The following procedure for 66 is representative. To 40 mL of methanol is a 125 mL Erlenmeyer flask was carefully added 3.0 g of NaH. After the addition was complete the sodium methoxide solution

was cooled to -78° C. To this solution with vigorous stirring were quickly injected via a 9 in. disposable pipet small aliquots of the ion solution (3 mL containing 6.9 mmol $SbF_5$ and 1.48 mmol 66 cooled in acetone slush.

After the addition was complete, the quench solution was warmed to room temperature and added to 150 mL of cold water. If necessary the solution was adjusted to a basic pH with saturated aqueous sodium bicarbonate. The aqueous solution was extracted with ether and the combined ether extracts dried over magnesium sulfate. After filtering and removal of the solvent, a yellow oil was obtained. Silica gel TLC with 50% ether/pentane eluent afforded 96 mg, 33%, of quench product. The product could be microdistilled at 62° C under 1 mm pressure. NMR ($DCCl_3$) δ (The ratios of the peaks are based on the assumption that the δ 3.23 peak is 3 protons), 6.97 (m, 0.60), 6.11 (m, 2.11), 5.36 (m, 1.90), 3.23 (s, 3.00), 2.26 (d, 0.64), 2.03 (d, 1.72), 1.98 (d, 0.94), 1.89 (d, 0.72), 1.83 (d, 0.67), 1.72 (m, 1.42), 1.28 (s, 5.60), (The multiplicities are a description of the peaks as they appear in the spectrum); UV (methanol) $\lambda_{max}$ 214 (ε = 3400), 248 (4100); IR ($CCl_4$) 3300 (m), 2970 (s), 2930 (s), 2820 (m), 1680 (m), 1636 (m), 1613 (m), 1500 (m), 1454 (m), 1400 (m), 1380 (s), 1377 (s), 1310 (m), 1250 (m), 1233 (m), 1198 (m, sh), 1185 (s), 1177 (s, sh), 1158 (m), 1152 (s), 1142 (s), 1113 (s), 1076 (s), 1050 (m, sh), 943 (m), 911 (m), 889 (m), 710 (m), 696 (m), 688 (m), 602 (m); mass spectrum, m/e (rel intensity) 216 (1), 205 (2), 196 (3), 73 (100).

Anal. Calcd for $C_{12}H_{17}FO$: C, 73.43; H, 8.73. Found: C, 73.42; H, 8.71.

A similar quenching of 65 yielded ketone 69 in 50% yield after silica gel chromatography with 50% ether/pentane eluent: NMR, see Table 3; IR ($CCl_4$) 3070 (m), 3030 (m), 2980 (m), 2920 (s), 2860 (m), 1670 (s), 1625 (m), 1585 (m), 1472 (m), 1440 (s), 1390 (m), 1375 (m), 1369 (s), 1323 (s), 1309 (m), 1294 (m), 1232 (m), 1228 (m), 1211 (m), 1183 (w), 1166 (m), 1115 (w), 1090 (w), 1029 (w), 1000 (m), 950 (m), 940 (m), 910 (m), 877 (m), 7700 (m, br), 680 $cm^{-1}$ (s); UV (methanol) $\lambda_{max}$ 209 nm ($\varepsilon$ = 2700), 237 (5200), 274 (2100); mass spectrum m/e (rel intensity) 162 (55), 147 (100).

E. Preparation of 2-methylene-4,8,8-trimethylbicyclo[3.2.1] octatriene (71).

To a 10 mL pear shaped flask with a sidearm was added 21.2 mg of ketone 69 in 5 mL ether. After the flask was purged with nitrogen and cooled in an ice-salt bath, 0.5 mL of 1.77 M methyllithium was injected through the serum cap of the sidearm. The solution was magnetically stirred at room temperature overnight. After again cooling the solution in an ice-salt bath, 0.3 mL of water was carefully injected. Enough 6 N HCl was added to make the solution acidic to litmus paper. As much of the aqueous layer as possible was removed via syringe and the acidic ethereal solution was stirred at 0° C for 1 h. The solution was then neutralized with 5% sodium carbonate solution.

After an additional 3 mL of ether was added to the flask, the aqueous layer was again removed via syringe. The ether was dried over $MgSO_4$ and filtered. Removal of the ether solvent afforded a yellow oil. Chromatography of the oil through a short alumina column

with pentane eluent yielded 20.2 mg of 71. The product can also be purified by VPC at 140° C employing column A with a helium flow rate of 50 mL/min and a retention time of 8 min. NMR, see Table 5; IR ($CCl_4$) 3060 (m), 2980 (m), 2915 (s), 2865 (m), 1638 (m), 1610 (m), 1590 (w), 1540 (w), 1472 (m), 1445 (m), 1436 (m), 1420 (w), 1385 (m), 1376 (m), 1365 (m), 1330 (m), 1315 (m), 1297 (m), 1128 (w), 955 (m), 908 (m), 881 (s), 871 (s), 860 (s), 710 (m), 637 (s); UV (methanol) $\lambda_{max}$ 216 ($\varepsilon$ = 6900), 241 (8700), 261 (5500); mass spectrum, m/e (rel intensity) 160 (39), 145 (100).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.53, H, 9.92.

F. Preparation of 2,4,8,8-tetramethylbicyclo[3.2.1]octa-2,6-dienylium ion (72).

Into a 10 mm NMR tube was added approximately 1/4 mL of $FSO_3H$. The NMR tube was placed in an acetone-liquid nitrogen slush and 2.5 mL of $FSO_2Cl$ were condensed on top of the acid. Next 20.2 mg of 71 in 1/2 mL $CD_2Cl_2$ was carefully layered on top of the $FSO_2Cl$ phase. After an additional 5 min of cooling the contents of the tube were stirred together with the supermixer. The spectrum was recorded at -85° C. NMR, see Table 5.

G. Preparation of fluorostyrene (81).

The methoxyether quench product obtained for ion 66 was dissolved in $CCl_4$ and injected onto column C at 170° C with a He flow rate of

50 mL/min. The injector and detector ports were at a temperature greater than 200° C. The product was trapped in 60% yield in a collection tube cooled in dry ice-acetone. NMR ($DCCl_3$) δ 6.98 (3, m), 6.20 (1, s, broad), 2.27 (3, d, J = 2.1 Hz), 1.88 (3, d, J = 1.6 Hz), 1.83 (3, d, J = 1.6 Hz); IR ($CCl_4$) 2965 (m), 2920 (m), 2850 (m), 1500 (s), 1450 (m), 1378 (m), 1248 (m), 1212 (s), 1178 (m), 1142 (m), 1112 (s), 903 (m), 888 (m); mass spectrum, m/e (rel intensity) 164 (75), 149 (100); UV (methanol) $\lambda_{max}$ 226 (ε = 11,000), 243 (12,000).

Anal. Calcd for $C_{11}H_{14}F$: C, 80.45; H, 7.98. Found: C, 80.29; H, 7.85.

H. Oxidation of fluorostyrene (81).

To 100 mL of water was added 2.1 g of $NaIO_4$ and 300 mg of $KMnO_4$.[12] A 25 mL aliquot of this stock solution was added to a 50 mL aqueous solution containing 61 mg of 81 and 200 mg sodium carbonate. After 2 h the excess oxidizing agent was destroyed by the addition of a sodium bisulfite solution. The mixture was acidified with 10 mL of 6 N HCl and it was then extracted with four 50-mL portions of ether. The combined ether extracts were dried over magnesium sulfate and filtered. Removal of the ether afforded 37 mg of the crude acid. Vacuum sublimation yielded 8.1 mg of pure acid 82. The NMR and IR spectra of this acid were identical to the spectra of the acid prepared from oxidation of the corresponding fluoroxylene 84.[54] NMR ($DCCl_3$) δ 9.83 (1, s, broad), 7.77 (2, m), 6.93 (1, m), 2.28 (3, d, J = 2 Hz); IR ($DCCl_3$) 3520 (w), 2920 (s, broad), 2600 (m, broad, sh), 1688 (s), 1612 (m, sh), 1592 (s), 1475 (m, broad, sh), 1423 (s), 1492 (m, broad, sh),

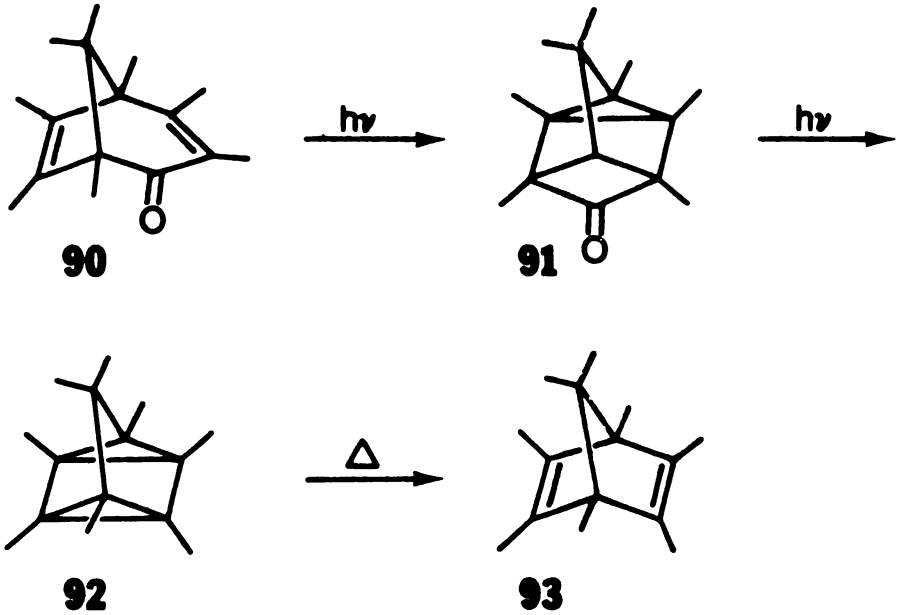
1292 (s), 1264 (s), 1248 (s, sh), 1190 (s), 1158 (m), 1170 (s), 1160 (s, sh), 835 (m) $cm^{-1}$.

