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STEREOCHEMISTRY OF ELECTROPHILIC ADDITIONS TO BENZO FUSED
7-ISOPROPYLIDENE- NORBORNENE AND -NORBORNADIENE SYSTEMS

The Ohio State University

Ph.D. 1980

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STEREOCHEMISTRY OF ELECTROPHILIC ADDITIONS
TO BENZO FUSED 7-ISOPROPYLIDENE-NORBORNENE AND
-NORBORNADIENE SYSTEMS

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Larry Wayne Hertel, M.S.

The Ohio State University
1980

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To my wife, Betty
ACKNOWLEDGMENTS

I wish to extend my appreciation and gratitude to Professor Leo A. Paquette, who proposed and oversaw this investigation, and whose personal attention and enthusiasm stimulated this author throughout.

Finally, I must thank my wife, Betty, for her unselfish support and encouragement throughout my graduate studies.
VITA

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INTRODUCTION

Electrophilic and nucleophilic reactions are fundamental to organic chemistry. Nucleophilic reactivities are determined in a large part by the intrinsic basicity and polarizability of the reagent. The quantitative equations developed by Swain and Scott and by Edwards for correlation of nucleophilic reactivity are discussed in most physical organic chemistry texts. Relative electrophilic reactivities are not well known. This is due principally to the fact that the fundamental nature of $S_N^2$ reactions permits the direct replacement of one nucleophile by another via transition states where both are intimately involved. No comparable electrophilic process is available.

We were interested in finding a method by which one could examine various electrophilic processes, decipher what parameters are important in their response to varying stereoselectivity demands, and to establish in a relative sense, their order of electrophilicity.

Linear free-energy relationships such as the Hammett and Taft correlations, as well as more recent multiple parameter versions, have been of limited use in establishing the rate-determining transition state structures.
involved in electrophilic addition reactions. This is because a single set of substituent steric and polar parameters is inadequate to cope simultaneously with both open and bridged-ion pathways.

Our intention was to utilize chemical probes which would be capable of reacting with various electrophilic species and give rise to different stereochemical isomers under these two sets of mechanistic circumstances. Importantly, the probe should allow for electronic alterations without the perturbation of other parameters such as conformational and steric effects. In this way, it should prove possible to establish if the rate-determining step for a particular electrophilic process involves substantial \( \Pi \)-bond distortion \( \text{A} \) as usually required by weak electrophiles, or more closely resembles the highly polarized open ion situation \( \text{B} \) commonly characteristic of more powerful electrophilic agents.

![Diagram](image)

Figure 1. Open and bridged ion pathways in electrophilic addition reactions.
With these goals in mind, several 7-isopropylidene benzonorbornenes and related molecules have been synthesized and allowed to react with various types of electrophiles. Theoretical calculations and correlations have been carried out in conjunction with the experimental results. Lastly, the mechanistic details made clear by the individual olefins and the various electrophiles are interpreted.
RESULTS AND DISCUSSION

I. Preparation of Olefins

9-Isopropylidene-1,4-dihydro-1,4-methanonaphthalene (1), a molecule previously reported, can easily be synthesized by aprotic diazotization of anthranilic acid with isoamyl nitrite and subsequent in situ decomposition to the highly reactive benzyne in the presence of 6,6-dimethylfulvene. Controlled catalytic hydrogenation of the Diels-Alder adduct (1) saturates only the endocyclic double bond and yields 9-isopropylidene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (2).

9-Ethylidene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (4) was prepared from 2 by ozonolysis of the exocyclic double bond to form 7-benzonorbornenone (3) followed by treatment with ethyltriphenylphosphonium ylide.
5,6,7,8-Tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (5) was made available by the reaction of tetrafluorobenzyne with 6,6-dimethylfulvene. The aryne was generated from pentafluorophenyllithium. In a similar manner, 5,6,7,8-tetrachloro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (6) was prepared by the reaction of tetrachlorobenzyne with 6,6-dimethylfulvene. In this instance, the aryne was similarly generated from pentachlorolithium. Catalytic hydrogenation of 5 and 6 was found to result initially in isomerization of the exocyclic double bond to an isopropenyl group, followed by saturation of this newly formed double bond and/or the endocyclic double bond. Therefore, selective saturation
of the endocyclic double bond was accomplished by diimide reduction, utilizing potassium azodicarboxylate and acetic acid in methanol-chloroform solution. In this way, both 7 and 8 were made available.

Scheme 2

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-ethylidene-1,4-methanonaphthalene (9) was prepared by ozonolysis of 7 to form 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalen-9-one followed by treatment with ethyltriphenylphosphonium ylide.
5,8-Dimethoxy-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (11) could be prepared by 0-methylation of the p-benzoquinone-6,6-dimethylfulvene adduct. The poor yields observed in this approach are attributed to the incursion of a retro [4+2] reaction whenever aromatization of the quinone ring was attempted under either acidic or basic conditions.
A better yielding synthesis was devised. The heating of p-benzoquinone with tetrachlorocyclopentadienone dimethyl ketal at 170°C yielded the aromatic dihydroxy adduct 12. Treatment of 12 with potassium tert-butoxide and dimethylsulfate gave dimethoxy compound 13, which was reduced to 14 by means of lithium and tert-butyl alcohol in tetrahydrofuran. The ketal hydrolysis, which was carried out with a two-phase system (6N HCl / ether), yielded 5,8-dimethoxy-9-benzonorbornenone (15). Reaction of 15 with isopropyltriphenylphosphonium ylide gave 5,8-dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (16).

The hydrocarbon 7-isopropylidenenorbornene (21) was obtained from a series of reactions which began with the condensation of 6,6-dimethylfulvene and acrylic acid at elevated temperatures to give the [4+2] adduct 17. Oxidative decarboxylation of this acid yielded 7-isopropylidenebicyclo[2.2.1]hept-5-en-2-one (18) whose hydride reduction gave alcohol 19. Treatment of 19 with p-toluene-sulfonyl chloride in pyridine formed the tosylate 20 which was reduced to hydrocarbon 21 with lithium aluminum hydride.
Scheme 5
The synthesis of 11-isopropylidene-9,10-dihydro-9,10-methanoanthracene \((\text{23})\) has been achieved by Tanida\(^{11}\) who utilized the bis-dehydrochlorination of \(\text{22}\), the \([4+2]\) adduct of 9-isopropylidene-1,4-dihydro-1,4-methanomethylnaphthalene \((\text{1})\) and 1,4-dichlorobutadiene. However, the dehydrochlorination step using potassium \(\text{t-butoxide}\) in dimethylsulfoxide was low yielding and variable.\(^{12}\)
When the same bis-dehydrochlorination conditions were applied to the [4+2] adduct (27) of 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (5) and 1,4-dichlorobutadiene, no desired product was obtained. When numerous variations in the reaction conditions were tried, the same unwanted product or products seemed to be formed. The product(s) was that obtained from initial abstraction of the hydrogen atom \( \alpha \) to the chlorine, followed by vinylogous chloride ion expulsion to form the chlorocyclohexadiene adduct 24. This unstable intermediate then underwent facile [3,3] sigmatropic rearrangement\(^\text{13} \) to deliver 25 and/or a [10+4] cycloreversion reaction to benzene and 8,8-dimethylbenzo-[6]fulvene (26).\(^\text{14} \) To circumvent this problem, dichloride

**Scheme 8**

\[ 24 \rightarrow \text{base} \rightarrow 25 \]

\[ \text{[6]} \rightarrow 26 \]

adduct 27 was selectively epoxidized at its exocyclic double bond to form both the syn (28) and anti isomer (29) in a ratio of 88:12.
The stereochemistry of the epoxides, as well as the stereochemistry of 29 (i.e., whether the four carbon bridge is exo or endo), was readily assigned on the basis of the $^1$H NMR spectra. The methyl signal of anti isomer 29 was upfield relative to that of the syn isomer (28), a circumstance attributable to shielding by the underlying aromatic ring. The signals from the protons α to the chlorine atoms in 29 were dramatically shifted downfield as compared to those of 28 due to the deshielding effect of the epoxide oxygen. This deshielding effect of the epoxide oxygen also gave evidence for the exo stereochemistry of 27.

Syn epoxide 28 could be 1,4-dechlorinated to the cyclohexadiene adduct 30 with zinc in refluxing tetrahydrofuran and then aromatized with palladium on carbon to deliver the desired dibenzo epoxide 31. This epoxide could be transformed into the isopropylidene compound 32 by deoxygenation using lower valent tungsten chloride formed from the treatment of tungsten hexachloride with two equivalents of n-butyllithium.15
As previously discussed, 5,8-dimethoxy-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene 11 is not readily available. Therefore, the synthesis of 11-isopropylidene-5,8-dimethoxy-9,10-methanoanthracene (39) had to be
accomplished by the following sequence. Dichloride 22 was epoxidized selectively at its exocyclic double bond to produce both the syn (33) and anti isomers (34) in a ratio of 2:1. 1,4-Dechlorination of 33 with zinc in refluxing tetrahydrofuran led to the cyclohexadiene adduct 35, whose reaction with singlet oxygen formed the expected endoperoxide. In the presence of triethylamine, this intermediate was isomerized to 36, whose oxidation with manganese dioxide gave a mixture of the enedione 37 and its aromatic tautomer. O-Methylation of this mixture was accomplished with potassium tert-butoxide and dimethyl sulfate, and the resulting 38 was deoxygenated with the lower valent tungsten chloride\(^1^5\) to form 39.

II. **Electrophilic Reactions with Olefins.**

Singlet oxygen was produced by the customary dye sensitization technique. In this procedure, ground state triplet oxygen is excited to the singlet (\(^1\Delta_g\)) state by energy transfer from the excited dye, in this case, rose bengal. Singlet oxygen interacts with the olefins to produce allylic hydroperoxides initially, and these were immediately reduced to allylic alcohols with sodium borohydride. No attempt was made to analyze products at the hydroperoxide stage.
Scheme 10

\[ \text{Methylene blue} \]

\[ \text{Zn, THF, } \Delta \]

\[ \text{1. hv, O}_2 \text{, methylene blue} \]

\[ \text{2. Et}_3\text{N} \]

\[ \text{MnO}_2, \text{CH}_2\text{Cl}_2 \]

\[ \text{KOH, Bu, (CH}_3)_2\text{SO}_4 \]

\[ \text{WCl}_6, \text{BuLi} \text{, (2 equiv.)} \]

\[ \text{THF} \]
When 16 was reacted with $^1\text{O}_2$, both possible isomers were formed. The stereochemistries of the products were assigned on the basis of (a) the higher field position of the methyl and vinyl signals in D, a circumstance attributable to shielding by the underlying aromatic ring; (b) upfield shifting of the exo protons on the ethano bridge in C relative to D as a result of the anisotropy of the isopropenyl group. Integration of the vinyl signals of the two different isomers, as taken from the $^1\text{H}$ NMR spectra of the crude reaction product, gave a syn:anti ratio of 17:83.

Figure 2. Syn and anti isomers in electrophilic addition reaction.
When 2, 7, and 8 were comparably reacted with $^{13}$O$_2$, both possible isomers were again formed. Through application of the identical criteria for stereochemical assignment and for determination of isomer ratios, the resulting product compositions were determined. A change in solvent from methanol to dichloromethane altered the stereochemical results very little (see Scheme 11).

Scheme 11

When the 9-ethylidene compounds 4 and 9 were treated with $^{13}$O$_2$, little change from the isomer ratios obtained for the 9-isopropylidene compounds 2 and 7 were observed (see Scheme 12). The syn to anti ratio found for 21 is also shown in Scheme 12.
Absolute rate constants for the reaction of $^1\text{O}_2$ with olefins 2, 7, 8, and 16 were obtained through the courtesy of Dr. M.A.J. Rodgers at the Center for Fast Kinetic Research, Austin, Texas. In their experiments, a laser flash was used to generate anthracene triplets in aerated dichloromethane solutions containing diphenylisobenzofuran (DPBF). The quenching of such triplets by $\text{O}_2$ ($^3\Sigma_g^-$) produced the $^1\Delta_g$ species, the reactivity of which was determined by time-resolved observation of DPBF bleaching. Upon addition of 16, 2, 8, and 7 to such reaction mixtures, the respective absolute rate constants ($k_g$) were determined to be $4.28 \times 10^6$, $1.36 \times 10^5$, $9.63 \times 10^4$ and $5.27 \times 10^4$ l mol$^{-1}$sec$^{-1}$, respectively.
Peracid epoxidation of the series of 9-isopropylidene compounds 2, 7, 8, 16, and 21 gave both possible stereoisomers in each case. The stereochemistries were assigned on the basis of the higher field position of the methyl signals in the anti isomer, a circumstance again attributable to shielding by the underlying aromatic ring. Further stereochemical proof was obtained by base promoted opening of the epoxides to the allylic alcohols of previously established stereochemistry. Integration of the methyl signals of the two different isomers, as determined from the $^1$H NMR spectra of the crude reaction mixtures, gave the syn:anti product ratios (see Scheme 13).

Peracid epoxidation of 32 yielded the two isomeric epoxides 31 and 64. The stereochemistry of these compounds was determined by direct comparison with epoxide 31 as obtained in the synthesis of 32 (see Scheme 9), whose stereochemistry was earlier deduced. The methyl signal in the $^1$H NMR spectrum of 31 appears upfield from the methyl signal in that of 64. This is attributable to the greater shielding effect of the more electron-rich aromatic ring.

When the 9-isopropylidene compounds 2, 7, 8, and 16 were treated with N-bromosuccinimide in 10% aqueous glyme, allylic bromides were formed. The $^1$H NMR spectra
of these products were closely similar to those of the allylic alcohols formed in the $^{1}O_2$ reactions. The stereochemical assignments and isomer ratios were determined as in the preceding work. The observed isomer ratios are shown in Scheme 14.

Scheme 14

On exposure of the 9-isopropylidene compounds 2, 7, 8, 16, and 21 to N-methyltriazolinedione, an "ene" reaction ensued to form allylic urazoles. Again, the stereochemical assignments and ratio determinations were handled as in the $^{1}O_2$ and bromination cases. The experimental data are recorded in Scheme 15.
All of the aforementioned stereochemical results are compiled in Table 1.

Table I. Electrophilic Additions to the 7-Isopropylidenebenzonorbornenes.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Singlet Oxygen</th>
<th>NBS, H2O-glyme</th>
<th>N-Methyltriazolinedione</th>
<th>m-Chloroperbenzoic Acid</th>
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<td>Compd</td>
<td>syn</td>
<td>anti&lt;sup&gt;a&lt;/sup&gt;</td>
<td>syn</td>
<td>anti&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>21</td>
<td>14</td>
<td>86</td>
<td>14</td>
<td>86</td>
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<sup>a</sup>The percentage values given were obtained from carefully integrated <sup>1</sup>H NMR spectra of reaction mixtures prior to isolation and characterization of the individual components and are normalized to 100%. In the case of the singlet oxygen reactions, analysis was made only after NaBH₄ reduction of the allylic hydroperoxide mixtures.
Acetylation of the 9-isopropylidene compounds 16, 17, 21 with acetyl chloride and aluminum chloride in dichloromethane at -10°C or with zinc chloride in acetic anhydride at room temperature led in high yield to single products. The presence of only lone acetyl methyl and lone vinyl methyl signals as well as one set of vinyl signals in the $^1$H NMR spectra of the crude reaction mixtures constituted the evidence for formation of one product in each instance. The exclusivity of syn attack in these examples was established in the following manner. Of the two methyl peaks in the $^1$H NMR spectrum of 84, [(δ,CDCl₃) 1.97(s) and 1.75(m, $\nu_2 = 3$Hz)], only the upfield isopropenyl signal remained after suitable hydrogen-deuterium exchange provided 88. Upon ozonolysis, both
$84$ and $88$ were converted to diacetyl derivatives $90$, whereas $90a$ showed a pair of methyl singlets at $\delta$ 2.19 and 1.91 (in CDCl$_3$), the spectrum of $90b$ was characterized by a lone absorption at 2.19. Since the more shielded methyl group in $90$ resides above the benzene ring, structural assignment to $84$ is confirmed. Exclusive syn attack in $21$ was established in the following manner. Controlled diimide reduction of $86$ permitted selective saturation of the norbornene double bond. The chemical change was accompanied by a downfield shift of the acetyl singlet ($\delta$ 2.03–2.13) while the isopropenyl methyl signal ($\delta$ 1.75) remained unaltered.

Scheme 17

\[
\begin{align*}
\text{CH}_3 \quad \text{NaOD, D}_2\text{O} & \quad \text{CD}_3 \quad \text{O}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
& \quad \text{CR}_3
\end{align*}
\]

Scheme 18

\[
\begin{align*}
\text{O}_3 & \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{HO}_\text{OC}_\text{H}_3 & \\
\text{HO}_\text{OC}_\text{H}_3 & \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{X} & = \text{H} \\
\text{X} & = \text{F}
\end{align*}
\]
The ozonolysis of 84 was complicated by the formation of two other products in addition to diacetyl compound 90. The identity of 92 was determined by spectral and combustion analysis. This peroxide could be converted to 90 by acid hydrolysis or catalytic hydrogenation. Epoxy ketone 93 was identified by spectral data as well as independent synthesis by peracid epoxidation of 84. The ozonolysis of 85 produced the diacetyl compound 91 as well as 94. No other product was observed.

Internal consistancy throughout the series was shown by independent ozonolysis of the syn and anti allylic alcohols 42 and 43 to form the isomeric pairs of acetyl

\[ \text{Scheme 19} \]
alcohols 95 and 96. The methyl peak in the 1H NMR spectrum of 95 appears as a singlet at 6 1.7. The methyl peak in the 1H NMR spectrum of 96 appears as a singlet at 6 2.25. The higher field position of the methyl signal in 95, a circumstance attributable to shielding by the underlying aromatic ring, is consistent with the stereochemical assignments of the allylic alcohols.

Scheme 20

Acetylation of 32 with acetyl chloride and aluminum chloride in dichloromethane at -10°C produced the two isomers 97 and 98 in a ratio of 47:53, respectively. In this instance, stereochemical assignment was made on the basis of the 1H NMR spectra. The vinyl methyl signal of 97 appeared upfield from the vinyl methyl signal of 98;
also, the acetyl methyl of 98 appeared upfield from the acetyl methyl of 97. This higher field shift is attributable to the greater shielding effect of the more electron-rich aromatic ring.

The response of the 9-isopropylidene compounds 2, 7, 16, and 21 to the Prins reaction (hydroxymethylation by means of the acid-catalyzed addition of formaldehyde) was similarly to give only one product, the structures of which were the cyclic ethers, 99-101. These products could
be obtained by initial addition of one equivalent of formaldehyde to form the hydroxymethyl compound 102, which could then add a second equivalent of formaldehyde to produce the dihydroxymethylated compound. Subsequent loss of water with ring closure then delivers the cyclized products 99-101.

