PART I
SYNTHESIS AND ACID-CATALYZED REARRANGEMENT OF EPOXYENONES

PART II
REGIOSPECIFICITY IN DI-π-METHANE PHOTOISOMERIZATIONS

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ABSTRACT

PART I

SYNTHESES
AND
ACID-CATALYZED REARRANGEMENT OF EPOXYENONES

PART II

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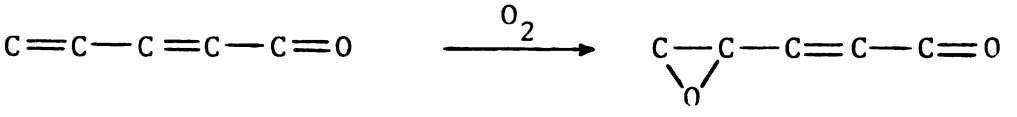
By

Paul B. Lavrik

The epoxidation of several conjugated dienones and diene esters with molecular oxygen was studied in Part I of this thesis. Compounds containing the moiety represented by 1 are easily epoxidized at the



1 2

γ,δ double bond to give 2 when heated in the presence of air or oxygen in a solvent which has readily abstractable hydrogen atoms. Thus, 4,5-epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone (24), 4,5-epoxy-3,4,6,6-tetramethyl-2-cyclohexenone (25), 4,5-epoxy-2,6,6-trimethyl-2-cycloheptenone (26), 4-(1,2-epoxy-2,6,6-trimethyl-1-cyclohexyl)-3-buten-2-one (27),

3α,4α-epoxy-5-cholesten-7-one (28), and methyl 4,5-epoxy-2-hexenoate (29) were prepared from their corresponding unsaturated precursors.

The acid-catalyzed rearrangement of epoxide 24, 3,5-epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone, was also studied in Part I of this thesis. In aqueous acid epoxide 24 rearranged quantitatively to 5-hydroxy-4-methylene-2,3,5,6,6-pentamethyl-2-cyclohexenone (32). In neat trifluoroacetic acid (TFA), 32 rearranged to 5-isopropenyl-4-methylene-2,3,5-trimethyl-2-cyclopentenone (36) which, on longer treatment with TFA, was dealkylated to 4-methylene-2,3,5-trimethyl-2-cyclopentenone (37) and acetone. When 24 was treated directly with neat TFA, there was formed, in addition to 36 and 37, a small yield of 2-acetyl-2,3,4,5,5-pentamethyl-3-cyclopentenone (34) and a larger amount of 4-acetyl-2,3,4,5,5-pentamethyl-2-cyclopentenone (35). Appropriate deuterium-labeling experiments allowed fairly complete mechanistic schemes to be postulated.

In Part II of this thesis, the acetone-sensitized di-π-methane photoisomerization of *syn*- and *anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s and 58a) was studied. Of the two possible products which might arise from such rearrangement, the product resulting from the diradical in which the unpaired electrons are close to rather than remote from the methyl substituent on the saturated bridge was preferred. The extent of the preference depended on the geometry of the methyl-substituent and the aromatic ring. When the methyl was *anti* to the aromatic ring the reaction was regiospecific and yielded *anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67a). When the methyl was *syn* to the aromatic ring, some *syn*-7-methyl-3,4-benzotricyclo [3.3.0.$0^{2,8}$]oct-3-ene (66s), was obtained, but the reaction was still

highly regioselective yielding mainly *syn*-6-methyl-3,4-benzotricyclo [3.3.0.$0^{2,8}$]oct-3-ene (67s). In addition to the di-π-methane products, photoreduction products of 58s and 58a were also obtained. The structures of all photoproducts were determined by independent syntheses.

PART I

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PART II

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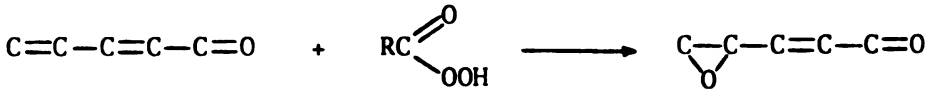
PART I

SYNTHESES
AND
ACID-CATALYZED REARRANGEMENT OF EPOXYENONES

INTRODUCTION

The preparation of γ,δ-epoxyenones from conjugated dienones can be carried out by a number of methods, the most frequently employed and generally applicable of which is peracid oxidation.[1] The versatility and selectivity of this reaction makes it the method of choice in most conversions of a double bond to the corresponding epoxide in a variety of monounsaturated or polyunsaturated systems.

The most common peracids used for the conversion of dienones represented by 1 to the epoxide 2 have been perbenzoic,[2] monoperphthalic,[3] and m-chloroperbenzoic acids.[4] Of these peracids,



1 2

m-chloroperbenzoic acid is the most convenient oxidizing agent. It is commercially available, reacts at a somewhat faster rate than perbenzoic acid, and is ideally suited for epoxidations which require long reaction times due to its excellent stability.

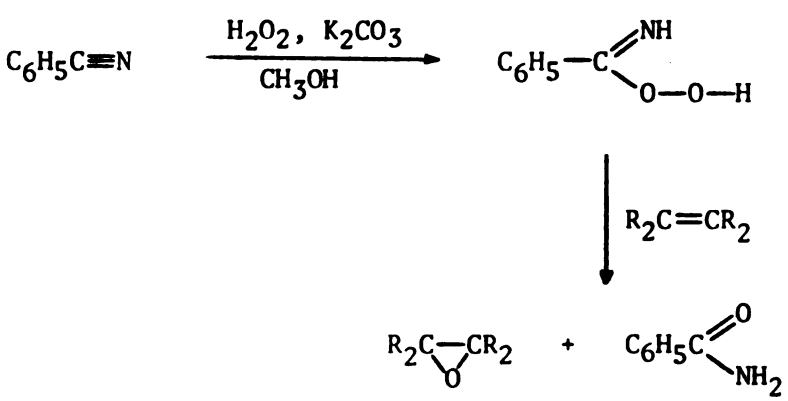
The preferential oxidation of the γ,δ-double bond over the α,β-double bond in conjugated dienones reflects the electrophilic nature of organic peracids. Epoxidation reactions proceed by an electrophilic attack of the peracid upon the double bond; thus the rate of epoxidation is very sensitive to the electron density at the olefinic site.[1] In a

system represented by 1 the γ,δ-double bond has a greater electron density than the α,β-double bond,[5] and selectivity is easily achieved.

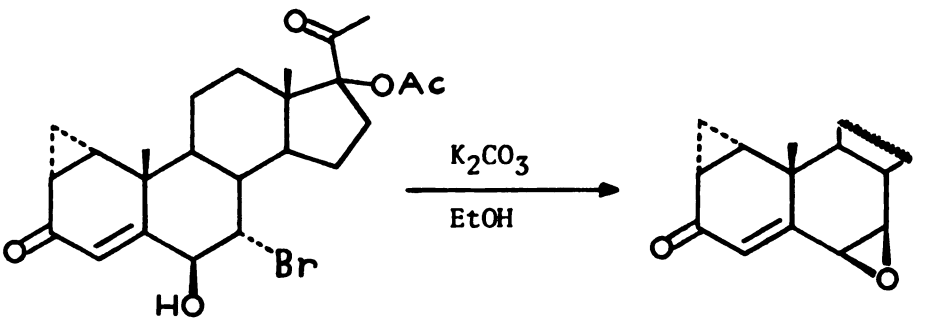
The generality of epoxidation with organic peracids is impaired when the olefin or the epoxide is unstable to the carboxylic acid formed as a by-product.[6] Also, it is essential that other functional groups present in the molecule be stable to the peracid employed. Finally, it should be noted that for systems such as 1, selectivity towards oxidation of the γ,δ-double bond is not achieved if a third double bond with similar or greater reactivity towards the peracid is present in the molecule.

A number of modifications have been employed to overcome these major difficulties encountered with normal peracid epoxidation. For instance, epoxidation with a peracid in dichloromethane-aqueous sodium bicarbonate biphasic system permits, in some cases, the epoxidation of acid-sensitive olefins or the epoxidation of olefins yielding acid-sensitive epoxides.[7]

Another useful variant of the peracid method which shows promise in the preparation of acid-sensitive γ,δ-epoxyenones is the reaction of benzonitrile with alkaline hydrogen peroxide. The probable path, illustrated in the following equations, involves a peroximidic acid intermediate which readily epoxidizes olefins under neutral conditions.[8]



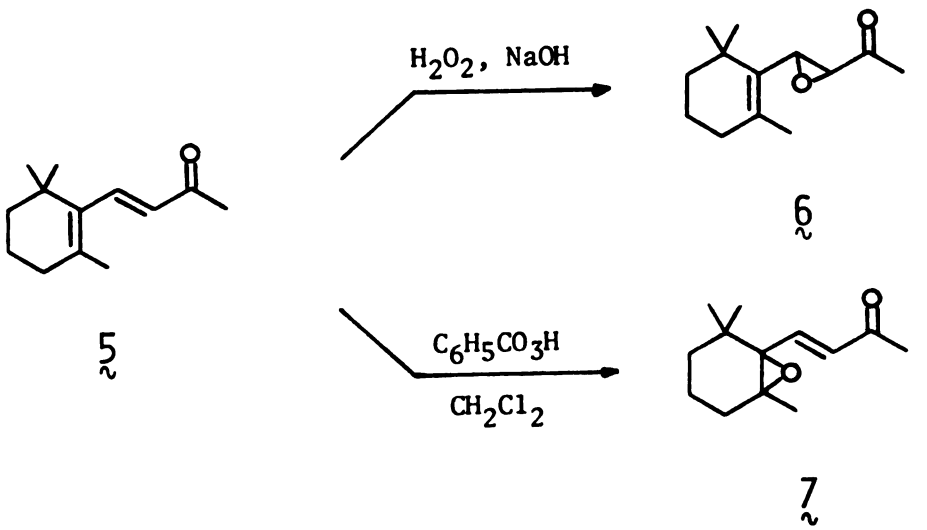
In addition to organic peracids, other methods of epoxidation have shown great promise in the synthesis of γ,δ-epoxyenones. A very effective route involves the dehydrohalogenation of bromohydrins or chlorohydrins.[9] This process is illustrated in the formation of a steroidal 6β,7β-epoxide 4 from the corresponding bromohydrin 3.[10]



3 4

A particularly significant aspect of this method, besides its effectiveness in the synthesis of acid-sensitive epoxides, is that it often leads to epoxides isomeric in configuration to those obtained by peracid epoxidation.[10]

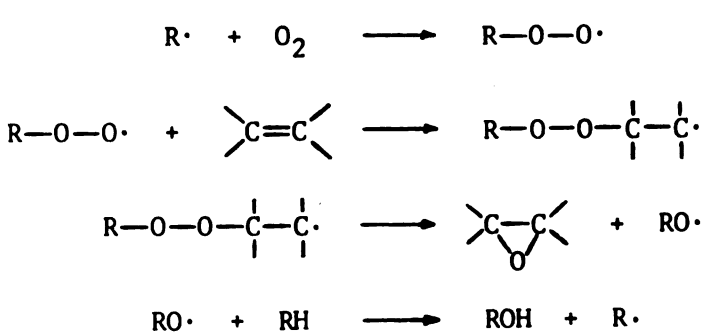
A method frequently employed for epoxidation of double bonds conjugated with a strong electron withdrawing group such as carbonyl is alkaline hydrogen peroxide.[1d,9] However, the selectivity of such a method is the reverse of organic peracids when applied to systems such as 1. Thus, when β-ionone 5 is treated with alkaline hydrogen peroxide, it yields only the α,β-epoxide 6. In contrast, when β-ionone is treated with perbenzoic acid it gives the γ,δ-epoxide 7.[3a] Similarly, treatment of eucarvone[11] or 4-benzoyl-1-phenylbuta-1,3-diene[12] with alkaline hydrogen peroxide, even in excess, yields only the α,β-monoepoxides.



5 6 7

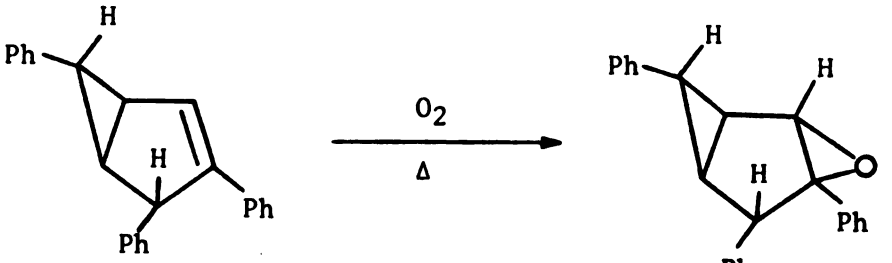
Olefins have also been epoxidized by reaction with peroxides in the presence of vanadium and molybdenum salts.[13] The neutral and mild conditions of this method offers a potentially useful route into acid-sensitive epoxyenones.

Besides the major epoxidation methods discussed above, other less general processes are available.[9] Among these is the autoxidation of olefins.[14] This autoxidation process is not well understood but probably involves a free radical mechanism of the following type:[15]



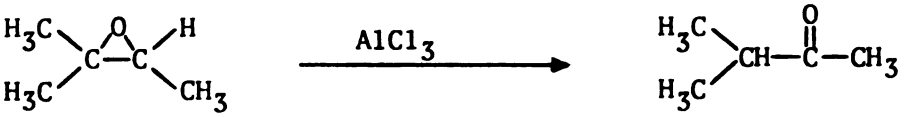
There are several examples of epoxide formation by this approach; however, because of competition among other free radical processes, high yields desirable for laboratory preparations are rare.[14]

Nevertheless, given a system where these competitive processes are minimized, the autoxidation of alkenes to epoxides may be of some synthetic and preparative value. The autoxidation of *exo,exo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene 8 to give epoxide 9 in 76% yield exemplifies this method.[16]



8 9

Among the synthetic uses of epoxidation products, the acid-catalyzed rearrangement of epoxides are of special interest, since they provide a simple means of converting olefins to carbonyl compounds.[6,17] Thus, in the presence of aluminum trichloride, trimethylethylene oxide 10 rearranges to methyl isopropyl ketone 11:[18]



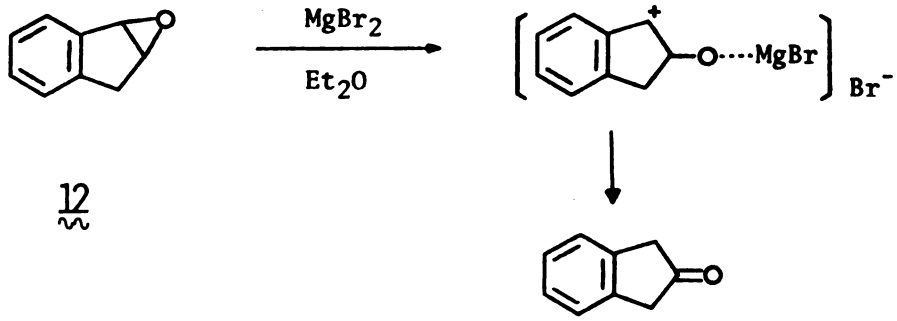
10 11

In general, Lewis acids (i.e., aluminum trichloride, magnesium bromide or boron trifluoride etherate) are the usual catalysts, although aqueous mineral acids and non-nucleophilic carboxylic acids such as trifluoroacetic

acid are also used. Rearrangement reactions of this kind become especially useful if one can predict in any particular case what the major product will be. The major product formed from the rearrangement of an epoxide is governed by two main factors: the direction of ring opening, and the relative migratory aptitudes of the different substituents.

The direction of ring opening in acid-catalyzed rearrangements may in general be predicted simply on the basis of the relative ease of ionization of the two carbon-oxygen bonds in question. By analogy with other situations in organic chemistry, the sequence is expected to be tertiary > secondary > primary. The rearrangement of trimethylethylene oxide 10 to methyl isopropyl ketone 11 illustrates this rule. Similarly, isobutylene oxide gives largely isobutyraldehyde and propylene oxide yields propionaldehyde.[18]

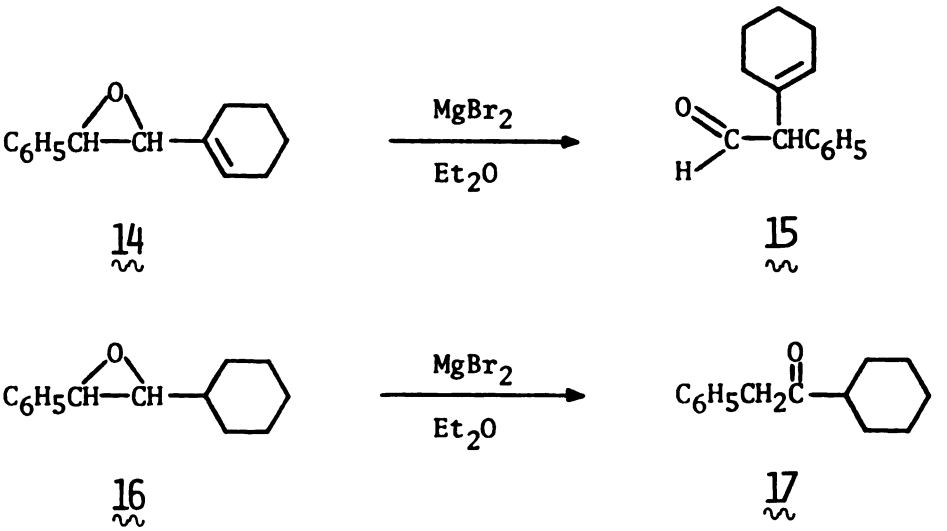
Aryl groups are superior to alkyl groups in increasing the ease of heterolysis of the carbon-oxygen bond. For example, in indene oxide 12 cleavage of the C-O bond which leads to an incipient benzylic carbonium ion is preferred, and 2-indanone 13 results.[19] In fact, monoaryl-substituted epoxides invariably rearrange to give nonconjugated ketones.



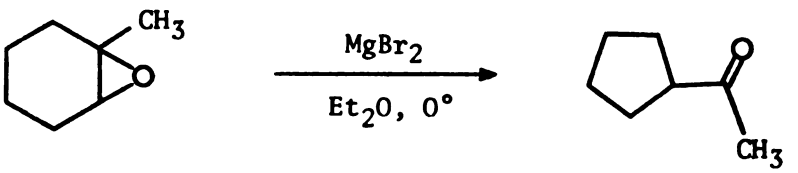
12

13

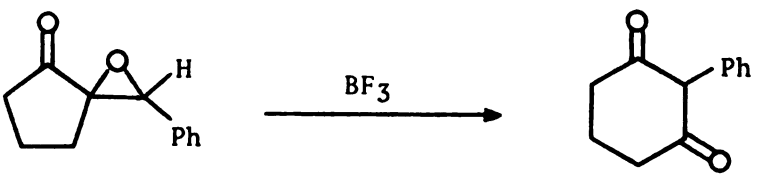
Vinyl substitution, like phenyl substitution, weakens a C-O bond with respect to ionization. However, there are a number of reports of rearrangement of epoxides involving cleavage of the bond to a vinyl rather than a phenyl substituted carbon atom.[6b] For example, the cyclohexenyl epoxide 14 rearranges to aldehyde 15, whereas the cyclohexyl analog 16 rearranges with cleavage of the other C-O bond to give ketone 17.[20]



Once the direction of ring opening has been decided, in epoxide 10, for example, by the circumstance that a tertiary carbonium ion is formed, there remains a choice between hydrogen migration or alkyl migration. This will be decided by the relative migratory aptitudes of the groups and in general this order is aryl > acyl > H > ethyl > methyl. Among the few exceptions to this order of migratory aptitudes, are those which occur when for steric reasons hydrogen migrates in preference to phenyl.[6] In certain cases, the rearrangement may constitute a ring expansion or ring contraction, as shown by the following two examples:[21,22]

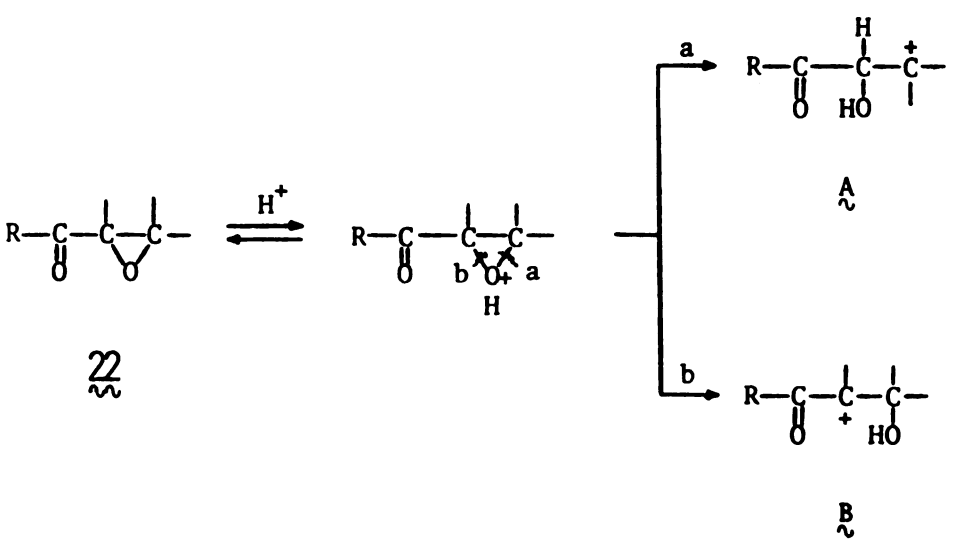


18 19



20 21

As illustrated by epoxide 20, acid-catalyzed rearrangement of α,β-epoxyketones is an extremely useful route to dicarbonyl compounds. This rearrangement has been intensively studied by House and co-workers.[23,24] As with other epoxides, the rearrangement of an α,β-epoxyketone (22) under the influence of acids can also proceed in two directions:



22

However, with only few exceptions,[25] the rearrangement proceeds through the more stable carbonium ion $\underset{\sim}{A}$ and the observed products depend only on the migratory aptitudes of the groups attached to the epoxide ring.

In contrast to α,β-epoxyketones, the acid-catalyzed rearrangement of γ,δ-epoxyenones such as $\underset{\sim}{2}$ have been completely neglected in the literature. A detailed study of this rearrangement should yield valuable information concerning its synthetic utility as well as information concerning the mode of epoxide ring opening and group migration in such systems.

It is the purpose of this part of this thesis to examine the generality of autoxidation of conjugated dienones to γ,δ-epoxyenones and to study the acid catalyzed rearrangement of such epoxides.

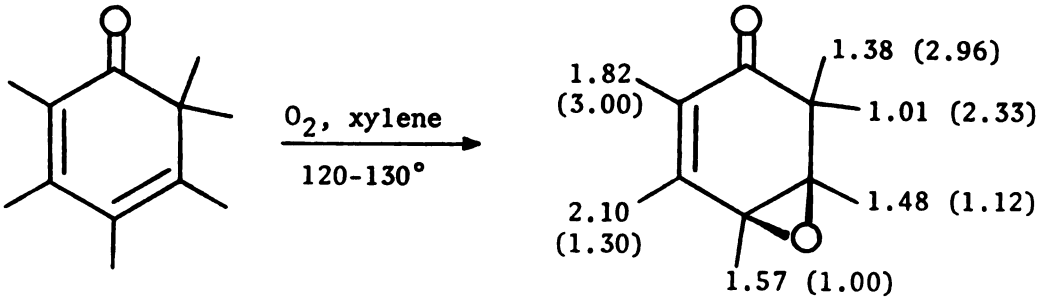
RESULTS AND DISCUSSION

A. Autoxidation of Conjugated Dienones and Diene Esters to γ,δ-Epoxyenones

In an attempt to obtain a Diels-Alder adduct between 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone 23 and hexamethyl-Dewar benzene by refluxing the two components in xylene, a white solid, mp 48-49.5°, was isolated which was identified as epoxide 24. The infrared spectrum showed a band at 840 cm^{-1} which is characteristic for epoxides[26] and a carbonyl band at 1680 cm^{-1}, indicating conjugation with a double bond. The conjugation of the carbonyl group was corroborated by the compound's ultraviolet spectrum, which showed λ_{max} (cyclohexane) 253 nm (ε 7230), 324 (240). The nmr spectrum (assignment and europium shift data are given below) was also consistent with structure 24. Finally, epoxide 24 was conclusively identified by independent synthesis using m-chloroperbenzoic acid.