# PART III

# MISCELLANEOUS

# INTRODUCTION

One of the original goals of this thesis work was to find a useful synthetic route to octamethylnorbornadiene 93. This known compound can be produced by prolonged photolysis of 90.[60] Unfortunately, the overall yield of 93 by this route is poor, thus prompting a search for a better synthetic method. The reason for wanting to prepare 93

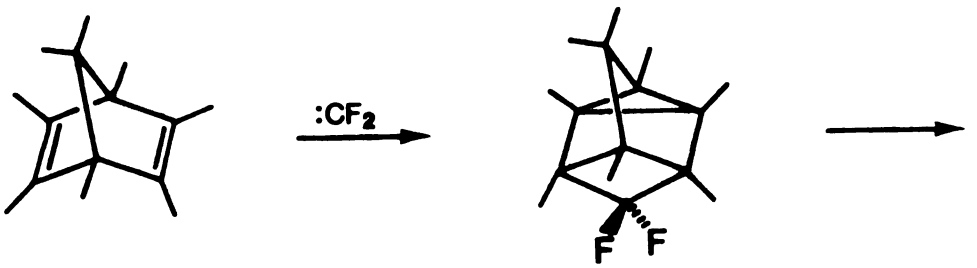



(22)

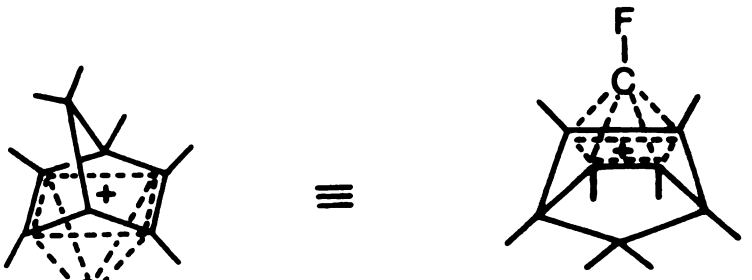
is that it is an attractive precursor to 94 which might possibly ionize to the pyramidal carbocation 95. We wanted to compare the stability of 95 with that of the known analog in which the apical position has a hydrogen rather than a fluoro substituent.

Since the Diels-Alder reaction provides the quickest entry into the bicyclo[2.2.1] system, the original synthetic strategy was to treat hexamethylcyclopentadiene 96 with an appropriate dienophile to produce

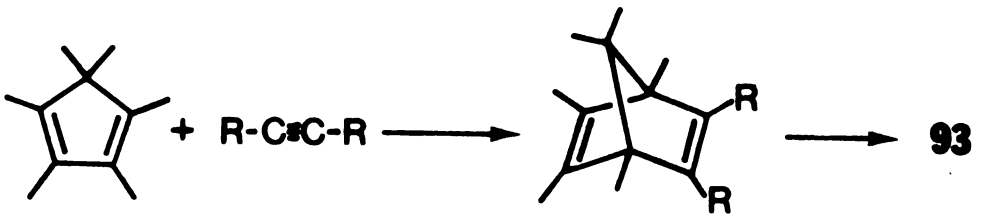
either 93 directly or a compound which could be chemically transformed into 93 (eq 24). Although a new synthesis of 93 was not achieved, the experiments in this section may be viewed as an exploratory study of the reactions of 96 with various dienophiles, as well as an investigation of the chemistry of the resultant Diels-Alder adducts.




93 94 (23)



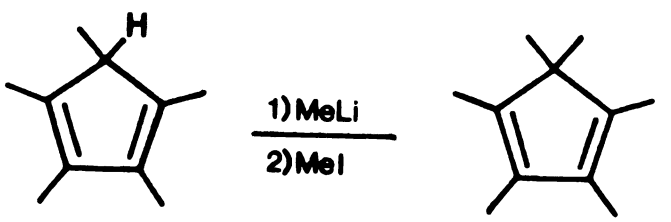

95




96 93 (24)

## RESULTS

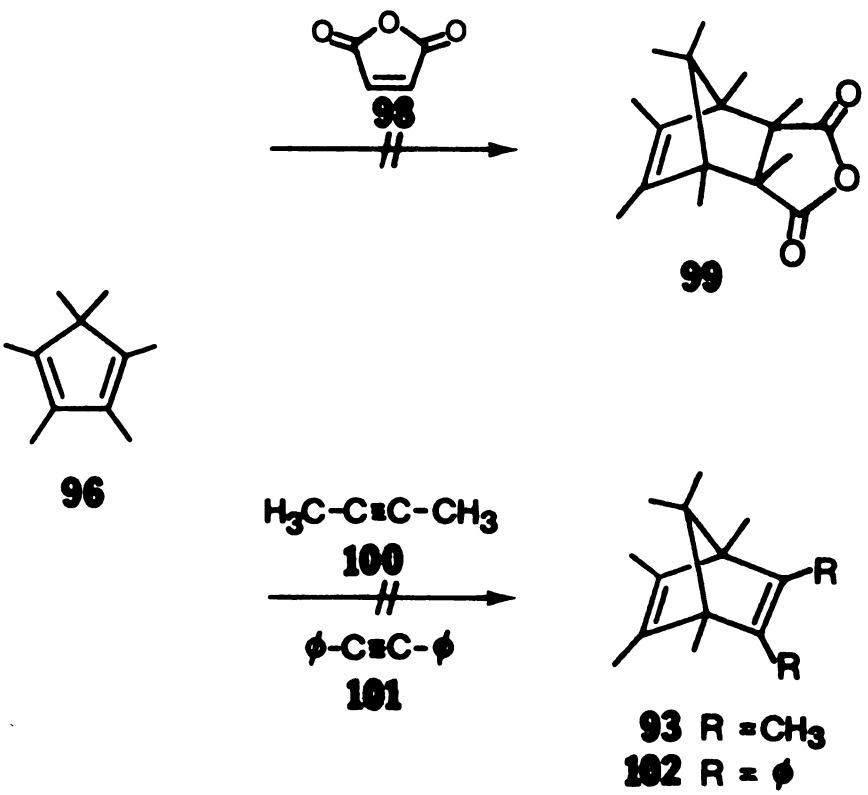
Hexamethylcyclopentadiene was prepared by treating the pentamethyl derivative with methyllithium in THF, followed by alkylation with methyl iodide. This method is superior to methylation with methyl iodide and sodamide in liquid ammonia, a procedure used by DeVries.[61]




97 96 (95%) (25)

Scheme 9 depicts several dienophiles which did not add to 97. It is unfortunate that 2-butyne 100 does not add, since 88 would be produced directly. Compound 96 was treated with an excess of 2-butyne in a sealed tube for days at room temperature or at temperatures up to 250° C without any NMR evidence for the formation of 93. At the higher temperatures 96 slowly decomposed. Similarly diphenylacetylene 101 and dimethylmaleic anhydride 98 also did not react with 96 under a variety of conditions. Since most Diels-Alder reactions involve addition of an electron deficient dienophile to an electron rich diene,

Scheme 9



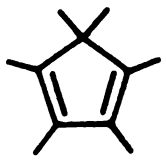

it is understandable why the electron rich 100 and 101 have little propensity for addition to 96, which is also electron rich.

Although 98 has an electron deficient double bond, it is sterically hindered and therefore unable to react with 96, which has methyl substituents at both termini of the diene moiety.

As expected, however, 96 readily reacts with less hindered electron deficient dienophiles (Scheme 10).

Dimethyl acetylenedicarboxylate 103 reacts exothermically with one equivalent of 96 without solvent to form 104 in 100% yield. Compound 104 was saponified in alcoholic KOH to the known dicarboxylic acid 114.[62]