The stereochemistry of 99-101 was elucidated by independent synthesis. Thus, haloform degradation of 84

Scheme 22

\[
\begin{align*}
84 & \xrightarrow{\text{NaOCl, NaOH, H}_2\text{O, dioxane}} 104 \\
102 & \xrightarrow{\text{CH}_2\text{N}_2, \text{LiAlH}_4} 100
\end{align*}
\]

to give carboxylic acid 104 followed by esterification and hydride reduction of the ester (105) provided 102. Independent submission of 102 to the Prins conditions
delivered \textbf{100} exclusively. To show that an acid catalyzed elimination of formaldehyde from \textbf{102}, followed by addition of formaldehyde in the opposite stereochemistry was not involved, \textbf{102} was subjected to the Prins conditions with the absence of formaldehyde. Only recovered \textbf{102} was obtained.

Ether \textbf{103} exhibits a methylene proton absorption ($\delta 4.82$, $2H$) differing little in chemical shift from that of \textbf{100} and its congeners ($\sim \delta 4.94$). This internal consistency comprises the reference point for this stereochemical assignment.

When \textit{tert-}butyl hypochlorite was allowed to react in the dark with olefins \textit{2}, \textit{7}, and \textit{16} in methylformate solution, allylic chlorides were formed. The stereochemical assignments of these products and their ratios were handled as in the \textbf{102} and other electrophilic reactions that formed "ene" type products. Changes in the solvent system to 12 equiv. of formic acid in methyl formate and formic acid-methyl formate (1:1) afforded the same allylic chlorides except in appreciably altered ratios (see Scheme 23).

Reaction of the 7-isopropyldiene compounds \textit{2}, \textit{7}, \textit{16}, and \textit{21} with dichlorocarbene, as generated from sodium
trichloroacetate in refluxing glyme-tetrachloroethylene (1:1), gave both possible isomeric dichlorocyclopropane adducts 112-119. Stereochemistry was determined through X-ray crystal analysis of the major isomer 114. The X-ray structure was determined by direct methods using standard X-ray program techniques. 18

Figure 3. X-Ray crystal structure of 114.
$^1$H NMR spectral comparisons clearly showed the methyl signals of anti isomers 114, 115, 117, and 119 to reside at a higher field position than those of the syn isomers (112, 114, 116, and 118), a circumstance attributed to shielding by the underlying aromatic ring or double bond. Also, the signals from the exo hydrogens on the ethano bridge in the anti isomers appeared at lower field than those of the syn isomers. This is attributed to the deshielding effect of the overhanging chlorine atoms.
The isomeric compositions of the dichlorocarbene addition products are listed in Scheme 24.

III. Factors Involved in Stereochemical Results

A. Steric Considerations

A certain level of steric bias is present in all of the bridged olefins. In benzonorbornenes $2$, $4$, $7$, $8$, $9$, and $16$, syn attack results in minimal buildup of steric inhibition due to the planar geometry of the bridging aromatic ring. Anti attack, on the other hand, is perturbed to some extent by the exo hydrogens on the ethano bridge. By selectively increasing the steric factor for electrophilic attack in one direction, an increase in electrophilic attack at the exocyclic double bond on the opposite side should be observed. This is dramatically illustrated when the exo hydrogens on the ethano bridge are replaced by an exo cyclohexene moiety. Thus, the peracid epoxidation of $2$ and $7$ occurs with a syn:anti ratio of $17:83$ and $37:63$, respectively (Scheme 13), whereas the epoxidation of $25$ and $27$ occurs with a syn:anti ratio of $67:33$ and $88:12$, respectively (Schemes 9 and 10). The steric factors prevailing in the two directions of attack on $21$ should be roughly comparable.
to those present in the benzo series. Steric differences in the two modes for attack in the dibenzo compounds 32 and 39 should be negligible.

B. Solvent Effects

Solvent effects in the \( ^{10}_2 \) reaction appear to be unimportant, as essentially identical product ratios were obtained in methanol, \(^{18}\) dichloromethane \(^{19}\) and acetonitrile. \(^{20}\) The bromination of 2 with N-bromosuccinimide in either 10% aqueous glyme or methyl formate–formic acid (1:1) gave essentially identical product ratios. Mukai \(^{21}\) has reported similar product ratios in the reaction of dichlorocarbene with 2. \(^{22}\)

C. Electrophilicity

Brominations with N-bromosuccinimide \(^{22}\) and "ene" reactions with N-methyltriazolinedione \(^{24}\) are classified as electrophilic reactions that proceed through highly dipolar transition states. The peracid oxidation of olefins is an electrophilic process which has less propensity than any of the above for charge buildup in the activated complex. \(^{25}\)

Acetylation is often pictured as the result of electrophilic attack by an acetylium cation. Whether the
attacking species is a separated or "tight" ion pair or a donor acceptor form seems to depend upon reaction conditions. Whatever the case, the reacting species must have a substantial amount of charge buildup at the attacking center.

The Prins reaction is generally accepted as proceeding by electrophilic attack of protonated formaldehyde upon a double bond. One can reasonably view the reaction of tert-butyl hypochlorite in an acidic medium as also involving attack by a protonated reagent. Protonation in this case, however, materializes chiefly on the oxygen atom adjacent to the attacking center (Cl atom) (see Figure 4).

Figure 4. Cationic electrophiles.
Carbenes have high electrophilicity and formally neutral charge character. The extent of polarization which develops in the transition state is said to depend upon the angle of attack and the reactivity of the olefin involved.  

D. Orbital Distortion

Heilbronner and Martin have reported the photoelectron spectrum of 7-isopropylidenenorbornene and have estimated the value of the orbital splitting resulting from interaction between the exocyclic and C₂-C₃ double bonds. Hoffmann and Kurz have observed polarization of the exocyclic double bond by measurement of the ¹³C NMR spectrum of 7-methylenenorbornene and have established that homoconjugation induced polarization of the exocyclic double bond exists.

In our systems, it was anticipated that homoconjugation would induce distortion of the N-orbitals of the exocyclic double bond, so that the two sides of the exocyclic double bond would have unequal electron densities.

The photoelectron spectra of 2, 7, and 16 consist of 3 peaks below 10 eV. On the basis of previous findings with 7-isopropylidenenorbornene and 7-isopropylidenebenzonorbornadiene, it is evident that these peaks
result from three \( \Pi \) MO's, two of which are localized predominantly on the benzene ring and the third on the exocyclic double bond. Full analysis of orbital sequencing was achieved through application of Koopman's theorem \((-e_J = I_{V_J})\), and utilization of both ZDO model and MINDO/3 procedures. The good agreement between calculation and experiment make evident substantial mixing of \( \Pi \) and \( \sigma \) orbitals (see Table 2). In 2, the HOMO is seen to be that MO having large coefficients at the benzene ring (Figure 5).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band</th>
<th>( I_{V,J} )</th>
<th>Assignment</th>
<th>ZDO</th>
<th>MINDO/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>8.20</td>
<td>( \sigma'(\sigma) )</td>
<td>8.18(( \sigma' ))</td>
<td>8.58(( \sigma' ))</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.70</td>
<td>( \sigma^*(\sigma) )</td>
<td>8.85(( \sigma^* ))</td>
<td>8.55(( \sigma^* ))</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.85</td>
<td>( \sigma'(\sigma) )</td>
<td>8.94(( \sigma^* ))</td>
<td>8.98(( \sigma' ))</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>7.70</td>
<td>( \sigma'(\sigma) )</td>
<td>7.69(( \sigma^* ))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.20</td>
<td>( \sigma'(\sigma) )</td>
<td>8.66(( \sigma^* ))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.70</td>
<td>( \sigma'(\sigma) )</td>
<td>8.93(( \sigma' ))</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>8.75</td>
<td>( \sigma^*(\sigma) )</td>
<td>9.14(( \sigma^* ))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.03</td>
<td>( \sigma'(\sigma) )</td>
<td>9.23(( \sigma' ))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.03</td>
<td>( \sigma'(\sigma) )</td>
<td>9.54(( \sigma' ))</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5. Comparison between theoretical and experimental orbital energies of 2. The ZDO wave functions of 2 are indicated at right.

The methoxy groups in 16 shift the a" orbital strongly, but leave the other two essentially unchanged; the fluorine substituents in 7 shift the first band toward yet higher energies (Figure 6). The resulting homoconjugation (for 2, \( \beta = 0.318 \) eV) leads to spectroscopically \(^{13}\text{C NMR}\) recognizable polarization of the exocyclic double bond. \(^{36}\)

Figure 6. Correlation of the first three bands in the PE spectra of 2, 7, and 16.
The shape of $\psi_2$, the wave function having a large coefficient at the exo methylene group is visualized in Figure 7. Linear combination between the exocyclic $\Pi$-orbital and a high lying $\sigma$-orbital causes distortion of the $\Pi$ orbital in such a way that overlap with an orbital approaching from the anti side is favored.

Figure 7. Interaction diagram between the exocyclic $\Pi$ orbital and a high lying $\sigma$ orbital to visualize the distortion of the resulting linear combination.
E. **Electrostatic Potential Fields**

When electron-withdrawing substituents are positioned on a benzene ring, they effectively reduce the electron density above and below the aromatic ring. This effect is most dramatically illustrated by contour diagram plots of the calculated electrostatic potential fields (EPF).[^37][^38] In Figure 8, the plot[^34] for 7 is seen to display an intensely positive region above and below the

![Figure 8](image-url)

**Figure 8.** Contour diagrams of the calculated electrostatic potentials of 2 (top) and 7. The maps are drawn parallel to the x,z-plane 1.5 Å above the benzene ring. The gap between the contours is 5 kcal/mol. Positive potentials are indicated by solid lines, negative ones with broken lines. Nodes are indicated by short dashes.
benzene ring, while that for 2 reflects the absence of meaningful long-range electrostatic interaction. The transition states for uniparticulate electrophilic additions and for those biparticulate electrophilic process where closely trailing δ-fragments are involved can be expected to receive added stabilization when the attacking reagent is positioned above the electron-deficient benzenoid portion of 7. The transition states which develop during syn attack shown in Figure 9 are representative.

Figure 9. Transition states for certain electrophilic additions.

F. Neighboring Group Participation

The Π electrons of the exocyclic double bond may experience partial rehybridization as they come under the influence of the electrostatic field provided by the approaching electrophile. Such external perturbation of
local electronic configurations could provide an opportunity for the aromatic ring to delocalize charge. Stabilizing bishomoconjugative interaction could then develop when the benzene ring is unsubstituted or endowed with electron-donating groups. The importance of this effect would be somewhat diminished by the presence of electron-withdrawing aryl substituents, as solvolytic studies on anti-7-benzonorbornenyl sulfonates have demonstrated. 40

Figure 10. Charge delocalization by the aromatic ring.

G. Secondary Orbital Interaction

No cases have been established for the importance of "orbital distortion" in transition states. The
distortions found in many more highly perturbed systems were found to be extremely small. "Secondary orbital interactions" may be more important. The attacking electrophile could experience antibonding interactions with the \( \text{C}_2-\text{C}_3 \) double bond on the syn side. The HOMO of our systems have the exocyclic double bond and the aryl orbitals mixed in an antibonding fashion, so that approaching electrophiles could experience repulsive secondary orbital interactions with the aromatic orbitals or the \( \text{C}_2-\text{C}_3 \) double bond. This interaction essentially disappears with \( \text{C}_7 \) and \( \text{C}_8 \), since the aromatic ring is a poorer donor.

\[ \text{Figure 11. Repulsive secondary orbital interaction.} \]

In the case of the carbene addition reaction, the origin of the stereoselectivity could be inverse orbital interaction \(^{43}\) shown in Figure 12.
Figure 12. Inverse orbital interaction.

These effects are difficult to distinguish from orbital distortion which also can be caused by \(\sigma-\Pi\) mixing induced by the aromatic orbitals. Both of these effects are difficult to distinguish from "neighboring-group participation" by the aromatic ring, when it is a good donor.

H. Charge Complex Formation

A contributing factor to the observed stereo-selectivity seen with strong cationic electrophiles could be prior \(\Pi\) coordination of these reagents to the benzo ring or norbornene double bond, with ensuing intramolecular delivery to the syn surface of the exocyclic double bond. Aromatic complexes with metals and cations have been
postulated ever since the initial discovery of the Friedel-Crafts reaction. Modern spectroscopic methods have convincingly shown the existence of Π complexes.\textsuperscript{25a}

If prior coordination with the aromatic rings was important, one could expect that Π complexes with the aromatic rings with donating substituents would contribute more than would be the case with the aromatic rings that were substituted with withdrawing groups.

IV. Conclusion

The 7-isopropylidenebenzonorbornenes have served as interesting model substrates within which electronic factors may be altered while steric and conformational factors remain constant throughout the series. There is agreement that approach of an electrophile from over the ethano bridge constitutes the more sterically hindered pathway in the 7-isopropylidenenorbornenes.\textsuperscript{49} Similar conclusions have been reached with benzonorbornenes.\textsuperscript{20,50}

The addition of singlet oxygen, N-bromosuccinimide, and N-methyl triazolinedione to olefins 2, 16, and 21 proceed with a strong contrasteric preference to provide high levels of anti products. Through manipulation of the electronic character of the aromatic ring as in 7 and 8,
the choice between the two bonding approaches to the
exocyclic $\Pi$ orbital becomes more closely equalized (see
Table 1).

Electrophilic reactions proceeding through more well
understood transition states than those involving singlet
oxygen, e.g., NBS and N-methyltriazolinedione additions,
gave proportions of syn to anti products identical within
experimental error to those realized for $^{1}O_2$. Since the
stereoselectivity of $^{1}O_2$ attack is essentially identical
to that of these model reactions, the intervention of
peroxide-like transition states is directly implicated
(see Figures 9 and 10). Clearly, the observed variable
stereoselectivity cannot be dictated by steric effects,
but must have an electronic origin. The electrostatic
potential map argument is an interesting one, but it is a
bit confusing regarding the question of whether the
positive or negative part of the electrophile is being
attracted or repelled by the electrostatic forces. E.P.F.
forces cannot be operative in the 7-isopropylidenenorbornene
21.

The most attractive rationale is found in neighboring
group participation by the aromatic ring or the endocyclic
double bond. This participation is well documented in the literature through solvolysis studies.\textsuperscript{40} If the transition state is dipolar, then bishomoconjugative interaction by the aromatic ring would stabilize this transition state (see Figure 10). The observed switch in syn:anti ratios when proceeding from electron-rich to the electron-deficient ring systems is consistent with this interpretation. When the ring is endowed with electron-withdrawing groups, the bishomoconjugative interaction should be less effective and therefore steric effects dictate stereoselectivity to a larger extent.

Peracid oxidation of olefins is an electrophilic process that has less propensity than any of the previously mentioned electrophiles for charge buildup in the activated complex.\textsuperscript{25} The long range electronic demands for this electrophile should be greater. Greater electronic push may be required from the aromatic ring in order for the oxidation to occur at an appreciable rate. The observed stereochemistry of the peracid epoxidation bears out this contention; i.e., regardless of ring substituents the stereochemistry of the formed epoxides are predominately the contrasteric anti isomer. The
stereoselectivity of peracid oxidation of unsymmetrical dibenzo compound \( \text{32} \) is also consistent with this contention (see Scheme 13).

When the strong cationic electrophiles react with our model systems, we observe attack from the less hindered side; i.e., syn. The stereoselectivity here is clearly not due to ring interaction with the exocyclic double bond, whether it be through-bond or through-space, because one would predict anti attack. On the basis of repulsive secondary orbital interactions, one would predict a predominance of anti attack. E.P.F. contours are not helpful in the interpretation of these results.

A change in the electrophilicity of the attacking electrophile modifies the preferred mode of attack, which is exemplified in the reaction with \( \text{t-butyl hypochlorite} \) with and without acid catalysis (see Scheme 23). This change in selectivity which accompanies the change in electrophilicity must involve a different mechanism than that involved in dipolar electrophilic reactions. This mechanistic situation can be pictured as the open ion pathway shown in Figure 1.

The selectivity shown by the strong electrophiles is most likely due to two causes, steric factors or prior II
coordination. Acetylation of the unsymmetrical dibenzo compound 32 shows essentially no preference in its directional attack (see Scheme 20). This result can be interpreted as evidence for steric control; however, prior Π coordination cannot be ruled out. Perhaps coordination of the cationic electrophiles and the aromatic rings take place irregardless to the substituents on the ring. In order to be more definitive, more experimental results will be necessary.

The carbene selectivity can involve a third factor not operative in the case of the other strong electrophiles and that is inverse orbital interaction (see Figure 12). More experimental evidence will be necessary in such instances to better understand the parameters involved.
EXPERIMENTAL

Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. Proton magnetic resonance spectra were recorded with Varian EM-360 and Varian T-60 spectrometers. Apparent splittings are given in all cases. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

All operations requiring dry conditions were performed in flame-dried glassware under an atmosphere of nitrogen. Organic solutions were dried over anhydrous magnesium sulfate unless otherwise stated. Evaporation of solvent was performed on a Buchi rotary evaporator applying heat when appropriate. In experiments requiring dry solvents, dioxane, ether, tetrahydrofuran and glyme were distilled from sodium-benzophenone. Benzene and diisopropylamine were distilled from calcium hydride and stored over molecular sieves. Dichloromethane was distilled from potassium carbonate and stored over molecular sieves.
Methanol was distilled from magnesium methylate and stored over molecular sieves. Methyl formate was freshly distilled before use. Low boiling petroleum ether (bp 35-65°C) was used unless otherwise specified.

9-Isopropylidene-1,4-dihydro-1,4-methanophthalene (I).

To a refluxing solution of 6,6-dimethylfulvene (53 g, 0.5 mol) and dry glyme (30 ml) was simultaneously added in dropwise fashion solutions of anthranilic acid (41.1 g, 0.3 mol) in glyme (140 ml) and of isoamyl nitrite (57.2 g, 0.5 mol) in glyme (60 ml) over a 1.5 hr period. The reaction mixture was refluxed for an additional 1 hr after the addition and allowed to cool. After removal of the volatiles under reduced pressure, the resulting black residue was purified by chromatography on silica gel (petroleum ether elution) to yield 21 g (39%) of I, mp 90-91.5°C (from ethanol) (lit. mp 91-91.5°C); \textsuperscript{1}H NMR (\delta, CDCl\textsubscript{3}) 7.2(m, 2H), 6.86(m, 4H), 4.35(m, 2H), and 1.55 (s, 6H).
9-Isopropylidene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (2). A mixture of 9-isopropylidene-1,4-dihydro-1,4-
methanonaphthalene (1.72g, 9.5 mmol) and 5% Pd/C (0.1g) in ethyl acetate (20 ml) at 0°C was stirred under an atmosphere of hydrogen until the theoretical amount of hydrogen was absorbed (230 ml, 9.5 mmol). The reaction mixture was filtered through a pad of Celite. After solvent removal from the filtrate, the resulting residue was purified by recrystallization from ethanol to give 1.58 g (90.5%) of 2, mp 91-92°C (from ethanol) (lit. mp 90.5-91.5°C); $^1$H NMR ($\delta$, CDCl$_3$) 7.0(m, 4H), 3.65(m, 2H), 1.85(m, 2H), 1.60(s, 6H), and 1.23(m, 2H).