The unexpected formation of epoxide 24 led to further investigation of this reaction. The hexamethyl-Dewar benzene obviously had nothing to do with the reaction and was omitted from further studies of the epoxidation. Additional attempts to effect a Diels-Alder addition of hexamethyl-Dewar benzene to dienone 23 in the absence of air were unsuccessful.

When dienone 23 was heated in xylene at 120-130° for 21 hr in the presence of air, epoxide 24 was formed in 65-75% yield. No reaction was observed when dienone 23 was heated in xylene at 120-130° under a



23 24

nitrogen atmosphere for 48 hr or when dienone 23 was refluxed in chlorobenzene for 48 hr in the presence of air. When dienone 23 was heated in cyclooctane, cumene or mesitylene at 120-130°, epoxide 24 was formed, generally more rapidly and in better yield than when xylene was used as solvent. However, xylene yielded relatively smaller amounts of side products, thus making it the most practical solvent for the reaction from a preparative viewpoint. These results are summarized in Table I.

When dienone 23 was heated in xylene for longer than 21 hr (36-48 hr), the yield of epoxide 24 decreased and a significant amount of polymer was formed. Also, there was very little advantage in reaction time, yield or reproducibility by bubbling air or oxygen through the reaction mixture.

To explore the generality and scope of this epoxidation method, the reaction was carried out using a variety of dienones. Table II lists several epoxides which have been prepared by autoxidation of the corresponding unsaturated precursors. In all cases, the dienone or diene ester was heated in xylene at 120-130° for 24 hr. No attempt

Table I. The Effect of Solvent on the Autoxidation of 1,2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone (23).

Solvent	Reaction Time	Yield of Epoxide 24[a]
Xylene	21 hr	65-75%
Cyclooctane	13	70-75
Mesitylene	14	80
Cumene	8	90-95
Chlorobenzene	48	0

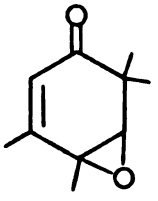
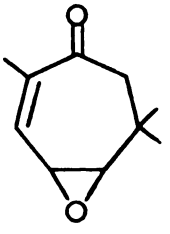
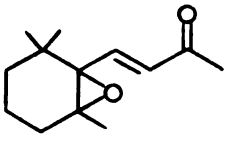
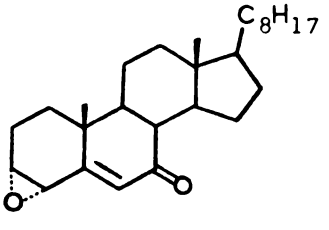
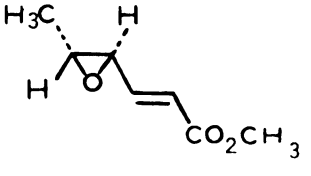
[a]Absolute yields obtained by nmr versus an internal standard.

was made to optimize yields. The reactions of 25-28 were performed on a 100 mg scale. When the oxidation of 29 was scaled up from 100 mg to 3 g, the yield improved from 49% to 90%.

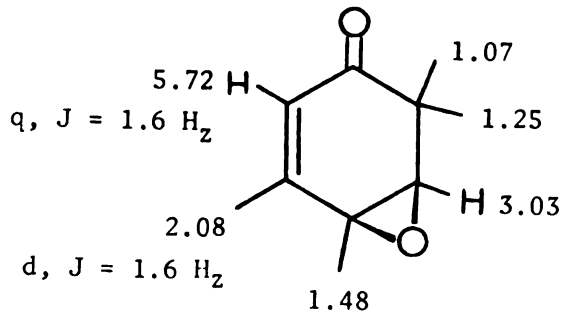
Epoxides 25 and 26 have not been previously described. Their structures were established by their spectral properties and independent synthesis using m-chloroperbenzoic acid. Epoxide 25, 4,5-epoxy-3,4,6,6-tetramethyl-2-cyclohexenone, was obtained as colorless crystals, mp 48.0-50.0°, from the corresponding dienone.[27] The infrared spectrum showed a carbonyl absorption at 1680 cm^{-1}, indicating conjugation with a double bond, and an epoxide band at 890 cm^{-1}. The ultraviolet spectrum also showed that the carbonyl and carbon-carbon double bond were conjugated; λ_{max} (95% ethanol) 247 nm (ε 7200), 326 (143). The nmr spectrum was consistent with the assigned structure.

Epoxide 26, 4,5-epoxy-2,6,6-trimethyl-2-cycloheptenone, was obtained from 2,6,6-trimethyl-2,4-cycloheptadienone (eucarvone)[28] as a clear liquid.

Table II. Epoxyenones Prepared Using Molecular Oxygen

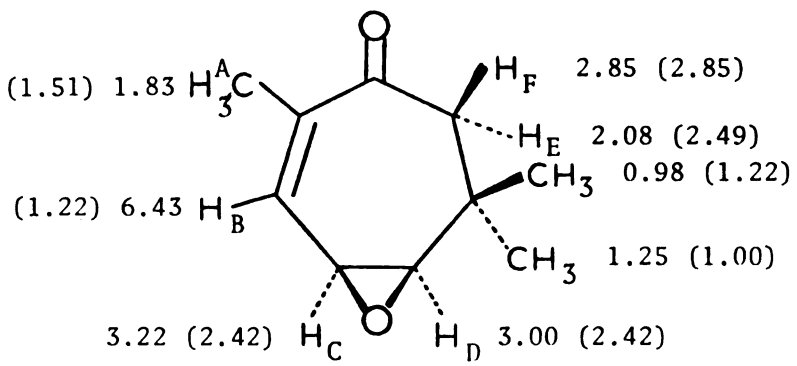
Epoxide	No.	Yield, %[a]
	25	51
	26	52
	27	72
	28	31
	29	90

[a]Yield of isolated epoxide, corrected for recovered starting material.



25

The infrared spectrum showed a carbonyl band at 1670 cm^{-1}, indicating conjugation with a double bond, and a band at 875 cm^{-1}, due to the asymmetric stretching of the epoxide ring. The ultraviolet spectrum showed a λ_{max} (95% ethanol) at 246 nm (ϵ 7920). The nmr assignment, based primarily on the splitting pattern and europium shift data, is shown below. The long range coupling between H_D and H_F and the assignment of protons H_E and H_F was confirmed by deuterium labeling. Preparation of 26 from eucarvone deuterated at C-7[29] gave 26-d_2, lacking methylene signals at δ 2.85 and 2.08. In addition, the signal at δ 3.00 changed from a "doublet of doublets" to a doublet.



26

H_A = d, J_{AB} = 1.6 Hz

H_B = q of d, J_{BC} = 6.1 Hz, J_{AB} = 1.6 Hz

H_C = d of d, J_{BC} = 6.1 Hz, J_{CD} = 4.2 Hz

H_D = d of d, J_{CD} = 4.2 Hz, J_{DE} = 1.4 Hz

H_E = d of d, J_{EF} = 13.0 Hz, J_{DE} = 1.4 Hz

H_F = d, J_{EF} = 13.0 Hz

Epoxides 27-29 have been previously described in the literature.[30-32] However, in order to confirm their structures, these epoxides were synthesized independently using m-chloroperbenzoic acid. In every case, the nmr and infrared spectra of the epoxide obtained with molecular oxygen was identical to the spectra of the epoxide obtained with m-chloroperbenzoic acid. The spectral properties of these epoxides are given in the experimental section.

To probe the effect of radical initiators on the epoxidation with molecular oxygen, the autoxidation of methyl sorbate in the presence of α,α'-azobis-iso-butyronitrile was studied. The results are summarized in Table III. There is some advantage in reaction time and yield by using a radical initiator. However, such a procedure is of little practical value since it increases the amount of undesired side-products making isolation of the epoxide more difficult.

The epoxidation with molecular oxygen can best be explained by a free radical mechanism as illustrated in Scheme 1. The autoxidation may be initiated by reaction of triplet oxygen with the hydrocarbon

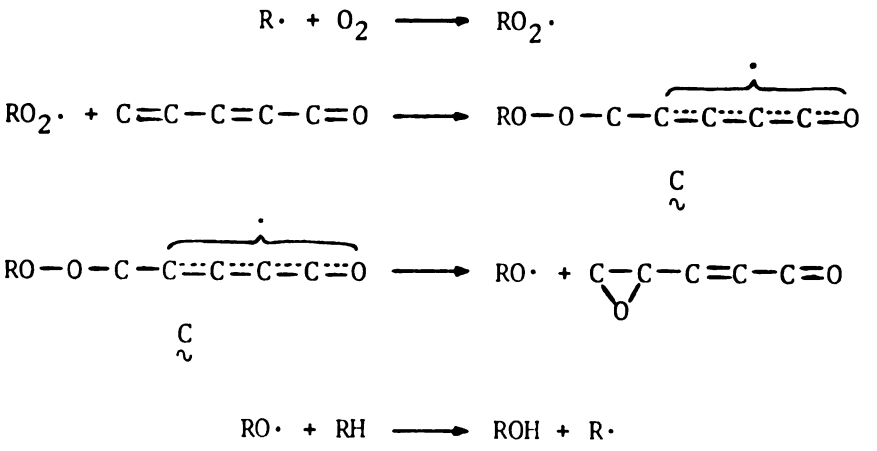
Table III. The Effect of a Radical Initiator on the Autoxidation of Methyl Sorbate in Xylene.

Concentration of AIBN, M	Reaction Temp.	Reaction Time, hr.	Epoxide 29, (% yield)[a]	% Unreacted Methyl Sorbate[a]
0.01	80-90	6.0	45.0	50.0
0.02	80-90	6.0	47.0	45.0
0.04	80-90	6.0	50.3	41.5
none	120-130	6.0	24.0	70.0
0.01	80-90	20.0	71.2	18.8
none	120-130	20.0	61.0	28.0

[a]Absolute yields obtained from the nmr spectrum of the crude reaction mixture.

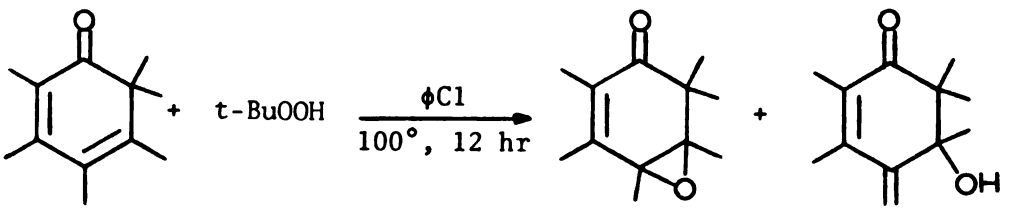
solvent to form a peroxy radical which in turn adds to the conjugated dienone. The epoxide can then be formed by an S_H2 reaction on the O-O

SCHEME 1



bond in radical C. Consistent with this mechanism is the lack of oxidation in chlorobenzene and the formation of typical oxidation products from the solvent (p-methylbenzyl alcohol from xylene, cumyl alcohol and acetophenone from cumene, etc.). Also, epoxide formation was completely suppressed by addition of 4-t-butylcatechol, a radical inhibitor, to the reaction mixture.

As a further probe into the nature of this autoxidation process, the reaction between t-butyl hydroperoxide and dienone 23 in chlorobenzene was examined. Under these conditions two products were observed,

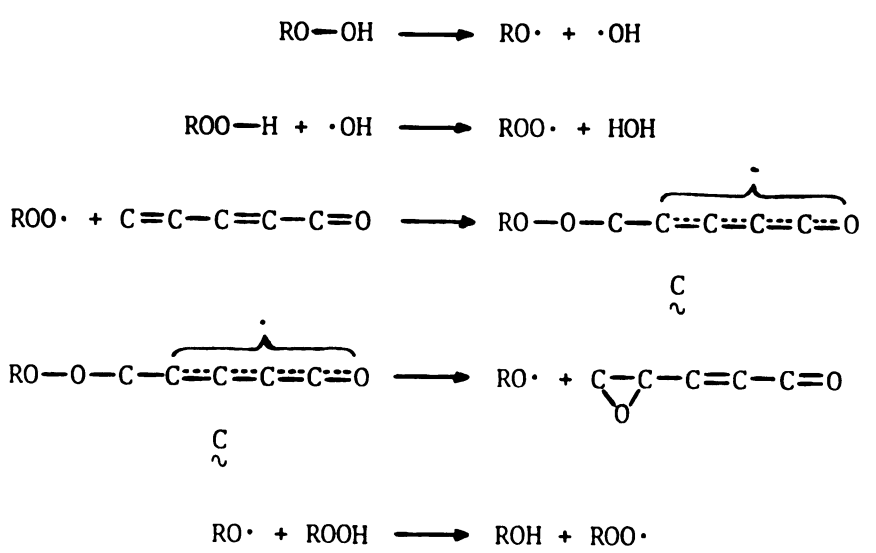


23 24, 35% 32, 48%

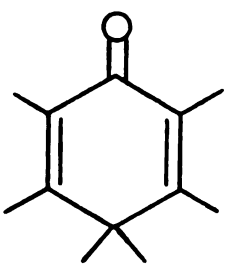
epoxide 24 and a hydroxy ketone assigned structure 32. A plausible mechanism for epoxide formation with an alkyl hydroperoxide is presented in Scheme 2. The formation of epoxide 24 with t-butylhydroperoxide clearly supports the mechanism presented in Scheme 1 in which the peroxy radical is the epoxidizing agent. A detailed discussion of the structure and formation of hydroxy ketone 32 will be presented later.

As illustrated by the reaction of 28 and 29, the autoxidation of dienones and diene esters to γ,δ-epoxides may be highly stereoselective. Thus, with 3,5-cholestadien-7-one the product is the α-epoxide and with methyl sorbate the E,E-epoxide 29 is the predominant product. In the case of methyl sorbate, however, the nmr spectrum shows traces of another isomer, probably *cis* at the epoxide ring.

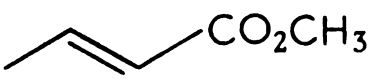
SCHEME 2



In all cases studied, the epoxides obtained by autoxidation are identical to those obtained using m-chloroperbenzoic acid. However, isolated double bonds or singly conjugated systems such as 30 and 31 are not oxidized by molecular oxygen, so that the method provides a selectivity not always available with a peracid. Thus, though dienone 30 is easily epoxidized with m-chloroperbenzoic acid even at 0°,[33]



30



31

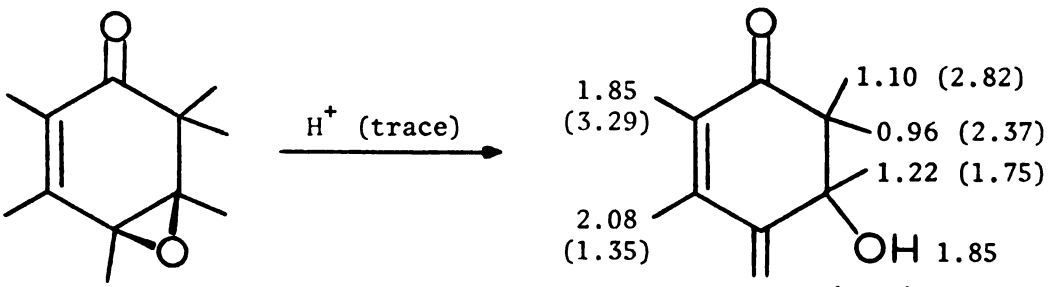
an equimolar mixture of 23 and 30, heated in xylene for 24 hr, gave a 70% yield of 24 and essentially quantitative recovery of unreacted 30.

Clearly, epoxidation of dienones and diene esters with molecular oxygen offers a valuable route to γ,δ-epoxyenones and γ,δ-epoxyenoates. The selectivity towards oxidation at the γ,δ-double bond, the neutral and mild reaction conditions, and the simplicity of this reaction makes it a potentially useful alternative to epoxidation of certain classes of compounds with organic peracids.

B. Acid-Catalyzed Rearrangement of 4,5-Epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone (24).

The epoxyenone 24, described in the previous section, was obtained in high yield by treating the corresponding dienone 23 with m-chloroperbenzoic acid. Epoxide 24 could be purified by chromatography over Florisil or neutral alumina but it was unstable to weakly acidic or basic conditions. For instance, chromatography on silica gel or treatment with a little aqueous acid, resulted in nearly quantitative rearrangement to a hydroxy ketone assigned structure 32, based on its spectral properties and further rearrangements in stronger acid (*vide infra*). Similarly, if after reacting dienone 23 with m-chloroperbenzoic acid, the reaction mixture is washed with 10% Na_2SO_3 and saturated $NaHCO_3$ solutions to remove excess peracid and acid, epoxide 24 is converted to hydroxy ketone 32. The infrared spectrum of 32 showed a carbonyl band at 1670 cm^{-1} which indicates conjugation with both double bonds, a terminal methylene group band at 960 and 930 cm^{-1}, and hydroxyl group bands at 3620 (sharp, free OH), 3590 (sharp, intramolecular π-H bond), 3500 cm^{-1} (broad, intermolecular H bond). The conjugation of the carbonyl

group with two double bonds is corroborated by the compound's uv spectrum which showed λ_{max} at 282 nm (ε 11,700), 273 (15,200) and 266 (14,500). The nmr data given below are also consistent with structure 32.

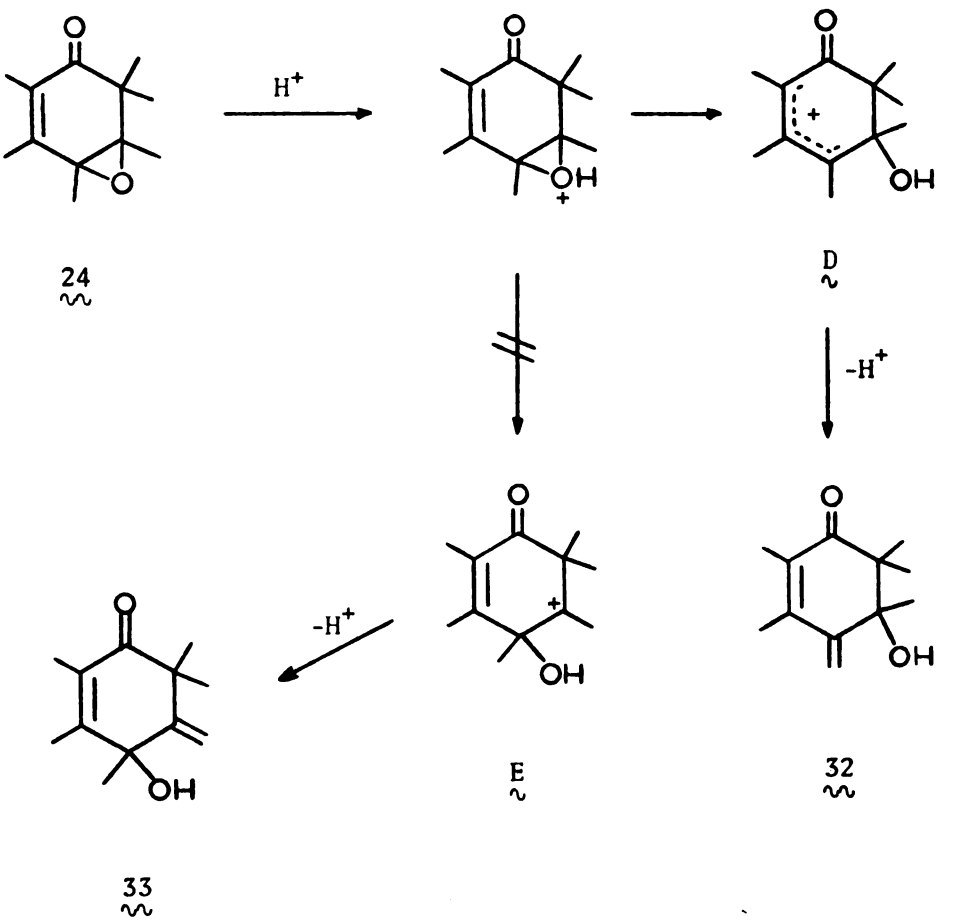


24 32

Hydroxy ketone 32 is undoubtedly formed from 24 by proton loss from the intermediate cation D (Scheme 3). The alternative epoxide ring-opening mode to give E would lead to structure 33, which is also reasonably consistent with the nmr spectrum, but which is less consistent with the uv and ir data and is conclusively eliminated by labeling results. Preparation of 24 from dienone 23 containing CD_3 at C-3 and C-5[34] gave the epoxide 24-d_6 lacking methyl signals at δ 1.48 and 2.10. Treatment of 24-d_6 with dilute acid gave the hydroxy ketone 32-d_6 lacking methyl signals at δ 1.22 and 2.08. If the hydroxy ketone had structure 33, the product would have contained only five deuteriums and would have lacked the vinyl proton signals.

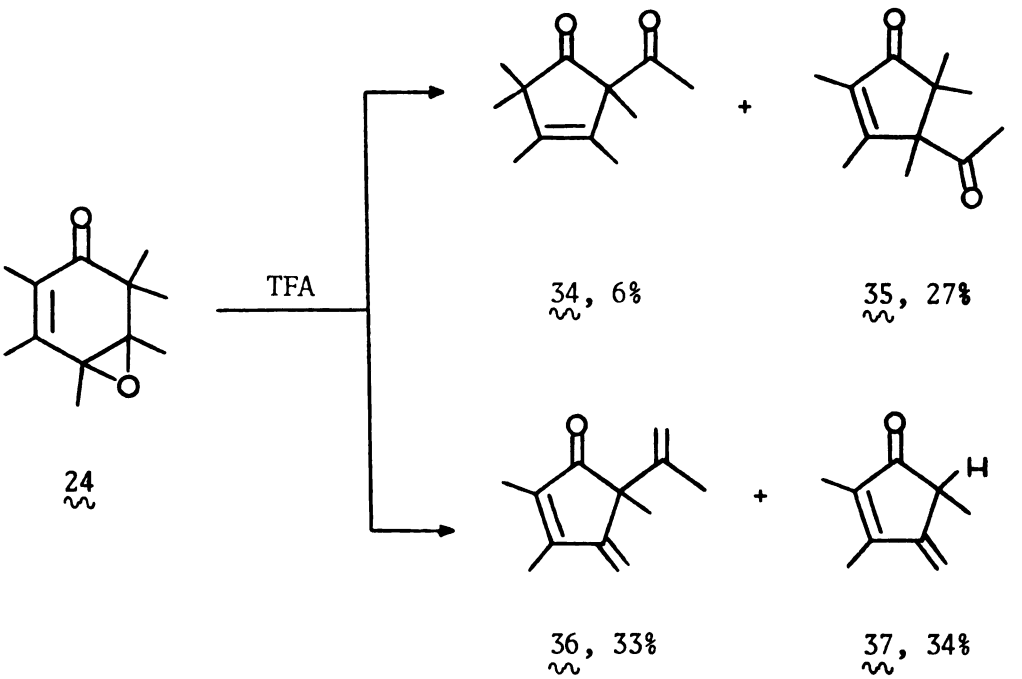
Treatment of epoxyenone 24 with neat trifluoroacetic acid gave four products, only two of which were isomers (mass spectrum) of the starting epoxide. These products were assigned structures 34-37. The

SCHEME 3



product ratios depend on reaction time and temperature, those shown being for 20 hr reaction time at room temperature.