Scheme 10

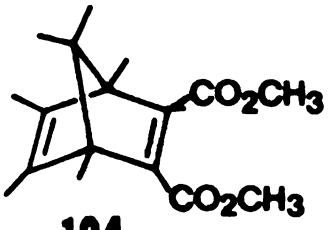


96

$CH_3O_2C-C{\equiv}C-CO_2CH_3$

**103**

RT

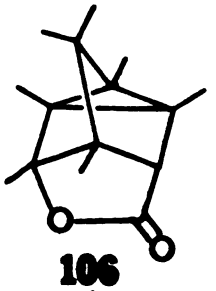


**104**

$CH_3C{\equiv}C-CO_2H$

**105**

155°C

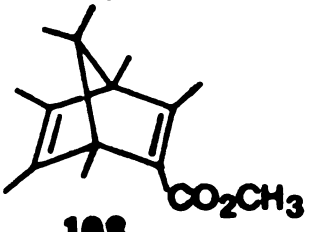


**106**

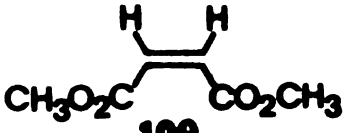
$CH_3C{\equiv}C-CO_2CH_3$

**107**

155°C

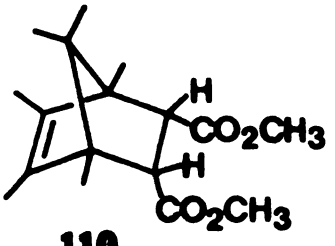


**108**



**109**

150°C



**110**

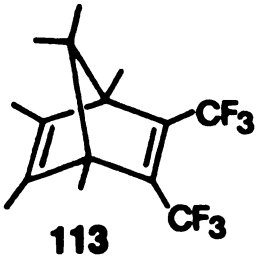
$^1O_2$

**111**

$CF_3-C{\equiv}C-CF_3$

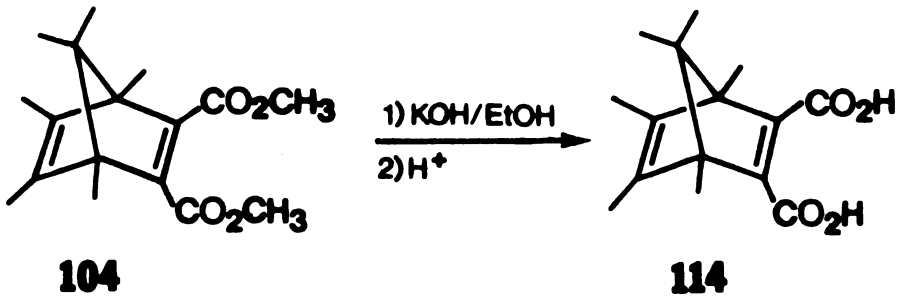
**112**

RT



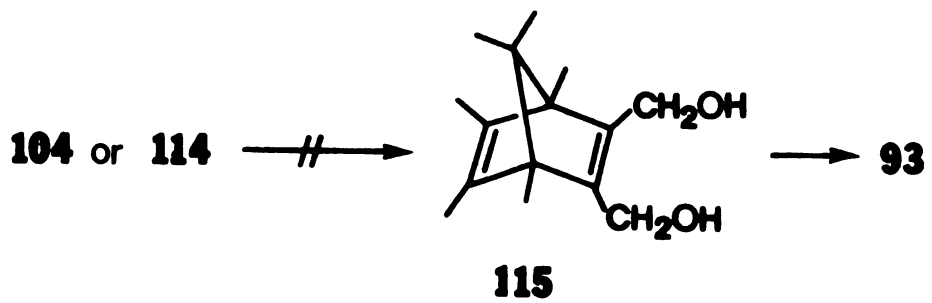
**113**

Unfortunately, all attempts to reduce either 104 or 114 (with a variety of reducing agents) to the corresponding dialcohol 115 were unsuccessful.[63] In general the starting material was consumed (by NMR) and an intractable mixture was obtained. Since the mass spectrum of the crude reduction products had a peak 2 mass units higher than starting material, at least one of the reactions was reduction of the electron deficient double bond, a known side reaction in the reduction of α,β-unsaturated esters.[12] Therefore, this particular route to 93 was abandoned.



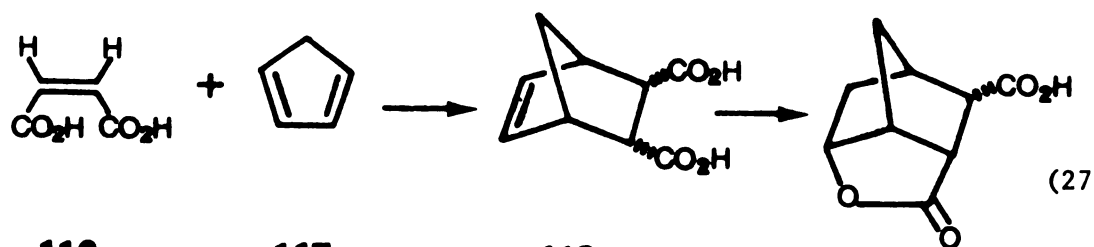

104 114 (26)

Tetrolic acid 105 and methyl tetrolate 107 which contain only one electron withdrawing group, are less reactive dienophiles than 103 towards 96. Thus it is necessary to heat these reagents in order to




115

initiate the Diels-Alder reaction. Under these conditions 105 first added then cyclized to give the lactone 106. This reaction is reminiscent of the addition of maleic acid 116 to cyclopentadiene 117, eq 27.[64] The structural assignment of 106 is based on spectral data. The IR spectrum showed no hydroxyl (OH) absorption that would be expected for a carboxylic acid. There was, however, a strong band




116 117 118 119 (27)

at 1776 $cm^{-1}$, characteristic of a γ-lactone.[65] The proton NMR spectrum had seven methyl group absorptions, and the most deshielded methyl group was at only δ 1.25 ppm, too far upfield for the methyl to be attached to a double bonded carbon. The compound therefore has no double bonds which implies that 106 is not the expected Diels-Alder adduct. This conclusion was verified by a carbon-13 NMR spectrum which contained no olefinic carbon absorptions. Furthermore, the δ 177.3 carbonyl carbon peak was consistent with the carbonyl chemical shift observed in other lactones.[44]

The reaction of 96 with 107 did produce the expected Diels-Alder adduct 108 along with a side product. VPC indicated that the ratio of 108 to side product was 3:2. Since the side product had vinyl proton absorptions in its NMR spectrum and had the same molecular weight as

108, it is probably some type of ene reaction product.[66] However, its exact structure was not established.

The structure of 108 rests on spectral data. In addition to a parent ion at m/e 248 in the mass spectrum, 108 also had a strong ester carbonyl absorption at 1752 $cm^{-1}$. This indicated that 108 was indeed a cyclo adduct of 96 and 107. The NMR spectral assignments were (Figure 10) also consistent with the structure.

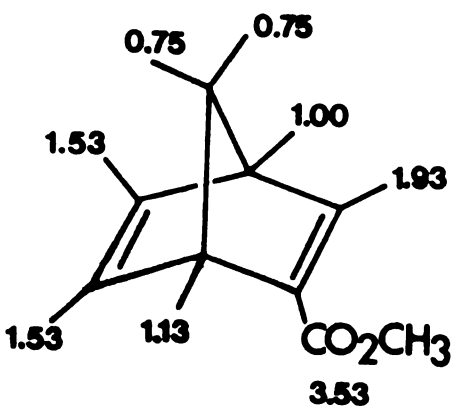
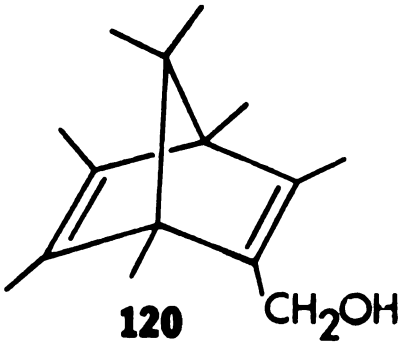



Figure 10. The proton chemical shift ($\delta$) assignments for 108.

Compound 108 could be reduced with either $HAl(iBu)_2$ or $AlH_3$ to what is believed to be the corresponding alcohol 120. The absence of a carbonyl absorption in the IR spectrum in addition to a hydroxyl absorption at 3610 $cm^{-1}$ indicated that 108 was reduced to an alcohol. However attempts to reduce this alcohol to the hydrocarbon by reduction of the tosylate[67] or by using Corey's pyridine sulfur trioxide method[68] resulted in an elimination reaction as indicated by the appearance of vinyl protons in the NMR spectrum. Furthermore a comparison of the NMR spectrum of 93 with the corresponding reaction mixtures clearly ruled out the presence of any 93.




In contrast to the lack of reaction of 96 with anhydride 98, compound 96 did react smoothly with dimethyl maleate 109 to form 110. The structure of 110 was evident from the spectral data. Figure 11 shows the proton NMR spectral assignments.

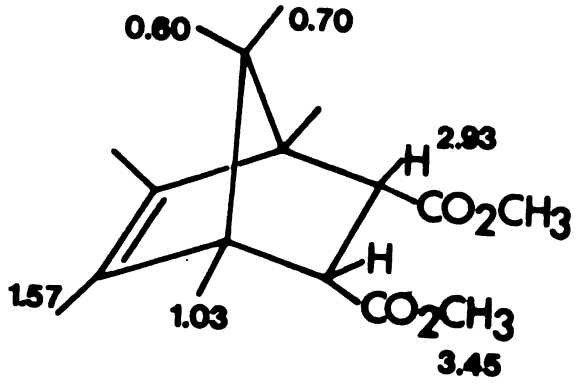
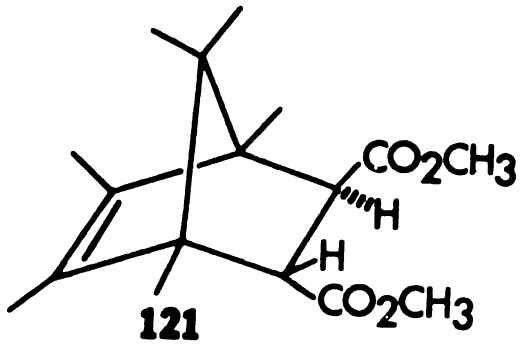



Figure 11. Chemical shift (δ) assignments for 110.