7-Benzo[bornenone (3). An ozone stream in oxygen was bubbled for 30 min through a solution of 1,2,3,4-tetrahydro-9-isopropylidene-1,4 methanonaphthalene (3g, 16.3 mmol) in methylenechloride (55 ml) with cooling from a salt-ice bath. Oxygen was then bubbled through the solution to remove excess dissolved ozone. In order to destroy the ozonide,
acetic acid (8.4 ml) was added slowly to the cold solution with stirring. Zinc powder (2.8 g) and water (2.8 ml) were added portionwise and in alternation and the solution was allowed to stir at room temperature. Survival of the ozonide was examined by addition of 1 drop of the above solution to iodide-starch solution. The reaction mixture was extracted three times with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water prior to drying. Removal of the solvent yielded 2.21 g (86%) of 3 as an oil (lit. \(^8\) bp 100-103°C, 7 mm); \(^1\)H NMR (δ, CDCl₃) 7.15(m, 4H), 3.25(m, 2H), 2.1 (m, 2H), and 1.3(m, 2H); \(\nu_{\text{max}}\) 1806 and 1792 cm\(^{-1}\).

1,2,3,4-Tetrahydro-9-ethylidene-1,4-methanonaphthalene (4).

To a solution of ethyltriphenyl-phosphonium bromide (1.25g, 3 mmol) in anhydrous tetrahydrofuran (25 ml) at 0°C was added 3.8 ml (3 mmol) of 0.79 M \(n\)-butyllithium in hexane. After being stirred for 15 min at 0°C, 1,2,3,4-tetrahydro-1,4-methanonaphthalene 9-one (0.47 g, 3 mmol) in tetrahydrofuran (5 ml) was added dropwise. After 1 hr at 0°C, the
reaction mixture was allowed to warm to room temperature and heated at reflux for 2 hr. The cooled reaction mixture was filtered through a pad of Celite and the filtrate was diluted with water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with saturated sodium bicarbonate solution, water, and brine prior to drying. After solvent removal, the residue was purified by chromatography on silica gel (petroleum ether elution) to give 0.4 g (78%) of 4 as an oil; \(^1\)H NMR (\(^6\) CDCl\(_3\)) 7.1 (br s, 4H), 4.88 (q, \(J = 7\) Hz, 1H), 3.8 (m, 1H), 3.45 (m, 1H), 1.78-2.04 (m, 2H), 1.6 (d, \(J = 7\) Hz, 3H), and 1.1-1.35 (2H, m). The analytical sample was prepared by preparative vpc (12 ft x 0.25 in. 5% SF96 on Chromosorb G, 140°C).

**Anal. Calcd. for C\(_{13}\)H\(_{14}\): C, 91.71; H, 8.29.**
**Found: C, 91.67; H, 8.37.**

5,6,7,8-Tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (5). Pentafluorobenzene (13.2 g, 0.079 mol) in anhydrous ether was treated with 50 ml (0.079 mol) of 1.6 M \(n\)-butyllithium in hexane at -70°C. After 1 hr,
6,6-dimethylfulvene (8.3 g, 0.079 mol) was added, the external cooling was discontinued, and the mixture was allowed to warm gradually to room temperature. After 12 hr, the mixture was cooled to 0°C and treated with 2 N hydrochloric acid (25 ml). The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with saturated sodium bicarbonate and 10% ammonium chloride solutions prior to drying. After removal of solvent, the residue was chromatographed on silica gel (petroleum ether elution) yielding 6.74 g (34%) of 5, mp 80.5-82°C (from 2-propanol)(lit.9 mp 80-82°C); \(^1\)H NMR (δ, CDCl\(_3\)) 6.9 (distorted t, J = 2 Hz, 2H), 4.7 (m, 2H), and 1.6 (s, 6H).

5,6,7,8-Tetrachloro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (6). Hexachlorobenzene (28.5 g, 0.1 mol) in anhydrous ether was treated with 50 ml (0.1 mol) of 2.0 M n-butyllithium in hexane at -5°C. At completion of the addition, no insoluble hexachlorobenzene remained. 6,6-Dimethylfulvene (10.6 g,
0.1 mol) was added, the external cooling was discontinued, and the mixture was allowed to warm gradually to room temperature. The reaction mixture was heated at reflux for 5 hr, cooled, and treated with 5% hydrochloric acid (250 ml). The ether layer was separated and dried. After removal of solvent, the residue was purified by chromatography on silica gel (petroleum ether elution) to yield 4.2 g (13.1%) of 6, mp 118-125°C (lit. mp 129-131°C)

\[ \text{H NMR (6, CDCl}_3) \ 6.92 (m, 2H), 4.63 (m, 2H), \text{ and 1.6 (s, 6H).} \]

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (7). To a solution of 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (6g, 23.6 mmol) and potassium azodicarboxylate (5.5 g, 28.3 mmol) in methanol (50 ml) and chloroform (15 ml) at room temperature was added dropwise acetic acid (3.4 g, 56.7 mmol) in methanol (3 ml). The reaction mixture was stirred at room temperature for 12 hr and diluted with water. The organic layer was separated and the aqueous layer was extracted twice.
with chloroform. The combined organic layers were dried and evaporated under reduced pressure. The resulting residue was purified by recrystallization from hot 2-propanol to yield 5.17 g (85.6%) of mp 98-99°C (lit.9 mp 97-99°C); 1H NMR (δ, CDCl₃) 3.9-4.1 (m, 2H), 1.72-2.05 (m, 2H), 1.6 (s, 6H), and 1.0-1.34 (m, 2H).

5,6,7,8-Tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (8). To a solution of 5,6,7,8-tetrachloro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (1.27 g, 4 mmol) and potassium azodicarboxylate (0.93 g, 4.8 mmol) in methanol (30 ml) and chloroform (10 ml) at room temperature was added dropwise acetic acid (0.56 g, 9.6 mmol) in methanol (2 ml). The reaction mixture was stirred at room temperature for 5 hr and diluted with water. The organic layer was separated and the aqueous layer was extracted twice with chloroform. The combined organic layers were dried and evaporated under reduced pressure. The resulting residue was purified by recrystallization from hot 2-propanol to
yield 1.0 g (77.5%) of 9, mp 149.5-150°C (lit. mp 154-
155°C); 1H NMR (δ, CDCl3) 4.07 (m, 2H), 1.98 (m, 2H), 1.65
(s, 6H), and 1.25 (m, 2H).

Anal. Calcd for C14H12Cl4: C, 52.21; H, 3.76.
Found: C, 52.46; H, 3.86.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-ethylidene-1,4-
methanonaphthalene (9). To a solution of ethyltriphenyl-
phosphonium bromide (1.82 g, 4.35 mmol) in anhydrous tetra-
hydrofuran (30 ml) at 0°C was added 2.7 ml (4.35 mmol) of
1.6 M n-butyllithium in hexane. After being stirred for 30 min
at 0°C, 5,6,7,8-tetrafluoro-
1,2,3,4-tetrahydro-1,4-methanonaphthalene-9-one (1 g,
4.35 mmol) in tetrahydrofuran (5 ml) was added dropwise.
After 1 hr at 0°C, the reaction mixture was allowed to
warm to room temperature and heated at reflux for 3 hr.
The cooled reaction mixture was filtered through a pad of
Celite and the filtrate was diluted with water. The
organic layer was separated and the aqueous layer was
extracted twice with ether. The combined organic layers
were washed with saturated sodium bicarbonate solution, water, and brine prior to drying. After solvent removal, the residue was purified by chromatography on silica gel (petroleum ether elution) to give 0.67 g (64%) of 9 as an oil; $^1$H NMR ($\delta$, CDCl$_3$) 4.98 (q, $J$ = 7 Hz, 1H), 4.15 (m, 1H), 3.77 (m, 1H), 1.8-2.12 (m, 2H), 1.66 (d, $J$ = 7 Hz, 3H), and 1.19-1.47 (m, 2H). The analytical sample was prepared by preparative vpc (12 ft x 0.25 in. 5% SF96 on Chromosorb G, 140°C).

Anal. Calcd. for C$_{13}$H$_{10}$F$_4$: C, 64.46; H, 4.16.
Found: C, 64.45; H, 4.20.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalen-9-one (10). An ozone stream in oxygen was bubbled for 30 min through a solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (3 g, 11.7 mmol) in methylene chloride (55 ml) with cooling from a salt-ice bath. Oxygen was then bubbled through the solution to remove excess dissolved ozone. In order to destroy the ozonide, acetic
acid (12 ml) was added slowly to the cold solution with stirring. Zinc powder (4 g) and water (4 ml) were added portionwise and in alternation and the solution was allowed to stir at room temperature. Survival of the ozonide was examined by addition of 1 drop of the above solution to iodide-starch solution. The reaction mixture was extracted three times with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water prior to drying. After removal of solvent, the residue was purified by recrystallization from hot petroleum ether to yield 1.82 g (67.4%) of 10, mp 82-86°C (lit. mp 96-97°C); \(^1\)H NMR (\(\delta, \text{CDCl}_3\)) 3.56-3.79 (m, 2H), 2.09-2.54(m, 2H), and 1.27-1.7(m, 2H); \(\nu_{\text{max}}^\text{mull}\) 1795 cm\(^{-1}\).

5,8-Dimethoxy-1,4-dihydro-9-isopropylidene-1,4-methanophthalene (11). A solution of p-benzoquinone (10.8 g, 0.1 mol) in anhydrous ether (100 ml) was treated with 6,6-dimethylfulvene (10.6 g, 0.1 mol) in ether (20 ml) at 0°C. After 1 hr at 0°C, chloroform (3 ml) was added and the solution was stirred at room temperature
for 12 hr. After removal of solvent, the residue was mixed with 10% sodium hydroxide solution (120 ml) and cooled to 0°C. Dimethyl sulfate (40 g, 0.32 mol) was added and the solution was allowed to warm to room temperature and stirred for 5 hr. Sodium hydroxide (6 g in 15 ml of water) was added to the reaction mixture along with dimethylsulfate (20 g, 0.15 mol) and stirring was continued for an additional 3 hr. More sodium hydroxide (3 g in 10 ml of water) was added and stirring was continued for 10 hr. The reaction mixture was acidified with 5% hydrochloric acid solution and extracted with ether. The ether extracts were dried and evaporated under reduced pressure. The resulting black residue was chromatographed on alumina (benzene elution) and the product was purified by recrystallization from hot ethanol to yield 1.66 g (7%) of 11, mp 137-137.5°C; $^1$H NMR (δ, CDCl$_3$) 6.85(m, 2H), 6.42(s, 2H), 4.6(m, 2H), 3.8(s, 6H), and 1.55(s, 6H).

**Anal. Calcd. for C$_{16}$H$_{18}$O$_2$:** C, 79.31; H, 7.49.

**Found:** C, 79.31; H, 7.61.
1,8,9,10-Tetrachloro-11,11-dimethoxytricyclo[6.2.1.0^2.7]-
undeca-2,4,6,9-tetraene-3,6-diol (12). p-Benzoquinone
(6.14 g, 56.8 mmol) and 1,2,3,4-
tetrachloro-5,5-dimethoxycycl-
pentadiene (15 g, 56.8 mmol)
were heated at 170°C for 12 hr. The resultant solid reaction
mixture was recrystallized from
chloroform to yield 14.9 g
(70.5%) of 12 as a white
crystalline solid, mp 202.5-203.5°C (from chloroform) (lit. 5
mp 203-204°C); \(^1\)H NMR (\(\delta\), acetone-\(\delta_6\)) 6.55(s, 2H), 3.58
(s, 3H), and 3.45(s, 3H); \(\nu_{\text{max}}\) \(\text{mull}\) 3360 cm\(^{-1}\).

1,2,3,4-Tetrachloro-5,8-dimethoxy-9-benzonorbornadienone
Dimethyl Ketal (13). 1,8,9,10-Tetrachloro-11,11-
dimethoxytricyclo[6.2.1.0^2.7]
undeca-2,4,6,9-triene-3,6-diol
(16 g, 43 mmol) and dimethyl
sulfate (16.24 g, 128.8 mmol)
in dry tetrahydrofuran at 0°C
under nitrogen were treated
with three portions of potassium
tert-butoxide (3 x 4.8 g, 128.6 mmol) at 1 hr intervals. The mixture was stirred overnight and then filtered through a pad of Celite. The filtrate was dried and concentrated to give a brown solid. The residue was purified by recrystallization from hot benzene-ethanol (1:1) to give 9.9 g (57.5%) of 13, mp 148-149°C (from ethanol/benzene, 1:1) (lit. mp 147°C; 1H NMR (δ, CDCl₃) 6.76(s, 2H), 3.82(s, 6H), 3.68(s, 3H), and 3.5(s, 3H).

5,8-Dimethoxy-9-benzonorbornenone Dimethyl Ketal (14).

To a stirred solution of 1,2,3,4-tetrachloro-5,8-dimethoxy-9-benzonorbornadieneone dimethyl ketal (1 g, 2.5 mmol), tert-butanol (2.04g, 26.9 mmol) and tetrahydrofuran (15 ml), under a nitrogen atmosphere, was added freshly cut lithium metal (0.48 g, 68.9 mg at). The mixture was stirred at reflux for 15 hr. The reaction mixture was cooled in an ice bath and the excess lithium was destroyed by the slow addition of methanol. After dilution with water, the organic layer was separated. The aqueous layer was reextracted with ether, and the combined
organic layers were washed with water and brine prior to drying. After solvent removal, the residue was purified by chromatography on silica gel (petroleum ether elution): 0.45 g (70%), mp 122.5-123.5°C (from ethanol); $^1$H NMR ($\delta$, CDCl$_3$) 6.62(s, 2H), 3.82(s, 6H), 3.57(m, 2H), 3.35 (s, 3H), 3.12(s, 3H), 2.1(m, 2H), and 1.15(m, 2H).

5,8-Dimethoxy-9-benzonorbornenone ($\text{15}$). A solution of 5,8-dimethoxy-9-benzonorbornenone dimethyl ketal (2.43 g, 9.3 mmol) in ether (75 ml) was stirred for 12 hr at room temperature with 6 N hydrochloric acid solution (50 ml). The ether phase was separated and evaporated under reduced pressure. The resulting residue was purified by recrystallization from hot ethanol to give 1.8 g (90%) of $\text{15}$, mp 107.5-108.5°C (from ethanol); $^1$H NMR ($\delta$, CDCl$_3$) 6.7(s, 2H), 3.82(s, 6H), 3.53(m, 2H), 2.17(m, 2H), and 1.37(m, 2H); $\nu_{\text{max}}$ 1782 and 1770 cm$^{-1}$.

Anal. Calcd. for C$_{13}$H$_{14}$O$_3$: C, 71.54; H, 6.47. Found: C, 71.35; H, 6.49.
5,8-Dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (16). To a solution of isopropyltriphenylphosphonium bromide (9.9 g, 25.7 mmol) in anhydrous tetrahydrofuran (250 ml) at 0°C was added 20 ml of 1.29 N n-butyllithium (25.7 mmol) in hexane. After 1.5 hr at 0°C, 5,8-dimethoxy-9-benzonorbornenone (5 g, 23.4 mmol) in tetrahydrofuran (40 ml) was added dropwise. After 1 hr at 0°C, the reaction mixture was allowed to warm to room temperature and heated at reflux for 16 hr. The cooled reaction mixture was filtered through a pad of Celite and the filtrate was diluted with water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with saturated sodium bicarbonate solution, water, and brine prior to drying. After solvent removal, the residue was purified by chromatography on silica gel (benzene elution) to give 3.66 g (65%) of 16, mp 129-130°C (from ethanol); 1H NMR (δ, CDCl₃) 6.57(s, 2H), 4.0(m, 2H), 3.82(s, 6H), 1.87(m, 2H), 1.64(s, 6H), and 1.24 (m, 2H).
Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_2$: C, 78.65; H, 8.25.  
Found: C, 78.58; H, 8.28.

7-Isopropylidenebicyclo[2.2.1]hept-5-ene-endo-2-carboxylic Acid (17). A solution of 6,6-dimethylfulvene (29.7 g, 0.28 mol) and acrylic acid (20.2 g, 0.28 mol) in tetrahydrofuran (50 ml) was heated at reflux for 19 hr. The cooled reaction mixture was diluted with ether and extracted with 10% sodium hydroxide solution. The alkaline aqueous layer was washed with ether and slowly acidified with 6 N hydrochloric acid. The acidic solution was extracted three times with ether. The combined ether layers were dried and evaporated under reduced pressure to yield 32.2 g (65%) of 17 as an oil. The product was carried on to the next step without further purification. $^1\text{H NMR} (\delta, \text{CDCl}_3)$ 11.93(s, 1H), 6.03-6.35(m, 2H), 3.47-3.65(m, 1H), 3.17-3.35(m, 1H), 2.7-3.05(m, 1H), 1.66-2.4(m, 2H), and 1.55 (s, 6H).
7-Isopropylidenebicyclo[2.2.1]hept-5-en-2-one (18). A solution of lithium diisopropylamine (0.44 mol) in tetrahydrofuran (175 ml) and HMPA (35 ml) at 0°C was added dropwise with stirring to a solution of 7-isopropylidenebicyclo[2.2.1]-hept-5-ene-2-carboxylic acid (31.3 g, 0.176 mol) in tetrahydrofuran (175 ml). After 3 hr, the dianion solution was cooled to -78°C and transferred via syringe to a reaction well containing ether (500 ml) cooled to -78°C into which dry oxygen was continuously bubbled. After addition of the dianion, oxygen was bubbled through the solution at -78°C for an additional 30 min. The reaction mixture was concentrated in vacuo to 200-250 ml, diluted with ether, and poured into cold aqueous 10% hydrochloric acid (250 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined ether layers were dried and an exchange of solvent was accomplished by removal of ether in vacuo and addition of methylene chloride to maintain a volume of 200-250 ml. To this solution at -78°C under
nitrogen was added dropwise a solution of dimethyl formamide dimethylacetal (50 g, 0.42 mol) in methylene chloride (175 ml), and the reaction mixture was then allowed to warm up slowly to room temperature. Stirring was continued until the starch-iodide test for peroxides was negative. The solvent was removed and the residue was diluted with saturated sodium chloride solution and ether. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether layers were dried and evaporated under reduced pressure. The resulting residue was distilled to yield 5.47 g (21%) of a yellow oil, bp 46°C (0.3 mm) (lit. 46°C, 0.3 mm); 1H NMR (δ, CDCl₃) 6.52-6.74(m, 1H), 6.08-6.3(m, 1H), 3.43-3.72(m, 2H), 1.96-2.1(m, 2H), 1.69(s, 3H), and 1.59 (s, 3H).