The product structures were established primarily by their spectral properties. Diketone 34[35] showed two carbonyl absorptions at 1740 and 1710 cm^{-1}, and only weak uv absorption, indicating that neither carbonyl group was conjugated with the double bond. The nmr spectrum, with europium shift data, is consistent with structure 34.

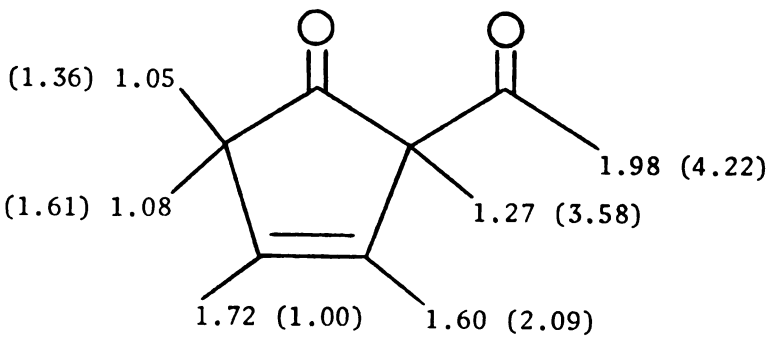


24

34, 6% 35, 27%

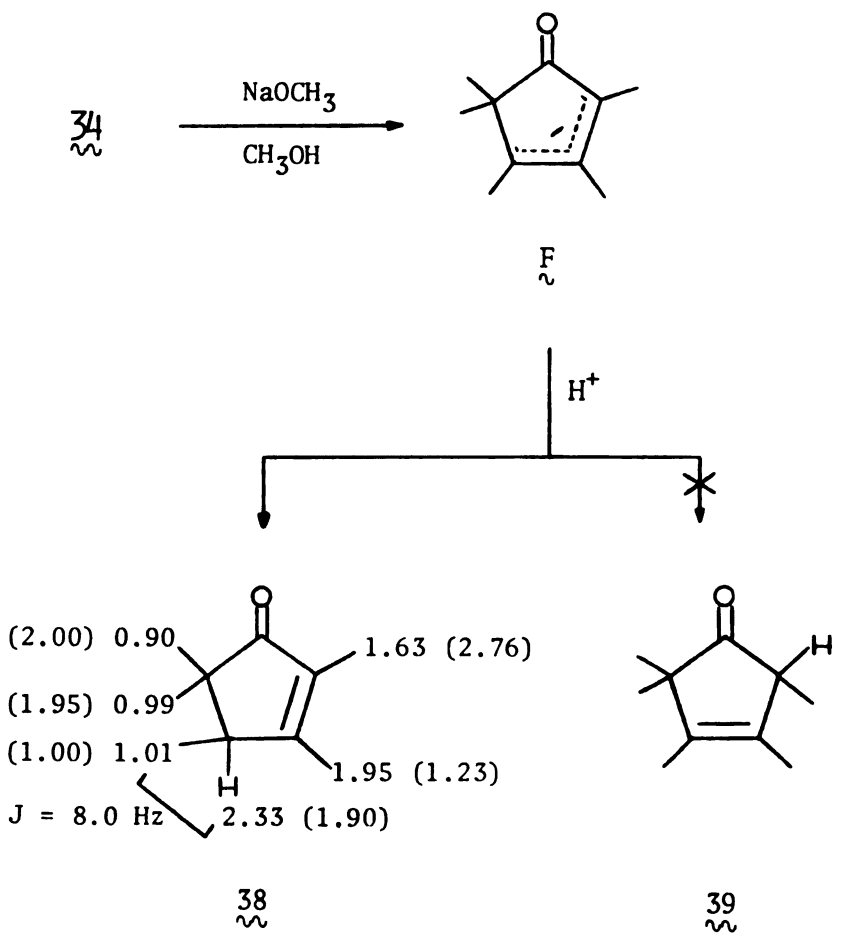
36, 33% 37, 34%

Cleavage of 34 with base supports the structural assignment. With sodium methoxide in methanol, 34 afforded the conjugated cyclopentenone 38. Cleavage of the acetyl group should give the allylic anion F, which



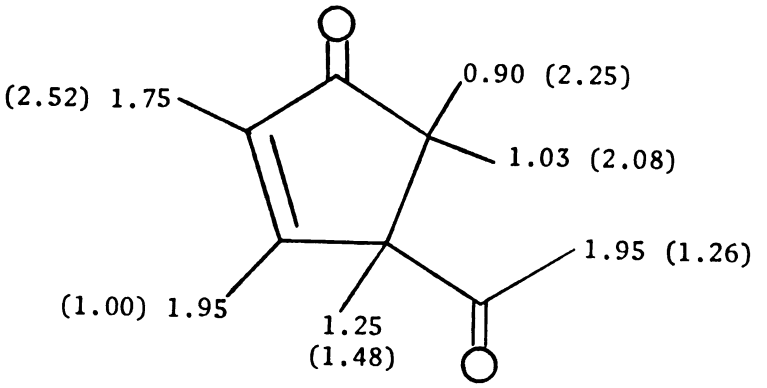
34

is protonated in the γ-position to give 38. Structure 39, which could be formed by α-protonation, is eliminated from consideration by the ir and uv data. The infrared spectrum of 38 showed a carbonyl band at 1700 cm^{-1}, indicating conjugation of a cyclopentanone carbonyl group with a double bond, and a band at 1650 cm^{-1} due to carbon-carbon double bond absorption. The uv spectrum showed a λ_{max} at 235 nm (ε 6000) also indicating conjugation with the carbonyl group. The nmr data given above are consistent with structure 38.



38 39

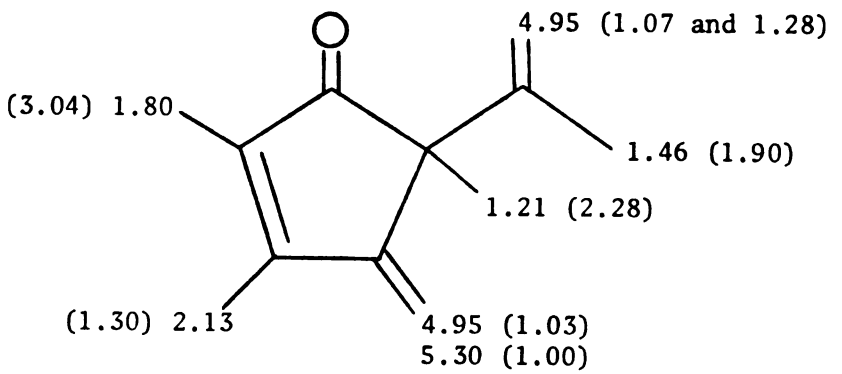
Diketone 35 also showed two carbonyl absorption bands at 1710 and 1660 cm^{-1}, but unlike 34, 35 showed a uv absorption at 237 nm (ε 7720),



35

indicating that one of the carbonyls was conjugated with the double bond. The nmr data are in agreement with the assigned structure; the shift reagent appears to coordinate primarily at the cyclopentenone carbonyl group. The base peak in the mass spectrum of 35 appeared at M-42 (loss of CH_2=C=O) and the next most intense peak (rel. intensity 60) was at M-57 (loss of CH_2=C=O and CH_3).

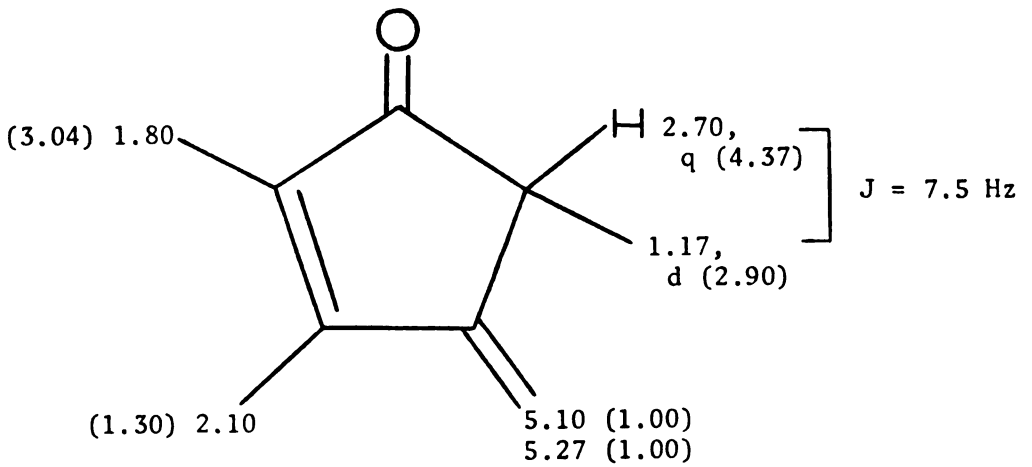
The product assigned structure 36 corresponded in analysis to loss of water from the epoxyenone 24. The infrared spectrum showed a carbonyl



36

absorption at 1710 cm^{-1} which is consistent with a cyclopentenone carbonyl, strong carbon-carbon double bond absorptions at 1645 and 1620 cm^{-1}, and a strong terminal methylene band at 915 cm^{-1}. The uv maxima [340 nm (ε 63), 270 (13,700)] were consistent with a conjugated dienone. The nmr data for structure 36 are given above.

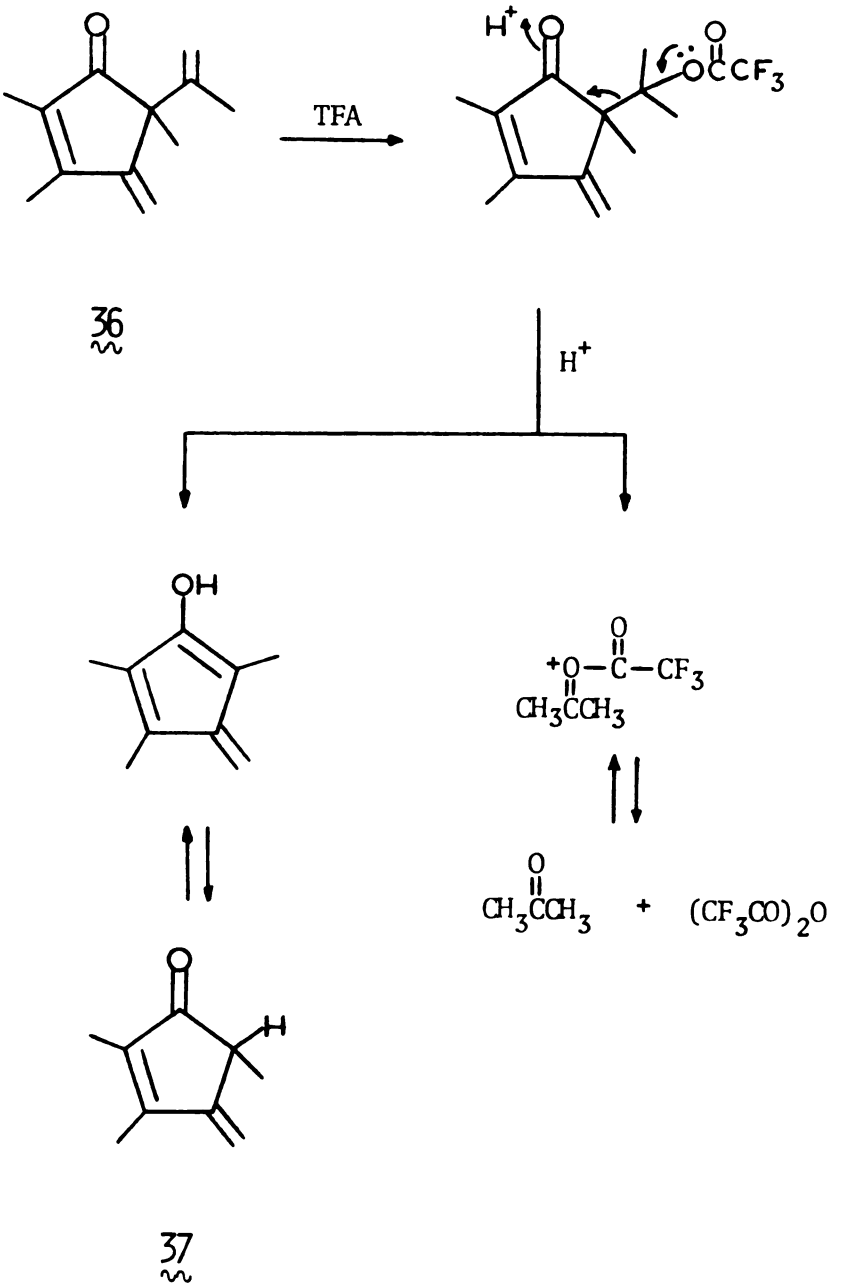
The product assigned structure 37 corresponded in analysis not only to loss of water from epoxyenone 24, but to loss of a C_3H_4 fragment as well. The uv spectrum was very similar to that of 36 [267 nm (ε 15,200)], as was the ir spectrum ($\nu_{C=O}$ 1710, $\nu_{=CH_2}$ 910 cm^{-1}). The nmr chemical shifts and europium shift data are consistent with structure 37. The proton at δ 2.70 was readily exchanged at room temperature in $NaOCH_3$-CH_3OD, causing collapse of the doublet at δ 1.17 to a singlet.



37

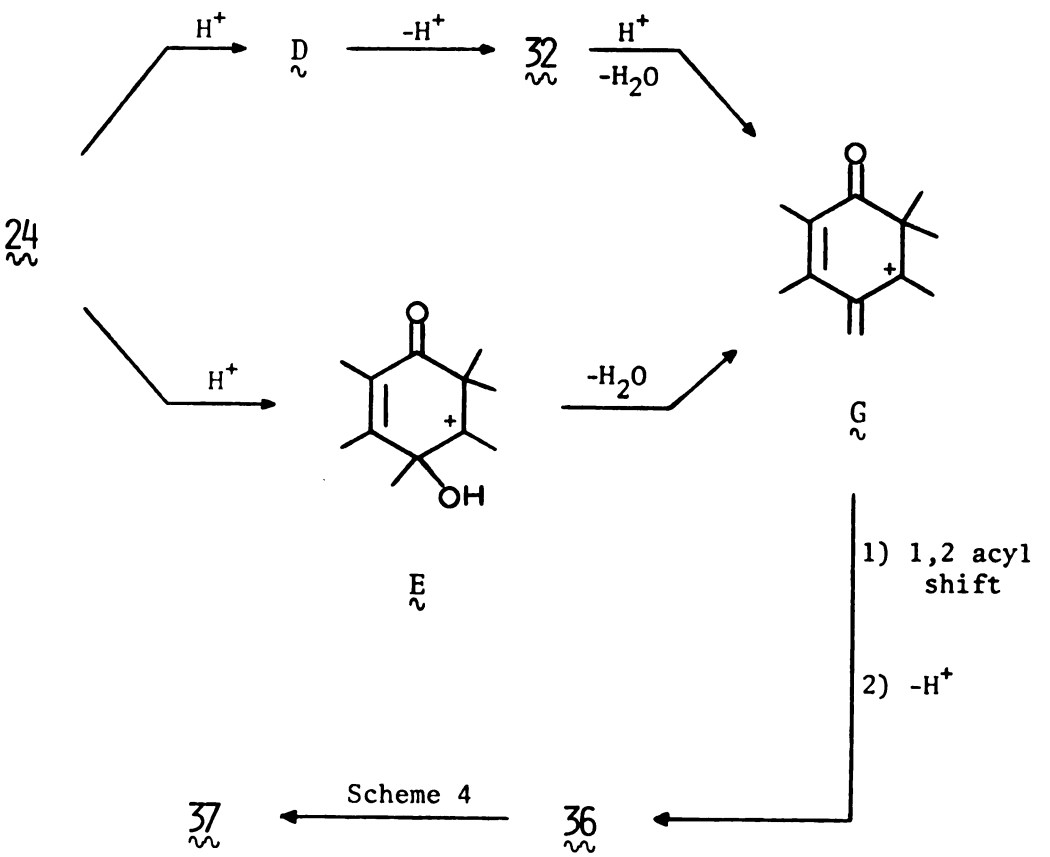
A plausible mechanism for the formation of 37 from 36 is given in Scheme 4. When the reaction was monitored by nmr, a sharp singlet, which increased in intensity as the reaction progressed, appeared at δ 2.33. This singlet was later shown to correspond to acetone in trifluoroacetic acid.

SCHEME 4



Products 36 and 37 were also formed by acid-catalyzed rearrangement of hydroxy ketone 32. Thus, independent treatment of 32 with trifluoroacetic acid at room temperature gave only 36 and 37, in ratios which depended on the reaction time. After 2 hr the product was 94% 36 and 6% 37, whereas after 46 hr it was 3% 36 and 97% 37. The formation of these products can be rationalized as in Scheme 5. Either 32 is a discrete intermediate as in the route 24 → 32 → 36 → 37 or it may be bypassed through the intermediacy of E. If the reaction proceeds via

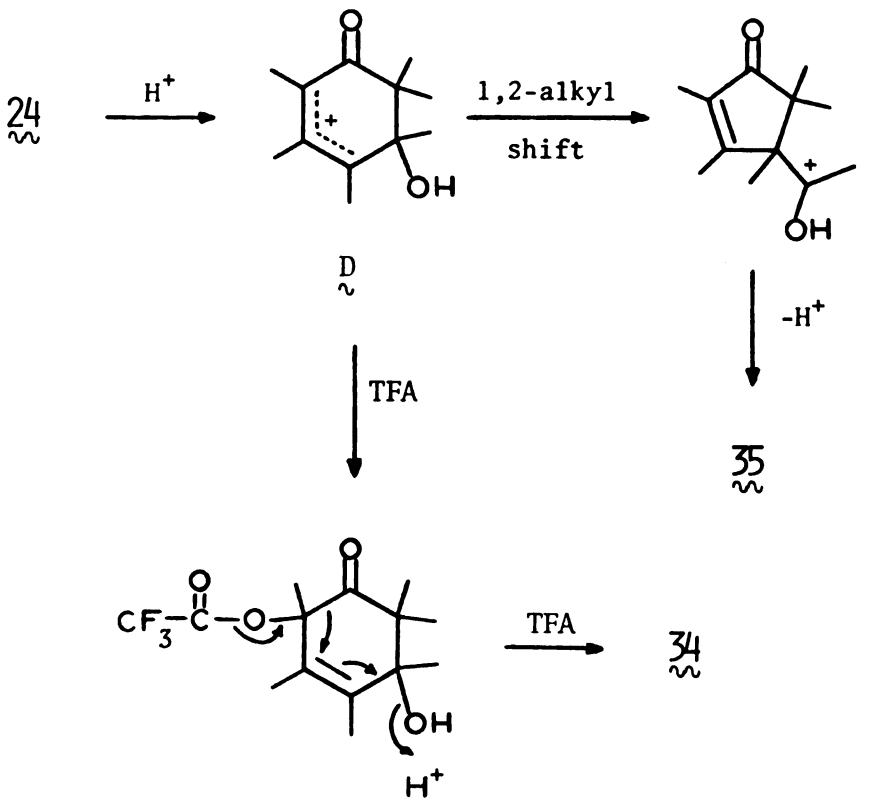
SCHEME 5



intermediate E, dehydration may precede 1,2-acyl shift as shown in Scheme 5, or the order of these steps may be reversed. Unfortunately, no simple experiment can distinguish between the two possible routes. It is clear, however, that the remaining two rearrangement products 34 and 35 are not produced from hydroxy ketone 32.

Possible routes to 34 and 35 are shown in Scheme 6. The first formed intermediate is once again D. Ring contraction and proton loss lead to 35, whereas attack of a nucleophile at the carbon α to the

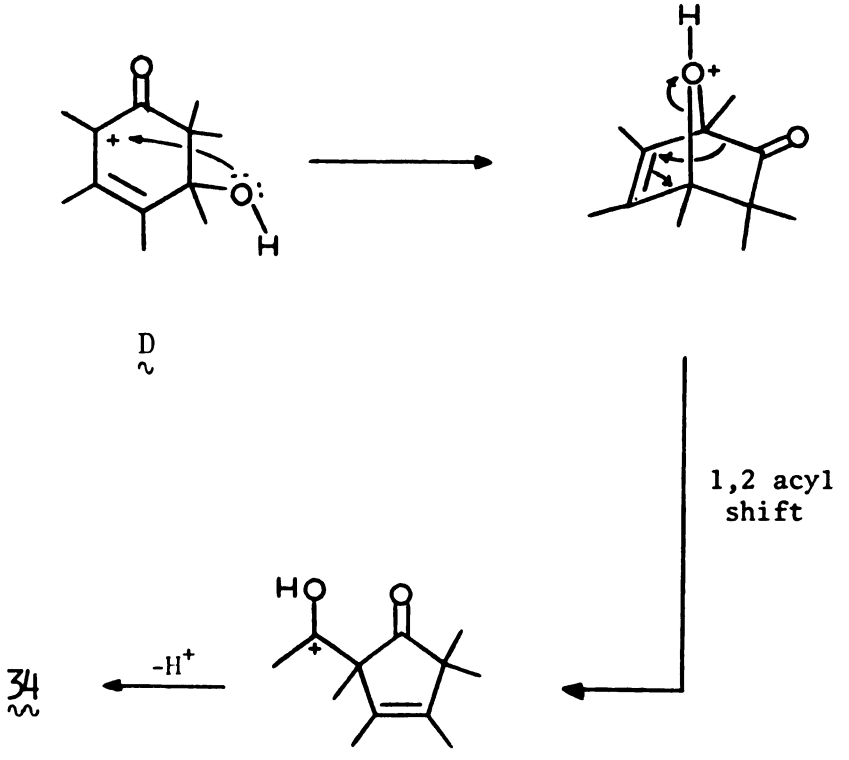
SCHEME 6



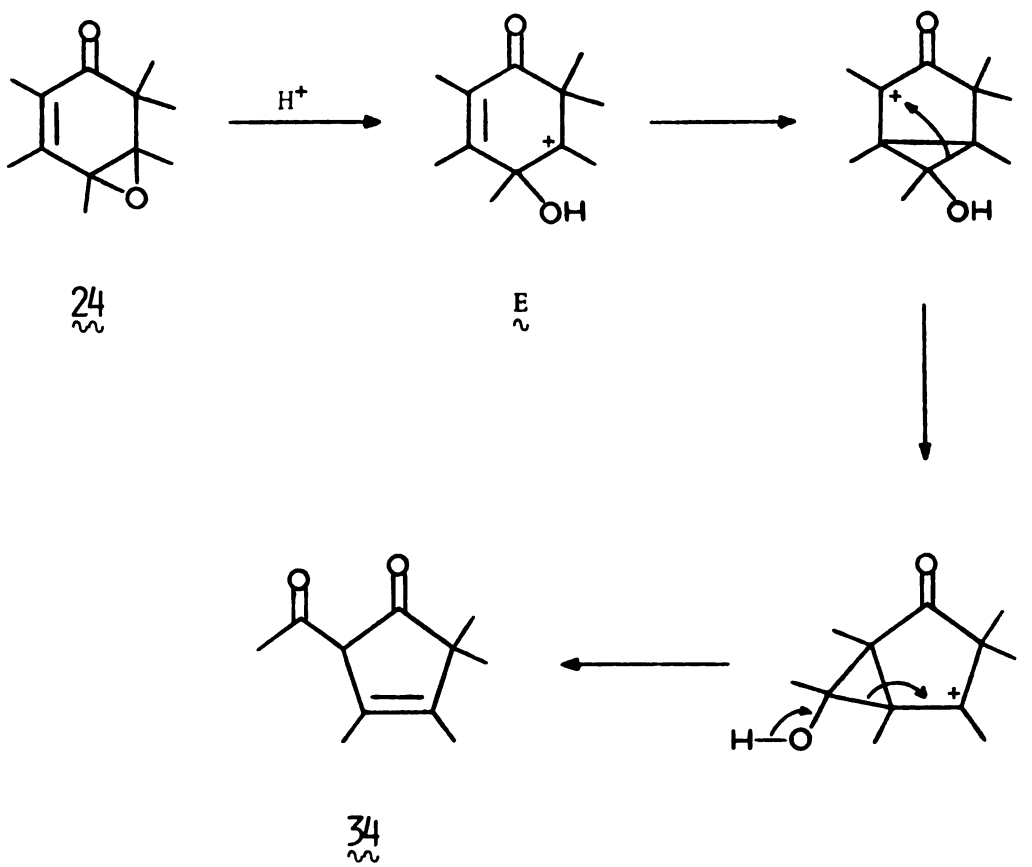
carbonyl group followed by an acyl shift and loss of hydroxyl lead to 34. The nucleophile shown in Scheme 6 is trifluoroacetic acid but it may also be water or even an intramolecular attack of the hydroxyl group at the C-5 position. This alternate route to 34 is shown in Scheme 7.