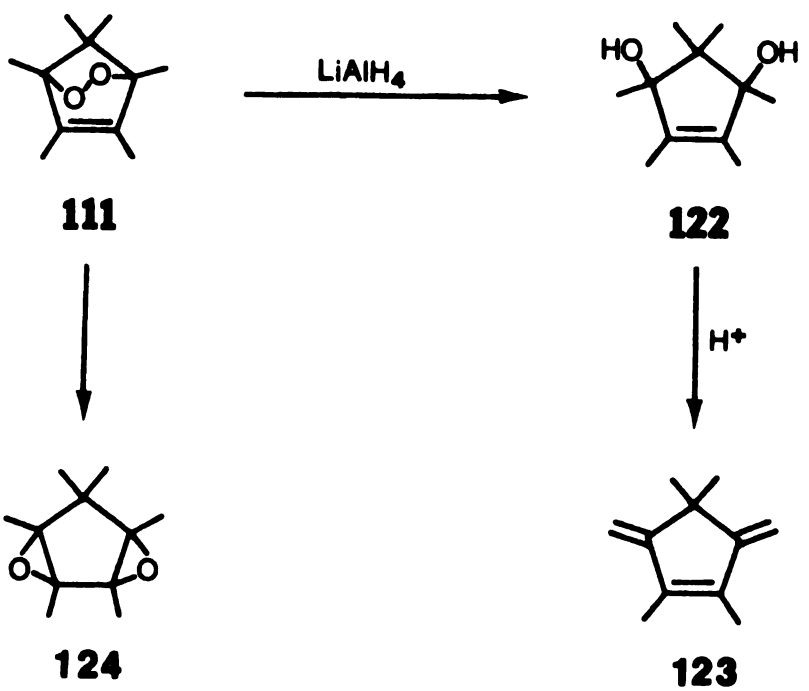
An attempt to methylate 110 by treatment with potassium hydride followed by the addition of methyl iodide resulted in only epimerization to the trans-diester 121. At this stage attempts to prepare the permethylated norbornadiene 93 were abandoned. The remainder of the experiments in this section are exploratory Diels-Alder reactions with diene 96.




**121**

The reaction of 96 with singlet oxygen produced the corresponding endo-peroxide 111. Although the reaction can be carried out at room temperature, photolysis at 0° C forms a cleaner reaction mixture which is important since the product decomposed upon attempted purification by silica gel chromatography. The structure of the endo-peroxide is based on spectral data and on subsequent chemical transformations (Scheme 11).

Scheme 11




**111** **122** **124** **123**

The symmetry of 111 was clear from both the proton and carbon-13 NMR spectra (assignments in Figure 12). Furthermore the proton chemical shifts were as expected for structure 111.

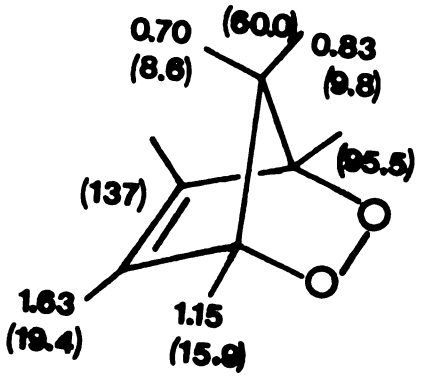



Figure 12. The proton and carbon-13 chemical shift (δ) assignments for 111 in parts per million from TMS. The carbon-13 shifts are in parentheses.

The structure of 111 was confirmed first by heating it in $CCl_4$, to form the diepoxide 124. This type of rearrangement is a known thermal reaction of endo-peroxides.[69] Epoxide formation was indicated in the NMR spectrum by a shift of the vinyl methyl protons (at δ 1.63 in 111) upfield to δ 1.32. Unfortunately 124 decomposed upon attempted purification by silica gel chromatogrpahy.

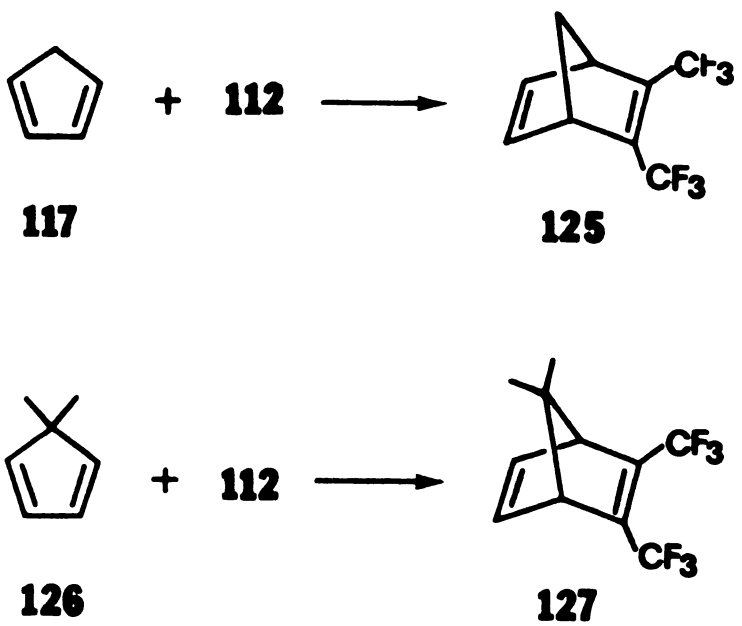
Reduction of 111 with lithium aluminum hydride gave the dialcohol 122. Compound 122, without further purification, was treated with a trace of acid in ether to form the known triene 123,[61b] thus confirming the structure of 111.

Hexafluoro-2-butyne 112 reacted exothermically with diene 96 to produce cycloadduct 113. Since it was also of interest to compare the reactions of adduct 113 with those of less methylated adducts, 125 and 127 were prepared by adding hexafluoro-2-butyne to cyclopentadiene 117

and 5,5-dimethylcyclopentadiene 126, respectively.

Adducts 113 and 127 like 125[70] underwent photolysis to the corresponding quadricyclic compounds 128 and 129 (Scheme 12). In general the structure assignments for 128 and 129 rest on the absence of the vinyl protons (or vinyl methyl groups) in the proton NMR spectra and on the analogy with the known photochemical reaction of 125. When 113 was irradiated in the presence of 1 M piperlyene 128 was still formed without any apparent quenching. Thus the $2\pi + 2\pi$ addition proceeds via the singlet state (or a very short lived triplet).

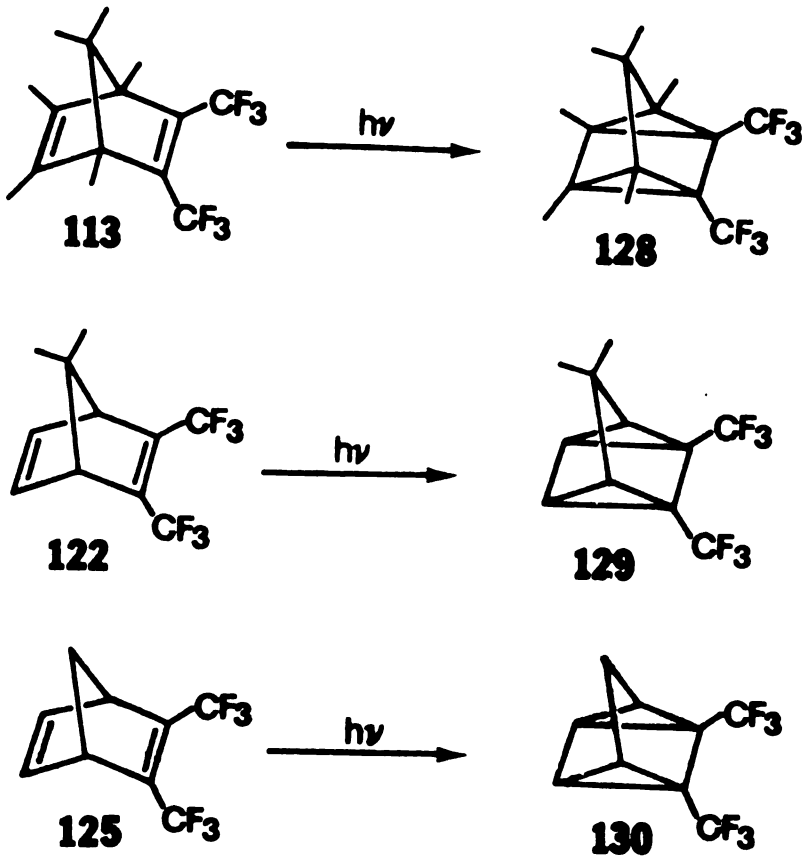
Scheme 12




In addition to photolysis other exploratory reactions were performed on these adducts. For example, these compounds were treated with various electrophiles.

Curiously, despite repeated attempts, adducts 113 and 125 would not

Scheme 13

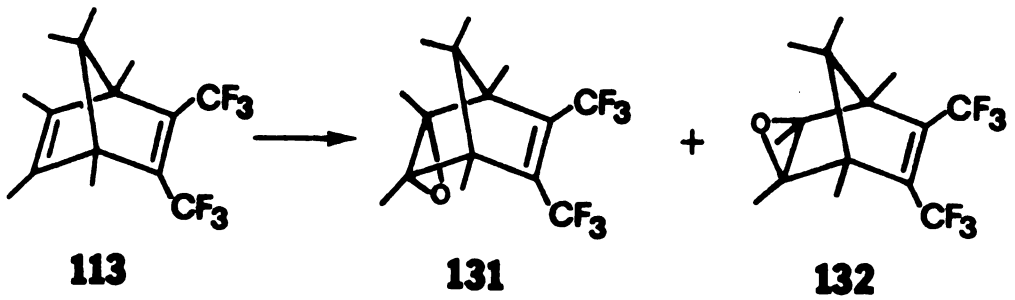



react with dihalocarbenes $:CX_2$ (X = F, Cl, Br). In every instance only starting material was recovered.

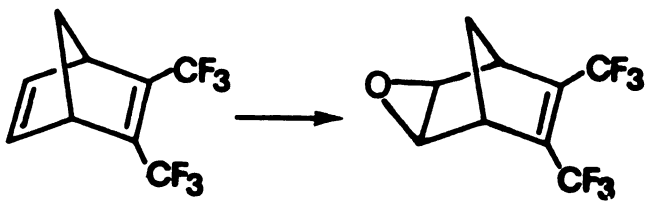
In contrast, however, treatment of 113 or 125 with m-chloroperbenzoic acid formed the corresponding epoxides 131, 132, and 133, Scheme 14).