**7-Isopropylidenebicyclo[2.2.1]hept-5-en-endo-2-ol (19).**

To a refluxing suspension of lithium aluminum hydride (1.3 g, 34.5 mmol) in anhydrous ether (50 ml) was added a solution of 7-isopropylidenebicyclo[2.2.1]-hept-5-en-2-one (5.1 g, 34.5 mmol) in ether (25 ml). The
suspension was refluxed for 15 hr. The reaction mixture was cooled and the excess hydride was quenched by cautious addition of small chunks of ice followed by 10% sulfuric acid solution until no precipitated salts remained. The solution was extracted three times with ether and the combined ether layers were washed with saturated sodium chloride solution prior to drying. Evaporation of the solvent gave 4.33 g (84%) of \( \text{19} \) as a white solid, which was carried on to the next step without further purification.

7-Isopropylidene-2-tosyloxybicyclo[2.2.1]hept-5-ene (20).

To a solution of 7-isopropylidene-bicyclo[2.2.1]hept-5-en-endo-2-ol (4.33 g, 28.9 mmol) in pyridine (50 ml) at \(-10^\circ\text{C}\) was added p-toluene-sulfonyl chloride (13.8 g, 72 mmol) in one portion. The flask was swirled until all had dissolved and was allowed to set at \(0^\circ\text{C}\) for 20 hr. Water was added to the cold solutions in portions \((1+1+1+2+5 \text{ ml})\) at intervals of 5 min. The solution was diluted with water (25 ml) and extracted with chloroform. The combined organic
layers were washed with cold 5% hydrochloric acid solution, water, and saturated sodium bicarbonate solution prior to drying. Evaporation of the solvent gave 6.53 g (74%) of 20 as a viscous oil, which was carried on to the next step without further purification.

7-Isopropylidenenorbornene (21). To a refluxing suspension of lithium aluminum hydride (0.82 g, 21.5 mmol) in anhydrous ether (30 ml) was added a solution of endo-7-isopropylidene-2-tosyloxybicyclo-[2.2.1]hept-5-ene (6.53 g, 21.5 mmol) in ether (40 ml). The suspension was refluxed for 16 hr. The reaction mixture was cooled and the excess hydride was quenched by cautious addition of small chunks of ice and 10% sulfuric acid solution was added until no precipitated salts remained. The solution was extracted three times with ether and the combined ether layers were washed with saturated sodium chloride solution prior to drying. Evaporation of the solvent and distillation of the residue gave 1.24 g (43%) of 21 as a yellow oil, bp 56-58°C (19 mm); (lit48 bp 70°C, 20 mm); 1H NMR (δ, CDCl₃) 6.14
(t, J = 2 Hz, 2H), 3.25(m, 2H), 1.58(s, 6H), and 0.7-1.75(m, 4H).

13-Isopropylidene-7,10-dichloro-5,6,7,10,11,12-hexahydro-
methanoanthracene (22). A thick-walled Carius tube was charged with a solution of 1,4-dihydro-9-isopropylidene-
1,4-methanonaphthalene (2.5 g, 13.6 mmol) and 1,4-dichloro-
butadiene (1.9 g, 15.6 mmol) in carbon tetrachloride (12 ml).
The tube was sealed under vacuum at -78°C and heated at 100°C in a copper tube furnace for 28 hr. Removal of the solvent gave 4.2 g (100%) of 22 which was carried on to the next step without further purification; mp 108-122°C (lit.11 mp 123-129°C); 1H NMR (δ, CDCl₃) 6.94-7.17(m, 4H), 5.81(s, 2H), 3.92-4.12(m, 2H), 3.82(s, 2H), 2.02-2.25(m, 2H), and 1.68(s, 6H).

13-Isopropylidene-1,2,3,4-tetrafluoro-7,10-dichloro-5,6,7,10,11,12-hexahydro-5,12-
methanoanthracene (27). A thick-walled Carius tube was charged with a solution of
5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-
methanonaphthalene (3.22 g, 12.7 mmol) and 1,4-dichloro-
butadiene (4.7 g, 38.2 mmol) in carbon tetrachloride
(20 ml). The tube was sealed under vacuum at -78°C and
heated at 100°C in a copper tube furnace for 30 hr. The
solvent was removed under reduced pressure. Chromato-
graphy of the residue on silica gel (petroleum ether
elution) gave 3.7 g (77%) of 27, mp 128-132°C; \(^1\)H NMR
(\(\delta\), CDCl\(_3\)) 5.83(s, 2H), 3.9-4.25(m, 4H), 2.05-2.3(m, 2H),
and 1.78(s, 6H); m/e calcd 376.0408, obs. 376.0414.

**Epoxidation of 13-Isopropylidene-1,2,3,4-tetrafluoro-7,10-
dichloro-5,6,7,10,11,12-hexahydro-5,12-methanoanthracene**

(28 and 29). A solution of
13-isopropylidene-1,2,3,4-
tetrafluoro-7,10-dichloro-
5,6,7,10,11,12-hexahydro-5,12-
methanoanthracene (0.5 g, 1.33
mmol) in methylene chloride was
reacted with m-chloroperbenzoic
acid (0.23 g, 1.33 mmol) for 16 hr at room temperature.

Water was added, the organic layer was separated, and the
aqueous layer was extracted twice with methylene chloride.
The combined organic layers were washed with saturated
sodium bicarbonate solutions and brine prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn epoxide 28: 308 mg (59.1%); mp 186-188°C (from 2-propanol); $^1$H NMR (δ, CDCl$_3$) 6.02(s, 2H), 4.1-4.33(m, 2H), 3.59(distorted t, $J_{app} = 2$Hz, 2H), 2.13-2.33(m, 2H), and 1.48(s, 6H).

Ana. Calcd. for C$_{16}$H$_{14}$Cl$_2$F$_4$O: C, 54.98; H, 3.59. Found: C, 54.70; H, 3.60.

Anti epoxide, 29: 62 mg (11.9%); $^1$H NMR (δ, CDCl$_3$) 5.90(s, 2H), 4.58-4.78(m, 2H), 3.45(distorted t, $J_{app} = 2$Hz, 2H), 2.19-2.4(m, 2H), and 1.3(s, 6H); m/e calcd. 392, obs 392.

Syn-epoxide of 13-Isopropylidene-5,6,11,12-1,2,3,4-tetrafluoro-5,6,11-12-tetrahydro-5,12-methanoanthracene (30).

A solution of syn epoxide 28 (100 mg, 0.254 mmol) in tetrahydrofuran was added dropwise to a refluxing suspension of zinc metal (83 mg, 1.27 mg-at) in tetrahydrofuran. Two additional portions of zinc metal (83 mg ea, 1.27 mg-at) were added at 45 min intervals and the reaction mixture was heated at reflux for a further 60 min after the final addition. The cooled reaction mixture
was diluted with saturated sodium chloride solution and extracted three times with ether. The combined organic layers were washed with 5% hydrochloric acid solution, saturated sodium bicarbonate solution, and brine prior to drying. Removal of the solvent gave 79.4 mg (97%) of 30 which was carried on to the next step without further purification, mp 180-195°C; \( ^1H \) NMR (\( \delta, \text{CDCl}_3 \)) 5.37-6.0 (m, 4H), 3.25 (m, 2H), 2.65 (m, 2H), and 1.35 (s, 6H); \( m/e \) calcd 322.0980, obs 322.0991.

**Syn-epoxide of 11-Isopropylidene-1,2,3,4-tetrafluoro-9,10-methanoanthracene (31).** To a solution of 31 (3.28 g, 10.2 mmol) in benzene was added 10% Pd/c (10 g) and this mixture was heated at reflux for 12 hr. The cooled reaction mixture was filtered through a pad of Celite. The solvent was removed from the filtrate and the residue was recrystallized from hot 2-propanol to yield 1.24 g (38%) of a white crystalline solid, mp 231-232°C; \( ^1H \) NMR (\( \delta, \text{CDCl}_3 \)) 7.03-7.5 (m, 4H), 4.45 (distorted t, \( J = 1 \) Hz, 2H) and 1.3 (s, 6H).
Anal. Calcd for C_{18}H_{12}F_{4}O:  C, 67.50; H, 3.78.
Found:  C, 67.25; H, 3.96.

11-Isopropylidene-1,2,3,4-tetrafluoro-9,10-dihydro-9,10-methanoanthracene (32). Tungsten hexachloride (1.6 g, 4.0 mmol) was added to 10 ml of tetrahydrofuran (freshly distilled from sodium and benzo-phenone and maintained under nitrogen) while cooled to -62°C in a Dry Ice-acetone bath. While this suspension was stirred at -62°C, 6.25 ml (10 mmol) of 1.6 M n-butyllithium in hexane was added slowly over a 5 min period. The mixture was allowed to warm slowly to room temperature. Shortly after reaching room temperature, the solution was homogeneous, at which time it was cooled to 0°C using an ice water bath. A solution of 31 (340 mg, 1.06 mmol) in tetrahydrofuran was added dropwise to the cold solution. After 45 min at 0°C, the reduction mixture was poured into 20 ml of an aqueous solution which was 1.5 M in sodium tartrate and 2 M in sodium hydroxide, and extracted three times with hexane. The combined organic layers were
washed with brine prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (petroleum ether elution) to yield 211 mg (65%) of a white crystalline solid, mp 218-219°C (from 2-propanol); $^1$H NMR ($\delta$, CDCl$_3$), 6.85-7.38 (m, 4H), 5.05 (distorted t, $J$ = 1 Hz, 2H), and 1.65 (s, 6H); m/e calcd 304.0875, obs 304.0880.

Epoxidation of 13-Isopropylidene-7,10-dichloro-5,6,7,10,11,12-hexahydro-5,12-methanoanthracene (33 and 34). A solution of 22 (250 mg, 0.814 mmol) in methylene chloride was reacted with m-chloroperbenzoic acid (141 mg, 0.814 mmol) for 17 hr at room temperature. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfate and saturated sodium bicarbonate solutions, and brine prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer
chromatography on silica gel (benzene elution). Syn epoxide: 117 mg (44.4%); mp 168-169°C (from 2-propanol); \(^1\)H NMR (\(\delta\), CDCl\(_3\)) 7.03-7.2(m, 4H), 5.95(s, 2H), 4.06-4.26 (m, 2H), 3.18(s, 2H), 2.07-2.28(m, 2H), and 1.43(s, 6H); m/e calcd. 320.0734, obs. 320.0743. Anti epoxide: 48 mg (18%); mp 111-112°C (from 2-propanol); \(^1\)H NMR (\(\delta\), CDCl\(_3\)) 7.1-7.22(m, 4H), 5.90(s, 2H), 4.66-4.85(m, 2H), 3.14(s, 2H), 2.16-2.36(m, 2H), and 1.28(s, 6H); m/e calcd 292.1463, obs. 292.1471.

**Syn-epoxide of 13-Isopropylidene-5,6,11,12-tetrahydro-5,12-methanoanthracene (35).** A solution of 33 (1.7 g, 5.23 mmol) in tetrahydrofuran was added dropwise to a refluxing suspension of zinc metal (508 mg, 7.76 mg-at) in tetrahydrofuran. Another portion of zinc (508 mg, 7.76 mg-at) was added after 45 min and the reaction mixture was refluxed for a further 60 min after the final addition. The cooled reaction mixture was diluted with saturated sodium chloride solution and extracted three times with
ether. The combined organic layers were washed with 5% hydrochloric acid solution, saturated sodium bicarbonate solution, and brine prior to drying. Removal of the solvent gave 1.32 g (100%) of 35 which was carried onto the next step without further purification. \(^1\text{H} \text{NMR (6, CDCl}_3\text{)} \) 6.9-7.1(m, 4H), 5.49-5.75(m, 4H), 2.95(s, 2H), 2.56(m, 2H), and 1.32(s, 6H).

**Syn-epoxides of 13-Isopropylidene-5,6,11,12-tetrahydro-5,12-methanoanthracene-7,10-dione and 11-Isopropylidene-5,8-dihydroxy-9,10-methanoanthracene (37 and 37a).** An ice-methanol cooled solution of 35 (590 mg, 2.34 mmol) and methylene blue (1 mg/ml) in methylene chloride (50 ml) was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution. The irradiation was carried out for 0.5 hr. Most of the solvent was removed under reduced pressure at a temperature below 15°C. The residue was dissolved in chloroform and triethylamine (222 mg, 2.2 mmol) was added. This solution was stirred
at room temperature for 12 hr, poured onto a column containing 25 g of neutral alumina (activity III), and filtered through with 150 ml of ethyl acetate. After solvent removal, the crude dark oil was dissolved in methylene chloride and stirred for 12 hr at room temperature with Attenburrow manganese dioxide (2.6 g, 30.0 mmol). After filtration and removal of solvent from the filtrate, the residue was purified by preparative layer chromatography on silica gel (chloroform elution) to yield 54 mg (8.2%) of $37^1H NMR (\delta, CDCl_3) 7.12-7.34 (m, 4H), 6.82(s, 2H), 3.55(s, 2H), 2.8(s, 2H), and 1.14 (s, 6H)]$ and 70 mg (10.6%) of $37a^1H NMR (\delta, DMSO-d_6) 8.22(br s, 2H), 6.77-7.34(m, 4H), 6.26(s, 2H), 4.35(s, 2H), and 1.28(s, 6H).

Syn-epoxide of 11-Isopropylidene-5,8-dimethoxy-9,10-methanoanthracene (38). The mixture of $37$ and $37a$ (20 mg, 0.07 mmol) and dimethyl sulfate (27 mg, 0.213 mmol) in dry tetrahydrofuran (3 ml) at 0°C under nitrogen was treated with three portions of potassium tert-butoxide (3 x 8 mg,
0.213 mmol) at 1 hr intervals. The mixture was stirred overnight and filtered through a pad of Celite. The filtrate was dried and concentrated to give a brown solid. The residue was purified by preparative layer chromatography on silica gel (chloroform elution) to give 16.7 mg (76%) of 38, mp 186-190°C (from 2-propanol); ¹H NMR (δ, CDCl₃) 6.84-7.39(m, 4H), 6.48(s, 2H), 4.33(s, 2H), 3.75(s, 6H), and 1.35(s, 6H). m/e calcd 308.1412, obs 308.1418.

11-Isopropylidene-5,8-dimethoxy-9,10-methanoanthracene (39).

Tungsten hexachloride (1.58 g, 3.98 mmol) was added to 5 ml of tetrahydrofuran (freshly distilled from sodium and benzophenone and maintained under nitrogen while cooled to -62°C in a Dry Ice-acetone bath. While this suspension was stirred at -62°C, 8.32 ml (9.96 mmol) of 1.2 M n-butyllithium in hexane was added slowly over a 5 min period. The mixture was allowed to warm slowly to room temperature. Shortly after reaching room temperature, the
solution was homogeneous, at which time it was cooled to
0°C using an ice water bath. A solution of 38 (122 mg,
0.39 mmol) in tetrahydrofuran was added dropwise to the
cold solution. After 30 min at 0°C, the mixture was
allowed to warm to room temperature. After 2.5 hr at room
temperature, the reduction mixture was poured into 25 ml
of an aqueous solution which was 1.5 M in sodium tartrate
and 2 M in sodium hydroxide, and extracted three times
with hexane. The combined organic layers were washed
with brine prior to drying. After removal of solvent,
the residue was purified by preparative layer chromato-
graphy on silica gel (chloroform elution) to yield 91 mg
(79%) of a white crystalline solid, mp 223-224°C; 1H NMR
(δ, CDCl₃), 7.14-7.34(m, 2H), 6.75-6.95(m, 2H), 6.4(s, 2H),
4.96(s, 2H), 3.75(s, 6H), 1.58(s, 6H); m/e calcd 292.1463,
obsv 292.1471.

5,8-Dimethoxy-1,2,3,4-tetrahydro-9-syn(anti)hydroxy-9-
anti(syn)-isopropenyl-1,4-methanonaphthalene (40 and 41).

A. A solution of 5,8-
dimethoxy-1,2,3,4-tetra-
hydro-9-isopropylidene-
1,4-methanonaphthalene
(100 mg, 0.41 mmol) and
rose bengal (1 mg/ml) in
in methanol was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The photolysis was carried out for 8 hr, at which time the reaction mixture was treated with sodium borohydride (155 mg, 4.1 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After the removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn hydroxy isomer: 15.6 mg (14.6%); mp 123-125°C (from ethanol); $^1$H NMR ($\delta$, CDCl$_3$) 6.7(br s, 2H), 5.17(m, 1H), 5.05(m, 1H), 3.80(s, 6H), 3.55(m, 2H), 1.88(br s, 3H), 1.7-2.0(m, 2H), 1.67(br s, 1H), and 1.0-1.3(m, 2H); m/e calcd 260.1412, obs 260.1417.

Anti hydroxy isomer: 41.8 mg (39%); mp 127-128°C (from ethanol); $^1$H NMR ($\delta$, CDCl$_3$) 6.57(s, 2H), 4.88(m, 1H), 4.7(m, 1H), 3.78(s, 6H), 3.46 (distorted t, $\tilde{J}$ = 2Hz, 2H), 2.15-2.45(m, 2H), 1.72(m, 4H), and 1.1-1.4(m, 2H).
Anal. Calcd for C_{16}H_{20}O_{3}: C, 73.82; H, 7.74.
Found: C, 73.87; H, 7.73.

B. A solution of 5,8-
I dimethoxy-1,2,3,4-tetra-
hydro-9-isopropylidene-
1,4-methanonaphthalene
(50 mg, 0.205 mmol) and
polymeric bound rose bengal
(200 mg) and dichloro-
methane (10 ml) was irradiated with a 500 W tungsten
filament projector bulb while oxygen was bubbled through
the solution which was being cooled by an ice water bath.
The irradiation was carried out for 3 hr, at which time
the polymeric bound rose bengal was filtered. The solvent
was removed from the filtrate and the resulting residue
was dissolved in methanol (15 ml). The solution was
treated with sodium borohydride (78 mg, 2.05 mmol) and
stirred at room temperature for 12 hr. The solvent was
removed under reduced pressure and the resulting residue
was dissolved in ether and water. The organic layer was
separated and the aqueous layer was extracted twice with
ether. The combined organic layers were washed with 5%
sodium hydroxide solution and water prior to drying. Removal of the solvent yielded a residue, 44 mg (82.5%), which was similar to that previously obtained.