Still another plausible route from 24 to 34, involving a cyclopropylcarbinyl rearrangement, is shown in Scheme 8. This mechanism, however, was eliminated as a consequence of deuterium labeling experiments (*vide infra*).

SCHEME 7



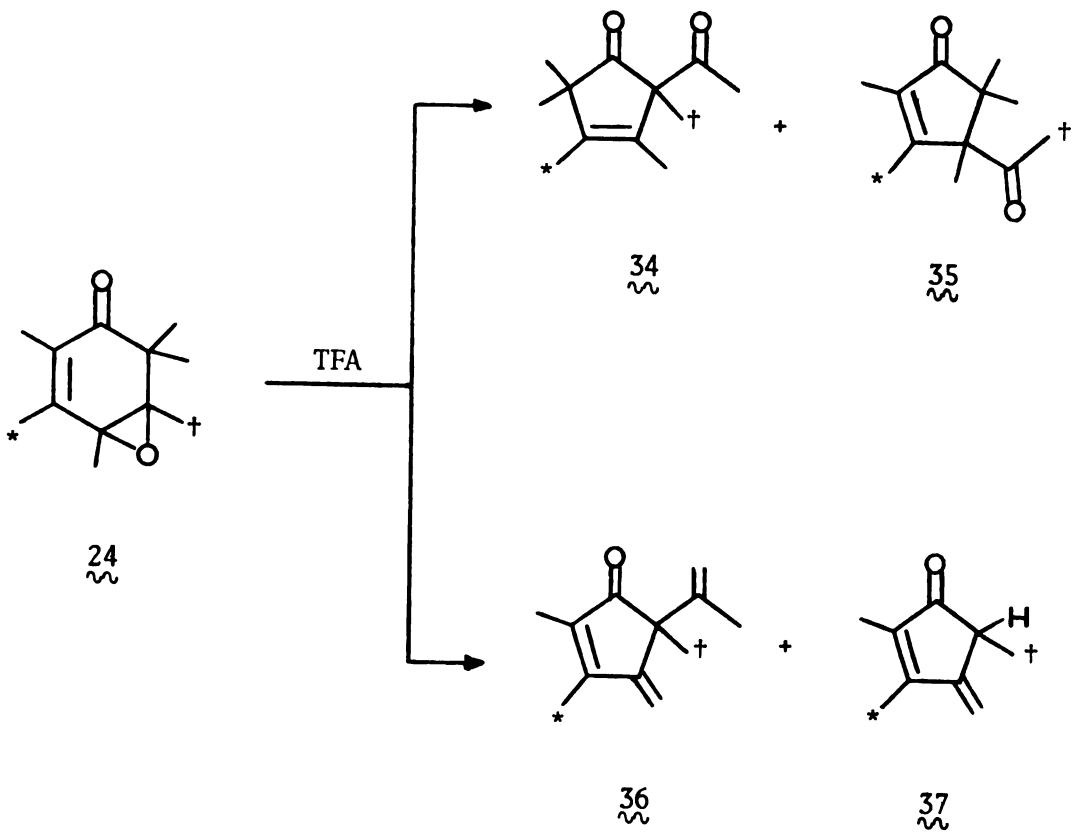
SCHEME 8



24 E 34

Several deuterium labeling experiments were carried out to test the mechanisms in Schemes 5-8. The results are shown in Scheme 9. Experiments were conducted with trideuterioepoxide (24*) containing a CD_3 group at C-3 and hexadeuterioepoxide (24*,†) containing CD_3 groups at C-3 and C-5. The mechanisms leading from epoxyenone 24 to 35-37 are fairly obvious, and the labeling results support the proposals in Schemes 5 and 6.

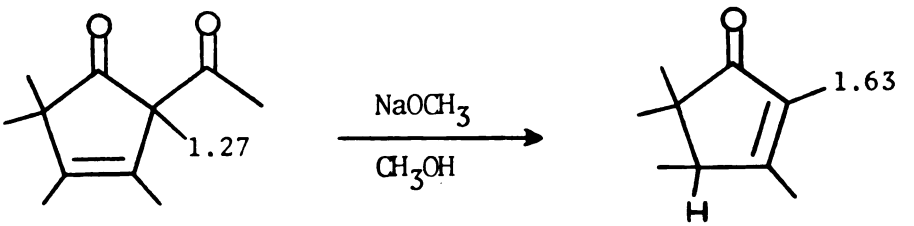
SCHEME 9



The route from 24 to 34 is less obvious, and in order to ascribe meaning to the labeling results it was necessary to establish unequivocally the nmr assignments of 34.

The europium shift data support the assignment shown in structure 34; however, there is some uncertainty because the molecule contains two functional groups with which coordination can occur. Since the nmr assignment of 38 is unambiguous from both chemical and europium shift data, the base cleavage of 34 to 38 was conveniently used in the nmr assignment of 34. Thus, when diketone 34 labeled with a CD_3 group at δ 1.27 (obtained from 24 containing a CD_3 group at C-3) was cleaved

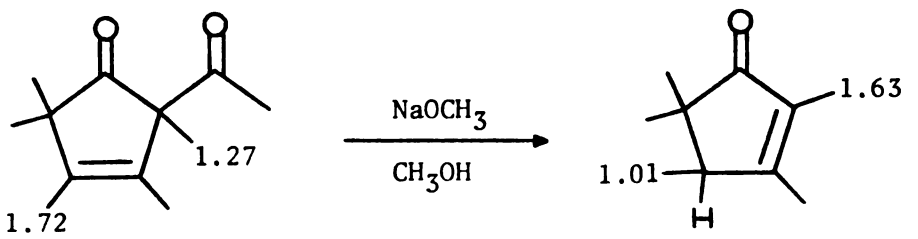
with base, the resulting cyclopentenone 38 lacked the allylic methyl signal at δ 1.63. Consequently, the methyl in 34 corresponding to the signal at δ 1.27 must be the methyl between the two carbonyl groups. The signals at δ 1.05 and 1.08 must therefore correspond to the gem-dimethyl group.



34 38

A similar procedure was used to assign the allylic methyl signals. Treatment of 24 containing CD_3 groups at C-3 and C-5 with acid gave a sample of 34 lacking the methyl signals at δ 1.27 and 1.72. Cleavage of this labeled 34 with base gave 38 lacking the allylic methyl signal at δ 1.63 and the doublet (J = 8.0 Hz) at δ 1.01. This result establishes unequivocally that the allylic methyl furthest from the acetyl group is at δ 1.72, and that all the other assignments for 34 are correct as shown in the first structure.

The labeling results clearly eliminate the mechanism in Scheme 8 as a possible route to 34. For the mechanism shown in Scheme 8 to be consistent with the labeling results, acid treatment of epoxyenone 24 containing CD_3 groups at C-3 and C-5 should yield 34 lacking allylic methyl signals at δ 1.72 and 1.60.



34 38

The labeling results fully support both the mechanisms in Schemes 6 and 7. A possible method to distinguish between these two routes to 34 would involve labeling the oxygen (^{18}O) in the epoxide ring of 24. The presence of ^{18}O in 34 would support the mechanism in Scheme 7 whereas the absence of ^{18}O would support the mechanism in Scheme 6.

In summary, the epoxyenone 24 rearranges quantitatively in dilute acid to the hydroxy ketone 32 through the allylic cation D (Scheme 3). In less basic solvents (such as trifluoroacetic acid) the same intermediate may rearrange by a 1,2-alkyl shift to give 35 or may, following nucleophilic attack α to the carbonyl group, undergo ring contraction to give 34 (Scheme 6 or 7). Product 36 may arise from protonation of 32 or may be formed by the alternate method of epoxide ring opening (via E, Scheme 5); product 37 is formed by dealkylation of 36 (Scheme 4).

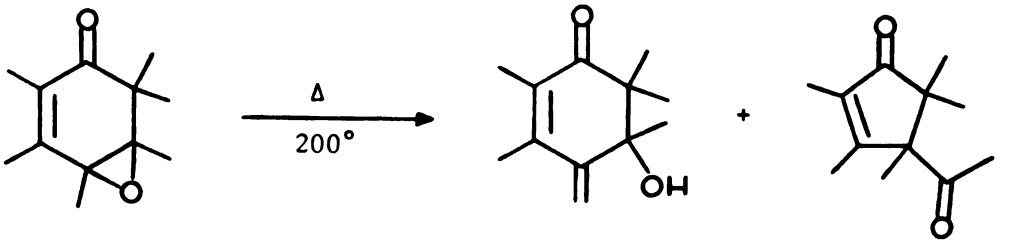
Although this is the first study of an acid-catalyzed rearrangement of a conjugated γ,δ-epoxyenone such as 24, it is clear that the preferential (if not exclusive) mode of epoxide ring opening is to give the allylic cation. Rearrangement invariably leads to ring contraction

products; consequently, such reactions can be useful for the synthesis of cyclopentenones. However, the manner in which the various methyl groups or other substituents, may determine the mode of the acid-catalyzed rearrangement of conjugated epoxyenones remains to be explored.

C. Thermal and Photochemical Rearrangements of γ,δ-Epoxyenones.

Several exploratory experiments were conducted on the thermal and photochemical rearrangement of conjugated γ,δ-epoxyenones. The results of these experiments are described in this section.

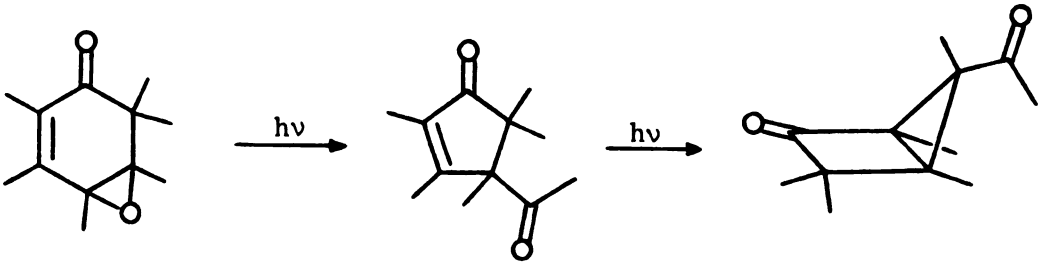
In general, thermal and photochemical rearrangements of epoxyketones parallel the acid-catalyzed rearrangement to the corresponding diketone.[9,17] This proved to be the case with epoxyenone 24. When epoxide 24 was heated in a sealed tube at 200° for 2 hr, either neat or in carbon tetrachloride, it rearranged to three products. The two major products were identified as hydroxy ketone 32 and diketone 35. The minor product was not isolated. Since hydroxyketone 32 is easily



24 32 35

formed from 24 by traces of acid or base (see previous section), it is not certain whether 32 formed under these conditions is truly the result of a thermal rearrangement.

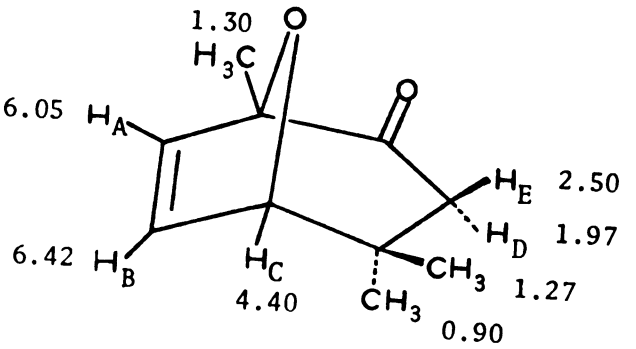
The photochemistry of epoxide 24 is more complex. Irradiation of 24 in cyclohexane with pyrex-filtered light gave diketone 35. However, the α,β-unsaturated diketone 35 is photolabile and under these same conditions rearranges further. Diketone 35 could be isolated in 10-20% yield using short photolysis times. On prolonged irradiation at approximately 10°, the diketone 35 seems to undergo an oxa-di-π-methane rearrangement to give a compound which was tentatively assigned structure 39 based on its spectral properties. The nmr spectrum of 39 showed no allylic methyl signals; instead it had five sharp methyl singlets, at δ 0.80, 1.12, 1.23, 1.27, and 1.33, and a sharp acetyl methyl singlet at δ 2.20. The infrared spectrum showed two carbonyl bands, at 1760 and 1710 cm^{-1}, corresponding respectively to the cyclobutanone and acetyl moieties.[36] Unfortunately, due to its thermal instability, isolation of pure 39 was not possible. Additional work is necessary if structure 39 is to be unambiguously characterized.



24 35 39

This type of photochemistry is not new. A diketone similar to 35, 2,5-di-t-butyl-4-pivaloyl-2-cyclopentenone, has been reported to undergo a similar oxa-di-π-methane rearrangement to give a bicyclo-[2.1.0]pentan-2-one derivative.[37] Nevertheless, the potential synthetic route from conjugated γ,δ-epoxyenones to strained systems such as 39 warrants further investigation of the photochemistry of 24 and other related epoxides.

An unusual thermal rearrangement was detected in the case of epoxide 26, 4,5-epoxy-2,6,6-trimethyl-2-cycloheptenone. When epoxide 26 was heated in a sealed tube at 180° or merely gas chromatographed at 170° (5 ft 10% FFAP column) it rearranged quantitatively to a new compound which was an isomer of 26 (mass spectrum). This isomer of 26 was assigned structure 40 based on its spectral properties. The infrared spectrum showed a carbonyl band at 1720 cm^{-1}, indicating no conjugation with the double bond, and a strong C-O-C stretch band at 1075 cm^{-1}. The nmr data given below support structure 40. Analogous isomerizations are common with vinyl cyclopropanes; however, these isomerizations are rare with vinyl epoxides.



40

H_A = d, J_{AB} = 6.0 Hz

H_B = d of d, J_{AB} = 6.0 Hz, J_{BC} = 2.0 Hz

H_C = d of d, J_{BC} = 2.0 Hz, J_{CD} = 1.3 Hz

H_D = d of d, J_{DE} = 17.0 Hz, J_{CD} = 1.3 Hz

H_E = d, J_{DE} = 17.0 Hz

The exploratory experiments described in this section clearly indicate the need for further research in this area. A more thorough investigation of the thermal and photochemical rearrangements of systems analogous to 24 may create new synthetic routes into cyclopentenones and highly strained compounds such as 39. Furthermore, a study of the photochemical and acid-catalyzed rearrangements of eucarvone oxide 26 as well as its thermal rearrangement product (40) might be of considerable synthetic and mechanistic interest.

EXPERIMENTAL

A. General Procedures

Except where otherwise noted, all nmr spectra were measured in $CDCl_3$ or CCl_4 solutions using TMS as an internal standard. The 60 MHz spectra were recorded on a Varian T-60 spectrometer and the 100 MHz spectra were recorded on a Varian HA-100 spectrometer. The small number placed next to protons in the structures in the discussion section are the nmr chemical shifts of those protons. The numbers beside the chemical shifts in parentheses are the normalized europium shift numbers. These were obtained by adding small increments of tris-(1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6-octanedione)Eu(III) to the CCl_4 or $CDCl_3$ solution of the compound being investigated. After each addition the nmr spectrum was scanned and the new frequency of each absorption was recorded. The shift for each absorption is the difference between the frequency of the shifted absorption and the original one. The normalized shift numbers are ratios obtained by dividing the shift of each signal in the spectrum by the shift of the least shifted signal.

Infrared spectra were recorded on a Perkin Elmer 237 grating spectrophotometer and calibrated against a polystyrene film. Ultraviolet spectra were obtained with a Unicam SP-800 in 95% ethanol, unless otherwise noted. Mass spectra were obtained from a Hitachi-

Perkin Elmer RMU-6 operated by Mrs. Ralph Guile. Melting points were determined with a Thomas-Hoover Melting Point Apparatus and are uncorrected. Varian Aerograph gas chromatographs were used. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

B. 4,5-Epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone (24).

Epoxidation With Molecular Oxygen. A solution containing 178 mg (1.0 mmol) of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (23)[34] in 10 ml of xylene was heated for 24 hr at 120-130° in a flask equipped with a reflux condenser. After removal of the solvent *in vacuo*, the residue was chromatographed on a Florisil column using 5% ether in hexane as the eluent, to afford 39 mg (22%) of recovered dienone 23 and 115 mg (0.60 mmoles, 77%) of epoxide 24: mp 48-49.5°; ir (KBr) 2970 (m), 2920 (m), 2860 (m), 1680 (s), 1465 (m), 1380 (m), 1310 (m), 1070 (m), 840 cm^{-1} (s); uv (cyclohexane) λ_{max} 253 nm (ε 7230); nmr ($CDCl_3$) see structure; all peaks had equal area; all were sharp singlets except those at δ 1.82 and 2.10, which were mutually coupled quartets, J = 1.0 Hz; mass spectrum (70 eV) m/e (rel intensity) 194 (14), 179 (14), 178 (19), 163 (18), 152 (46), 151 (70), 147 (21), 137 (29), 135 (25), 126 (29), 124 (29), 123 (27), 109 (31), 91 (16), 81 (30), 43 (100).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.10; H, 9.34

Found: C, 74.06; H, 9.32

The autoxidation of 23 in cyclooctane, mesitylene, cumene and chlorobenzene was carried out following the procedure described above. The yield of epoxide 24 was obtained by nmr for integration of the

methyl signal at δ 1.01 and comparing it against an internal standard (CH_2Cl_2). The results are given in Table I.

Epoxidation With m-Chloroperbenzoic Acid. To a solution of 0.600 g (3.37 mmol) of dienone 23 in 10 ml of methylene chloride was added, at 0°, a solution of 0.620 g (3.60 mmol) of m-chloroperbenzoic acid in 10 ml of methylene chloride. The mixture was stirred for 2 hr at 0°, during which time m-chlorobenzoic acid precipitated from solution. The solvent was evaporated, petroleum ether (bp 30-60°) was added to the residue, and the m-chlorobenzoic acid was removed by filtration. Evaporation of the solvent from the filtrate left 0.648 g of a light yellow oil; an nmr spectrum of the crude material showed it to be >90% 24. The crude product was chromatographed on a Florisil column using 5% ether in hexane as the eluent, to give 0.523 g (2.70 mmol, 80%) of epoxide 24: mp 48-49.5°. The nmr and ir spectra were identical to the epoxide obtained by autoxidation of 23.

Similar oxidation of 23 with a CD_3 group at C-3[34] gave 24* whose nmr spectrum lacked the quartet at δ 2.10, and with the quartet at δ 1.82 sharpened to a singlet. Oxidation of 23 with CD_3 groups at C-3 and C-5[34] gave 24*,† whose nmr spectrum, in addition to the changes just cited, lacked the singlet at δ 1.48.

C. 4,5-Epoxy-3,4,6,6-tetramethyl-2-cyclohexenone (25).

A solution of 166 mg (1.1 mmol) of 3,4,6,6-tetramethyl-2,4-cyclohexadienone[27] in 10 ml of xylene was autoxidized following the same procedure used for the autoxidation of dienone 23 (*vide supra*). After column chromatography on Florisil using 5% ether in hexane as the eluent, the reaction yielded 39 mg (0.26 mmol, 26%) of recovered dienone and

70 mg (0.42 mmol, 51%) of epoxide 25: mp 48-50°; ir (CCl_4) 2960 (s), 2920 (m), 2840 (w), 1680 (s), 1640 (w), 1470 (m), 1455 (m), 1440 (m), 1430 (m), 1360 (w), 1315 (m), 1235 (w), 1220 (w), 1170 (m), 920 (m), 890 cm^{-1} (m); uv (95% ethanol) λ_{max} 247 nm (ϵ 7200), 326 (143); nmr (CCl_4) see structure; the peaks at δ 2.08 (3H) and 5.72 (1H) were mutually coupled doublet and quartet respectively, J = 1.6 Hz, all other peaks were sharp three protons singlets with the peak at δ 3.03 being a sharp one proton singlet; mass spectrum (70 eV) m/e (rel intensity) 166 (8), 150 (39), 135 (37), 123 (36), 119 (32), 107 (100), 96 (35), 91 (72), 79 (44), 67 (51), 65 (26), 43 (46).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49

Found: C, 72.20; H, 8.56

Epoxide 25 was also prepared with m-chloroperbenzoic acid in 89% yield following the same procedure for the epoxidation of dienone 23 (*vide supra*). The nmr and ir spectra were identical to the epoxide obtained by autoxidation.

D. 4,5-Epoxy-2,6,6-trimethyl-2-cycloheptenone (26).

A solution of 113 mg (0.755 mmol) of 2,6,6-trimethyl-2,4-cycloheptadienone (eucarvone)[28] in 7 ml of xylene was autoxidized following the same procedure for the autoxidation of dienone 23 (*vide supra*). After preparative thick-layer chromatography on neutral alumina using 10% ether in hexane as the eluent, the reaction yielded 33 mg (0.22 mmol, 29%) of recovered eucarvone and 48 mg (0.29 mmol, 52%) of epoxide 26, a clear liquid. The ir spectrum (CCl_4) showed bands at 2960 (s), 2920 (m), 2860 (w), 1670 (s), 1470 (m), 1440 (m), 1380 (m), 1310 (w), 1250 (w), 1220 (w), 1110 (w), 1070 (w), 1030 (w), 935 (m),

875 cm^{-1} (m); uv (95% ethanol) λ_{max} 246 nm (ε 7920); nmr (CCl_4) see structure; mass spectrum (70 eV) m/e (rel intensity) 166 (50), 123 (65), 109 (33), 107 (30), 82 (600), 81 (100), 54 (96), 53 (52), 43 (96), 41 (59), 39 (86).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49

Found: C, 72.20; H, 8.50

Following the same procedure for the epoxidation of dienone 23, epoxide 26 was prepared with m-chloroperbenzoic acid in 76% yield. The nmr and ir spectra were identical to the epoxide obtained by autoxidation.