VPC analysis with column A indicated that epoxides 131 and 132 are formed in a 10:1 ratio. The structure assignments are based on the chemical shifts of the syn- and anti-methyl groups at C-8. For 131 the syn- and anti-methyls appeared at δ 0.85 and δ 0.78, respectively, whereas for 132 they were at δ 0.93 and δ 0.80. In epoxide 132, the methyl group syn to the epoxide ring is expected to be farther down field (deshielded) than the syn-methyl group of epoxide 131, due to the

Scheme 14




**113** **131** **132**

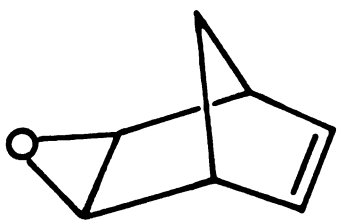



**125** **133**

deshielding effect of the oxygen atom. This deshielding by the epoxide oxygen has been observed in other systems[71] and is further illustrated by the larger chemical shift difference ($\delta$ 0.13) between the syn- and anti-methyls of epoxide 132 as opposed to the smaller chemical shift difference ($\delta$ 0.07) between the syn- and anti-methyls of epoxide 131. Furthermore the endo attack (caused by the steric hindrance of the bridge methyl groups) observed in 113, is also found in other systems when dimethyl substitution on the bridge position prevents the normal exo attack,[72] so the assignment of the endo configuration to the major product, 131, seems reasonable.

In contrast to adduct 113, unhindered adduct 125 is attacked on the exo (normal) side. Exo addition is indicated in the proton NMR spectrum

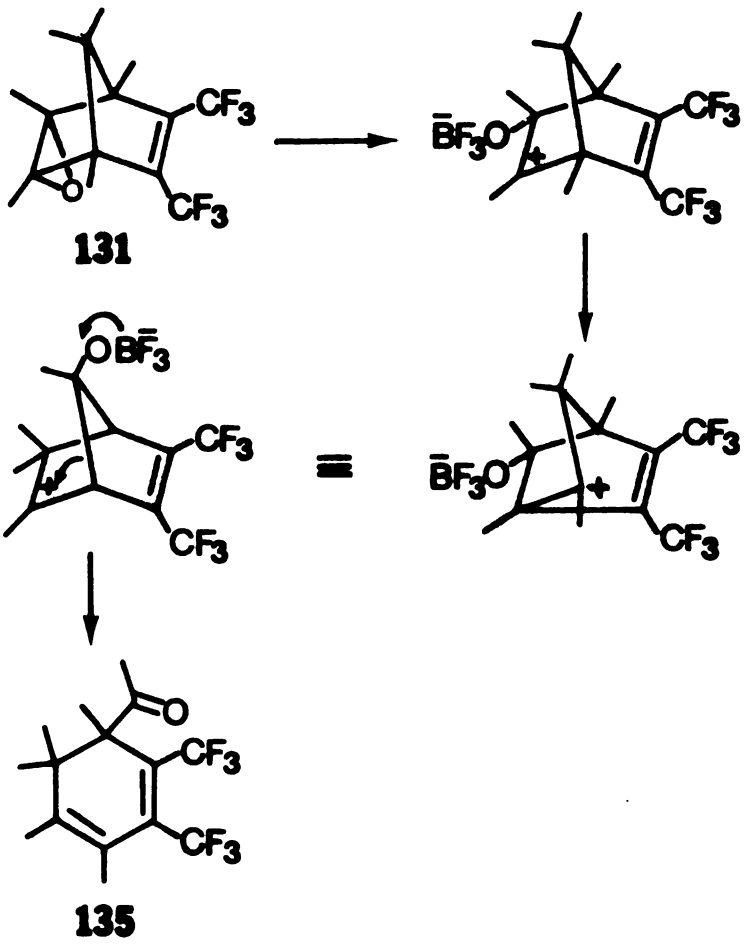
by the epoxide protons ($\delta$ 3.50) appearing as a singlet which implies there is little (if any) coupling between the bridgehead and endo-protons. This small coupling constant ($J \approx 0$), is characteristic for the couplings observed between the bridgehead and endo-protons in other bicyclic[2.2.1] systems[73] and agrees with the epoxide protons of 134 also appearing as a singlet.



**134**

Compound 131 proved to be a fairly stable epoxide in contrast to epoxide 134.[74] For example, it did not rearrange upon VPC and it was unaffected upon refluxing with trifluoroacetic acid in tetrahydrofuran. However, upon treatment with $BF_3$ etherate in benzene, 131 smoothly rearranged to a diene assigned structure 135. The mechanism of the rearrangement is depicted in Scheme 15. The spectral evidence for 135 is as follows: 1) the proton NMR spectrum indicated six methyl groups; from the chemical shifts, two of the methyls are attached to vinyl carbons while one methyl group is attached to a carbonyl carbon; 2) the presence of a carbonyl group was clear from the strong 1717 $cm^{-1}$ absorption in the IR spectrum; 3) the trifluoromethyl groups appeared in the fluorine NMR spectrum of 135 as two quartets (long range fluorine-fluorine splitting); thus the molecule is not symmetric with respect to these groups; 4) the carbon-13 spectrum confirms the presence of two methyl substituted vinyl carbons; 5) the mass spectrum had the expected

Scheme 15




m/e 328 value for the parent ion.

Although the spectral data could possible fit two other structures 136 and 137, structure 135 is favored on mechanistic grounds.

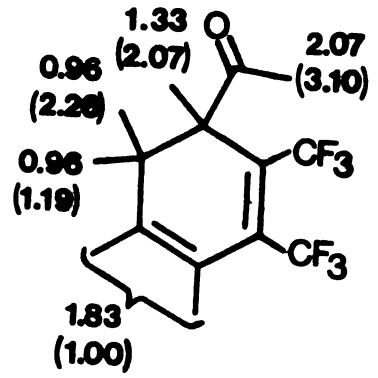
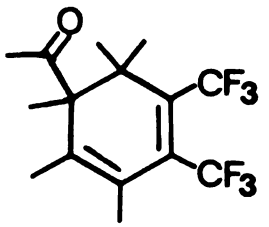
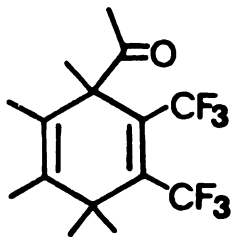



Figure 13. The proton chemical shifts (δ) of 135 in ppm from TMS. Europium shifts are in parentheses.

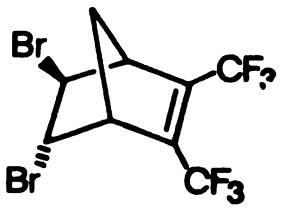


136

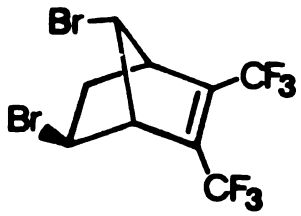


137

Finally treatment of diene 125 with one equivalent of bromine gave only one major addition product which is assigned structure 138.



138

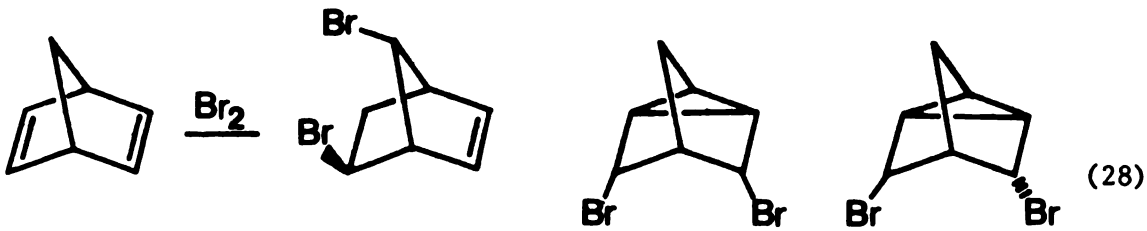


139

The assignment is based on spectral data. The bridge, bridgehead, endo- and exo-protons have chemical shifts which are consistent with the structure. In 138 the exo-proton appeared as a doublet of doublets (J = 3 Hz, J = 4 Hz) whereas the endo-proton which has a smaller coupling with the bridgehead proton appeared as a broadened singlet. Furthermore the magnitudes of the coupling constants found for the exo-proton were consistent with the exo-proton coupling constants in other bicyclic[2.2.1] systems.[73b] This ruled out the possible structure 139. In compound 139 one

of the protons attached to a bromine substituted carbon is in the endo position and would be expected to have different coupling constants than those found in 138. Further evidence for 138 is that the trifluoromethyl groups appear as two quartets in the fluorine NMR spectrum, which indicates that the molecule is not symmetric with respect to these groups.

The results of bromine addition to diene 125 contrasts dramatically with those of bromine addition to norbornadiene 140 in which three rearrangement products are observed.[75] Thus the trifluoromethyl groups so deactivate the double bond to which they are attached that the double bond cannot readily stabilize the intermediate carbonium ion




(28)

**140** **141** **142** **143**

formed in the bromine addition reaction. As a result carbonium ion rearrangements, like those found in 140, are not observed in 125.

# EXPERIMENTAL

## A. General

The fluorine NMR spectrum were obtained on a Varian model A-56/60 NMR instrument with $FCCl_3$ as an internal standard. The fluorine chemical shifts ($\phi$) are in parts per million. A minus sign indicates a signal upfield from $FCCl_3$.