C. To an ice cold solution of lithium diethylamide (1.9 mmol), prepared from diethylamine (0.14 g, 1.9 mmol) and 1.2 ml (1.9 mmol) of 1.6 M n-butyllithium, was added a mixture of 5,8-dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene syn(anti)-oxides, (54 and 55, 50 mg, 0.19 mmol) in anhydrous ether (5 ml). After the addition, the solution was allowed to warm to room temperature and stirred for 12 hr. Water was added, the organic layer was separated, and the aqueous phase was extracted twice with ether. The combined organic layers were washed with 10% ammonium chloride solution, saturated sodium bicarbonate solution, and water prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn isomer 40: 3 mg (6%); anti isomer 41: 28 mg (56%).
A. A solution of 1, 2, 3, 4-tetrahydro-9-isopropylidene-1, 4-methanonaphthalene (72.5 mg, 0.394 mmol) and rose bengol (1 mg/ml) in methanol was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 6 hr, at which time the reaction mixture was heated with sodium borohydride (149 mg, 3.94 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After the removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn hydroxy isomer: 7.8 mg (9.9%); mp 83-83.5°C (from
petroleum ether); $^1$H NMR (δ, CDCl$_3$) 7.23 (br s, 4H), 5.16 (m, 1H), 5.06 (m, 1H), 3.35 (distorted t, $J$ = 2Hz, 2H), 1.94-2.27 (m, 2H), 1.94 (m, 3H), 1.65 (s, 1H), and 1.0-1.3 (m, 2H).

**Anal.** Calc for C$_{14}$H$_{16}$O: C, 83.96; H, 8.05.

Found: C, 84.03; H, 8.04.

Anti hydroxy isomer: 29.5 mg (37.4%); mp 128.5-129°C (from petroleum ether); $^1$H NMR (δ, CDCl$_3$) 7.08 (s, 4H), 4.8 (m, 1H), 4.7 (m, 1H), 3.2 (m, 2H), 2.1-2.45 (m, 2H), 1.72 (m, 4H), and 1.0-1.3 (m, 2H); m/e calcd 200.1201, obs 200.1204.

B. A solution of 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (75 mg, 0.41 mmol) and polymeric bound rose bengal (200 mg) and dichloromethane (10 ml) was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 3 hr, at which time the polymeric bound rose bengal was filtered. The solvent was removed from
the filtrate and the resulting residue was dissolved in methanol (15 ml). The solution was treated with sodium borohydride (90 mg, 2.38 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. Removal of the solvent yielded a residue, 32 mg (40%), which was similar to that previously obtained.

C. To an ice cold solution of lithium diethylamide (4.2 mmol), prepared from diethylamine (0.31 g, 4.2 mmol) and 2.62 ml (4.2 mmol) of 1.6 M n-butyllithium, was added a mixture of 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene-syn(anti)-oxides, (56 and 57, 0.84 g, 2.5 mmol) in anhydrous ether (50 ml). After the addition, the solution was allowed to warm to room temperature and
stirred for 12 hr. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 10% ammonium chloride solution, saturated sodium bicarbonate solution, and water prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn isomer 42: 80.6 mg (9.6%); anti isomer 43: 565 mg (67%).

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-syn(anti)-hydroxy-9-anti(syn)-isopropenyl-1,4-methanonaphthalene (44 and 45). A. A solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (100 mg, 0.39 mmol) and rose bengal (1 mg/ml) in methanol was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 12 hr, at which time the reaction mixture
was treated with sodium borohydride (147 gm, 3.9 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After the removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn hydroxy isomer: 32.5 mg (30%); mp 130-130.5°C (from petroleum ether); \(^1\)H NMR (\(\delta\), CDCl\(_3\)) 5.0-5.15(m, 2H), 3.62(m, 2H), 1.92-2.2(m, 2H), 1.92(m, 3H), 1.45(br s, 1H), and 1.3-1.07(m, 2H).

**Anal. Calcd for C\(_{14}\)H\(_{12}\)F\(_4\)O:** C, 61.77; H, 4.44.

**Found:** C, 61.23; H, 4.55.

Anti hydroxy isomer: 20.2 mg (19%); mp 86-88.5°C; \(^1\)H NMR (\(\delta\), CDCl\(_3\)) 4.90-4.72(m, 2H), 3.55(m, 2H), 2.25-2.5(m, 2H), 1.72(m, 4H), and 1.15-1.43(m, 2H); m/e calcd 272.0824, obs 272.0833.

B. A solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (75 mg, 0.29 mmol) and
polymeric bound rose bengal (200 mg) and dichloromethane (10 ml) was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution which was being cooled by an ice water bath. The irradiation was carried out for 6 hr, at which time the polymeric bound rose bengal was filtered. The solvent was removed from the filtrate and the resulting residue was dissolved in methanol (15 ml). The solution was treated with sodium borohydride (111 mg, 2.93 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. Removal of the solvent yielded a residue, 59.2 mg (74.3%), which was similar to that previously obtained.

C. To an ice cold solution of lithium diethylamide (5.2 mmol), prepared from diethylamine (0.38 g, 5.2 mmol) and 3.2 ml (5.2 mmol) of 1.6 M n-butyl lithium, was added a mixture of
5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene syn(anti)-oxides (58 and 59, 151.4 mg, 0.56 mmol) in anhydrous ether (15 ml). After the addition, the solution was allowed to warm to room temperature and stirred for 12 hr. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 10% ammonium chloride solution, saturated sodium bicarbonate solution, and water prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (chloroform elution). Syn isomer 44: 29 mg (19.3%); anti isomer 46: 46 mg (30.4%).

5,6,7,8-Tetrachloro-1,2,3,4-tetrahydro-9-syn(anti)-hydroxy-9-anti(syn)-isopropenyl-1,4-methanonaphthalene (46 and 47).

A. A solution of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (100 mg, 0.31 mmol) and rose bengal (1 mg/ml) in methanol was irradiated
with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 12 hr at which time the reaction mixture was treated with sodium borohydride (117 mg, 3.1 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After the removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (chloroform elution). Syn hydroxy isomer: 21.8 mg (21%); mp 143.5-144.5°C (from hexane); $^1$H NMR ($\delta$, CDCl$_3$) 5.02-5.20(m, 2H), 3.63(distorted t, $J = 2$Hz, 2H), 1.9-2.2(m, 2H), 1.9(m, 3H), 1.50(br s, 1H), and 1.0-1.3(m, 2H).

**Anal.** Calcd for C$_{14}$H$_{12}$Cl$_4$O: C, 49.74; H, 3.58.

Found: C, 49.89; H, 3.76.

Anti hydroxy isomer: 17.1 mg (16.5%); mp 118-119.5°C (from petroleum ether); $^1$H NMR ($\delta$, CDCl$_3$) 4.83(m, 1H), 4.72 (m, 1H), 3.54(m, 2H), 2.27-2.53(m, 2H), 1.70(m, 4H), and 1.15-1.37(m, 2H); $m/e$ calcd 355.9642, obs 335.9650.
B. A solution of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (75 mg, 0.233 mmol) and polymeric bound rose bengal (200 mg) and dichloromethane (15 ml) was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 5 hr, at which time the polymeric bound rose bengal was filtered. The solvent was removed from the filtrate and the resulting residue was dissolved in methanol (15 ml). The solution was treated with sodium borohydride (88 mg, 2.33 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. Removal of the solvent yielded a residue, 45.5 mg (58%), which was similar to that previously obtained.
C. To an ice cold solution of lithium diethylamide (3 mmol), prepared from diethylamine (0.22 g, 3 mmol) and 3.5 ml (3 mmol) of 0.86 M \( n \)-butyllithium, was added a mixture of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropyldene-1,4-methanonaphthalene syn(anti)-oxides (60 and 61, 100 mg, 0.3 mmol) in anhydrous ether (10 ml). After the addition, the solution was allowed to warm to room temperature and stirred for 12 hr. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 10% ammonium chloride solution, saturated sodium bicarbonate solution, and water prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (chloroform elution). Syn isomer 46: 13.5 mg (13.5%); anti isomer 47: 39.9 mg (39.9%).
A solution of 1,2,3,4-tetrahydro-9-syn(anti)-hydroxy-9-anti-(syn)-vinyl-1,4-methanonaphthalene (48 and 49). A solution of 1,2,3,4-tetrahydro-9-ethyldene-1,4-methanonaphthalene (100 mg, 0.59 mmol) and rose bengal (1 mg/ml) in methanol was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 4 days at which time the reaction mixture was treated with sodium borohydride (223 mg, 5.9 mmol) for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was reextracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After the removal of the solvent, the residue was purified and the isomers were separated by preparative layer chromatography (benzene elution). The isomers were further purified by preparative vpc (12 ft x 0.25 in. 5% SF96 on Chromosorb G, 140°C). Syn isomer:
7.63 mg (7%); mp 57.5-58.5°C; \(^1\)H NMR (δ, CDCl₃) 7.21 (m, 4H), 6.0-6.5 (series of m, 1H), 5.17-5.73 (series of m, 2H), 3.12 (distorted t, \(J = 2\) Hz, 2H), 1.92-2.28 (m, 2H), 1.76 (s, 1H), and 1.04-1.4 (m, 2H); m/e calcd 186.1044, obs 186.1048. Anti isomer: 30.5 mg (28%); mp 86-87°C; \(^1\)H NMR (δ, CDCl₃) 7.03 (s, 4H), 5.55-6.05 (series of m, 1H), 4.84-5.42 (series of m, 2H), 3.03 (t, \(J = 2\) Hz, 2H), 2.17-2.5 (m, 2H), 1.86 (s, 1H), and 1.1-1.4 (m, 2H).

**Anal.** Calcd for C₁₃H₁₄O: C, 83.83; H, 7.58. Found: C, 83.47; H, 7.49.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-syn-(anti)-hydroxy-9-anti-(syn)-vinyl-1,4-methanonaphthalene (50 and 51).

A solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-ethylidene-1,4-methanonaphthalene (82 mg, 0.34 mmol) and rose bengal (1 mg/ml) in methanol was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 5 hr.
at which time the reaction mixture was treated with sodium borohydride (128 mg, 3.4 mmol) and stirred at room temperature for 12 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After the removal of solvent, the residue was purified and the isomers separated by preparative vpc (12 ft x 0.25 in. 5% SF 96 on Chromosorb G, 140°C). Syn isomer: 23.2 mg (26.6%); mp 71-74°C; \(^1H\) NMR (\(\delta\), CDCl\(_3\)) 5.95-6.48(series of m, 1H), 5.18-5.69(series of m, 2H), 3.44(m, 2H), 1.83-2.32(m, 2H), 1.58(br s, 1H), and 1.0-1.37(m, 2H).

**Anal.** Calcd for C\(_{13}\)H\(_{10}\)F\(_4\)O: C, 60.47; H, 3.90.

Found: C, 60.60; H, 4.12.

Anti isomer: 18.6 mg (21.4%); mp 55.5-57°C; \(^1H\) NMR (\(\delta\), CDCl\(_3\)) 5.58-6.08(series of m, 1H), 4.93-5.45(series of m, 2H), 3.37(m, 2H), 2.26-2.54(m, 2H), 1.84(s, 1H), and 1.08-1.42(m, 2H); m/e calcd 258.0667, obs 258.0673.
7-anti-Hydroxy-7-syn-isopropenynorbornene (53) and
7-syn-Hydroxy-7-anti-isopropenynorbornene (52).

A. A solution of 7-isopropylidenenorbornene (50 mg, 0.373 mmol) and rose bengal (1 mg/ml) in methanol was irradiated with a 500 W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 2 hr at which time the reaction mixture was treated with sodium borohydride (140 mg, 3.73 mmol) and stirred at room temperature for 4 hr. The solvent was removed under reduced pressure and the resulting residue was dissolved in ether and water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn hydroxy isomer 52:
5 mg (9%); \(^1\)H NMR (\(\delta, \text{CDCl}_3\)) 6.08 (t, \(J = 2\) Hz, 2H), 4.98 (m, 2H), 2.82 (m, 2H), 1.8 (m, 3H), and 0.88-2.15 (series of m, 5H). Anti hydroxy isomer \(53\); 18 mg (32%); \(^1\)H NMR (\(\delta, \text{CDCl}_3\)) 5.92 (t, \(J = 2\) Hz, 2H), 4.86 (m, 2H), 2.7 (m, 2H), 1.78 (m, 3H), and 0.82-2.2 (series of m, 5H).

B. To an ice cold solution of lithium diethylamide (2.23 mmol), prepared from diethylamine (163 mg, 2.23 mmol) and 1.4 ml (2.23 mmol) of 1.6 M n-butyl-lithium, was added a mixture of 7-isopropylidenenorbornene syn(anti)-oxides (62 and 63, 99 mg, 0.66 mmol) in anhydrous ether (5 ml). After the addition, the solution was allowed to warm to room temperature and stirred for 12 hr. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 10% ammonium chloride solution, saturated sodium bicarbonate solution, and water prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative
layer chromatography on silica gel (benzene elution). Syn isomer 52: 11 mg (11%); anti isomer 53: 30 mg (30%).

5,8-Dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-14-methanonaphthalene syn (anti)-oxides (54 and 55). A solution of 5,8-dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (0.94 g, 3.85 mmol) in methylene chloride was reacted with M-chloroperbenzoic acid (0.73 g, 4.24 mmol) for 12 hr at room temperature. Water was added, the organic layer was separated and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, and brine prior to drying. After the removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn epoxide: 60 mg (6%); mp 160-162°C; $^1$H NMR ($\delta$, CDCl$_3$) 6.63(s, 2H), 3.80(s, 6H), 3.24(m, 2H), 1.77 (m, 2H), 1.40(s, 6H), and 1.1-1.5(m, 2H); m/e calcd 260.1412, obs 260.1417.
Anti epoxide: 620 mg (62%); mp 138.5-139°C (from ethanol); 
\(^1\)H NMR (δ, CDCl\(_3\)) 6.63 (s, 2H), 3.80 (s, 6H), 3.20 (m, 2H), 2.02-2.4 (m, 2H), 1.15-1.43 (m, 2H), and 1.34 (s, 6H). 

Anal. Calcd for C\(_{16}\)H\(_{20}\)O\(_3\): C, 73.82; H, 7.74. 
Found: C, 73.92; H, 7.73.

1,2,3,4-Tetrahydro-9-isopropylidene-1,4-methanonaphthalene syn(anti)-Oxides (56 and 57). A solution of 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (1 g, 5.43 mmol) in methylene chloride was reacted with \textit{m}-chloroperbenzoic acid (1.03 g, 5.97 mmol) for 12 hr at room temperature. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, and brine prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn epoxide: 50 mg (4.6%);
mp 96-115°C; \(^1\)H NMR (\(\delta\), CDCl\(_3\)) 7.15 (br s, 4H), 3.0 (m, 2H), 1.83-2.15 (m, 2H), 1.4 (s, 6H), and 1.05-1.48 (m, 2H); m/e calcd 200.1201, obs 200.1204.

Anti epoxide: 440 mg (40.5%); mp 134-134.5°C (from ethanol); \(^1\)H NMR (\(\delta\), CDCl\(_3\)) 7.15 (s, 4H), 2.98 (m, 2H), 2.05-2.48 (m, 2H), 1.06-1.42 (m, 2H), and 1.32 (s, 6H).

**Anal.** Calcd for C\(_{14}\)H\(_8\)O: C, 83.96; H, 8.05.

**Found:** C, 83.81; H, 8.07.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene syn(anti)-Oxides (58 and 59).

A solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (277 mg, 1.08 mmol) in methylene chloride was reacted with m-chloroperbenzoic acid (224 mg, 1.3 mmol) for 12 hr at room temperature. Water was added, the organic layer was separated and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfite solution, saturated
sodium bicarbonate solution, and brine prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (petroleum ether–benzene (4:1) elution).

Syn epoxide: 108 mg (36.5%); mp 91–94°C (from 2-propanol); $^1$H NMR ($\delta$, CDCl$_3$) 3.19–3.4(m, 2H), 1.9–2.35(m, 2H), 1.16–1.47(m, 2H), and 1.43(s, 6H); m/e calcd 272.0824, obs 272.0833.

Anti epoxide: 120 mg (40.6%); mp 106.5–107°C (from 2-propanol); $^1$H NMR ($\delta$, CDCl$_3$) 3.08–3.28(m, 2H), 2.05–2.37 (m, 2H), 1.06–1.43(m, 2H), and 1.37(s, 6H).

Anal. Calcd for C$_{14}$H$_{12}$F$_4$: C, 61.77; H, 4.44. Found: C, 61.41; H, 4.62.

5,6,7,8-Tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene syn(anti)-Oxides (60 and 61).

A solution of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (75 mg, 0.233 mmol) in methylene chloride was reacted with m-chloroperbenzoic acid (44 mg,
0.26 mmol) for 20 hr at room temperature. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, and brine prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (petroleum ether-benzene (4:1) elution). Syn epoxide: 33 mg (41%); mp 183-184°C (from 2-propanol); \( ^1H \text{ NMR (}\delta, \text{CDCl}_3) 3.15-3.32(m, 2H), 2.0-2.28(m, 2H), 1.13-1.5(m, 2H), \) and 1.4(s, 6H); m/e calcd 335.9642, obs 335.9650.

Anti epoxide: 45.4 mg (57%); mp 165.5-166°C (from 2-propanol); \( ^1H \text{ NMR (}\delta, \text{CDCl}_3) 3.27 \) (distorted t, \( J = 2Hz, 2H), 2.17-2.47(m, 2H), 1.15-1.53(m, 2H), \) and 1.35(s, 6H).

**Anal. Calcd for C\(_{14}\)H\(_{12}\)Cl\(_4\)O: C, 49.74; H, 3.58.**

**Found: C, 49.83; H, 3.66.**

7-Isopropylidenenorbornene syn(anti)-Oxides (62 and 63).

A solution of 7-isopropylidenenorbornene (100 mg, 0.75 mmol) in methylene chloride cooled to -23°C using a dry-ice carbon-tetrachloride bath was
reacted with m-chloroperbenzoic acid (129 mg, 0.75 mmol) for 2 hr at -23°C and then for 12 hr at room temperature. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, and brine prior to drying. After removal of solvent, the residue was analyzed by $^1$H NMR spectroscopy and then carried on, without further purification, to the base promoted opening to the allylic alcohol.

1,2,3,4-Tetrafluoro-9,10-dihydro-11-isopropylidene-9,10-methanoanthracene-syn(anti)-oxides (31 and 64). A solution of 1,2,3,4-tetrafluoro-9,10-dihydro-11-isopropylidene-9,10-methanoanthracene (40 mg, 0.13 mmol) in methylene chloride was reacted with m-chloroperbenzoic acid (25 mg, 0.14 mmol) for 18 hr at room temperature. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined
organic layers were washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, and brine prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn epoxide: 28.8 mg (68.4%); mp 231-232°C (from isopropanol): $^1$H NMR ($\delta$, CDCl$_3$) 7.03-7.5 (m, 4H), 4.45 (distorted t, $\delta$ = 1 Hz, 2H), and 1.3 (s, 6H).

Anal. Calcd for C$_{18}$H$_{12}$F$_4$O: C, 67.50; H, 3.78. Found: C, 67.25; H, 3.96.

Anti epoxide: 9.9 mg (23.5%); mp 145-150°C; $^1$H NMR ($\delta$, CDCl$_3$) 7.03-7.5 (m, 4H), 4.45 (distorted t, $\delta$ = 1 Hz, 2H), and 1.34 (s, 6H); m/e calcd 320, obs 320.