Treatment of d_2-eucarvone[29] with m-chloroperbenzoic acid as described above gave 26-d_2 with the following nmr spectrum: δ 0.98 (s, 3H), 1.25 (s, 3H), 1.83 (d, 3H, J = 1.6 Hz), 3.00 (d, 1H, J = 4.2 Hz), 3.22 (d of d, 1H, J = 6.1 Hz, J = 4.2 Hz), 6.43 (q of d, 1H, J = 6.1 Hz, J = 1.6 Hz).

E. 4-(1,2-Epoxy-2,6,6-trimethyl-1-cyclohexyl)-3-buten-2-one (27).

A solution of 105 mg (0.55 mmol) of 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone) in 4 ml of xylene was autoxidized following the same procedure for the autoxidation of dienone 23 (*vide supra*). After preparative thick-layer chromatography on neutral alumina using 10% ether in hexane as the eluent, the reaction yielded 32 mg (0.17 mmol, 30%) of recovered β-ionone and 57 mg (0.27 mmol, 72%) of epoxide 27: mp 45.5-47° (lit.[30] mp 46°); ir (KBr) 2950 (s), 2920 (s), 2860 (w), 1690 (m), 1680 (s), 1625 (m), 1455 (m), 1380 (w), 1365 (m), 1255 (s), 1175 (w), 1070 (w), 1050 (w), 990 (m), 910 cm^{-1} (w); uv (95% ethanol) λ_{max} 233 nm (ε 11,200); nmr (CCl_4) δ 0.90 (s, 3H, methyl), 1.12 (s, 3H, methyl), 1.15 (s, 3H, methyl), 1.15-2.10 (m, 6H, cyclohexyl H's), 2.20 (s, 3H, methyl α to carbonyl), 6.18 (d, 1H, J = 16.5 Hz,

vinyl H), 6.95 (d, 1H, J = 16.5 Hz, vinyl H); mass spectrum (70 eV) m/e (rel intensity) 208 (1.5), 193 (7), 165 (16), 135 (50), 123 (400), 109 (28), 107 (28), 95 (33), 91 (26), 81 (21), 79 (28), 77 (21), 69 (28), 67 (24), 65 (14), 55 (52), 53 (23), 41 (70), 39 (39).

Following the same procedure for the epoxidation of dienone 23, epoxide 27 was prepared with m-chloroperbenzoic acid in 76% yield. The nmr and ir spectra were identical to the epoxide obtained by autoxidation.

F. 3α,4α-Epoxy-5-cholesten-7-one (28).

A solution of 205 mg (0.54 mmol) of 3,5-cholestadiene-7-one[38] in 7 ml of xylene was autoxidized following the same procedure for the autoxidation of dienone 23 (*vide supra*). Thus, after column chromatography on neutral alumina using 25% ether in hexane as the eluent, the reaction yielded 45 mg (0.12 mmol, 22%) of recovered dienone and 55 mg (0.14 mmol, 31%) of epoxide 28: mp 129-130° (lit.[31] mp 127-128°; ir (CCl_4) 2950 (s), 2860 (m), 1675 (s), 1470 (m), 1380 (m), 1340 (w), 1280 (m), 1175 (m), 960 (w), 880 (w), 860 cm^{-1} (w); uv (95% ethanol) λ_{max} 239 nm (ε 12,100); nmr (CCl_4) δ 0.66-2.50 (m, 39H), 3.30 (broad s, 2H, epoxide ring H's), 5.96 (s, 1H, vinyl H); mass spectrum (70 eV) showed a base peak of m/e 174 and a parent peak of m/e 398.

Epoxide 28 was also prepared with m-chloroperbenzoic acid in 60% yield following the same procedure for the epoxidation of dienone 23 (*vide supra*). The nmr and ir spectra were identical to the epoxide obtained by autoxidation.

G. Methyl 4,5-epoxy-2-hexenoate (29).

A solution of 3.00 g (23.5 mmol) of methyl 2,4-hexadienoate in 150 ml of xylene was autoxidized following the same procedure for the autoxidation of dienone 23 (*vide supra*). After column chromatography on neutral alumina using 10% ether in hexane as the eluent, the reaction yielded 1.12 g (8.89 mmol, 37.3%) of recovered dienoate and 1.62 g (11.4 mmol, 90.5%) of epoxide 29.[32] The infrared spectrum (neat) showed bands at 2980 (m), 2940 (m), 2920 (w), 1725 (s), 1660 (m), 1440 (s), 1380 (m), 1350 (m), 1320 (s), 1275 (s), 835 cm^{-1} (s); nmr (CCl_4) δ 1.27 (d, 3H, J = 5.3 Hz, epoxide ring methyl), 2.88 (d of q, 1H, J = 5.3 Hz, J = 1.9 Hz, C-5 H), 3.08 (d of d, 1H, J = 6.7 Hz, J = 1.9 Hz, C-4 H), 3.72 (s, 3H, carboxylate methyl), 6.07 (d, 1H, J = 16.0 Hz, C-2 H), 6.68 (d of d, 1H, J = 16.0 Hz, J = 6.7 Hz, C-3 H), the nmr spectrum also showed several small peaks at δ 1.23, 3.17-3.54 and 6.75 which are due to traces of another isomer, probably *cis* at the epoxide ring.

Epoxide 29 was also prepared with m-chloroperbenzoic acid in 85% yield following the same procedure for the epoxidation of dienone 23 (*vide supra*). The nmr and ir spectra were identical to the epoxide obtained by autoxidation.

H. Autoxidation of Methyl 2,4-Hexadienoate in the Presence of α,α'-Azobis-iso-butyronitrile.

A solution of 300 mg (2.38 mmol) of methyl 2,4-hexadienoate (methyl sorbate) in 10 ml of xylene containing α,α'-azobis-iso-butyronitrile was heated in a flask equipped with a reflux condenser. The reaction temperature, time and the concentration of α,α'-azobis-iso-butyronitrile

in xylene are given in Table III. After removal of the solvent *in vacuo*, the crude reaction mixture was analyzed by nmr. The yield of epoxide 29 was obtained from integration of the methyl doublet at δ 1.27 and comparing it against an internal standard (CH_2Cl_2). Similarly, the yield of recovered dienoate was obtained by integration of the allylic methyl doublet at δ 1.90. The results are given in Table III.

I. Autoxidation of Methyl 2,4-Hexadienoate in the Presence of 4-t-Butylcatechol.

To a flask equipped with a reflux condenser was added 300 mg (2.38 mmol) of methyl 2,4-hexadienoate and 10 ml of 0.01M solution of 4-t-butylcatechol in xylene. The mixture was heated at 120-130° for 24 hr, after which time, the solvent was removed *in vacuo*. Analysis of the crude reaction mixture by nmr showed no peaks at δ 1.27 and 2.88-3.08 indicating no formation of epoxide 29.

J. Autoxidation of 2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone (23) and 2,3,4,4,5,6,-Hexamethyl-2,5-cyclohexadienone (30).

A solution containing 178 mg (1.0 mmol) of conjugated dienone 23[34] and 178 mg (1.0 mmol) of cross-conjugated dienone 30[34] in 15 ml of xylene was heated at 120-130° in a flask equipped with a reflux condenser, for 24 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on a Florisil column using 5% ether in hexane as the eluent to afford 45 mg (25%) of conjugated dienone 23, 102 mg (0.52 mmol, 70% of epoxide 24 and 155 mg (87%) of cross-conjugated dienone 30.

K. Autoxidation of Methyl 2-Butenoate (31).

A solution of 176 mg (2.0 mmol) of methyl 2-butenoate (methyl crotonate) in 10 ml of xylene was heated at 120-130° in a flask equipped with a reflux condenser, for 33 hr. After removal of the solvent *in vacuo*, analysis of the crude mixture (nmr and vpc) showed no epoxide formation. Preparative thick layer chromatography on neutral alumina yielded 144 mg (82%) of recovered 31.

L. 4-Methylene-5-hydroxy-2,3,5,6,6-pentamethyl-2-cyclohexenone (32).

To a solution of 24 (0.250 g, 1.29 mmol) in ether (15 ml) at 0° was added a solution of trifluoroacetic acid (0.5 ml) in water (5 ml). After the mixture was stirred for 0.5 hr, the layers were separated, and the ether layer was washed successively with saturated $NaHCO_3$ solution, water, saturated NaCl solution, and dried ($MgSO_4$). Evaporation of the ether left 0.238 g (95%) of the hydroxy ketone 32 as a colorless liquid which was not purified. Ir (CCl_4) 3620 (w, sharp), 3590 (w, sharp), 3500 (m, br), 2980 (s), 2930 (m), 2870 (w), 1670 (s), 1590 (w), 1460 (w), 1380 (s), several weak bands from 1350-1170, 1150 (m), 1130 (w), 1070 (m), 1040 (m), 1010 (w), 960 (m), 930 cm^{-1} (m). The bands at 3620 and 3590 cm^{-1} did not change in relative intensity as a function of the concentration of 32 in CCl_4, whereas the intensity of the band at 3500 cm^{-1} decreased drastically with decrease in concentration of 32. Uv (cyclohexane) λ_{max} 282 nm (ϵ 11,700, sh), 273 (15,200), 266 (14,500, sh); nmr (CCl_4) see structure; the peaks at δ 1.85 and 2.08 were broadened, all other peaks being sharp singlets; mass spectrum (70 eV) m/e (rel intensity) 194 (29), 179 (31), 176 (8), 161 (16), 151 (100), 137 (30),

133 (44), 123 (15), 121 (15), 109 (26), 105 (15), 91 (23), 83 (16), 79 (23), 78 (25), 67 (13), 65 (15), 56 (18), 54 (26), 51 (15), 43 (80), 39 (42).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.05; H, 9.36

Treatment of 24*,† with aqueous trifluoroacetic acid as above gave 32-d_6 with the following nmr spectrum (CCl_4): δ 0.96 (s, 3H), 1.10 (s, 3H), 1.85 (s, 3H), 5.43 (s, 1H), 5.64 (s, 1H).

M. Rearrangement of 4,5-Epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone (24) in Neat Trifluoroacetic Acid.

A solution of 0.100 g (0.515 mmol) of 24 in 2 ml of ice-cold trifluoroacetic acid was stirred at 0° for 1 hr, then at room temperature for 20 hr. The reaction was monitored by nmr after the spectrum of each product had been determined. The reaction was quenched by pouring the mixture into ice and saturated $NaHCO_3$ solution. The products were extracted with ether, and combined ether layers were washed successively with saturated $NaHCO_3$ solution, water, saturated NaCl solution and dried ($MgSO_4$). Evaporation of the solvent left 0.092 g of a light yellow liquid which was analyzed by vpc (5 ft x 1/8 in, 10% FFAP on chromosorb W, AW-DMCS 80/100, 160°, 30 ml/min). Four products (ret time in min, % yield) were observed: 34 (1.5, 6%), 35 (4.4, 27%), 36 (1.8, 33%), 37 (1.2, 34%). At 150° the ret times were, respectively, 3.5, 10.9, 4.0 and 2.5 min. After only 30 min reaction time, the yields were 34 (7%), 35 (32%), 36 (53%), 37 (8%). After 20 hr, the respective yields were 6, 27, 33 and 34%. The ratio of 34/35/(36 + 37) was time independent, but the yield of 37 increased at the expense of 36.

The products from this and larger scale experiments were separated by preparative vpc (10 ft x 0.25 in, 20% FFAP on chromosorb W P/G 30/60, 160°).

2-Acetyl-2,3,4,5,5-pentamethyl-3-cyclopentenone (34): ir (neat) 2960 (m), 2920 (m), 2860 (w), 1740 (s), 1710 (s), 1470 (m), 1450(m), 1380 (m), 1360 (m), several weak bands from 1300 to 900 cm^{-1}; uv (95% ethanol) λ_{max} 282 nm (ε 81), 203 (35,660); nmr (CCl_4) see structure; the peaks at δ 1.60 and 1.72 were mutually coupled quartets, J = 1.5 Hz; mass spectrum (70 eV) m/e (rel intensity) 194 (<1), 152 (94), 137 (100), 123 (22), 109 (12), 91 (12), 81 (27), 67 (14), 43 (55).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 73.94; H, 9.41

4-Acetyl-2,3,4,5,5-pentamethyl-2-cyclopentenone (35): ir (CCl_4) 2970 (s), 2940 (m), 2860 (w), 1710 (s), 1660 (s), several medium intensity bands from 1475-1400, 1380 (m), 1350 (m), 1320 (m), 1215 (m), 1150 (m), 1075 (m), 1025 (m), 960 cm^{-1} (w); uv (cyclohexane) λ_{max} 237 nm (ε 7,720), 209 (6,000); nmr (CCl_4) see structure; the bands at δ 1.75 and 1.95 were mutually coupled, J = 1.0 Hz; mass spectrum (70 eV) m/e (rel intensity) 194 (1.5), 179 (1.0), 166 (1.0), 152 (100), 137 (60), 123 (53), 109 (9), 95 (8), 93 (9), 91 (12), 81 (35), 67 (12), 55 (12), 53 (12).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.25; H, 9.29

5-Isopropenyl-4-methylene-2,3,5-trimethyl-2-cyclopentenone (36): ir (CCl_4) 3080 (w), 2965 (s), 2910 (s), 2865 (m), 1710 (s), 1645 (s), 1620 (s), 1455 (s), 1400 (s), 1370 (m), 1340 (w), 1290 (m), 1175 (w), 1160 (w), 1120 (w), 1030 (m), 1010 (w), 915 cm^{-1} (s); uv (cyclohexane) λ_{max} 278 (ε 10,030, sh), 270 (13,700), 262 (11,070, sh); nmr (CCl_4)

see structure; the band at δ 1.46 was a doublet, J = 1.7 Hz, those at δ 1.83 and 2.13 were broadened by mutual coupling, that at δ 4.95 was a multiplet (3 vinyl protons) and that at δ 5.30 was a broadened singlet. The peak at δ 1.21 was a sharp singlet; mass spectrum (70 eV) m/e (rel intensity) 176 (13), 161 (34), 148 (24), 133 (100), 105 (31), 91 (35), 79 (19), 77 (26), 65 (16), 53 (14), 51 (19), 41 (37), 39 (41).

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

Found: C, 81.72; H, 9.11

4-Methylene-2,3,5-trimethyl-2-cyclopentenone (37): ir (CCl_4) 3080 (w), 2960 (m), 2925 (m), 2860 (w), 1710 (s), 1640 (s), 1620 (s), several medium intensity bands from 1460-1375, 1340 (w), 1310 (m), 1265 (m), 1145 (w), 1120 (m), 1050 (m), 990 (m), 905 cm^{-1} (s); uv (cyclohexane) λ_{max} 275 nm (ε 10,020, sh), 267 (15,200), 258 (13,450, sh); nmr (CCl_4) see structure; the peaks at δ 1.80 and 2.10 were broadened by mutual coupling, and the singlets at δ 5.10 and 5.27 were also broad; mass spectrum (70 eV) m/e (rel intensity) 136 (35), 121 (13), 93 (100), 91 (37), 79 (19), 77 (36), 67 (16), 65 (13), 55 (11), 54 (23), 53 (25), 52 (12), 51 (23), 50 (10), 41 (18), 39 (44).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88

Found: C, 79.15; H, 9.04

A solution of 37 (50 mg, 0.368 mmol) in 4 ml of CH_3OD containing 54 mg (1.0 mmol) of sodium methoxide was stirred for 1 hr at room temperature, then quenched with 15 ml of D_2O and extracted 3x with pentane (10 ml). The combined organic layers were washed with water (2x), saturated NaCl solution, and dried ($MgSO_4$). Evaporation of the solvent left 45 mg of 37-d_1 with the following nmr (CCl_4): δ 1.17 (s, 3H), 1.80 (br s, 3H), 2.10 (br s, 3H), 5.10 (br s, 1H), 5.27 (br s, 1H).

N. Cleavage of 2-Acetyl-2,3,4,5,5-pentamethyl-3-cyclopentenone (34) With Base.

A solution of 34 (100 mg, 0.515 mmol) and sodium methoxide (20 mg, 0.555 mmol) in 3 ml of methanol was stirred at room temperature for 8 hr. The mixture was poured into ice-water and extracted with ether, the combined ether extracts were washed with water, saturated NaCl solution, and dried ($MgSO_4$). After evaporation of the solvent, the residue was analyzed by vpc (5 ft x 0.125 in, 20% FFAP, 120°) and showed that all of 34 was consumed, the sole product being 2,3,4,5,5-pentamethyl-2-cyclopentenone (38), ret time 1.4 min. Pure 38 was collected by preparative vpc. Ir (neat) 2980 (m), 2880 (w), 1700 (s), 1650 (s), 1460 (m, br), 1400 (m), 1335 (m), 1040 cm^{-1} (m, br); uv (95% ethanol) λ_{max} 235 nm (ε 6,000); nmr (CCl_4) see structure; the peaks at δ 1.01 (3H) and 2.33 (1H) were a mutually coupled doublet and quartet respectively, J = 8.0 Hz and the peaks at δ 1.63 and 1.95 were mutually coupled quartets, J = 1.0 Hz. Treatment of 34 with sodium methoxide in excess methanol-d for 8 hr at room temperature, followed by workup, gave 34-d_4 whose nmr spectrum lacked the quartets at δ 1.95 (3H) and 2.33 (1H), the three proton peaks at δ 1.01 and 1.63 now becoming sharp singlets.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59

Found: C, 78.75; H, 10.71

Cleavage of 34-d_3 lacking the singlet at δ 1.27 (*vide infra*) gave 38-d_3 lacking the signal at δ 1.63 and with the peak at δ 1.95 a sharp singlet. Cleavage of 34-d_6 lacking the methyl signals at δ 1.27 and 1.72 (*vide infra*) gave 38-d_6 lacking the quartet at δ 1.63 and the doublet at δ 1.01, and having the signal at δ 1.95 a sharp singlet and that at δ 2.33 a broadened one-proton singlet.

O. Treatment of 5-Isopropenyl-4-methylene-2,3,5-trimethyl-2-cyclopentenone (36) With Trifluoroacetic Acid.

A solution of 36 (60 mg, 0.34 mmol) in 1 ml of trifluoroacetic acid was allowed to stand at room temperature for 20 hr, the reaction being monitored by nmr. During the reaction, a sharp singlet appeared at δ 2.33, shown to correspond to acetone in trifluoroacetic acid. The reaction was quenched by pouring it into ice and saturated $NaHCO_3$ solution. The mixture was extracted with ether, and the ether extract was worked up and analyzed as in the rearrangement of 24. The sole components (determined by vpc) after 20 hr were 36 (55%) and 37 (45%). When the reaction was carried out at higher temperatures, conversion to 37 was quantitative.

P. Rearrangement of 5-Hydroxy-4-methylene-2,3,5,6,6-pentamethyl-2-cyclohexenone (32) in Trifluoroacetic Acid.

A solution of 32 (0.100 g, 0.515 mmol) in 1.5 ml of trifluoroacetic acid was stirred at room temperature. Aliquots were withdrawn at various time intervals, quenched and worked up as usual, and analyzed by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW DMCS 80/100, 150°, N_2 flow rate 30 ml/min). Only two components were present, 36 (4.0 min) and 37 (2.5 min), identified by nmr and ir. The relative amounts at various time intervals were: 2 hr, 94% 36, 6% 37; 26 hr, 32% 36, 68% 37; 46 hr, 3% 36, 97% 37.

Q. Rearrangement of Labeled 4,5-Epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone in Trifluoroacetic Acid.

A solution of 24* (lacking the signal at δ 2.10; 500 mg, 2.58 mmol) in 5 ml of trifluoroacetic acid was stirred at room temperature for 21 hr, then quenched and worked up as described for unlabeled 24. The products had the following nmr spectra (CCl_4): 34, δ 1.05 (s, 3H), 1.08 (s, 3H), 1.60 (m, 3H), 1.72 (m, 3H), 1.98 (s, 3H); 35, δ 0.90, 1.03, 1.25, 1.75 and 1.95, all s, 3H; 36, δ 1.21 (s, 3H), 1.46 (d, 3H, J = 1.7 Hz), 1.83 (s, 3H), 4.95 (m, 3H), 5.30 (br s, 1H); 37, δ 1.17 (d, 3H, J = 7.5 Hz), 1.80 (s, 3H), 2.70 (q, 1H, J = 7.5 Hz), 5.10 (br s, 1H), 5.27 (br s, 1H).

A solution of 24*,† (lacking the signals at δ 2.10 and 1.48) in trifluoroacetic acid was allowed to rearrange in the amounts and manner described for 24*. The products had the following nmr spectra (CCl_4): 34, δ 1.05, 1.08, 1.60, and 1.98, all s, 3H; 35, δ 0.90, 1.03, 1.25 and 1.75, all s, 3H; 36, δ 1.46 (d, 3H, J = 1.7 Hz), 1.83 (s, 3H), 4.95 (m, 3H), 5.30 (br s, 1H); 37, δ 1.80 (s, 3H), 2.70 (br s, 1H), 5.10 (br s, 1H), 5.27 (br s, 1H).

R. Thermal Rearrangement of 4,5-Epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone (24).

A solution of 24 (55 mg, 0.31 mmol) in 0.5 ml of CCl_4 was sealed in an nmr tube and heated at 200-210°. After 2 hr no starting epoxide was detected by nmr. Analysis of the crude reaction mixture by tlc showed three products. The mixture was separated by preparative thick-layer chromatography on neutral alumina using 10% ether in hexane,

yielding two products, 25 and 32, which were identified by nmr. Only traces of the third product could be isolated, no attempt was made to identify it.

A similar rearrangement of epoxide 24 in the absence of solvent yielded the same products.

S. Photochemical Rearrangement of 4,5-Epoxy-2,3,4,5,6,6-hexamethyl-2-cyclohexenone (24).

A solution of 250 mg (1.29 mmol) of 24 in 400 ml of anhydrous ether was flushed with nitrogen and irradiated under nitrogen (Hanovia 450 W, Pyrex) for 1.5 hr. Analysis of the crude reaction mixture by tlc showed two products. After evaporation of the solvent, the mixture was separated by preparative thick-layer chromatography on neutral alumina using 10% ether in hexane yielding 126 mg (51%) of unreacted starting material and 26 mg (10%) of diketone 35, identified by nmr.

Similar irradiation of epoxide 24 at 10-15° for 8 hr followed by evaporation of the solvent *in vacuo* yielded a light yellow oil which was not purified. All attempts to purify the crude product resulted in decomposition. Nmr analysis of the crude oil showed it to consist mainly of one product which was tentatively assigned structure 39. Ir (CCl_4) 1760 (s) and 1710 cm^{-1} (s); nmr (CCl_4) δ 0.80, 1.12, 1.23, 1.27, 1.33 and 2.20, all sharp three protons singlets.

T. Irradiation of 4-Acetyl-2,3,4,5,5-pentamethyl-2-cyclopentenone (35).

A solution of 28 mg (0.14 mmol) of 35 in 20 ml of ether was placed in a Pyrex tube which was then stoppered with a serum cap. The solution

was flushed with nitrogen (using syringe needles) for 15 min and then irradiated for 2 hr with a 450 W Hanovia lamp. The solvent was removed *in vacuo* and the residue analyzed by nmr which showed small amounts of unreacted starting material and six sharp methyl peaks corresponding to 39 (*vide supra*).