In general the Diels-Alder reactions were performed by weighing out the dieneophile into a heavy walled Pyrex tube, then adding the appropriate amount of diene 96. The mixture was cooled in dry ice-acetone bath and the tube sealed with a torch. After warming to room temperature the tube was heated to the desired temperature in an oven.

The following VPC columns were used: A) 10 ft x .125 in. column of 10% FFAP on 80/100 mesh chromasorb W, B) 10 ft x .250 in. column of 10% FFAP on 80/100 chromasorb W, C) 10 ft x .375 in. column of carbowax 20 M on 80/100 mesh chromasorb W.

## B. Preparation of 1,2,3,4,5,5-hexamethylcyclopentadiene (96)

To a 3-necked 250-mL flask was added 5.0 g (33.3 mmol) of 1,2,3,4,5-pentamethylcyclopentadiene[76] along with 100 mL of freshly distilled THF (tetrahydrofuran). The flask was swept with nitrogen and cooled in an ice bath. Upon the careful addition of 20 mL of 2 M

methyllithium, a white precipitate formed. The mixture was magnetically stirred for an additional 0.5 h whereupon 2 mL of methyl iodide was added. After the mixture was stirred overnight at room temperature, a clear yellow solution remained. The reaction mixture was carefully quenched with water at 0° C, extracted with methylene chloride and dried over magnesium sulfate. Removal of the solvent afforded 5.2 g (95%) of a light yellow oil. NMR[61a] ($CCl_4$) δ 1.70 (12, s), 0.83 (6, s).

C. Attempted preparation of 1,2,3,4,5,6,7,7-octamethylbicyclo[2.2.1]-hepta-2,5-diene (93).

The following procedure is representative. Into a 7 mm x 8 in. Pyrex tube was added 200-300 mg of 2-butyne 100 followed by 100 mg of diene 96. The tubes prepared in this manner were then heated to the following temperatures: 200° C for 15 h, 240° C for 15 h, 200° C for 96 h. In each case the reaction mixture darkened. However, an NMR spectrum indicated only starting material.

D. Attempted preparation of 1,2,3,4,7,7-hexamethyl-5,6-diphenyl-bicyclo[2.2.1]hepta-2,5-diene (102).

The following procedure is representative. Into a 7 mm x 8 in. Pyrex tube was added 264 mg of 101 followed by 225 mg diene 96. After adding 20 mg hydroquinone (radical trap), enough benzene was added to dissolve the diphenylacetylene 101.

The tubes prepared in this manner were then heated to the following temperatures: 140° C for 15 h, 200° C for 24 h, 210° C for 72 h, room

temperature for approximately one year. In each case the NMR spectrum indicated starting material.

E. Preparation of 5,6-di(carbomethoxy)-1,2,3,4,7,7-hexamethyl-bicyclo[2.2.1]hepta-2,4-diene (104).

Into a 10 mL flask were weighed out 0.5 g (3.3 mmol) of 96 and 0.47 g (3.3 mmol) of dimethyl acetylenedicarboxylate 103. The mixture became warm upon stirring. After 3 h the reaction was complete. NMR ($CCl_4$) δ 3.60 (6, s, O-methyl), 1.60 (6, s, vinyl methyl), 1.13 (6, s, bridgehead methyl), 0.93 (3, s, anti-methyl), 0.77 (3, s, syn-methyl).

F. Saponification of diester (104).

The diester (1.0 g) along with 0.5 g KOH was refluxed in 40 mL of 90% ethanol for 4 h. The solution was cooled and most of the ethanol removed under reduced pressure.

The solution was added to 50 mL water and the mixture acidified with 10% HCl. The aqueous solution was then extracted with ether. The ether was dried over magnesium sulfate, filtered, and evaporated under reduced pressure to yield 0.6 g of 114 as yellowish crystals. Compound 114 was recrystallized once from methylene chloride to yield 0.54 g of white crystals (60%). Even though the melting point was low 202-206° C (lit[62b] 216-217) the NMR spectrum was consistent with the structure. The product was not further purified: NMR ($DCCl_3$) δ 1.63 (6, s), 1.23 (6, s), 0.93 (3, s), 0.83 (3, s).

G. Attempted reduction of diester (104).

To a 10 mL sidearm flask was added 50 mg of $LiAlH_4$, followed by 4 mL dry THF. The flask was swept with nitrogen and cooled to 0° C. After the addition of 105 mg of diester 104 in 1 mL THF, the mixture was stirred magnetically at room temperature for 4 h. The solution was again cooled to 0° C and quenched by the careful addition of a saturated aqueous ammonium chloride solution. The precipitate was filtered and washed with ether. The combined ether-THF solutions were dried over magnesium sulfate, filtered, and evaporated under reduced pressure to yield 80 mg of an oil. An NMR spectrum of the oil indicated that starting material was consumed (the ester methyl groups disappeared). However the spectrum was extremely complex and uninterpretable. An IR spectrum contained absorptions at 3400 $cm^{-1}$ (OH) and 1720 $cm^{-1}$ (carbonyl ?). Since separation of the mixture could not be accomplished with silica gel TLC with a variety of eluents the reaction was not further investigated.

H. Reaction of tetrolic acid with (96).

Diene 96 (341 mg, 2.28 mmol) and tetrolic acid 105 (236 mg, 1.81 mmol) were heated at 155° C in approximately 2 mL benzene for 24 h. TLC chromatography (silica gel) with 10% ether/hexane eluent gave 394 mg (74%) of product: Proton NMR ($CCl_4$) δ 2.25 (1, s), 1.25 (3, s), 1.05 (3, s), 0.95 (3, s), 0.87 (3, s), 0.83 (3, s), 0.75 (3, s); carbon-13 NMR ($DCCl_3$) δ 177.3 (carbonyl), 97.6, 59.9 (methine), 51.9, 47.0, 43.0, 36.2, 31.9, 20.7 (methyl), 19.2 (methyl), 14.4 (methyl), 8.5 (methyl), 6.3 (methyl), 5.8 (methyl), 4.2 (methyl); IR ($CCl_4$) 2985 (s), 2875 (s), 1776 (s), 1673 (m),

1452 (m), 1388 (s), 1380 (s), 1303 (m), 1276 (m), 1229 (m), 1180 (m), 1150-1140 (m, br), 937 (m), 915 $cm^{-1}$ (m); mass spectrum m/e (rel intensity) 234 (33), 175 (100).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.42; H, 9.14.

I. Preparation of 2-(carbomethoxy)-1,3,4,5,6,7,7-heptamethylbicyclo[2.2.1]hepta-2,5-diene (108).

Compound 96 (5.0 g, 33.3 mmol) and methyl tetrolate 107 (3.6 g, 36.7 mmol) were heated at 150° C in 5 mL benzene for 48 h. Distillation at 98° C under 2.5 mm Torr provided 5.6 g (68%) of reasonably pure 108. Adduct 108 was also purified by preparative VPC with column B at 150° C: Proton NMR ($CCl_4$) see Figure 10; carbon-13 NMR ($DCCl_3$) δ 169.4 (carbonyl), 144.1 (vinyl), 140.2 (vinyl), 139.2 (vinyl), 102.3 (vinyl), 77.8, 66.6, 63.5, 50.0 (O-methyl), 18.2 (2, methyls ?), 14.4 (methyl), 11.4 (methyl), 11.2 (methyl), 9.00 (methyl), 7.2 (methyl); IR ($CCl_4$) 3030 (m), 1700 (s), 1612 (m), 1433 (s), 1380 (s), 1314 (s), 1290 (s), 1198 (s), 1170 (m), 1075 (m), 1050 $cm^{-1}$ (s); mass spectrum m/e (rel intensity) 248 (45), 233 (100).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.63; H, 9.74.

J. Reduction of 2-(carbomethoxy)-1,3,4,5,6,7,7-heptamethylbicyclo[2.2.1]-hepta-2,5-diene (108).

Into a 25 mL sidearm pear-shaped flask fitted with a serum cap, was added a 7 mL hexane solution containing 300 mg (1.21 mmol) of 108.

The solution was purged with nitrogen and cooled in an ice-salt bath. A 20% hexane solution (6 mL) of cold di-isobutylaluminum hydride was slowly injected into the flask. The magnetically stirred solution was allowed to warm to room temperature. After 15 h, the solution was again cooled in an ice-salt bath and carefully quenched with 10% water-methanol. The white precipitate which formed was filtered and washed with 10 mL methanol and 75 mL ether. The combined ether-methanol-hexane solutions were washed twice with brine and dried over sodium sulfate. Removal of the solvent afforded 220 mg (86%) of 120 as a colorless oil which yellowed on standing: NMR ($CCl_4$) $\delta$ 3.90 (2, s), 1.63 (3, s), 1.53 (6, s), 1.37 (3, s), 1.05 (3, s), 0.96 (3, s), 0.72 (3, s); IR (neat) OH at 3610 $cm^{-1}$; mass spectrum m/e (rel intensity) 220 (12), 187 (100).

## K. Attempted reduction of ester 108 to hydrocarbon 93.

The ester (509 mg) was reduced with di-isobutylaluminum hydride by the previously described method. The alcohol in turn was treated with three equivalents of p-toluenesulfonyl chloride for 5 days by the method outlined by Fieser.[12] After work up 456 mg of a light yellow oil was obtained. The IR spectrum had no hydroxyl absorption, but it did have a sharp doublet at 1193 $cm^{-1}$ and 1180 $cm^{-1}$ characteristic of a tosylate.

The tosylate was dissolved in dry THF and treated with lithium triethylborohydride by the method outlined by Brown.[77] After work up an oil was obtained which had a complex NMR spectrum with many new vinyl proton peaks between 4-5 ppm. Comparison of this spectrum with an authentic spectrum for 93 (NMR $\delta$ 1.55 (12, s), 0.97 (6, s), 0.70 (6, s)) clearly indicated that the desired product was not formed.