5,8-Dimethoxy-1,2,3,4-tetrahydro-9-synthesis(bromo-9-anti-(syn)-isopropenyl-1,4-methanonaphthalene (65 and 66). A solution of 5,8-dimethoxy 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (75 mg, 0.31 mmol) in 10% aqueous glyme (5 ml) was reacted with N-bromosuccinimide (63 mg, 0.36 mmol) for 12 hr at room temperature. The reaction mixture was treated with 10% sodium bisulfite solution and
stirred for 15 min, at which time most of the solvent was removed under reduced pressure. The resulting residue was diluted with water and extracted three times with chloroform. The combined organic layers were washed with saturated sodium chloride solution prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (petroleum ether, followed by petroleum ether-benzene (4:1), and finally benzene elution). Syn bromide: trace; $^1$H NMR ($\delta$, CDCl$_3$) 6.60(s, 2H), 5.25(m, 1H), 5.05(m, 1H), 3.80(s, 6H), 3.5(m, 2H), 2.0(m, 3H), 1.80-2.2 (m, 2H), and 1.0-1.4 (m, 2H).

Anti bromide: 28.9 mg (29%); mp 126-126.5°C (from petroleum ether); $^1$H NMR ($\delta$, CDCl$_3$) 6.6(s, 2H), 4.9(m, 1H), 4.7(m, 1H), 3.8(s, 6H), 3.45(m, 2H), 2.1-2.5(m, 2H), 1.70 (m, 3H), and 1.0-1.4 (m, 2H); m/e calcd 322.0568, obs 322.0576.

1,2,3,4-Tetrahydro-9-syn(anti)-bromo-9-anti(syn)-isopropenyl-1,4-methanonaphthalene (67 and 68). A solution of 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (430 mg, 2.34 mmol) in 10% aqueous glyme (15 ml) was reacted with
N-bromosuccinimide (479 mg, 2.69 mmol) for 4 hr at room temperature. The reaction mixture was treated with 10% sodium bisulfite solution and stirred for 15 min, at which time most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted three times with chloroform. The combined organic layers were washed with saturated sodium chloride solution prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4) elution). Syn bromide: 32 mg (5%); mp 146-148.5°C (from ethanol); $^1$H NMR ($^6$, CDCl$_3$) 7.17(s, 4H), 5.2 (m, 1H), 4.98(m, 1H), 3.65(distorted t, $J$ = 2Hz, 2H), 1.82-2.17(m, 2H), 2.0(m, 3H), and 1.0-1.35(m, 2H); m/e calcd 262.0357, obs 262.0364.

Anti bromide: 264 mg (40%); mp 158.5-159°C (from petroleum ether); $^1$H NMR ($^6$, CDCl$_3$) 7.08(s, 4H), 4.83(m, 1H), 4.7 (m, 1H), 3.21(distorted t, $J$ = 2 Hz, 2H), 2.1-2.45(m, 2H), 1.69(m, 3H), and 1.0-1.3(m, 2H).

**Anal. Calcd for C$_{14}$H$_{15}$Br: C, 63.89; H, 5.74.**

**Found:** C, 63.69; H, 5.86.
A solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-syn(anti)-brom-9-anti(syn)-isopropenyl-1,4-methanonaphthalene (69 and 70) in 10% aqueous glyme (5 ml) was reacted with N-bromosuccinimide (65 mg, 0.37 mmol) for 12 hr at room temperature. The reaction mixture was treated with 10% sodium bisulfite solution and stirred for 15 min, at which time most of the solvent was removed under reduced pressure. The resulting residue was diluted with water and extracted three times with chloroform. The combined organic layers were washed with saturated sodium chloride solution prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (petroleum ether elution). Syn bromide: 21.6 mg (20.2%); mp 134-135.5°C (from petroleum ether); $^1$H NMR (δ, CDCl₃) 4.94-5.32 (m, 2H), 3.99 (m, 2H), 1.9-2.34 (m, 2H), 2.0 (m, 3H), and 1.04-1.43 (m, 2H).

Found: C, 50.15; H, 3.34.

Anti bromide: 12.9 mg (12%); mp 138-139°C (from petroleum ether); ¹H NMR (δ, CDCl₃) 4.63-4.9 (m, 2H), 3.82 (m, 2H), 2.34-2.68 (m, 2H), 1.75 (m, 3H), and 1.18-1.48 (m, 2H); m/e calcd 333.9980, obs 333.9988.

5,6,7,8-Tetrachloro-1,2,3,4-tetrahydro-9-syn(anti)-bromo-9-anti(syn)-isopropenyl-1,4-methanonaphthalene (71 and 72).

A solution of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (44 mg, 0.137 mmol) in 10% aqueous glyme (5 ml) was reacted with N-bromo-succinimide (28 mg, 0.16 mmol) for 18 hr at room temperature. The reaction mixture was treated with 10% sodium bisulfite solution and stirred for 15 min, at which time most of the solvent was removed under reduced pressure. The resulting residue was diluted with water and extracted three times with chloroform. The combined organic layers were washed with saturated sodium chloride solution prior to drying. After removal of solvent, the
residue was purified and the isomers were separated by preparative layer chromatography on silica gel (petroleum ether elution). Syn bromide: 20 mg (36%); mp 143-143.5°C (from petroleum ether); $^1$H NMR ($\delta$, CDCl$_3$) 5.26 (m, 1H), 5.08 (m, 1H), 4.0 (m, 2H), 1.88-2.28 (m, 2H), 2.0 (m, 3H), and 1.14-1.42 (m, 2H).

**Anal.** Calcd for C$_{14}$H$_{11}$Cl$_4$Br: C, 41.94; H, 2.76.

Found: C, 41.75; H, 2.90.

Anti bromide: 20.3 mg (37%); mp 185-186°C (from petroleum ether); $^1$H NMR ($\delta$, CDCl$_3$) 4.95 (m, 1H), 4.75 (m, 1H), 3.93 (m, 2H), 2.3-2.7 (m, 2H), 1.73 (m, 3H), 1.1-1.4 (m, 2H);

m/e calc 397.8798, obs 397.8805.

5,8-Dimethoxy-1,2,3,4-tetrahydro-9-anti(syn)-isopropenyl-9-syn(anti)-[1'-(4'-methyl-1',2',4'-triazoline-3',5'-dione)]-1,4-methanonaphthalene (73 and 74). 5,8-Dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (66 mg, 0.27 mmol) in anhydrous ether (5 ml) was treated with 4-methyl-1,2,4-triazoline-3,5-dione (30.6 mg, 0.27 mmol) in
anhydrous methylene chloride (5 ml) at room temperature. After 12 hr, the solvent was removed and the residue was recrystallized from hot ethyl acetate to yield 55 mg (57%) of the anti isomer, mp 250-251.5°C; $^1$H NMR ($\delta$, CF$_3$CO$_2$D) 6.87(s, 2H), 5.05(m, 1H), 4.88(m, 1H), 4.35(m, 2H), 4.96(s, 6H), 3.21(s, 3H), 2.41-2.12(m, 2H), 1.7(m, 3H), and 1.29-1.7(m, 2H); m/e calcd 357.1688, obs 357.1695. From the mother liquor was isolated the syn isomer; 9 mg (9.4%); mp 203-236°C; $^1$H NMR ($\delta$, CF$_3$CO$_2$D) 6.98(s, 2H) 5.27-5.48(m, 2H), 4.45(m, 2H), 4.03(s, 6H), 3.05(s, 3H), 2.05-2.41(m, 2H), 1.92(m, 3H), and 1.21-1.53(m, 2H); m/e calcd 357.1698, obs 357.1695.

$^{1234}$-Tetrahydro-9-anti(syn)-isopropenyl-9-syn(anti)-[1'-(4'-methyl-1',2',4'-triazoline-3',5'dione)]-4-methanonaphthalene (75 and 76). $^{1234}$-Tetrahydro-9-isopropylidene-1,4-methanonaphthalene (46.5 mg, 0.253 mmol) in anhydrous ether (10 ml) was treated with 4-methyl-1,2,4-triazoline-3,5-dione (28.5 mg, 0.253 mmol) in anhydrous methylene
chloride (10 ml) at room temperature. After 4 hr, the solvent was removed and the residue was recrystallized from hot methanol:acetic acid (1:1) to yield 46 mg (61%) of the anti isomer, mp 318-321°C; $^1$H NMR (δ, CF$_3$CO$_2$D) 7.15 (s, 4H), 5.03(m, 1H), 4.87(m, 1H), 4.07(m, 2H), 3.23(s, 3H), 2.02-2.39(m, 2H), 1.74(m, 3H), and 1.27-1.74(m, 2H).

Anal. Calcd for C$_{17}$H$_{19}$N$_2$O: C, 68.67; H, 6.44. Found: C, 68.97; H, 6.62.

From the mother liquor was isolated the syn isomer: 10 mg (13%); mp 250-260°C; $^1$H NMR (δ, CF$_3$CO$_2$D) 7.15(br s, 4H), 5.19-5.4(m, 2H), 4.07(m, 2H), 3.0(s, 3H), 1.9-2.3(m, 2H), 1.92(m, 3H), and 1.27-1.74(m, 2H); m/e calcd 297.1477, obs 297.1483.

5,6,7,8-Tetrafluoro-1,2,3,4-Tetrahydro-9-anti(syn)-isopropenyl-9-syn(anti)-[1'-(4'-methyl-1',2',4'-triazoline-3',5'-dione)]-1,4-methanonaphthalene (77 and 78). 5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (200 mg, 0.78 mmol) in anhydrous ether (15 ml) was treated with 4-methyl-1,2,4-
triazoline-3,5-dione (88 mg, 0.78 mmol) in anhydrous methylene chloride (15 ml) at room temperature. After 12 hr, the solvent was removed, the residue was purified, and the isomers were separated by preparative layer chromatography on silica gel (ether elution). Syn isomer: 182 mg (63%); mp 236-237°C (from ethanol); $^1H$ NMR (δ, CDCl$_3$) 9.37 (br s, 1H), 5.18 (m, 2H), 4.37 (m, 2H), 2.93 (br s, 3H), 1.6-2.25 (m, 2H), 1.8 (m, 3H), and 1.02-1.48 (m, 2H).

Anal. Calcd for C$_{17}$H$_{15}$F$_4$N$_2$O$_2$: C, 55.29; H, 4.09. Found: C, 55.18; H, 4.17.

Anti isomer: 104 mg (36%); mp 248-285°C (from ethanol); $^1H$ NMR (δ, CDCl$_3$) 9.56 (br s, 1H), 4.9 (m, 1H), 4.77 (m, 1H), 4.3 (m, 2H), 3.05 (s, 3H), 2.08-2.38 (m, 2H), 1.6 (m, 3H), and 1.08-1.48 (m, 2H); m/e calcd 369.1100, obs 369.1107.

5,6,7,8-Tetrachloro-1,2,3,4-tetrahydro-9-anti(syn)-isopropenyl-9-syn(anti)-[1'-(4'-methyl-1',2',4'-triazoline-3',5'-dione)]-1,4-methanonaphthalene (79 and 80). 5,6,7,8-Tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (200 mg, 0.62 mmol) in anhydrous ether (15 ml) was treated
with 4-methyl-1,2,4-triazoline-3,5-dione (100 mg, 0.88 mmol) in anhydrous methylene chloride (15 ml) at room temperature. After 4 hr, the solvent was removed, the residue was purified, and the isomers were separated by preparative layer chromatography on silica gel (ether elution). Syn isomer: 139 mg (51.5%); mp 273-277°C (from ethanol); $^1$H NMR ($\delta$, CDCl$_3$) 5.17 (m, 2H), 4.3 (m, 2H), 2.94 (s, 3H), 1.96-2.3 (m, 2H), 1.83 (m, 3H), and 1.1-1.45 (m, 2H).

Anal. Calcd for C$_{17}$H$_{15}$Cl$_4$N$_3$O$_2$: C, 46.92; H, 3.47. Found: C, 46.92; H, 3.49.

Anti isomer: 89.4 mg (33%); mp 215-218°C; $^1$H NMR ($\delta$, CDCl$_3$) 4.9 (m, 1H), 4.77 (m, 1H), 4.33 (m, 2H), 3.03 (s, 3H), 2.0-2.43 (m, 2H), 1.63 (m, 3H), and 1.1-1.43 (m, 2H); m/e calcd 432.9918, obs 432.9927.

7-anti(syn)-Isopropenyl-7-syn(anti)-[1'(4'-methyl-1',2',4'-triazoline-3',5'-dione)]-norbornene (81 and 82).

7-Isopropylidenenorbornene (300 mg, 2.24 mmol) in anhydrous ether (6 ml) was treated with 4-methyl-1,2,4-triazoline-3,5-dione (253 mg, 2.24 mmol) in anhydrous methylene chloride
(6 ml) at room temperature. After 1 hr, the solvent was removed and the residue was recrystallized from hot ethyl acetate to yield 425 mg (77%) of the anti isomer, mp 244.5-246°C; 1H NMR (δ, CDCl3) 9.7 (br s, 1H), 6.0 (m, 2H), 5.06 (m, 1H), 4.93 (m, 1H), 3.33-3.77 (m, 2H), 3.07 (s, 3H), 1.75-2.23 (m, 2H), 1.75 (br s, 3H), and 0.95-1.37 (m, 2H).

Anal. Calcd for C_{13}H_{17}N_{3}O_{2}: C, 63.14; H, 6.93.

Found: C, 62.98, H, 6.95.

The syn isomer could not be isolated, but its endocyclic olefinic protons could be observed in the 1H NMR spectrum of the crude product at δ 6.14.

5,8-Dimethoxy-1,2,3,4-tetrahydro-11-syn-9-acetyl-anti-9-isopropenyl-1,4-methanonaphthalene (83). A. To a stirred suspension of aluminum chloride (155 mg, 1.16 mmol) in dichloromethane (8 ml) was added a solution of acetyl chloride (101 mg, 1.29 mmol) in dichloromethane (10 ml). Most of the aluminum chloride dissolved. The stirred mixture was cooled in an ice-salt bath to -15°C and to this mixture
was added 5,8-dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (250 mg, 1.03 mmol) in dichloromethane (10 ml) over a 15 min period. After completion of the addition, the mixture was stirred at -10°C for 5 min, poured onto ice and a little concentrated hydrochloric acid, and diluted further with dichloromethane. After the ice had melted, the phases were separated, and the aqueous layer was extracted twice with dichloromethane. The combined dichloromethane solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (benzene elution): 150 mg (51.4%), mp 96.5°-97.5°C (from petroleum ether); 1H NMR (δ, CDCl₃) 6.55(s, 2H), 5.08-5.22(m, 2H), 3.88-4.05(m, 2H), 3.77(s, 6H), 1.88-2.2(m, 5H, a distinct s at 1.93), 1.73(m, 3H), and 1.15-1.33(m, 2H).


Found: C, 75.46; H, 7.68.
B. To a stirred solution of 5,8-dimethoxy-1,2,3,4-tetrahydro-9-isopropyldiene-1,4-methanonaphthalene (50 mg, 0.207 mmol) in acetic anhydride (2 ml) was added anhydrous zinc chloride (28.2 mg, 0.207 mmol). The mixture was stirred at room temperature for 8 hr, at which time it was poured into 10% sodium carbonate solution (50 ml) and stirred for 15 min. The aqueous mixture was extracted three times with ether and the combined organic layers were dried. After solvent removal, the residue was purified by preparative layer chromatography on silica gel (benzene elution) to yield 32.3 mg (54.6%) of the previously obtained syn acetyl compound.

1,2,3,4-Tetrahydro-syn-9-acetyl-anti-9-isopropenyl-1,4-methanonaphthalene (84). A. To a stirred suspension of aluminum chloride (0.82 g, 6.2 mmol) in dichloromethane (10 ml) was added a solution of acetyl chloride (0.53 g, 6.8 mmol) in dichloromethane (10 ml).
Most of the aluminum chloride dissolved. The stirred mixture was cooled in an ice-salt bath to -15°C, and to this mixture was added 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (1 g, 5.44 mmol) in dichloromethane (10 ml) over a 20 min period. After completion of the addition, the mixture was stirred at -10°C for 10 min. It was then poured onto ice and a little concentrated hydrochloric acid, and the mixture was diluted further with dichloromethane. After the ice had melted, the phases were separated and the aqueous layer was extracted twice with dichloromethane. The combined dichloromethane solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by chromatography on silica gel (benzene elution) to yield 0.72 g (58.3%) of a white crystalline solid, mp 95-102°C (lit. mp 101-105°C); \(^1\)H NMR (δ, CDCl\(_3\)) 7.03(m, 4H), 5.13 (m, 2H), 3.66(m, 2H), 1.92-2.25(m, 2H), 1.93(s, 3H), 1.75(m, 3H), and 1.0-1.28(m, 2H); m/e calcd 226.1357, obs 226.1363.
B. To a stirred solution of 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (100 mg, 0.54 mmol) in acetic anhydride (2 ml) was added anhydrous zinc chloride (74 mg, 0.54 mmol). The mixture was stirred at room temperature for 18 hr at which time it was poured into 10% sodium carbonate solution (50 ml) and stirred for 15 min. The aqueous mixture was extracted three times with ether and the combined organic layers were dried. After solvent removal, the residue was purified by preparative layer chromatography on silica gel (benzene elution) to yield 74 mg (60.3%) of the previously obtained syn acetyl compound.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-syn-9-acetyl-anti-9-isopropenyl-1,4-methanonaphthalene (85). A. To a stirred suspension of aluminum chloride (147 mg, 1.1 mmol) in dichloromethane (5 ml) was added a solution of acetyl chloride (96 mg, 1.22 mmol)
in dichloromethane (5 ml). Most of the aluminum chloride dissolved. The stirred mixture was cooled in an ice-salt bath to $-15^\circ C$ and 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (250 mg, 0.977 mmol) in dichloromethane (10 ml) was added over a 15 min period. After completion of the addition, the mixture was stirred at $-10^\circ C$ for 15 min, poured onto ice and a little concentrated hydrochloric acid, and diluted further with dichloromethane. After the ice had melted, the phases were separated, and the aqueous layer was extracted twice with dichloromethane. The combined dichloromethane solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was recrystallized from hot petroleum ether to yield 118.4 mg (41%) of a white crystalline solid, mp 127.5-128.5$^\circ C$; $^1H$ NMR ($\delta$, CDCl$_3$) 5.2(m, 2H), 4.03(m, 2H), 2.0-2.3(m, 2H), 2.0(s, 3H), 1.78(m, 3H), and 1.05-1.35(m, 2H).