U. Thermal Rearrangement of 4,5-Epoxy-2,6,6-trimethyl-2-cycloheptenone (26).

A solution of 26 (50 mg, 0.30 mmol) in 0.5 ml of CCl_4 was sealed in an nmr tube and heated at 180-185° for 4 hr, the reaction being monitored by nmr. After 4 hr the reaction mixture consisted of only one product which was assigned structure 40 based on the following spectral data: ir (neat) 2960 (s), 2930 (s), 2870(m), 1720 (s), 1470 (m), 1440 (m), 1410 (m), 1375 (m), 1365 (m), several small bands from 1325-1100, 1075 (s), 1010 (m), 975 (w), 915 (m), 880 (m), 860 (m), 760 (s), 720 cm^{-1} (s); nmr (CCl_4) see structure peaks at δ 1.30, 1.27 and 0.90 were sharp three proton singlets; mass spectrum (70 eV) m/e (rel intensity) 166 (17), 151 (1.5), 123 (28), 109 (17), 95 (9.0), 82 (100), 54 (36), 43 (43), 39 (44).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49

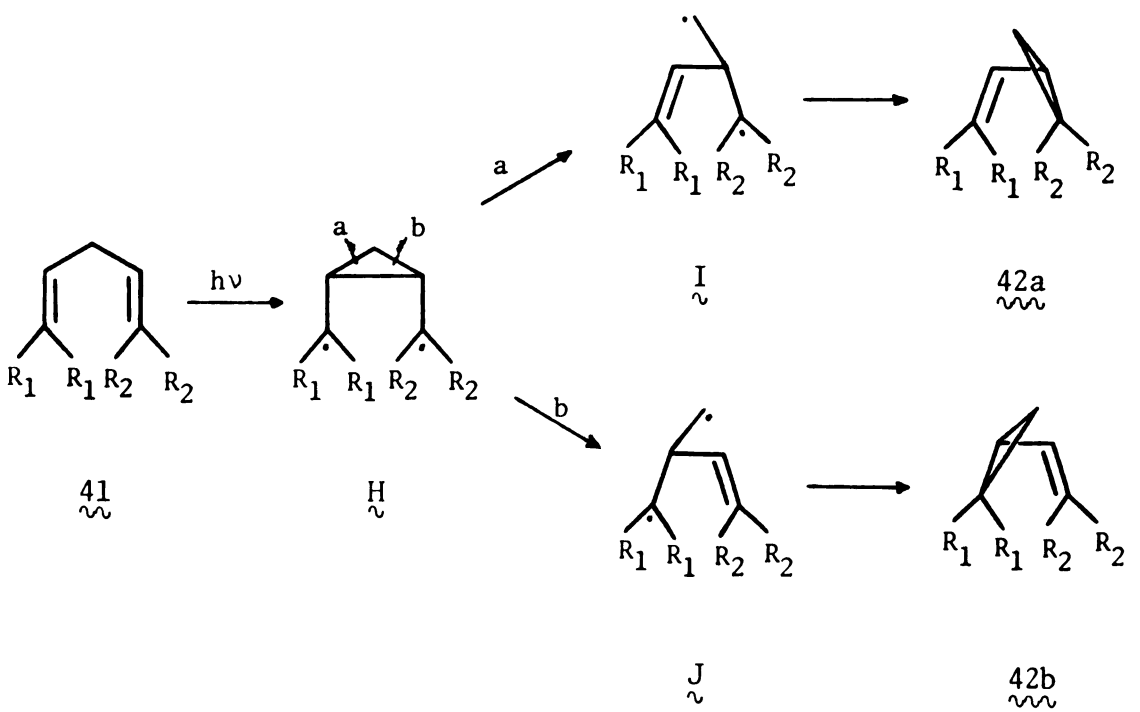
Found: C, 72.20; H, 8.50

PART II

REGIOSPECIFICITY IN DI-π-METHANE PHOTOISOMERIZATIONS

INTRODUCTION

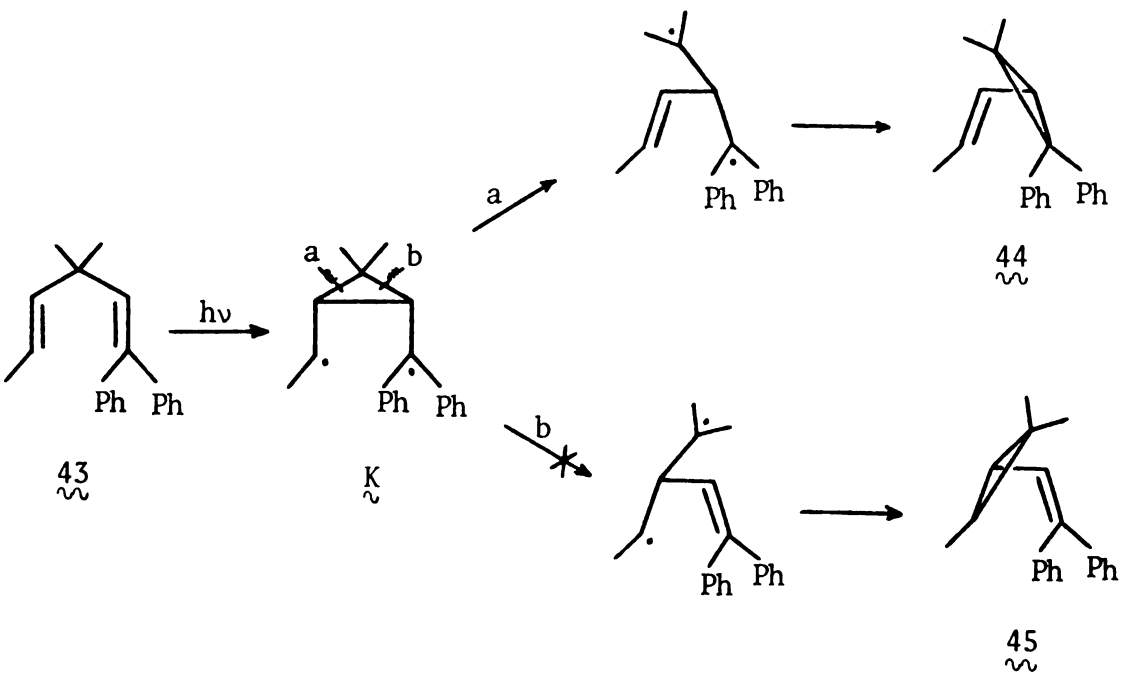
The generality of the di-π-methane photorearrangement was first recognized by Zimmerman.[39] The reaction involves the conversion of two π moieties bonded to a single saturated carbon atom into a π-substituted cyclopropane. The rearrangment is illustrated in the scheme below.



Although two vinyl groups are used for simplicity, the π moiety may alternatively include phenyl or carbonyl groups.[40]

In unsymmetric di-π-methane systems, *i.e.*, when $R_1 \neq R_2$, two products (42a and/or 42b) are possible depending upon whether bond a or bond b is broken along the reaction route. Several cases are known in which the reaction follows only one of these two possible routes.[40] For example,

direct irradiation of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (43) gave 1,1-diphenyl-2,2-dimethyl-3-propenylcyclopropane (44), but no 1,1,2-trimethyl-3-(2,2-diphenylvinyl)cyclopropane (45).[41] Thus, "intermediate" K cleaved exclusively at bond a.



Another type of regiospecificity has been observed in bicyclic di-π-methanes.[42] Sensitized irradiation of carbomethoxydibenzobarrelene 46 gave dibenzosemibullvalene 47, but no 48. In this case, the mode of initial bonding determines the structure of the reaction product. Thus, the observed product results from "intermediate" L not M.

These two types of regiospecificity can be easily rationalized. The reactions proceed along routes which maintain maximum odd-electron stabilization. In the first example, cleavage of bond b leads to loss of benzhydryl delocalization while cleavage of bond a does not. Similarly, in the second example, odd-electron stabilization by the carbomethoxy group makes L the favored bridged species.

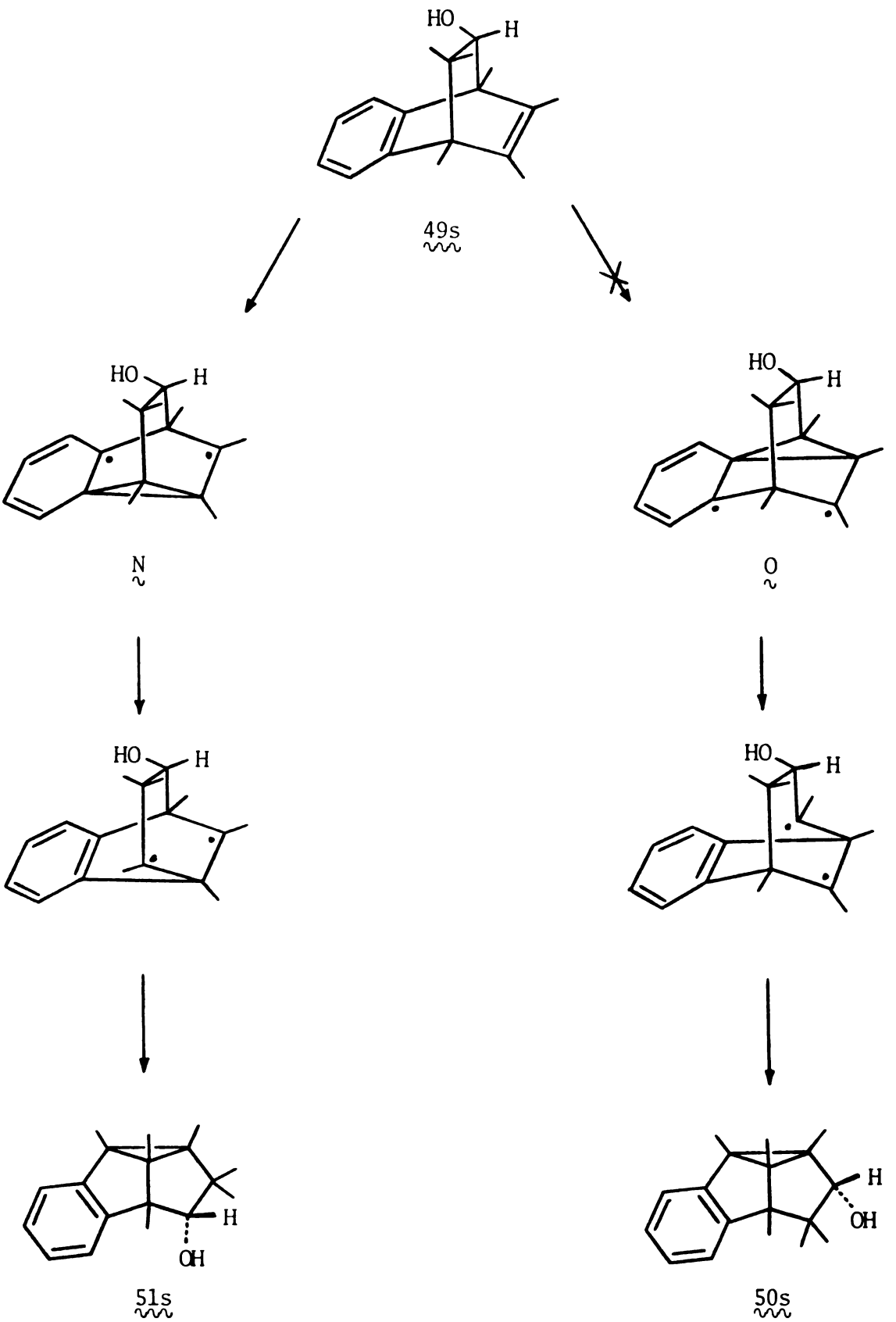
The substituent effect does not seem to be associated with a particular excited state multiplicity, since the first reaction proceeds from a singlet state, and the second from a triplet.[39,42]

It should be noted that this rationale to account for the regiospecificity in the di-π-methane rearrangement does not require a nonconcerted mechanism. In fact, it has been proposed that the di-π-methane rearrangement, especially from the singlet state, may be concerted.[43] Hence, formulations such as H-M do not mean to imply that the species along the reaction route necessarily are intermediates and correspond to energy minima. In some instances such discrete diradicals may be involved; in other cases, these may just be points along the hypersurface leading from excited state of reactant to ground state of product. Nevertheless, such qualitative valence-bond structures are useful in depicting odd-electron disposition along the reaction coordinate and one can expect predictions based on such models to correlate with experiment.

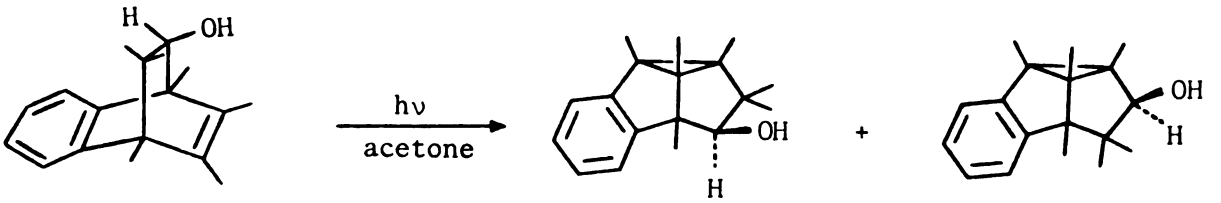
Still a third and less well understood type of regiospecificity in di-π-methane photoisomerizations has been observed by Hart and Murray.[44] Acetone-sensitized irradiation of secondary alcohol 49s gave 50s, but no 51s. This process is shown in detail in Scheme 10. In this case also, the mode of initial bonding determines the reaction product. Thus, the observed product results from intermediate N not O.

Irradiation of the epimeric alcohol 49a was also regioselective, but the directive effect was less dramatic than with the *syn* isomer 49s.

Since the hydroxyl group in the saturated bridge is not bonded to any of the atoms directly involved in the rearrangement, this directive effect may be a result of "through space" rather than a "through bond" interaction. Hart and Murray[44] suggested that this apparent stabilization of N over O could arise from charge transfer and/or hydrogen bonding



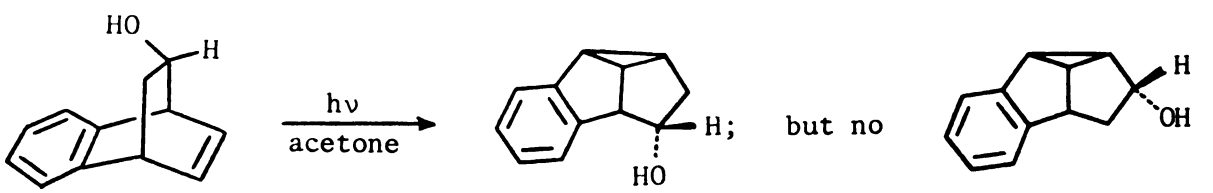
SCHEME 10: The di-π-methane rearrangement of 49s.



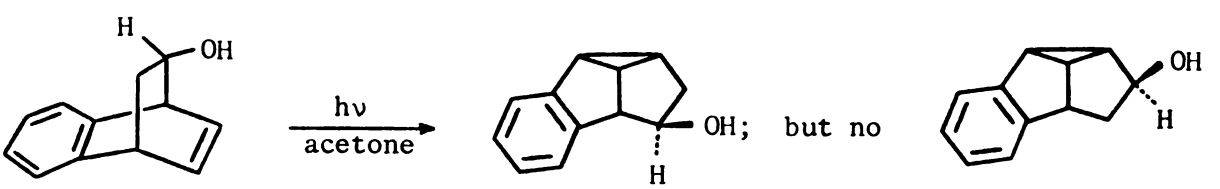
49a 50a, 60% 51a, 40%

interaction of the hydroxyl moiety with the delocalized π-system "beneath" it. Subsequent results,[45] however, indicated that the corresponding acetates show similar selectivity, thus eliminating the hydrogen bond explanation.

The same substituent effect was observed in the photochemistry of the epimeric alcohols 52s and 52a.[45] Irradiation of 52s in acetone gave



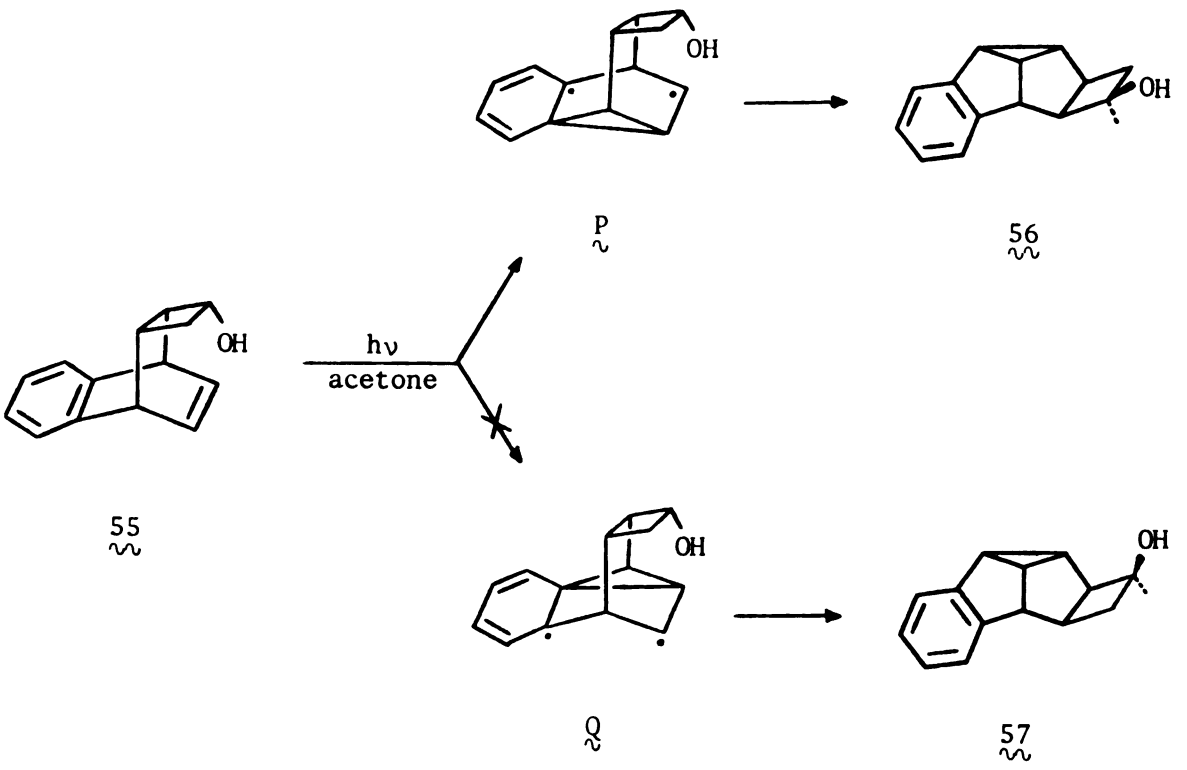
52s 53s 54s



52a 53a 54a

53s and an unidentified minor product in a ratio of 7:1. Similarly, irradiation of 52a gave a single photoproduct 53a.

In another case, Murata and Sugihara[46] observed a similar substituent effect. Sensitized irradiation of secondary alcohol 55 gave 56 but no 57. In this case also, of the two possible di-π-methane intermediates P and Q,

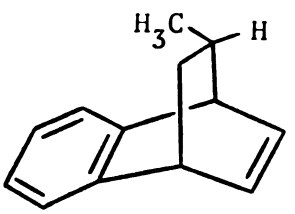


the reaction proceeds via the former. The explanation given to account for this substituent effect was also hydrogen bonding or charge-transfer interaction between a developing radical and the oxygen.

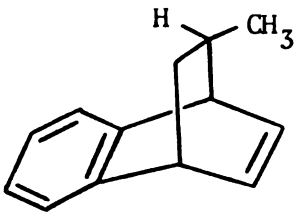
The purpose of this part of this thesis was to examine this unusual substituent effect with the hope of learning more about the nature of the stabilization of triplet excited states by groups not directly bonded to any of the atoms with odd electron density.

RESULTS AND DISCUSSION

One of the proposals of Hart and Murray for the selective formation of intermediate N rather than O in the photolysis of alcohol 49s was a charge-transfer interaction between a lone pair on the oxygen and the proximal unpaired electrons. To test this explanation two epimeric methyl substituted 1,4-dihydro-1,4-ethanonaphthalene 58s and 58a were prepared and irradiated.