L. Preparation of endo-cis-5,6-di(carbomethoxy)-1,2,3,4,7,7-hexamethylbicyclo[2.2.1]hepta-2-ene (110).

Diene 96 (3.0 g, 20 mmol) and dimethyl maleate 108 (2.88 g, 20 mmol) were heated in 5 mL benzene at 150° C for 24 h. Removal of the solvent afforded 110 which was used without further purification. Proton NMR ($CCl_4$) δ 3.45 (6, s, O-methyl), 2.93 (2, s), 1.57 (6, s, vinyl methyl), 1.03 (6, s, bridgehead methyl), 0.70 (3, s, anti-methyl), 0.60 (3, s, syn-methyl).

M. Epimerization of cis-5,6-di(carbomethoxy)-1,2,3,4,7,7-hexamethylbicyclo[2.2.1]hepta-2-ene (110).

To a dry 50 mL 3-necked flask was added 0.68 g (3.4 mmol) of 20% KH in oil. The KH was washed twice under nitrogen with 3 mL portions of pentane. The pentane was removed with a syringe. To the KH was added 10 mL of freshly distilled THF followed by a 2 mL THF solution of 1.0 g (3.4 mmol) of 110. A gas bubbler attached to the flask indicated that hydrogen was slowly evolved. After 0.5 h, 0.22 mL (3.5 mmol) of methyl iodide was added to the solution. The solution was magnetically stirred overnight during which time a white precipitate formed. The reaction was carefully quenched with water and the aqueous phase extracted with ether. The combined ether-THF phases were dried over magnesium sulfate. Removal of the solvent afforded 0.75 g (75%) of 121: NMR ($CCl_4$) δ 3.57 (3, s, O-methyl), 3.53 (3, s, O-methyl), 3.12 (1, d, J = 6 Hz), 2.48 (1, d, J = 6 Hz), 1.53 (3, s broad, vinyl methyl), 1.37 (3, m, vinyl methyl), 1.10 (3, s bridgehead methyl),

1.02 (3, s bridgehead methyl), 0.73 (3, s, anti-methyl), 0.60 (3, s, syn-methyl); mass spectrum m/e (rel intensity) 294 (12), 150 (100).

N. Photooxidation of 1,2,3,4,5,5-hexamethylcyclopentadiene (96).

Into a 200 mL round-bottomed flask was added 1.0 g of 96, 300 mg of methylene blue and 125 mL of methylene chloride. The flask was cooled in an ice-salt bath and a steady stream of oxygen was bubbled through the solution. The solution was then irradiated by light from a Kodak 800 carousel slide projector. The reaction was monitored by VPC with column A at 90° C by observing the disappearance of starting material. After 2 h the solvent was removed and the residue was extracted with ether. The ether solution was filtered through a bed of Celite filter aid to remove the last traces of methylene blue. Removal of the ether afforded 0.97 g (80%) of 111 as a reddish oil. Proton NMR ($CCl_4$) and carbon-13 NMR ($DCCl_3$) see Figure 12; mass spectrum m/e (rel intensity) 182 (5), 151 (100).

O. Preparation of cis-1,2,3,4-di(epoxy)-1,2,3,4,5,5-hexamethylcyclopentane (124).

Into an NMR tube was added 120 mg of 111 in $CCl_4$. The tube was then heated in an oil bath at 80° C for 2 h: Proton NMR ($CCl_4$) $\delta$ 1.32 (6, s, epoxide methyl), 1.07 (6, s, epoxide methyl), 0.95 (3, s, syn-methyl), 0.88 (3, s, anti-methyl). Chromatography with silica gel resulted in decomposition of the product.

P. Preparation of cis-1,2,3,4,4,5-hexamethylcyclopent-1-ene-3,5 diol(122).

Into a 25 mL sidearm flask with a serum cap attached was added 220 mg $LiAlH_4$ (5.5 mmol) and 10 mL dry ether. The flask was cooled in an ice-salt bath and 520 mg (2.85 mmol) of 111 in 5 mL dry ether were slowly injected into the solution. The solution was magnetically stirred under nitrogen at room temperature overnight whereupon the solution was again cooled in an ice-salt bath and the reaction quenched by the careful addition of 0.2 mL water, 0.2 mL 15% NaOH solution, and 0.7 mL water. The solution was filtered and the precipitate washed with ether. The combined ether solutions were dried over magnesium sulfate and filtered. Removal of the ether afforded 319 mg (61%) of 122: NMR ($CCl_4$) $\delta$ 2.70 (2, s broad, hydroxyl), 1.57 (6, s, vinyl methyl), 1.02 (6, s, hydroxyl methyls), 0.88 (3, s, syn-methyl), 0.67 (3, s, anti-methyl); IR ($CCl_4$) hydroxyl absorptions at 3616, 3540 (shoulder), 3430 $cm^{-1}$.

Q. Preparation of 1,2,4,4-tetramethyl-3,5-dimethylenecyclopentene(123).

Dialcohol 122 (319 mg, 1.73 mmol) was dissolved in 15 mL of ether. Two drops of 6 N HCl solution were added and the mixture was stirred for 3 h. The ether solution was washed with 10% sodium bicarbonate and was dried over magnesium sulfate. Removal of the ether afforded 49 mg (19%) of 123 as a yellow oil: Proton NMR ($CCl_4$) $\delta$ 4.62 (2, s, exo-methylene), 4.50 (2, s, exo-methylene), 1.80 (6, s, vinyl methyl), 1.05 (6, s, gem-dimethyl). Lit..[61b] NMR (neat) 4.75 (2, s), 4.65 (2, s), 1.81 (6, s), 1.09 (6, s).

R. Preparation of 1,2,3,4,7,7-hexamethyl-5,6-di(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene(113).

Diene 96 (19.4 g, 129 mmol) and hexafluoro-2-butyne (21.5 g, 133 mmol) in 20 mL benzene solution were allowed to stand in a sealed tube overnight at room temperature. Distillation afforded 37.7 g (93%) of 113 as a colorless oil: bp 47-48° C (1.5 mm). Proton NMR ($CCl_4$) δ 1.60 (6, s, vinyl methyls), 1.17 (6, s, bridgehead methyls), 0.96 (3, s, anti-methyl), 0.78 (3, s, syn-methyl); carbon-13 NMR (acetone-$d_6$) δ 157.2 (m, vinyl carbons), 143.8 (vinyl carbons), 132.5 (q, $J_{C-F}$ = 272 Hz, trifluoromethyl), 81.3 (bridge), 67.8 (bridgehead), 18.4 (methyl), 11.5 (methyl), 8.70 (methyl); fluorine NMR ($CCl_4$) ϕ -60.0 (6, s); IR ($CCl_4$) 2990 (m), 1658 (m), 1460 (m), 1440 (m), 1400 (w), 1390 (m), 1370 (m), 1322 (s), 1307 (s), 1245 (s), 1180 (s), 1143 (s, sh), 1120 (s), 1020 (w), 925 (m), 702 (w), 675 $cm^{-1}$ (m); UV (cyclohexane) $\lambda_{max}$ 223 (ε = 1500); mass spectrum m/e (rel intensity) 312 (11), 41 (100).

Anal. Calcd for $C_{15}H_{18}F_6$: C, 57.69; H, 5.81. Found: C, 57.63; H, 5.73.

S. Preparation of 7,7-dimethyl-2,3-di(trifluoromethyl)bicyclo[2.2.1]-hepta-2,5-diene (127).

Diene 126[78] (2.1 g, 22.4 mmol) and hexafluoro-2-butyne 112 (4.1 g, 25.3 mmol) in 10 mL of benzene were allowed to stand in a sealed tube at room temperature for 24 h. Distillation at atmospheric pressure afforded 3.5 g (61%) of 127 as a colorless liquid: bp 145-147° C. Proton NMR ($CCl_4$) δ 6.72 (2, m, vinyl), 3.40 (2, m, bridgehead), 1.23

(3, s, anti-methyl), 1.17 (3, s, syn-methyl); fluorine NMR ($CCl_4$) $\phi$ -63.6 (6, s); IR ($CCl_4$) 3000 (m), 2960 (m), 1683 (m), 1472 (w), 1449 (w), 1428 (w), 1393 (w), 1378 (m), 1352 (s), 1300 (s), 1250 (m), 1232 (m), 1200 (m, sh), 1182 (s), 1097 (m, sh), 1002 (w), 960 $cm^{-1}$ (m); mass spectrum m/e (rel intensity) 256 (2), 241 (100).

Anal. Calcd for $C_{11}H_{10}F_6$: C, 51.57; H, 3.93. Found: C, 51.57; H, 4.07.

T. Preparation of 2,3-di(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (125).

Cyclopentadiene 117 (6.8 g, 103 mmol) and hexafluoro-2-butyne 112 (17.0 g, 105 mmol) were allowed to stand in a sealed tube at room temperature for 24 h. Distillation at atmospheric pressure afforded 16.8 g (72%) of 125 as a colorless liquid[79]: bp 125° C.