**Anal. Calcd for C$_{16}$H$_{14}$F$_4$O: C, 64.64; H, 4.73.**

**Found:** C, 64.26; H, 4.73.
B. To a stirred solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methano-naphthalene (50 mg, 0.195 mmol) in acetic anhydride (2 ml) was added anhydrous zinc chloride (26.6 mg, 0.195 mmol). The mixture was stirred at room temperature for 2 days, at which time it was poured into 10% sodium carbonate solution (50 ml) and stirred for 15 min. The aqueous mixture was extracted three times with ether and the combined organic layers were dried. After solvent removal, the residue was purified by preparative layer chromatography on silica gel (benzene elution) to yield 28 mg of recovered starting material and 14 mg (54.7%) of the previously obtained syn-acetyl compound.

7-syn-Acetyl-7-anti-isopropenyl-norbornene (86). A. To a stirred suspension of aluminum chloride (113 mg, 0.85 mmol) in dichloromethane (3 ml) was added a solution of acetyl chloride (73 mg, 0.933 mmol) in
dichloromethane (3 ml). Most of the aluminum chloride dissolved. The stirred mixture was cooled in a dry ice-acetone bath to -78°C, and to this mixture was added 7-isopropylidenenorbornene (100 mg, 0.746 mmol) in dichloromethane (4 ml) over a 5 min period. After completion of the addition, the mixture was stirred at -78°C for 5 min, poured onto ice and a little concentrated hydrochloric acid, and diluted further with dichloromethane. After the ice had melted, the phases were separated and the aqueous layer was extracted twice with dichloromethane. The combined dichloromethane solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (benzene elution) to yield 68.9 mg (52.5%) of 8, mp 44-45.5°C after preparative vpc (12 ft x 0.25 in. 5% SF96 on Chromosorb G at 150°C); $^1$H NMR ($\delta$, CDCl$_3$) 6.05 (t, $J$ = 2Hz, 2H), 5.17(m, 1H), 4.94(m, 1H), 3.2(m, 2H), 2.02(s, 3H), 1.65(m, 3H), and 0.75-2.68(series of m, 4H).

Anal. Calcd for C$_{12}$H$_{16}$O: C, 81.77; H, 9.15.

Found: C, 81.60; H, 9.11.
B. To a stirred solution of 7-isopropylidene-norbornene (300 mg, 2.24 mmol) in acetic anhydride (6 ml) was added anhydrous zinc chloride (305 mg, 2.24 mmol). The mixture was stirred at room temperature for 9 hr, at which time it was poured into 10% sodium carbonate solution (50 ml) and stirred for 15 min. The aqueous mixture was extracted three times with ether and the combined organic layers were dried. After solvent removal, the residue was purified by preparative layer chromatography on silica gel (benzene elution) to yield 169 mg (43%) of the previously obtained syn acetyl compound. 

5,8-Dimethoxy-1,2,3,4-tetrahydro-syn-9-trideuterio-acetyl-anti-9-isopropenyl-1,4-methanonaphthalene (87).

To deuterium oxide (2 ml) at 0°C under nitrogen was added freshly cut sodium (52.8 mg, 2.3 mg at). To the cold solution was added 5,8-dimethoxy-1,2,3,4
tetrahydro-syn-9-acetyl-anti-9-isopropenyl-1,4-methanono-
naphthalene (25 mg, 0.088 mmol) in anhydrous tetrahydro-
furan (3 ml). The reaction mixture was allowed to warm
to room temperature and stirred for 4 days. The organic
layer was separated and the aqueous layer was extracted
twice with ether. The combined organic layers were dried
and evaporated under reduced pressure to give (19.5 mg,
77%) of solid product. The $^1$H NMR spectrum was identical
with that of the starting material except that the acetyl
peak at $\delta$ 1.93 was no longer present.

$\text{1,2,3,4-Tetrahydro-syn-9-trideuterioacetyl-anti-9-}$
isopropenyl-1,4-methanonaphthalene (88). To deuterium
oxide (2 ml) at 0°C under nitrogen was added freshly
cut sodium (63 mg, 2.72
mg-at). To the cold
solution was added 1,2,3,4-
tetrahydro-syn-9-acetyl-
anti-9-isopropenyl-1,4-methanonaphthalene (30 mg, 0.133
mmol) in anhydrous tetrahydrofuran (3 ml). The reaction
mixture was allowed to warm to room temperature and
stirred for 3 days. The organic layer was separated and
the aqueous layer was extracted twice with ether. The
combined organic layers were dried and evaporated under reduced pressure. The resulting solid product (30.1 mg, 98.7%) was carried on to the next step without further purification. The $^1$H NMR spectrum was identical with that of the starting material except that the acetyl peak at $\delta$ 1.93 was no longer present.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-syn-9-tride terio-
anti-9-isopropenyl-1,4-methanonaphthalene (89). To deuterium oxide (2 ml) at 0°C under nitrogen was added freshly cut sodium (77 mg, 3.35 mg-at). To the cold solution $^4$ was added 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-syn-9-acetyl-anti-9-

isopropenyl-1,4-methanonaphthalene (50 mg, 0.168 mmol) in anhydrous tetrahydrofuran (3 ml). The reaction mixture was allowed to warm to room temperature and stirred for 4 days. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were dried and evaporated under reduced
pressure. The resulting solid product (40.9 mg, 81%) was carried on to the next step without further purification. The \(^1\)H NMR spectra was identical with starting material except the acetyl peak at δ 2.0 was no longer present.

**Ozonolysis of \(\text{84} \).** A. Oxygen containing ozone was bubbled through a solution of 1,2,3,4-tetrahydro-syn-9-acetyl-anti-9-isopropenyl-1,4-methanonaphthalene (400 mg, 1.77 mmol) in methanol (50 ml), with cooling from a dry ice acetone bath, for 15 min. Oxygen was then bubbled through the solution to remove excess dissolved ozone. To the cold reaction mixture was added a solution of sodium iodide (0.88 g), acetic acid (0.4 ml), methanol (1.8 ml), and water (18 ml). After the addition, the mixture was allowed to warm to room temperature, at which time the liberated iodine was destroyed by introduction of solid sodium bisulfite. The resulting solution was extracted three times with ether. The combined ether solutions were washed with saturated
sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (chloroform elution). For 90: 72.5 mg (18%); mp 145.5–146.5°C (from ethanol); $^1$H NMR ($\delta$, CDCl$_3$) 7.07 (m, 4H), 3.9 (distorted t, $J = 2$ Hz, 2H), 1.8–2.25 (m, two distinct s at 1.91 and 2.19, 8H), and 1.07–1.34 (m, 2H).

**Anal.** Calcd for C$_{15}$H$_{16}$O$_2$: C, 78.92; H, 7.06.

Found: C, 78.51; H, 6.95.

For 93: 54.6 mg (13%); mp 91–99°C; $^1$H NMR ($\delta$, CDCl$_3$) 7.03 (m, 4H), 3.41 (m, 2H), 2.94 (d, $J = 5$ Hz, 1H), 2.58 (d, $J = 5$ Hz, 1H), 2.39–2.05 (m, 2H), 1.9 (s, 3H), 1.40 (s, 3H), and 1.07–1.4 (m, 2H); m/e calcd 242.1306, obs 242.1313.

For 92: 132 mg (27%); mp 154–156°C (from ethanol); $^1$H NMR ($\delta$, CDCl$_3$) 7.14 (s, 4H), 3.5 (m, 2H), 3.35 (s, 3H), 2.46 (br s, 1H), 2.06–2.34 (m, 2H), 1.54 (s, 3H), 1.05–1.35 (m, 2H), and 0.69 (s, 3H).

**Anal.** Calcd for C$_{16}$H$_{20}$O$_4$: C, 69.55; H, 7.30.

Found: C, 69.66, H, 7.23.
B. A mixture of the crude product from the ozonolysis of 1,2,3,4-tetrahydro-syn-9-acetyl-anti-9-isopropenyl-1,4-methanonaphthalene (25 mg) in ethyl acetate (3 ml) and 10% Pd/c (25 mg) was stirred at room temperature under an atmosphere of hydrogen for a short time. The reaction mixture was filtered through a pad of Celite. After solvent removal from the filtrate, the resulting residue was purified by preparative layer chromatography (chloroform elution) to give 15 mg (53%) of diacetyl derivative 90a.

1,2,3,4-Tetrahydro-syn-9-trideuterioacetyl-anti-9-acetyl 1,4-methanonaphthalene (90b). Oxygen containing ozone was bubbled through solution of 1,2,3,4-tetrahydro-syn-9-trideuteriacetyl-anti-9-isopropenyl-1,4-methanonaphthalene (30.1 mg, 0.133 mmol) in methanol (5 ml)
with cooling from a dry ice-acetone bath, for 15 min.
Oxygen was then bubbled through the solution to remove
excess dissolved ozone. To the cold reaction mixture
was added a solution of sodium iodide (67 mg), acetic
acid (0.03 ml), methanol (0.14 ml), and deuterium oxide
(1.4 ml). After the addition, the mixture was allowed to
warm to room temperature at which time the liberated
iodine was destroyed by introduction of solid sodium
bisulfite. The resulting solution was extracted three
times with ether. The combined ether solutions were
washed with saturated sodium bicarbonate and saturated
sodium chloride solutions prior to drying. Removal of
solvent yielded 11.3 mg (37%) of 90b. The $^1$H NMR
spectrum was identical with that of the crude from the
ozonolysis of the nondeuterio acetyl compound except that
the methyl peak at $\delta$ 1.91 was absent.

Ozonolysis of 85. Oxygen containing ozone was bubbled
through a solution of
5,6,7,8-tetrafluoro-1,2,3,4-
tetrahydro-syn-9-acetyl-
anti-9-isopropenyl-1,4-
methanonaphthalene (154 mg,
0.516 mmol) in methanol
(40 ml), with cooling from a dry ice-acetone bath, for
15 min. Oxygen was then bubbled through the solution to
remove excess dissolved ozone. To the cold reaction
mixture was added a solution of sodium iodide (0.26 g),
acetic acid (0.12 ml), methanol (0.53 ml), and water
(5.3 ml). After the addition, the mixture was allowed to
warm to room temperature, at which time the liberated
iodine was destroyed by introduction of solid sodium
bisulfite. The resulting solution was extracted three
times with ether. The combined ether solutions were washed
with saturated sodium bicarbonate and saturated sodium
chloride solutions prior to drying. After removal of
solvent, the residue was purified by preparative layer
chromatography on silica gel (chloroform elution). For
91a: 71.8 mg (46.4%); mp 122-123°C (from ethanol); 1H NMR
(δ, CDCl₃) 4.17-4.33(m, 2H), 1.87-2.20(m, two distinct s
at 1.97 and 2.20, 8H), and 1.17-1.40(m, 2H).

Anal. Calcd for C₁₅H₁₂F₄O₂: C, 60.00; H, 4.03.
Found: C, 59.83; H, 4.01.

For 94: 30.4 mg (16.9%); mp 123-128°C; 1H NMR (δ, CDCl₃)
3.79(m, 2H), 3.3(s, 3H), 2.61(br s, 1H), 2.1-2.44(m, 2H),
1.55(s, 3H), 1.07-1.43(m, 2H), and 0.86(s, 3H); m/e
calcd 348.0984, obs 348.0991.
Oxygen containing ozone was bubbled through a solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-syn-9-trideuterioacetyl-anti-9-acetyl-1,4-methanonaphthalene (91b). Oxygen containing ozone was bubbled through a solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-syn-9-trideuterioacetyl-anti-9-isopropenyl-1,4-methanonaphthalene (40 mg, 0.133 mmol) in methanol (10 ml) with cooling from a dry ice-acetone bath for 15 min. Oxygen was then bubbled through the solution to remove excess dissolved ozone. To the cold reaction mixture was added a solution of sodium iodide (67.8 mg), acetic acid (0.04 ml), methanol (0.15 ml), and deuterium oxide (1.4 ml). After the addition, the mixture was allowed to warm to room temperature, at which time the liberated iodine was destroyed by introduction of solid sodium bisulfite. The resulting solution was extracted three times with ether. The combined ether solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. Removal of solvent yielded 37.3 mg (93%) of 91b. The $^1$H NMR spectrum was identical with that of
the crude obtained from the ozonolysis of the nondeuterio acetyl compound except that the methyl peak at δ 1.97 was absent.

1,2,3,4-Tetrahydro-syn-9-acetyl-anti-9-hydroxy-1,4-methanonaphthalene (95). Oxygen containing ozone was bubbled through a solution of 1,2,3,4-tetrahydro-syn-9-isopropenyl-anti-9-hydroxy-1,4-methanonaphthalene (100 mg, 0.5 mmol) in methanol (40 ml) with cooling from a dry ice-acetone bath for 15 min. Oxygen was then bubbled through the solution to remove excess dissolved ozone. To the cold reaction mixture was added a solution of sodium iodide (248 mg), acetic acid (0.11 ml), methanol (0.51 ml), and water (0.1 ml). After the addition, the mixture was allowed to warm to room temperature, at which time the liberated iodine was destroyed by introduction of solid sodium bisulfite. The resulting solution was extracted three times with ether. The combined ether solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by
preparative layer chromatography on silica gel (chloroform elution). For 9: 38.4 mg (38%); mp 84-87°C; 
$^1$H NMR ($\delta$, CDCl$_3$) 7.15(s, 4H), 4.0(br s, 1H), 3.25 (distorted t, $J = 2$ Hz, 2H), 2.19-2.51(m, 2H), 1.67(s, 3H), 
and 1.07-1.37(m, 2H); m/e calcd 202.0993, obs 202.0998. 
For 3: 16.3 mg (20.6%); identical to that previously synthesized.

1,2,3,4-Tetrahydro-syn-9-hydroxy-anti-9-acetyl-1,4-methanonaphthalene (96). Oxygen containing ozone was 
bubbled through a solution of 1,2,3,4-tetrahydro-syn-9-hydroxy-anti-9-isopropenyl-1,4-methanonaphthalene (79 mg, 
0.393 mmol) in methanol (10 ml) with cooling from a dry ice-acetone bath for 15 min. Oxygen was then bubbled through 
the solution to remove excess dissolved ozone. To the cold reaction mixture was added a solution of sodium 
iodide (195 mg), acetic acid (0.1 ml), methanol (0.4 ml), 
and water (4 ml). After the addition, the mixture was allowed to warm to room temperature, at which time the 
liberated iodine was destroyed by introduction of solid sodium bisulfite. The resulting solution was extracted
three times with ether. The combined ether solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (chloroform elution) gave 14.3 mg (18%) of 96 as a colorless oil; $^1$H NMR ($^5$, CDCl$_3$) 7.25(m, 4H), 3.35(m, 2H), 2.26(s, 3H), 1.8-2.17(m, distinct s at 2.05, 3H), and 1.15-1.33(m, 2H); m/e calcd 202.0993, obs 202.0998.

1,2,3,4-Tetrafluoro-9,10-dihydro-11-syn(anti)-acetyl-11-anti(syn)-isopropenyl-9,10-methanoanthracene (97 and 98). To a stirred suspension of aluminum chloride (15.3 mg, 0.115 mmol) in dichloromethane (1 ml) was added a solution of acetyl chloride (9.8 mg, 0.125 mmol) in dichloromethane (1 ml). Most of the aluminum chloride dissolved. The stirred solution was cooled in an ice-salt bath to -15°C, and to this mixture was added 1,2,3,4-tetrafluoro-9,10-dihydro-11-isopropylidene-9,10-methanoanthracene
(30.4 mg, 0.1 mmol) in dichloromethane (2 ml) over a 5 min period. After completion of the addition, the mixture was stirred at -10°C for 15 min, poured onto ice and a little concentrated hydrochloric acid, and diluted further with dichloromethane. After the ice had melted, the phases were separated, and the aqueous layer was extracted twice with dichloromethane. The combined dichloromethane solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn acetyl: 8.8 mg (25.4%); mp 114-118°C, ¹H NMR (δ, CDCl₃) 6.84-7.3(m, 4H), 4.98(m, 4H), 2.05(s, 3H), and 1.57(m, 3H); m/e calcd 346.0980, obs 346.0987.

Anti acetyl: 8 mg (23%); mp 68-71°C; ¹H NMR (δ, CDCl₃) 6.89-7.4(m, 4H), 5.02(m, 4H), 1.98(s, 3H), and 1.61(m, 3H); m/e calcd 346.0980, obs 346.0987.

Prins Reaction of 16. To 5,8-dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanophthalene (300 mg, 1.24 mmol) and paraformaldehyde (372 mg, 12.4 mmol) was added anhydrous
dioxane (13 ml) containing concentrated sulfuric acid (1.22 g, 12.4 mmol), with external cooling from an ice bath. After completion of the addition, the mixture was stirred at room temperature for 3 hr, diluted with water, and extracted three times with ether. The combined organic layers were washed with 10% ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (petroleum ether-acetone, 9:1) to yield 171.5 mg (48.4%) of 99, mp 120.5-121.5°C (from ethanol); $^1$H NMR (δ, CDCl$_3$) 6.53(s, 2H), 4.88(br s, 2H), 3.45-3.8(m, a distinct s at 3.75, 10H), 3.2(s, 2H), 1.97-2.39(m, a distinct t at 2.26, J = 6 Hz, 4H), and 0.93-1.25(dd, 2H).

Anal. Calcd for C$_{18}$H$_{22}$O$_3$: C, 75.50; H, 7.74.
Found: C, 75.59; H, 7.74.

Prins Reaction of 2. To 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (1 g, 5.4 mmol) and paraformaldehyde (1.63 g, 5.4 mmol) was added anhydrous dioxane (55 ml) containing concentrated sulfuric acid (5.33 g, 54 mmol), with
external cooling from an ice bath. After completion of the addition, the mixture was stirred at room temperature for 2.5 hr, diluted with water, and extracted three times with ether. The combined organic layers were washed with 10% ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was recrystallized from hot ethanol to yield 100, 0.9 g (75%), as a white crystalline solid, mp 70.5-71.5°C; $^1$H NMR (δ, CDCl$_3$) 7.13 (br s, 4H), 4.94(br s, 2H), 3.7(t, J = 6 Hz, 2H), 3.35(t, J = 2 Hz, 2H), 3.17(s, 2H), 2.0-2.45(m with a distinct t at δ 2.3, J = 6 Hz, 4H), and 0.97-1.27(dd, 2H).

Anal. Calcd for C$_{16}$H$_{18}$O: C, 84.91; H, 8.02.
Found: C, 84.81; H, 8.03.

Prins Reaction of 7. To 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (250 mg, 0.98 mmol) and paraformaldehyde (292 mg, 9.8 mmol) was added anhydrous dioxane (10 ml) containing concentrated sulfuric acid (957 mg, 9.8 mmol) with external cooling from an ice bath. After completion of the addition, the mixture
was stirred at room temperature for 12 hr, diluted with water, and extracted three times with ether. The combined organic layers were washed with 10% ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (benzene elution) to yield 31.3 mg of recovered starting material and 171 mg (67%) of 101, mp 105.5-106.5°C (from ethanol); $^1$H NMR (δ, CDCl$_3$) 4.83-5.02(m, 2H), 3.55-3.78(m, 4H), 3.15(s, 2H), 2.03-2.4 (m, 4H), and 0.96-1.3(m, 2H).