58s

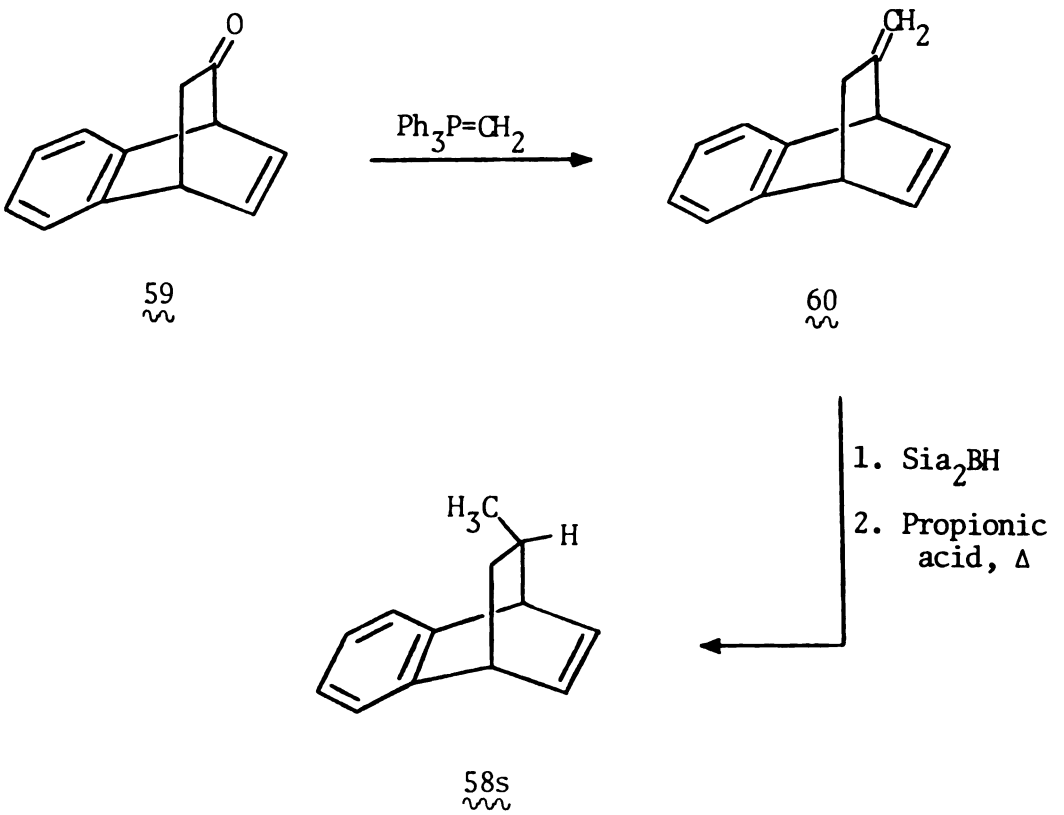


58a

A. Synthesis of *Syn*- and *Anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene, 58s and 58a.

The initial phase of this investigation was concerned with the transformation of ketone 59[45] to both epimers of 58 (Scheme 11). Treatment of 59 with methylenetriphenylphosphorane by the modified Corey procedure[47] proved to be highly efficient, leading to the isolation of 9-methylene-1,4-dihydro-1,4-ethanonaphthalene (60) in 84.0% yield. However, selective reduction of 60 with disiamylborane followed by treatment with propionic

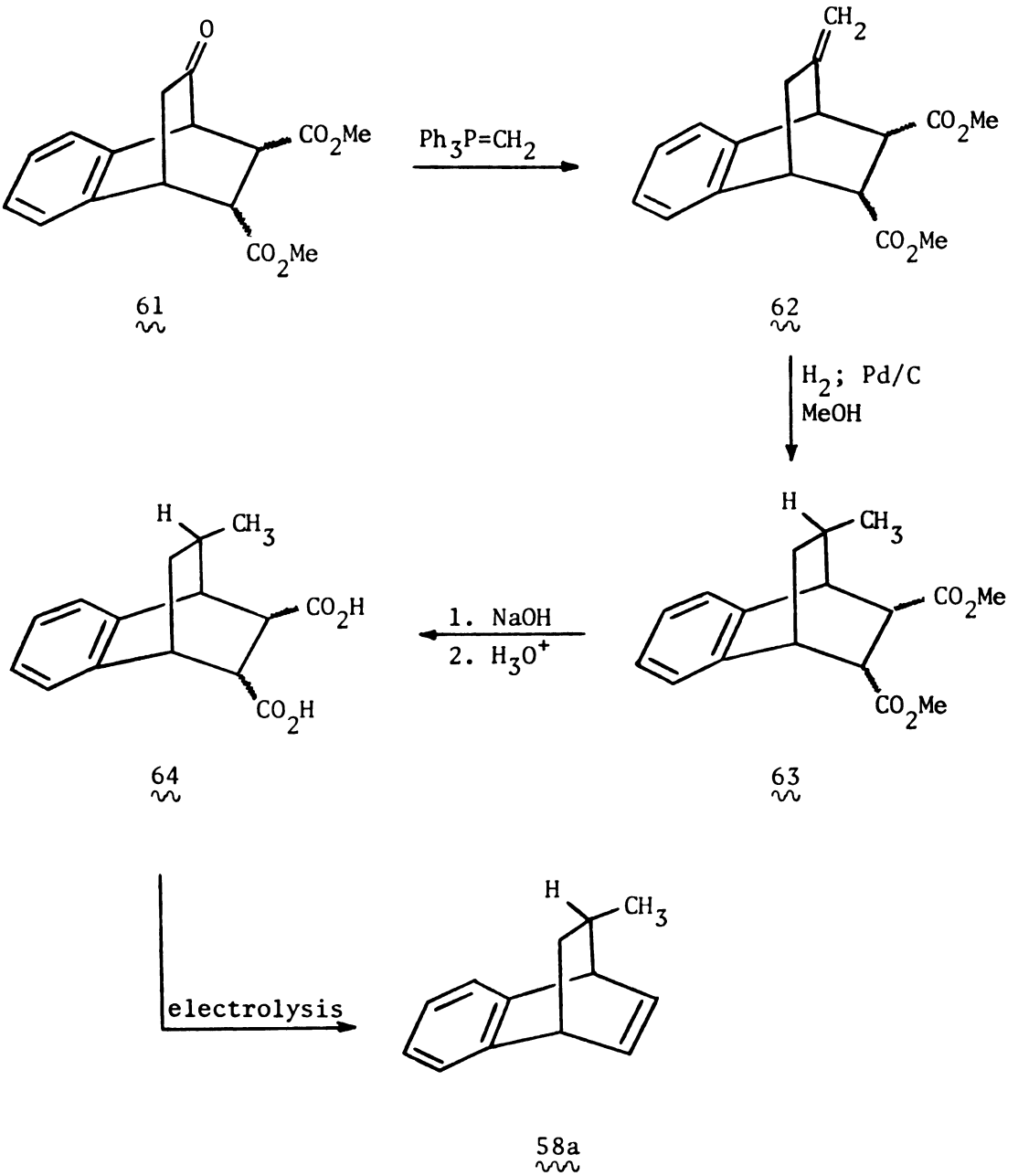
SCHEME 11



acid unexpectedly gave only one product, *syn*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s) in 63.0% yield.

Several attempts to synthesize the *anti*-isomer 58a from 60 by other reduction methods were unsuccessful. For example, catalytic hydrogenation with palladium on charcoal or treatment of 60 with tris-(triphenylphosphine)rhodium chloride catalyst lead to preferential reduction of the Δ^2-double bond, yielding 9-methylene-1,2,3,4-tetrahydro-1,4-ethanonaphthalene. The synthesis of *anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58a) was finally accomplished by the sequence of steps described in Scheme 12.

SCHEME 12



61 62 63 64 58a

Reaction of keto-diester 61[48] with methylenetriphenylphosphorane resulted in the formation of methylene-diester 62 in 70.7% yield. Reduction of 62 with palladium on charcoal in methanol was completely stereospecific, giving only the isomer with the methyl substituent *anti* to the aromatic ring, 63, in 91.5% yield. Saponification of diester 63 followed by

electrolytic decarboxylation of the diacid 64 in pyridine-water-triethylamine solution conveniently gave only the *anti*-isomer 58a in 34.5% yield.

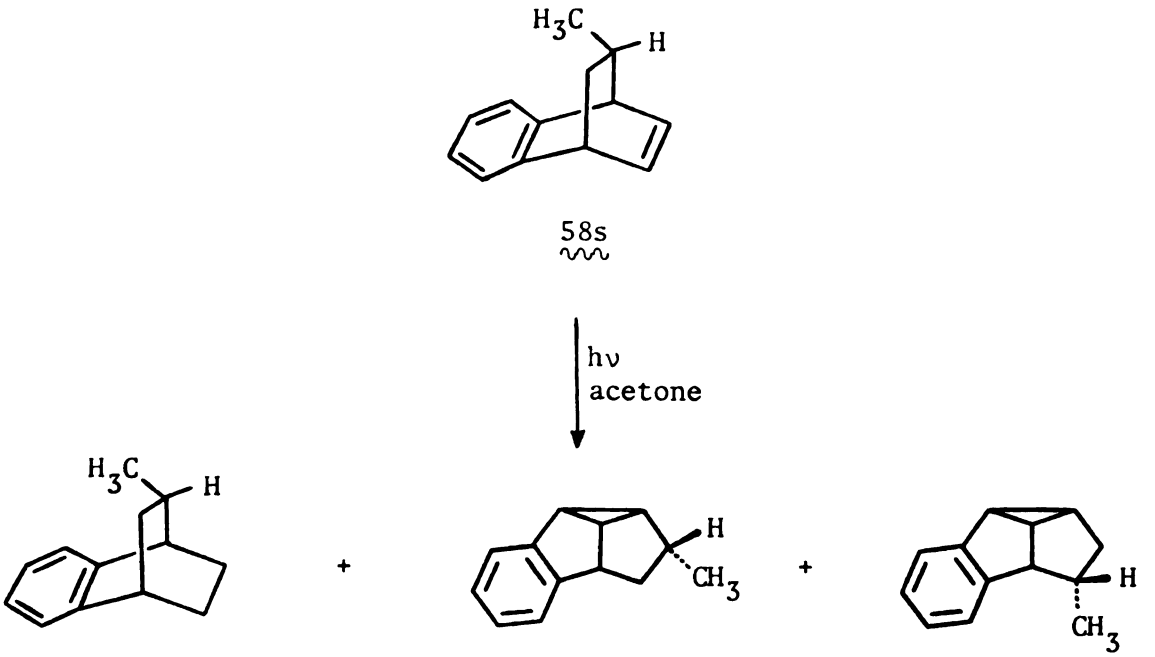
The structure of 58s and 58a follow from their method of synthesis and spectroscopic properties. Their spectral properties are given in the experimental section. The configuration assignments of 58s and 58a are based on their nmr spectra. In general, the methyl substituent in 2,3-benzobicyclo[2.2.2]octa-2,5-dienes appears at higher field when the methyl is *syn* to and "over" the aromatic π system, than when the methyl has the *anti* geometry.[45] Thus in 58s the methyl doublet appears at δ 0.62, whereas in 58a it appears at δ 0.98.

B. Photolysis of *Syn*- and *Anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene, 58s and 58a.

Epimers 58s and 58a were photolyzed in acetone through a pyrex filter, the reaction being monitored by vpc. The photoproducts were separated by preparative vpc and their yields determined by vpc using a calibrated internal standard. Irradiation of the *syn*-epimer 58s gave three products which were identified from their 100 MHz nmr spectra and by independent syntheses. These photoproducts together with their respective absolute yields are given in Scheme 13.

In contrast to 58s, irradiation of the *anti*-epimer 58a gave only two products which were also identified from their nmr spectra and by independent syntheses. These photoproducts together with their respective absolute yields are given in Scheme 14.

SCHEME 13

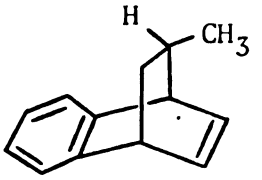


65s, 22.7% + 66s, 10.8% + 67s, 63.8%

Photoproducts 65s and 65a were determined to result from photoreduction of 58s and 58a, respectively. Their nmr spectra were consistent with the structures, and the assignment was corrobarated by their mass spectra which displayed a parent ion peak at m/e 172, an increase of two mass units compared to 58s and 58a (parent peak m/e 170). The spectral properties of 65s and 65a are given in the experimental section. Finally, 65s and 65a were conclusively identified by comparison with authentic speciments obtained by separate hydrogenation of 58s and 58a with 10% Pd/C in methanol.

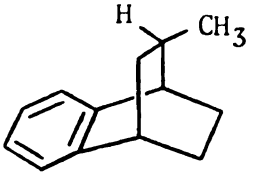
Photoproduct 66s was identified from its 100 MHz nmr spectrum which showed, in addition to the four aromatic protons at δ 6.73-7.17 and the methyl doublet at δ 0.48, a complex spectrum for an additional seven protons. The nmr assignments were based on double irradiation experiments;

SCHEME 14

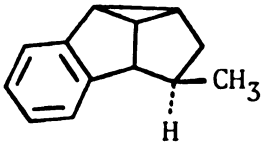


58a

hν
acetone



+



65a, 11.7%

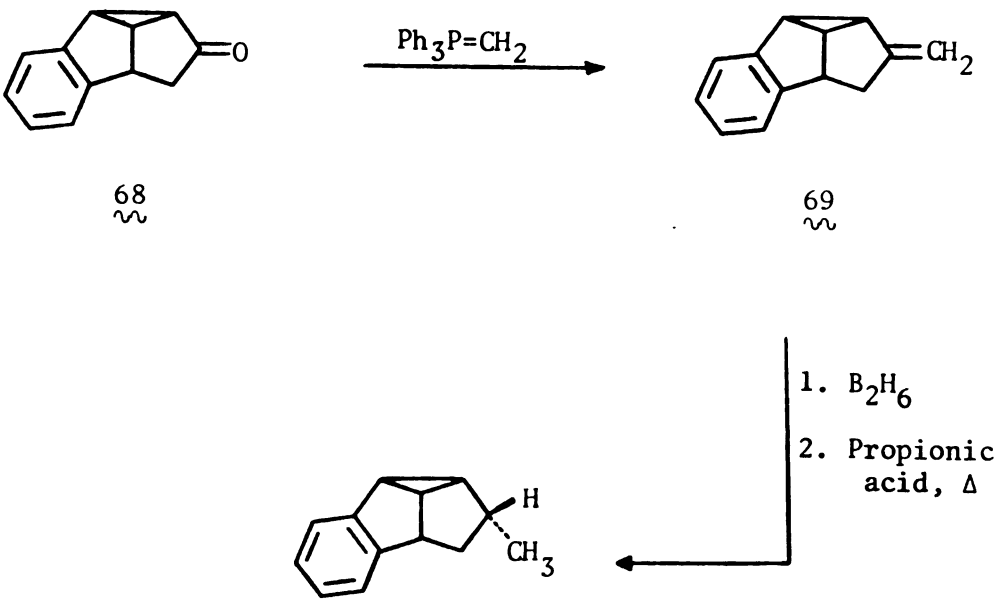
67a, 81.8%

however, due to long range coupling and the complexity of the spectrum, a complete analysis of the coupling constants could not be made. The double irradiation results and other spectral properties are given in the experimental section.

In order to confirm its structure, photoproduct 66s was synthesized from 3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-7-one (68)[49] as outlined in Scheme 15.

Treatment of ketone 68 with methylenetriphenylphosphorane by the modified Corey procedure[47] gave 7-methylene-3,4-benzotricyclo[3.3.0.$0^{2,8}$] oct-3-ene (69), in 70.0% yield as colorless crystals, mp 55-56°. Its 60 MHz nmr spectrum showed in addition to the four aromatic protons at δ 6.83-7.28 and a multiplet for two vinyl protons at δ 4.73-4.97, a complex spectrum for an additional six protons with a pattern similar to ketone 68. Hydroboration of 69 with B_2H_6 in tetrahydrofuran followed by

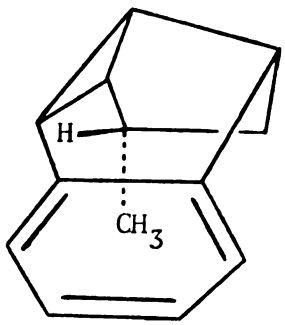
SCHEME 15



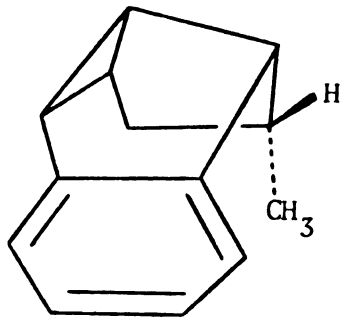
68 69 66s

treatment with propionic acid gave a single product (60.5% yield) with ir and nmr spectra identical to photoproduct 66s.

The major photoproduct from irradiation of 58s was assigned as *syn*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67s) also by analysis of its 100 MHz nmr spectrum. Thus, the nmr spectrum showed four aromatic protons at δ 6.85-7.37, a three-proton doublet for the methyl substituent at δ 0.74 and a complex spectrum for the remaining seven protons. A complete assignment was made based on double irradiation experiments. The double irradiation results and other spectral properties are given in the experimental section. In addition to the double irradiation results, a comparison of the methyl chemical shift of isomers 66s and 67s clearly indicates their respective positions. As the three dimensional drawings indicate, the methyl substituent in 66s is expected to be shielded by the aromatic ring current to a greater extent and, therefore,



66s

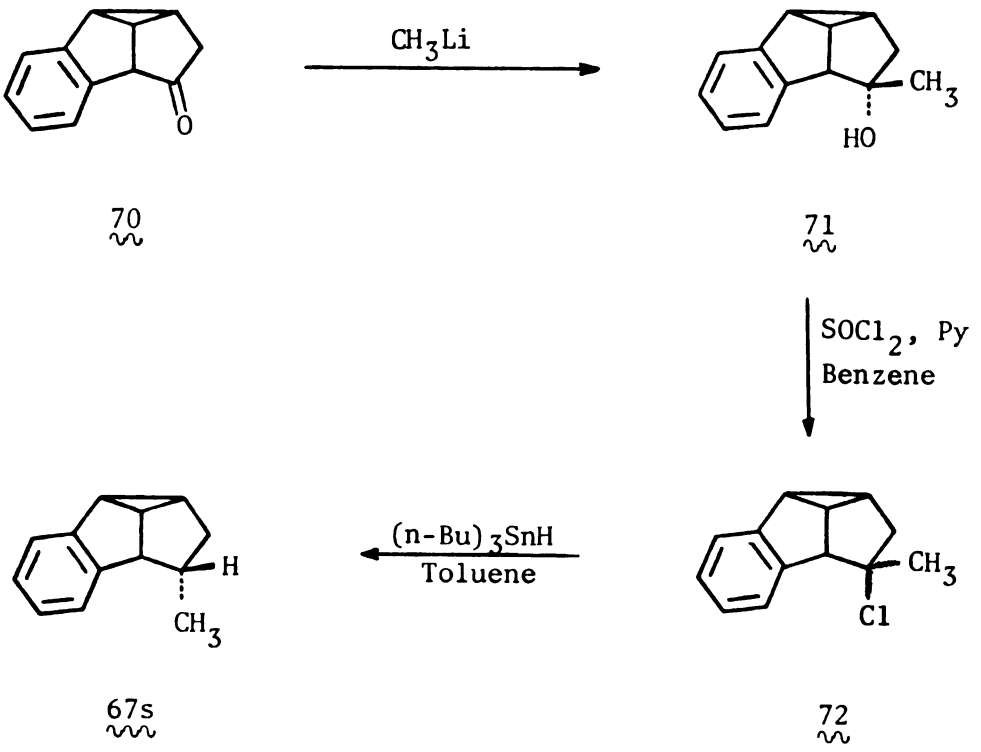


67s

absorb at higher field than the methyl substituent in 67s. Thus in 66s the methyl doublet appears at δ 0.43, whereas in 67s it appears at δ 0.74. Finally, the structure of 67s was conclusively established by comparison with an authentic sample obtained from 3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-6-one (70)[45] as outlined in Scheme 16.

Reaction of ketone 70 with methyllithium resulted in the formation of a single alcohol (97.0% yield) with the hydroxyl group *syn* to the aromatic ring. The stereochemical assignment is based on the nmr and infrared spectra. The 60 MHz nmr showed a methyl doublet at δ 0.95 which is predictably at lower field than if the methyl were *syn* to the aromatic ring. The infrared spectrum showed a band at 3575 cm^{-1} which after concentration studies was attributed to internal hydrogen bonding with the aromatic ring. Such intramolecular hydrogen bonding would not be expected if the hydroxyl were *anti* to the aromatic ring. Treatment of alcohol 71 with thionyl chloride followed by reduction with tri-n-butyltin

SCHEME 16



70 71 67s 72

hydride in toluene gave a single product (85% yield) with nmr and ir spectra identical to photoproduct 67s.

The formation of a single alcohol from ketone 70 and also the formation of a single product from reduction of chloride 72 is not unreasonable, since attack of methyllithium and also of the hydrogen atom from tri-n-butyltin hydride is expected to take place from the convex face of the cupped molecule to produce, respectively, *syn*-alcohol 71 and the *syn*-isomer 67s. The same stereospecific attack occurred in the reaction of alkene 69 with borane (*vide supra*).

The major photoproduct from irradiation of 58a was assigned as *anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67a) based on its spectral properties and by degradation to a relay compound which was synthesized independently. The 100 MHz nmr spectrum was considerably more complex than the nmr spectra of photoproducts 66s and 67s and showed, in addition to the four aromatic protons at δ 6.92-7.37 and the methyl doublet at δ 1.08, a half-proton multiplet at δ 3.46-3.60, a half-proton doublet at δ 3.17, one-proton multiplets at δ 2.70-2.93 and 2.26-2.48, and an extremely complex four proton multiplet at δ 1.25-2.16. The complexity of the spectrum prevented a complete proton assignment, similar to those of photoproducts 66s and 67s. However, similarities between the nmr spectrum of 67a and the nmr spectra of 66s and 67s in the aromatic region, in the low field multiplet at approximately δ 3.5 (benzylic methine proton at C_5), and in the "quartet-like" multiplet at δ 2.8 (cyclopropyl methine proton at C_1) indicated that photoproduct 67a was also a methyl-substituted 3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene. This gross structural assignment was suggested by the similarity in the infrared spectra of 67a, 66s and 67s, and by their identical mass spectra. However, photoproduct 67a could have the *anti*-methyl substituent located at either C_6 or C_7.

In an attempt to establish the position of the methyl substituent in 67a, a 270 MHz nmr spectrum was determined and double irradiation was performed.[50] The results are given in Table IV and shown in the Appendix section (Figures 10 and 11). Examination of the spectrum clearly indicates that it still remained second-order and unambiguous analysis was not possible. For instance, with the exception of the signals at δ 1.03, 2.72-2.82 and 2.26-2.38 all other signals integrate to fractions of a proton. The total integration agrees with structure 67a. However, as

Table IV. 270 MHz NMR and Spin Decoupling of *Anti*-6-methyl-3,4-benzotricyclo[3.3.0.0^{2,8}]oct-3-ene (67a).[a]

Signal position, δ	Rel. area	Signal description and assignment	Signal irradiated[b]	Decoupling result[c]
3.47-3.55	0.4	apparent triplet, benzyl methine, H-5	2.72-2.82, H-1 1.66-1.86, *anti* H-7	doublet doublet
3.14	0.6	doublet, benzylic cyclopropyl H, H-2	2.72-2.82, H-1	singlet
2.72-2.82	1.0	apparent doublet of a quartet, cyclopropyl methine, H-1	3.47-3.55, H-5 3.14, H-2 2.26-2.38, H-8 1.41-1.60	triplet triplet triplet quartet
2.26-2.38	1.0	two partially overlapping "triplets", cyclopropyl adj to methylene, H-8	2.72-2.82, H-1 1.66-1.86, *anti* H-7 1.41-1.60	triplet d of d d of d
1.97-2.08	0.5	apparent quintet, methine, H-6	1.18-1.37, *syn* H-7 1.03, methyl	quartet doublet
1.66-1.86	1.4	multiplet, *anti* H at C-7	3.47-3.55, H-5 2.26-2.38, H-8 1.18-1.37, *syn* H-7	incomp[d] incomp[d] incomp[d]
1.41-1.60	0.7	"triplet" superimposed on a multiplet, unassigned	2.72-2.82, H-1 2.26-2.38, H-8 1.18-1.37, *syn* H-7 1.66-1.86, *anti* H-7 1.03, methyl	doublet[e] doublet[e] doublet[e] incomp[d] incomp[d]
1.18-1.37	1.4	multiplet, *syn* H at C-7	1.97-2.08, H-6 1.66-1.86, *anti* H-7 1.41-1.60	incomp[d] incomp[d] incomp[d]
1.03	3.0	doublet, methyl	1.97-2.08, H-6 1.41-1.60	incomp[d] incomp[d]

[a]Run in $CDCl_3$ with TMS as internal standard. [b]Signal irradiated that affects signal in column 1. [c]Result of irradiation in spin decoupling. [d]Incomplete decoupling. [e]Multiplet remained unchanged.

shown in Table IV, if one assumes that each multiplet corresponds to one proton, an assignment based on spin decoupling seems to place the *anti*-methyl substituent at C_6.

The position of the methyl substituent was clarified mainly by the long range coupling between H-5 and *anti* H-7.[45] These protons are geometrically fixed in the "W" configuration for coupling through four bonds.[51] Thus, irradiation at *anti* H-7 showed it to be coupled to H-8, H-5 and *syn* H-7. If the *anti*-methyl substituent were at C_7 such long range coupling would not be observed. Furthermore, the splitting pattern for H-8 would be simplified considerably since it would have one less vicinal hydrogen.

The presence of two half-proton signals at δ 3.47-3.55 and 3.14 still remained a puzzling problem. Since these signals are far removed from the rest of the spectrum and do not seem to be mutually coupled, one would expect this region of the spectrum to differ only slightly from a first order spectrum. This problem raised the possibility that photoproduct 67a is a mixture of two isomeric products (*anti*-methyl substituent at C_6 and C_7). However, since no other product was detected by vpc using three different columns (3% SE-30, 10% FFAP and 20% DEGS on chromosorb W) at various temperatures and flow rates, and only one methyl doublet was observed in the 270 MHz nmr spectrum, this possibility seemed unlikely. Nevertheless, in view of the spectral ambiguities, it was important that structure 67a be established more firmly, preferably by independent synthesis.