U. Photolysis of 1,2,3,4,7,7-hexamethyl-5,6-di(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene (113).

A 350-mg (1.12 mmol) sample of 113 in 75 mL pentane was added to a 100 mL Vycor test tube which was sealed with a serum cap. The sample was irradiated with a 450 W Hanovia medium pressure mercury lamp in a quartz immersion well fitted with a Vycor filter. After approximately 3 h the photolysis was stopped and the solvent removed. A light yellow solid (345 mg) was obtained.[80] The product was purified by VPC with column C at 130° C to yield 128 as a waxy white solid: mp 138-140° C. Proton NMR ($CCl_4$) $\delta$ 1.28 (6, s), 1.08 (6, s), 1.02 (3, s), 0.87 (3, s);

fluorine NMR ($CCl_4$) $\phi$ -57.5 (6, s); IR ($CCl_4$) 2970 (m), 2930 (m), 2875 (w), 1470 (w), 1425 (m), 1386 (w), 1368 (w), 1343 (m), 1310 (m), 1185 (s), 1175 (s, sh), 1150 (s), 1115 (m, sh), 1050 $cm^{-1}$ (w); mass spectrum m/e (rel intensity) 312 (26), 41 (100).

Anal. Calcd for $C_{15}H_{18}F_6$: C, 57.69; H, 5.81. Found: C, 57.49; H, 5.68.

V. Photolysis of 7,7-dimethyl-2,3-di(trifluoromethyl)bicyclo[2.2.1]-hepta-2,5-diene (127).

A 500 mg (1.95 mmol) sample of 117 in 75 mL pentane was photolysed by the previously described method. Purification by VPC with column C at 110° C afforded 129 as a clear oil. Proton NMR ($CCl_4$) $\delta$ 2.25 (2, d, J = 5 Hz), 1.62 (2, d, J = 5 Hz), 1.31 (3, s), 1.27 (3, s); fluorine NMR $\phi$ -64.2 (6, s); IR ($CCl_4$) 2960 (m), 2920 (m), 2860 (m), 1463 (s), 1448 (s), 1400 (w, sh), 1386 (m), 1368 (m), 1335 (s), 1232 (m, sh), 1210 (s), 1185 (s), 1150 (s), 1081 (s), 1073 (s), 1010 (w), 998 (m), 925 $cm^{-1}$ (w); mass spectrum m/e (rel intensity) 256 (4), 241 (100).

Anal. Calcd for $C_{11}H_{10}F_6$: C, 51.57; H, 3.93. Found: C, 51.35; H, 3.76.

W. Attempted carbene addition to 125.

To 3.1 g (26 mmol) of chloroform was added 2.0 g (8.8 mmol) of diene 125. To this solution was added 50 mg of cetyltrimethylammonium bromide (phase transfer catalyst)[81] and 3.5 g of 50% aqueous sodium hydroxide. The mixture was vigorously stirred and warmed in an oil bath

at 50° C. The reaction was followed by NMR by taking small aliquots and adding them to $CCl_4$. After 24 h the chloroform signal disappeared with the starting material signals still present and no indication of any product signals.

X. Preparation of endo-5,6-epoxy-1,4,5,6,7,7-hexamethyl-2,3-di(trifluoromethyl)bicyclo[2.2.1]hepta-2-ene (131).

To a solution of 1.31 g (6.45 mmol) of 85% m-chloroperbenzoic acid in 50 mL methylene chloride was added 2.00 g (6.41 mmol) of 113. The solution was magnetically stirred overnight at room temperature. The precipitated m-chlorobenzoic acid was filtered and the methylene chloride solution was washed twice with 10% sodium bisulfite, twice with 10% sodium hydroxide and once with water. The solution was then dried over sodium sulfate and filtered. Removal of the solvent afforded 1.71 g (81%) of a colorless oil which solidified on standing. Preparative VPC with column B at 130° C gave 131 and 132 in a 10:1 ratio: For 131 proton NMR ($DCCl_3$) δ 1.35 (6, s, epoxide methyls), 1.17 (6, s broad, bridgehead methyls), 0.85 (3, s, syn-methyl, to the epoxide ring), 0.78 (3, s, anti-methyl); carbon-13 NMR[82] (acetone-$d_6$) δ 123 (q, J = 274 Hz, trifluoromethyl), 74.3, 63.8, 61.1, 18.9 (methyl), 16.6 (methyl), 12.4 (methyl), 9.3 (methyl); IR ($CCl_4$) 2900 (m), 1660 (m), 1471 (m), 1455 (m), 1400 (m), 1391 (m), 1386 (m), 1379 (m), 1362 (m), 1340 (m), 1311 (s), 1239 (m), 1172 (s), 1145 (s), 959 (s), 700 (m), 672 $cm^{-1}$ (m); UV (cyclohexane) $\lambda_{max}$ 215 nm (ε = 900); mass spectrum m/e (rel intensity) 328 (6), 41 (100).

Anal. Calcd for $C_{15}H_{18}F_6O$: C, 54.88; H, 5.53. Found: C, 54.82; H, 5.61.

For 132 proton NMR ($DCCl_3$) δ 1.38 (6, s, epoxy methyls), 1.27 (6, s broad, bridgehead methyls), 0.93 (3, s, syn-methyl, to epoxide ring), 0.80 (3, s, anti-methyl).

Y. Preparation of exo-5,6-epoxy-2,3-di(trifluoromethyl)bicyclo[2.2.1]-hepta-2-ene (133).

To a 40 mL solution of methylene chloride containing 4.5 g (22.2 mmol) of 85% m-chloroperbenzoic acid was added 5.0 g (20.5 mmol) of 125. After being stirred magnetically at room temperature for 24 h, the methylene chloride solution was filtered, washed twice with 10% sodium bisulfite, twice with 10% sodium hydroxide and once with brine. Then the solution was dried over magnesium sulfate, filtered and distilled. There was obtained 3.08 g (58%) of 133 as a colorless liquid, bp 150-152° C: Proton NMR ($CCl_4$) δ 3.53 (2, s, epoxide protons), 3.28 (2, s broad, bridgehead protons), 1.88 (1, d, J = 9 Hz syn-proton), 1.61 (1, d, J = 9 Hz anti-proton); fluorine NMR ($CCl_4$) ϕ -61.8 (6, s); carbon-13 NMR[82] ($DCCl_3$) δ 121.3 (q, $J_{C-F}$ = 270 Hz, trifluoromethyl), 57.7 (epoxide carbons), 46.3 (bridgehead), 40.2 (bridge); IR ($CCl_4$) 3150 (w), 3120 (w), 1723 (w), 1673 (w), 1450 (w), 1386 (m), 1362 (m), 1353 (m), 1301 (s), 1292 (s, sh), 1268 (m), 1242 (m), 1185 (s), 1167 (s), 1152 (s), 1042 (m), 1014 (m), 934 (m), 660 (w), 610 $cm^{-1}$ (w); UV (cyclohexane) $\lambda_{max}$ 233 nm (ε = 1600); mass spectrum m/e (rel intensity) 244 (35), 204 (100).

Anal. Calcd for $C_9H_6OF_6$: C, 44.28; H, 2.48. Found: C, 44.32; H, 2.51.

Z. Preparation of 1-acetyl-1,4,5,6,6-pentamethyl-2,3-di(trifluoromethyl)cyclohexa-2,4-diene (135).

To 50 mL benzene containing 1.05 g (3.2 mmol) of 131 was added 1.1 mL of $BF_3$ etherate. The solution was stirred at room temperature for 3 h before quenching with saturated sodium bicarbonate. The benzene layer was dried over magnesium sulfate and filtered. Removal of the solvent afforded 968 mg of crude 135. Purification was accomplished by silica gel chromatogrpahy with 30% ethyl acetate/hexane eluent: carbon-13 NMR[82] ($DCCl_3$) δ 218 (carbonyl), 143.6 (vinyl), 121.5 (vinyl), 57.7, 40.8, 29.8 (methyl), 21.8 (methyl), 15.2 (methyl), 15.1 (methyl), 14.3 (methyl); fluorine NMR ($CCl_4$) ϕ -57.4 (3, q, J = 7 Hz), -59.4 (3, q, J = 7 Hz); IR ($CCl_4$) 2995 (m), 2960 (m), 1717 (s), 1560 (m, broad), 1468 (m), 1404 (w), 1382 (m), 1372 (m), 1360 (m), 1323 (m), 1290 (s), 1272 (s), 1170 (s), 1152 (s), 1140 (s), 1090 (m), 1060 (w), 960 (w), 932 (w), 903 (w), 702 (w), 680 (w), 672 (w) $cm^{-1}$; mass spectrum m/e (rel intensity) 328 (6), 41 (100).

Anal. Calcd for $C_{15}H_{18}F_6O$: C, 54.88; H, 5.33. Found: C, 54.89; H, 5.47.

AA. Bromination of diene 125 .

Diene 125 (0.50 g, 2.2 mmol) was dissolved in 10 mL methylene chloride. The solution was cooled to -5° C and one equivalent of bromine in 1.5 mL methylene chloride was slowly added. After allowing the solution to warm to room temperature, a VPC of the reaction mixture using column A at 150° C indicated three peaks in the ratio of 20:1:1.

Removal of the solvent afforded 0.85 g (100%) of a light yellow oil. Microdistillation under 0.2 mm pressure afforded 0.75 g (88%) of 138 as a colorless oil: bp 43° C. Proton NMR ($CCl_4$) δ 4.37 (1, d, d, J = 4 Hz, J = 3 Hz), 3.87 (1, s broad), 3.53 (1, m), 3.40 (1, m), 2.23 (2, m); fluorine NMR ($CCl_4$) ϕ -65.1 (3, q, J = 4 Hz), -66.9 (3, q, J = 4 Hz); IR ($CCl_4$) 1422 (m), 1457 (s), 1387 (m), 1324 (m), 1296 (s), 1260 (s), 1050 (m), 975 (w), 948 (m).

Anal. Calcd for $C_9H_6F_6Br_2$: C, 27.86; H, 1.56; Br, 41.19. Found: C, 27.76; H, 1.54; Br, 41.22.

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