**Anal.** Calcd for C$_{16}$H$_{14}$F$_4$O: C, 64.43; H, 4.73.

Found: C, 64.59; H, 4.72.

**Prins Reaction of 21.** To 7-isopropylidenenorbornene (100 mg, 0.75 mmol) and paraformaldehyde (224 mg, 7.45 mmol) was added anhydrous dioxane (7.6 ml) containing concentrated sulfuric acid (731 mg, 7.45 mmol), with external cooling from an ice bath. After completion of the addition, the mixture was stirred at room temperature for 6 hr, diluted with water, and extracted three times with
ether. The combined organic layers were washed with 10% ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative vpc (12 ft x 0.25 in.5% SF96 on Chromosorb G, 150°C) to give 75 mg (57%) of \(103\) as an oil; \(^1\)H NMR (\(\delta, CDCl_3\)) 5.95 (t, \(J = 2\) Hz, 2H), 5.68–5.86 (m, 2H), 3.65 (t, \(J = 5\) Hz, 2H), 3.58 (s, 2H), 2.82 (distorted t, \(J = 2\) Hz, 2H), 2.22 (t, \(J = 5\) Hz, 2H), 1.73–2.0 (m, 2H), and 0.95–1.3 (m, 2H).

**Anal.** Calcd for \(C_{12}H_{16}O\): C, 81.77; H, 9.15.

Found: C, 81.90; H, 9.16.

### 1,2,3,4-Tetrahydro-anti-9-isopropenyl-1,4-methanonaphthalene-syn-9-carboxylic Acid (104)

A solution of 1,2,3,4-tetrahydro-syn-9-acetyl-anti-9-isopropenyl-1,4-methanonaphthalene (0.84 g, 3.7 mmol), sodium hydroxide (0.45 g, 11.2 mmol), 5% sodium hypochlorite solution (17 ml, 11.2 mmol) and dioxane (17 ml) were heated at reflux for 7 hr. At this point, more sodium hydroxide (0.45 g, 11.2 mmol, 5% sodium hypochlorite solution (17 ml, 11.2 mmol) and dioxane (17 ml) were added and reflux was continued for an additional
12 hr. The cooled solution was treated with sodium thiosulfate (6 g) and acidified with concentrated hydrochloric acid with external cooling. The reaction mixture was extracted three times with ether and the combined ether layers were washed with 10% ammonium chloride solution. The ether phase was extracted three times with 5% sodium hydroxide solution. The basic extracts were acidified with concentrated hydrochloric acid while externally cooled and extracted three times with ether. The combined ether layers were dried and evaporated under reduced pressure to give 0.33 g (76%) of 104 which was carried on to the next step without further purification: ¹H NMR (δ, CDCl₃) 9.73 (br s, 1H), 7.05 (m, 4H), 5.1 (m, 2H), 3.6 (m, 2H), 1.81-2.17 (m, 5H), and 0.96-1.23 (m, 2H).

**Methyl 1,2,3,4-tetrahydro-anti-9-isopropenyl-1,4-methanonaphthalene-syn-9-carboxylate (105).** To a solution of 1,2,3,4-tetrahydro-anti-9-isopropenyl-1,4-methanonaphthalene-syn-9-carboxylic acid (0.33 g, 1.45 mmol) in ether, cooled to 0°C, was added an ether solution of
diazomethane (5.95 mmol). The solution was stirred at 0°C for 5 min and the solvent was removed under reduced pressure. The resulting residue was purified by recrystallization from hot ethanol to give 0.25 g (71%) of 105, mp 94.5-95.5°C; 1H NMR (δ, CDC13) 7.14(m, 4H), 5.13(m, 2H), 3.72(t, J = 2 Hz, 2H), 3.35(s, 3H), 1.84-2.21(m, 5H), and 0.95-1.27(m, 2H); \nu_{\text{max}} 1722 cm^{-1}.

Anal. Calcd for C_{16}H_{18}O_{2}: C, 79.31; H, 7.49.
Found: C, 79.25; H, 7.53.

1,2,3,4-Tetrahydro-syn-9-hydroxymethyl-anti-9-isopropenyl-1,4-methanonaphthalene (102). To a stirred suspension of lithium aluminum hydride (50 mg, 1.32 mmol) in anhydrous tetrahydrofuran (5 ml) was added a solution of methyl 1,2,3,4-tetrahydro-anti-9-isopropenyl-1,4-methanonaphthalene-syn-9-carboxylate (50 mg, 0.21 mmol) in tetrahydrofuran (5 ml). The suspension was refluxed for 1 hr and stirred for 12 hr at room temperature. The reaction mixture was cooled in an ice bath and 10% sulfuric acid solution was added cautiously at first and then until no precipitated salts
remained. The solution was extracted three times with ether and the combined ether layers were washed with saturated sodium chloride solution prior to drying. Evaporation of the solvent gave 30.4 mg (68%) of 102, mp 51-58°C, which was carried on to the next step without further purification; $^1$H NMR ($\delta$, CDCl$_3$) 7.05 (br s, 4H), 5.1 (m, 1H), 4.9 (m, 1H), 3.26 (m, 2H), 3.08 (s, 2H), 1.85-2.2 (m, 3H), 1.80 (m, 3H), and 0.95-1.3 (m, 2H); m/e calcd 214.1357, obs 214.1362.

Prins Reaction of 102. To 1,2,3,4-tetrahydro-syn-9-hydroxymethyl-anti-9-isopropenyl-1,4-methanonaphthalene (30 mg, 0.142 mmol) and paraformaldehyde (43 mg, 1.42 mmol) was added anhydrous dioxane (2 ml) containing concentrated sulfuric acid (139 mg, 1.42 mmol) with external cooling from an ice bath. After completion of the addition, the mixture was stirred at room temperature for 17 hr, diluted with water, and extracted three times with ether. The combined organic layers were washed with 10% ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride solutions prior to drying. Removal of the solvent
yielded 22 mg (68.5%) of 100, identical in all respects with the material obtained directly from 2.

**syn-(anti)-9-Chloro-anti(syn)-9-isopropenyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (106 and 107).**

A. To a solution of 9-isopropylidene-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (100 mg, 0.41 mmol) in freshly distilled methyl formate (2 ml) was added tert-butyl hypochlorite (44.5 mg, 0.41 mmol). The solution was stirred at room temperature in the dark for 6 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4). Syn isomer: 11.2 mg (18.7%) (based on recovered 16), mp 158-160°C (from hexane); $^1$H NMR ($\delta$, CDCl$_3$) 6.6 (s, 2H), 5.1-5.2 (m, 1H), 4.9-5.02 (m, 1H), 3.67-3.87 (m, a distinct s at 3.75, 8H), 1.81-2.2 (m, a distinct 3H m at 1.95, 5H), and 1.02-1.33 (m, 2H).

**Anal. Calcd for C$_{16}$H$_{19}$O$_2$Cl: C, 68.94; H, 6.87. Found: C, 68.67; H, 6.91.**
Anti isomer: 34.3 mg (57.4%) (based on recovered 16), mp 126.5-127°C (from hexane); $^1$H NMR ($^6$, CDCl$_3$) 6.52(s, 2H), 4.8-4.9(m, 1H), 4.6-4.7(m, 1H), 3.75(s, 6H), 3.35-3.48 (distorted t, $\nu$ = 2 Hz, 2H), 2.15-2.43(m, 2H), 1.72(m, 3H), and 1.05-1.3(m, 2H).

**Anal.** Calcd for C$_{16}$H$_{19}$O$_2$Cl: C, 68.94; H, 6.87.

**Found:** C, 68.48; H, 6.95.

B. To a solution of 9-isopropylidene-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (250 mg, 1.03 mmol) in methyl formate (5 ml) and formic acid (0.48 ml, 12.60 mmol) was added tert-butyl hypochlorite (112 mg, 1.03 mmol). The solution was stirred at room temperature in the dark for 4.5 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 123.1 mg (42.9%). Anti isomer: 98.5 mg (34.3%).
C. To a solution of 9-isopropylidene-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (50 mg, 0.207 mmol) in methyl formate (2 ml) and formic acid (2 ml) was added tert-butyl hypochlorite (22.4 mg, 0.207 mmol). The solution was stirred at room temperature in the dark for 20 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 22.8 mg (39.5%); Anti isomer: 12 mg (20.8%).

syn-(anti)-9-Chloro-anti(syn)-9-isopropenyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene (108 and 109).

A. To a solution of 9-isopropylidene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (150 mg, 0.82 mmol) in freshly distilled methyl formate (3 ml) was added tert-butyl hypochlorite (88.5 mg, 0.82 mmol). The solution was stirred at room temperature in the dark for 9 hr. After removal
of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 19.1 mg (10.8%); mp 152.5-154°C (from hexane); \(^1\)H NMR (δ, CDCl\(_3\)) 7.13(br s, 4H), 4.96-5.18(m, 2H), 3.52-3.62(distorted t, \(\delta = 2\) Hz, 2H), 1.87-2.18(m, a distinct 3H-m at 1.95, 5H), and 1.04-1.34(m, 2H).

**Anal.** Calcd for C\(_{14}\)H\(_{15}\)Cl: C, 76.88; H, 6.91.  
Found: C, 76.75; H, 6.93.

Anti isomer: 133.7 mg (76.7%); mp 83-86°C (preparative vpc (6 ft x 0.25 in, 5% SE 30 on Chromosorb G, 180°C)); \(^1\)H NMR (δ, CDCl\(_3\)) 7.0(br s, 4H), 4.56-4.69(m, 2H), 3.39-3.5 (distorted t, \(\delta = 2\) Hz, 2H), 2.16-2.48(m, 2H), 1.65(m, 3H), and 1.05-1.33(m, 2H).

**Anal.** Calcd for C\(_{14}\)H\(_{15}\)Cl: C, 76.88; H, 6.91.  
Found: C, 76.54; H, 6.86.

![Chemical structure](image)

B. To a solution of 9-isopropylidene-1,2,3,4-tetrahydro-1,4-methano-naphthalene (100 mg, 0.54 mmol) in methyl formate (1.5 ml) and formic acid (0.25 ml, 6.6 mmol) was added tert-butyl hypochlorite (58.6 mg, 0.54 mmol). The solution was stirred at room
temperature in the dark for 1.5 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 39.2 mg (33.2%); Anti isomer, 54.3 mg (46%).

C. To a solution of 9-isopropylidene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (150 mg, 0.815 mmol) in methyl formate (6 ml) and formic acid (6 ml) was added tert-butyl hypochlorite (88.4 mg, 0.815 mmol). The solution was stirred at room temperature in the dark for 8 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 80.2 mg (45%); Anti isomer: 14.8 mg, (8.3%).

**syn(anti)-9-Chloro-anti(syn)-9-isopropenyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene** (110 and 111). A. To a solution of 9-isopropylidene-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (100 mg, 0.39 mmol) in freshly distilled methyl formate (4 ml)
was added tert-butyl hypochlorite (42.3 mg, 0.39 mmol). The solution was stirred at room temperature in the dark for 16 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 42.5 mg (37.4%); mp 82-84°C (preparative vpc (6 ft x 0.25 in. 5% SE30 on Chromosorb G, 180°C)); $^1$H NMR ($\delta$, CDCl$_3$) 5.0–5.2 (m, 2H), 3.77–3.95 (m, 2H), 1.85–2.22 (m, a distinct 3H-m at 1.95, 5H), and 1.1–1.44 (m, 2H).

**Anal.** Calcd for C$_{14}$H$_{11}$ClF$_4$: C, 57.85; H, 3.81.

Found: C, 57.74; H, 3.83.

Anti isomer: 50.5 mg (44.5%); mp 130.5–131.5°C (preparative vpc (6 ft x 0.25 in. 5% SE30 on Chromosorb G, 180°C)); $^1$H NMR ($\delta$, CDCl$_3$) 4.7–4.9 (m, 2H), 3.7–3.9 (m, 2H), 2.34–2.68 (m, 2H), 1.75 (m, 3H), and 1.19–1.53 (m, 2H).

**Anal.** Calcd for C$_{14}$H$_{11}$ClF$_4$: C, 57.85; H, 3.81.

Found: C, 57.65; H, 3.89.

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B. To a solution of 9-isopropylidene-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (50 mg, 0.195 mmol)
in methyl formate (2 ml) and formic acid (110 mg, 2.39 mmol) was added tert-butyl hypochlorite (21.2 mg, 0.195 mmol). The solution was stirred at room temperature in the dark for 16 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 20 mg (35.3%); Anti isomer: 18.7 mg (33%).

C. To a solution of 9-isopropylidene-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (50 mg, 0.195 mmol) in methyl formate (1 ml) and formic acid (1 ml) was added tert-butyl hypochlorite (21.2 mg, 0.195 mmol). The solution was stirred at room temperature in the dark for 18 hr. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene-petroleum ether (1:4)). Syn isomer: 31.5 mg (55.6%); Anti isomer: 3.4 mg (6%).

**Dichlorocyclopropanation of 16.** A solution of 5,8-

\[
\begin{align*}
\text{Cl} & \text{Cl} & \text{CH}_3 & \text{CH}_3 \\
\text{Cl} & \text{Cl} & \text{H}_3\text{C} & \text{Cl}
\end{align*}
\]

\[14-(\text{OCH}_3)_2\]

dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (200 mg, 0.82 mmol) and
sodium trichloroacetate (3.0 g, 16.5 mmol) in 20 ml of tetrachloroethylene:glyme (1:1) was heated at reflux for 10 hr. The reaction mixture was diluted with water and extracted three times with ether. The combined organic layers were washed with saturated sodium bicarbonate, 10% ammonium chloride, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). Syn isomer (112): 147 mg (55%); mp 147.5-148.5°C (from hexane); $^1$H NMR ($\delta$, CDCl$_3$) 6.6(s, 2H), 3.75(s, 6H), 3.42(distorted t, 2H), 1.74-2.1(m, 2H); and 1.13-1.45(m, a distinct s at 1.3, 8H).

Anal. Calcd for C$_{17}$H$_{20}$Cl$_2$O: C, 62.39; H, 6.16. Found: C, 62.38; H, 6.16.

Anti isomer (113): 32 mg (12%); mp 120-125°C; $^1$H NMR ($\delta$, CDCl$_3$) 6.58(s, 2H), 3.75(s, 6H), 3.33(distorted t, 2H), 2.08-2.37(m, 2H), and 1.15-1.43(m, a distinct s at 1.15, 8H); m/e calcd 326.0840, obs 326.0847.

Dichlorocyclopropanation of 2. A solution of 1,2,3,4-tetrahydro-9-isopropyldene 1,4-methanonaphthalene (250 mg, 1.36 mmol) and sodium
trichloroacetate (5g, 27 mmol) in 50 ml of tetrachloroethylene:glyme (1:1) was heated at reflux for 18 hr. The reaction mixture was diluted with water and extracted three times with ether. The combined organic layers were washed with saturated sodium bicarbonate, 10% ammonium chloride, and saturated sodium chloride solution prior to drying. After removal of solvent the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (petroleum ether elution). Syn isomer (114): 153 mg (55%, based on recovered 2); mp 173.5-174.5°C (from hexane); $^1$H NMR ($\delta$, CDCl$_3$) 7.17(m, 4H), 3.2(distorted t, $J = 2$Hz, 2H), 1.85-2.2(m, 2H), and 1.2-1.5(m, a distinct s at 1.3, 8H).

Anal. Calcd for C$_{15}$H$_{16}$Cl$_2$: C, 67.43; H, 6.04.

Anti isomer (115): 80 mg (29%, based on recovered 2); mp 121.0-122.5°C; $^1$H NMR ($\delta$, CDCl$_3$) 7.1(m, 4H), 3.14 (distorted t, $J = 2$Hz, 2H), 2.1-2.44(m, 2H), and 0.97-1.47 (m, a distinct s at 1.22, 8H); m/e calcd 266.0628, obs 266.0636.
Dichlorocyclopropanation of 7.

A solution of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (100 mg, 0.391 mmol) and sodium trichloroacetate (1.5 g, 8.1 mmol) in 20 ml of tetrachloroethylene:glyme (1:1) was heated at reflux for 15 hr. The reaction mixture was diluted with water and extracted three times with ether. The combined organic layers were washed with saturated sodium bicarbonate, 10% ammonium chloride, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (petroleum ether elution). Syn isomer (116): 36 mg (49%, based on recovered 7); mp 156.5-157.5°C (from hexane); $^1$H NMR ($\delta$, CDCl$_3$) 3.5(m, 2H), 1.9-2.2(m, 2H), and 1.22-1.56(m, a distinct s at 1.3, 8H).


Anti isomer (117): 6 mg (7.7%, based on recovered 7); mp 155-161°C; $^1$H NMR ($\delta$, CDCl$_3$) 3.5(m, 2H), 2.12-2.5(m, 2H), 2.8-3.5(m, 2H), 1.8-2.2(m, 2H).
1.2-1.5 (m, a distinct s at 1.24, 8H); m/e calcd 338.0252, obs 338.0259.

Dichlorocyclopropanation of 21. A solution of 7-isopropylidenenorbornene (100 mg, 0.75 mmol) and sodium trichloroacetate (2.8 g, 14.9 mmol) in 20 ml of tetrachloroethylene:glyme (1:1) was heated at reflux for 15 hr. The reaction mixture was diluted with water and extracted three times with ether. The combined organic layers were washed with saturated sodium bicarbonate, 10% ammonium chloride, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative vpc (12ft x 0.25 in. 5% SF96 on Chromosorb G, 140°C). Syn isomer (118): 29.4 mg (18.3%); mp 100.5-101°C (from methanol); $^1$H NMR ($\delta$, CDCl$_3$) 6.24 (t, $J = 2$ Hz, 2H), 2.72 (m, 2H), 1.23 (s, 6H) and 0.74-2.0 (series of m, 4H); m/e calcd 216.0472, obs 216.0476.

Anal. calcd for C$_{11}$H$_{14}$Cl$_2$: C, 60.8; H, 6.50

Found: C, 60.57; H, 6.51.
Anti isomer (119): 6.8 mg (4.2%); oil; $^1$H NMR ($\delta$, CDCl$_3$) 6.1(t, $J = 2$ Hz, 2H), 2.65(m, 2H), 1.25(s, 6H), and 0.9-2.35(series of m, 4H); m/e calcd 216.0472, obs 216.0476.
Figure 13. 60 MHz $^1$H NMR spectra of 33 and 34 (δ, CDCl$_3$, TMS).
Figure 14. 60 MHz $^1$H NMR spectra of $\mathfrak{u}$ and $\mathfrak{s}$ ($\delta$, CDCl$_3$, TMS).
Figure 15. 60 MHz $^1$H NMR spectra of 108 and 109 ($\delta$, CDCl$_3$, TMS).
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