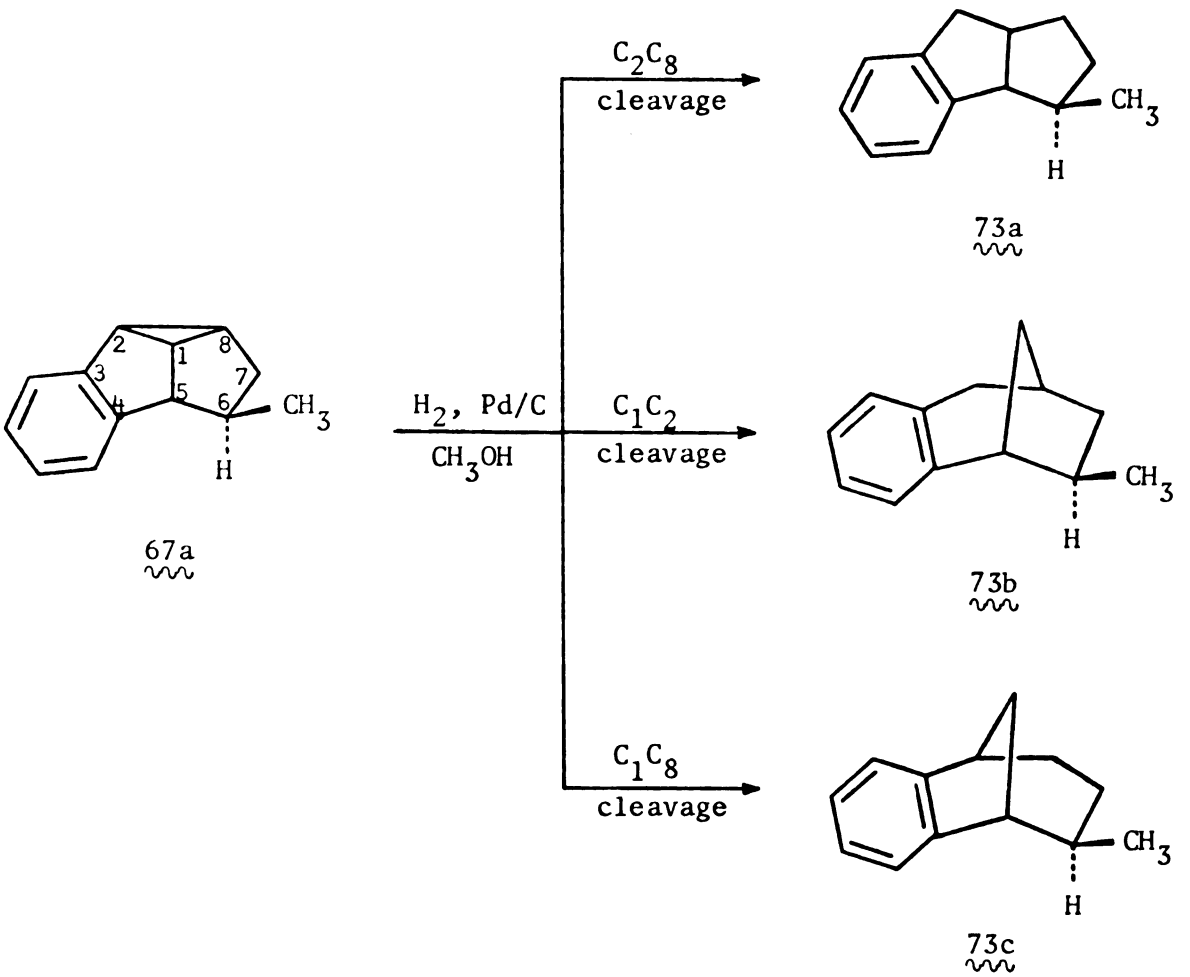
Since reduction of chloride 72 afforded only photoproduct 67s, several attempts were made to synthesize 67a from methyl ketone 74 (*vide infra*). Unfortunately, Wolff-Kishner reduction of ketone 74 or conversion of 74 to the respective chloride followed by tri-n-butyltin hydride

reduction resulted in opening of the cyclopropane ring. This difficulty was overcome by hydrogenation of photoproduct 67a and comparing its product with an authentic sample obtained by independent synthesis. Thus, hydrogenation of 67a with 10% palladium on charcoal resulted in the uptake of one equivalent of hydrogen. The mass spectrum showed a parent peak at m/e 172, corroborating the addition of one equivalent of hydrogen to photoproduct 67a. The nmr spectrum of the dihydro photoproduct showed four aromatic protons at δ 6.68-7.08, a methyl doublet at δ 1.00 and an extremely complex spectrum for the remaining nine protons. Analytical gas chromatography showed the hydrogenation of photoproduct 67a to consist of a single product; however, the nmr spectrum showed a small doublet at δ 1.17 and a multiplet at δ 6.95-7.10 corresponding to approximately 5% of a second product.

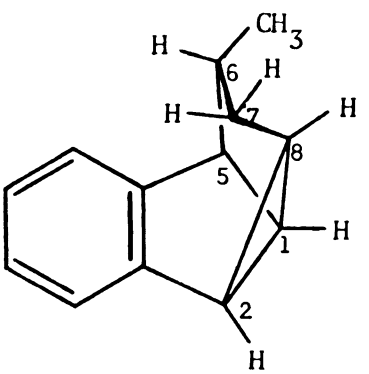
The presence of a second product is not surprising in view of the fact that three isomeric products can result from catalytic hydrogenation of photoproduct 67a (Scheme 17). Of these three possible hydrogenation products, 73a and 73b are most likely to be formed since the C_1-C_2 and C_2-C_8 bonds are activated by the adjacent phenyl group. Furthermore, based on steric considerations, one might expect product 73b to be the major product. As depicted in the three dimensional drawing below, molecular models of 67a clearly indicate that the C_7 methylene restricts the approach of the C_2-C_8 bond to the catalyst surface, while the C_1-C_2 bond is noticeably less hindered to such an approach.

A convenient synthetic entry to one of the possible hydrogenation products (73a) is outlined in Scheme 18. Addition of ketone 68 to a solution of hexamethyldisilazane and n-butyllithium followed by treatment with methyl iodide proved highly stereospecific, leading to the formation of *anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-7-one (74) in

SCHEME 17

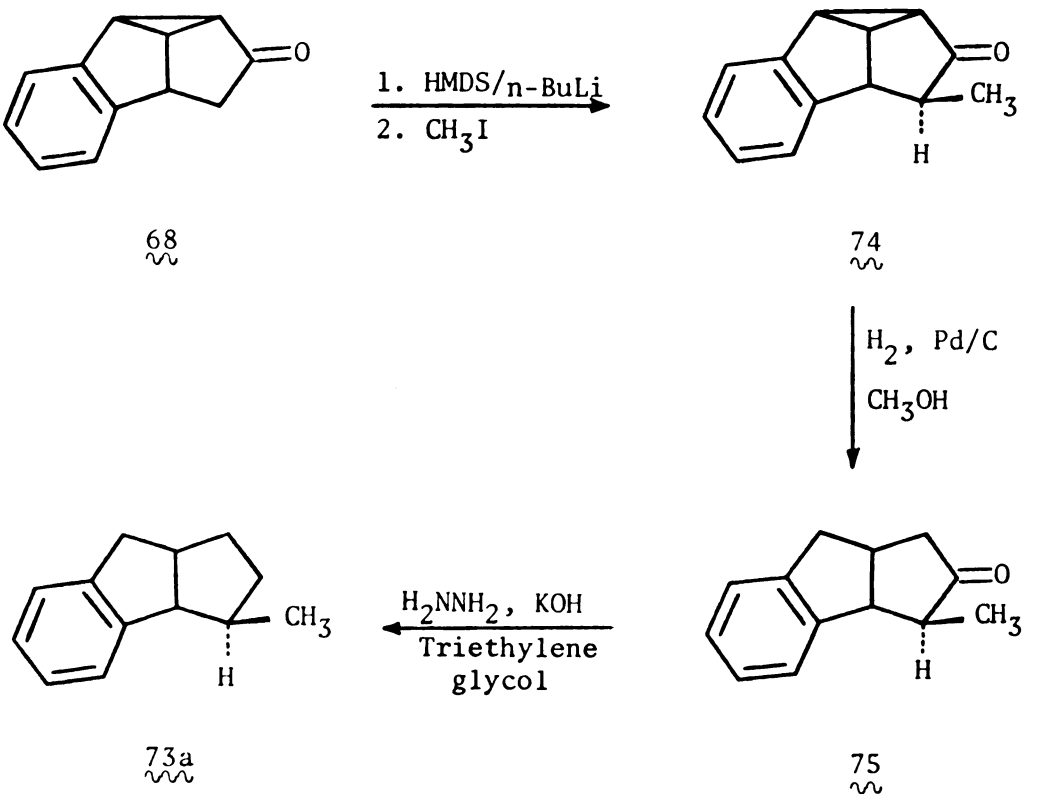


98% yield. As with other reactions in this ring system, attack of methyl iodide on the enolate ion of 68 occurred only from the convex face of the cupped shape molecule. Reduction of ketone 74 with 10% palladium on



67a

SCHEME 18

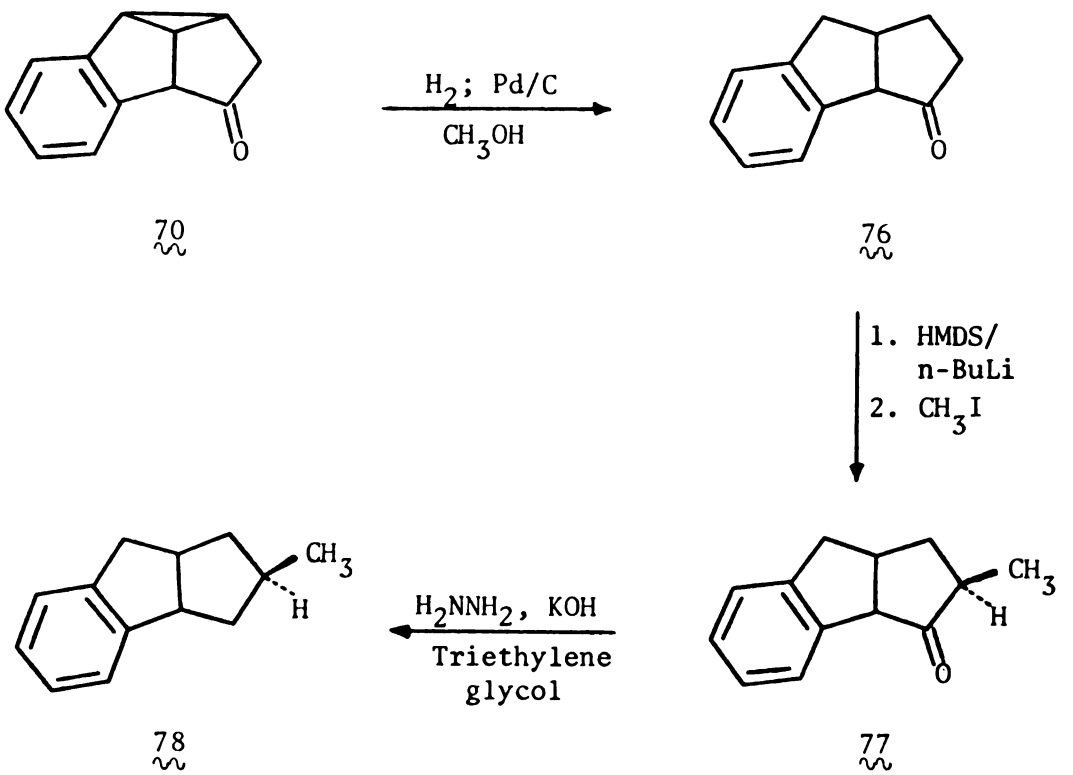


68 74 75 73a

charcoal in methanol gave only one product which was assigned structure 75 based on an analogous reduction of ketone 68.[49] Also, in analogy to the parent ketone (less methyl substituent),[49] Wolff-Kishner reduction of 75 gave 80% of 73a. Although this compound (73a) had an identical vpc retention time with the material obtained from reduction of photoproduct 67a, their nmr and ir spectra differed considerably.

In order to eliminate the possibility that the *anti*-methyl substituent in photoproduct 67a is at C_7, *anti*-7-methyl-3,4-benzobicyclo[3.3.0]-oct-3-ene (78) was synthesized from ketone 70 by a sequence of steps similar to the synthesis of 73a (Scheme 19). In this case, however, hydrogenation preceded methylation due to the instability of the enolate

SCHEME 19



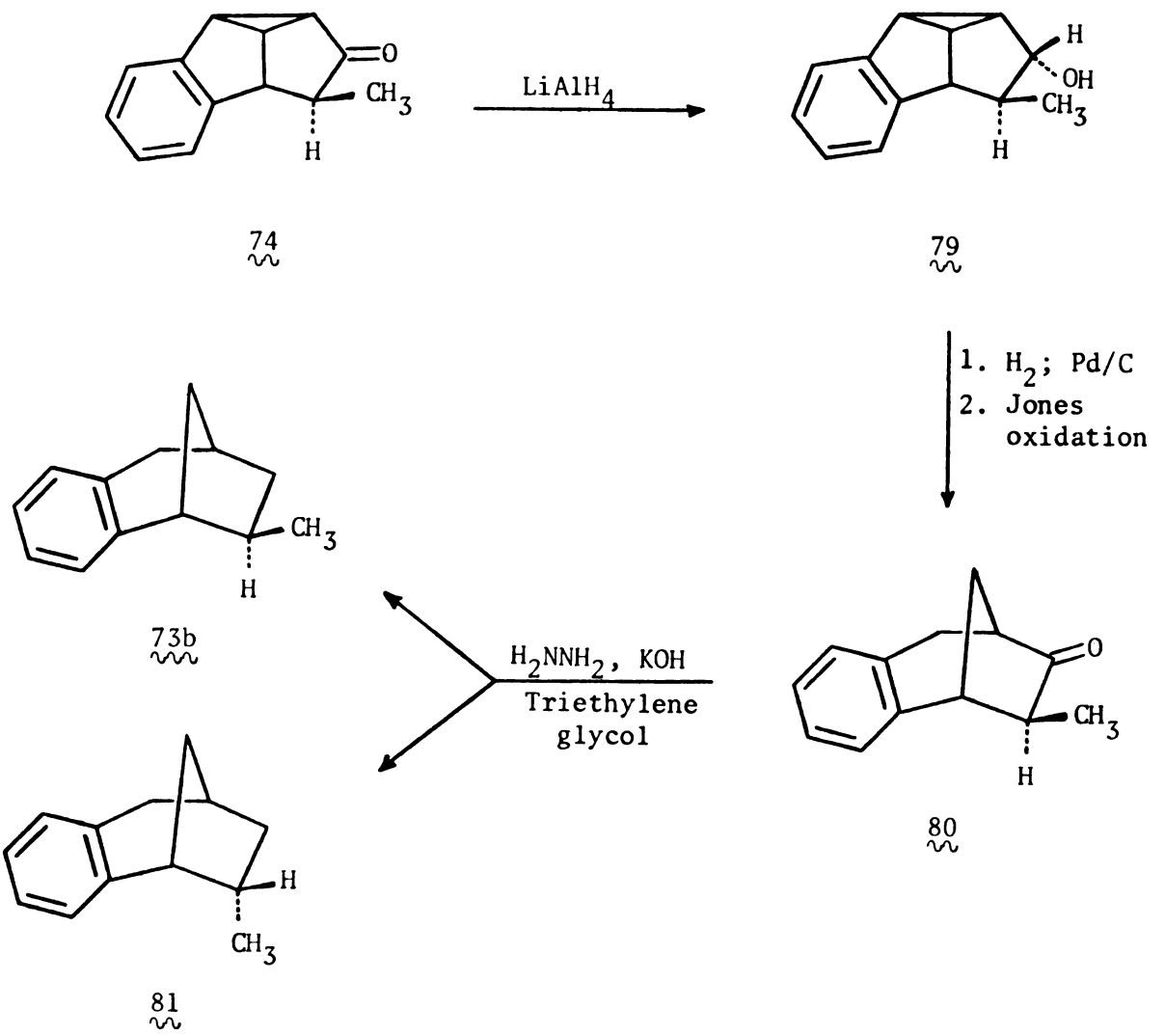
70 76 78 77

ion resulting from ketone 70. Thus, hydrogenation of ketone 70 with 10% palladium on charcoal in methanol resulted in the uptake of one equivalent of hydrogen. Vapor-phase chromatography showed the presence of two products in a ratio of 3:1. The major product gave a 2,4-dinitrophenylhydrazone derivative whose melting point was in close agreement with the literature value for the 2,4-dinitrophenylhydrazone derivative of ketone 76.[52] The minor product was not identified. Methylation of ketone 76 was stereospecific and gave only the *anti*-methyl ketone 77 in 67% yield. Finally, Wolff-Kishner reduction of 77 afforded 78 as the sole product in 74% yield. This compound (78) differed in every respect

(ir, nmr, and vpc retention time) with the sample obtained from reduction of photoproduct 67a.

Authentic *anti*-6-methyl-3,4-benzobicyclo[3.2.1]oct-3-ene (73b) was conveniently produced by a sequence of steps similar to the synthesis of 73a (Scheme 20). In this sequence, however, ketone 74 was reduced to *syn*-alcohol 79 in order to control the direction of hydrogenation. The *syn*-hydroxyl substituent at C_7 impedes approach of the catalyst to the C_2C_8 bond so that hydrogenation takes place preferentially at the C_1C_2 bond to yield the bicyclo[3.2.0]octane derivative. Thus, reduction

SCHEME 20

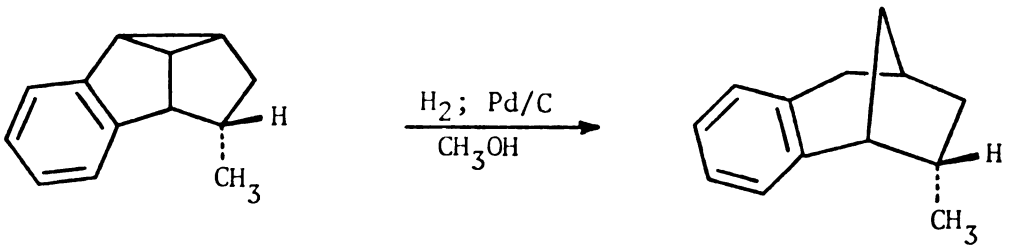


of 79 over palladium on charcoal in methanol followed by Jones oxidation of the crude hydrogenation mixture yielded ketones 75 and 80 in a ratio of 1:3. Separation of these isomeric ketones by preparative thick-layer chromatography was followed by Wolff-Kishner reduction of ketone 80 to afford two hydrocarbons in approximately 3:2 ratio. Separation of the two components by vapor-phase chromatography gave 73b and 81. The infrared spectrum and vpc retention time of the major component (73b) was identical to that of the material obtained from hydrogenation of photoproduct 67a. The nmr spectrum of 73b lacked the small doublet at δ 1.17 and the multiplet at δ 6.95-7.10 observed in the dihydro photoproduct, but the remaining spectrum was identical. This comparison establishes the structure of the dihydro photoproduct which in turn, then, firmly establishes the structure of the major photoproduct from 58a as *anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67a).

The structures of compounds 73-81 are based on their method of synthesis and on their spectral properties which are given in the experimental section. The configuration of the methyl substituent is based on its nmr chemical shift. In general, methyl substituent *syn* to the aromatic π system is expected to be more shielded and appear at higher field than when the methyl has the *anti* geometry. The configuration of the hydroxyl group in 79 is based on its infrared spectrum which showed bands at 3640 and 3590 cm^{-1} attributed to free O-H stretching and internal hydrogen bonding with the aromatic ring. As in the case of alcohol 71, such intramolecular hydrogen bonding is not expected when the hydroxyl is *anti* to the aromatic ring.

Additional evidence supporting structures 73b and 81 was obtained from the previously identified photoproduct 67s (*vide supra*). As shown

in Scheme 20, Wolff-Kishner reduction of ketone 80 conveniently caused epimerization of the methyl substituent giving rise to *syn*-methyl-3,4-benzotricyclo[3.2.1]oct-3-ene (81). In analogy to photoproduct 67a, then, 81 should be identical to the product resulting from hydrogenation of photoproduct 67s. Thus, as with photoproduct 67a, hydrogenation of 67s over 10% palladium on charcoal in methanol resulted in the uptake of one equivalent of hydrogen. The mass spectrum showed a parent peak



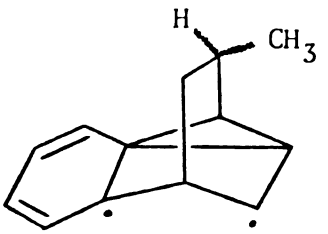
67s 81

at m/e 172, corroborating the addition of one equivalent of hydrogen to photoproduct 67s. The nmr spectrum showed four aromatic protons at δ 6.65-7.07, a methyl doublet at δ 0.63 and a complex spectrum for the remaining nine protons. This nmr spectrum was identical to that of 81. However, similar to the reduction of 67a, the nmr spectrum of the material obtained from hydrogenation of 67s showed a small doublet at δ 0.88 and a multiplet at δ 6.95-7.02 corresponding to approximately 15% of a second product. This additional doublet and multiplet were not present in the nmr spectrum of the material obtained from the Wolff-Kishner reduction.

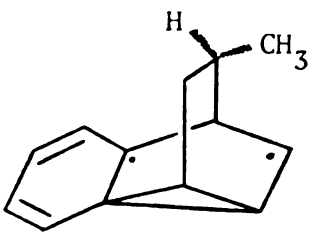
The discrepancies between the nmr spectrum of 73b and dihydro photoproduct 67a and similar discrepancies between the nmr spectrum of 81 and dihydro photoproduct 67s are most likely due to small amounts of product formed by reduction of either the C_1-C_2 or C_2-C_8 bonds in the respective photoproducts (*vide supra*). A comparison between the product obtained from hydrogenation of 67a and 73a showed them to have identical vpc retention times and the small methyl doublet at δ 1.17 in the nmr spectrum of dihydro photoproduct 67a had the same chemical shift as the methyl doublet of 73a, thus indicating possible formation of small amounts of 73a during hydrogenation of photoproduct 67a. A similar reduction could have taken place during hydrogenation of 67s.

C. Conclusions

The results of the experiments reported here may be summarized by examining the two benzo-vinyl intermediates R and S. The di-π-methane photoisomerization of compounds 58s and 58a proceed preferrentially through intermediate S in which the unpaired electrons are closest in space to the methyl substituent. The extent of the preference depends



R



S

on the relation between the methyl substituent and the aromatic ring. When the methyl was *anti* to the aromatic ring the reaction was regiospecific. When the methyl was *syn* to the aromatic ring some product corresponding to intermediate R was obtained, but the reaction was still rather highly regioselective.

Clearly, since the methyl substituent has no lone pair of electrons to share, this uneven distribution of di-π-methane photoproducts rules out any charge transfer interaction between the substituent and the proximal unpaired electrons as originally suggested by Hart and Murray.[44] As with the systems containing hydroxyl and acetoxyl substituents at C_9,[45] the methyl substituent can be the only directive influence on the reaction since it is the only dissymmetric element in the reaction of 58s and 58a. Furthermore, the influence must be through space rather than through bonds. If the directive effect of the methyl substituent occurred through bonds one might have expected the *syn* and *anti* epimers (58s and 58a) to react similarly.

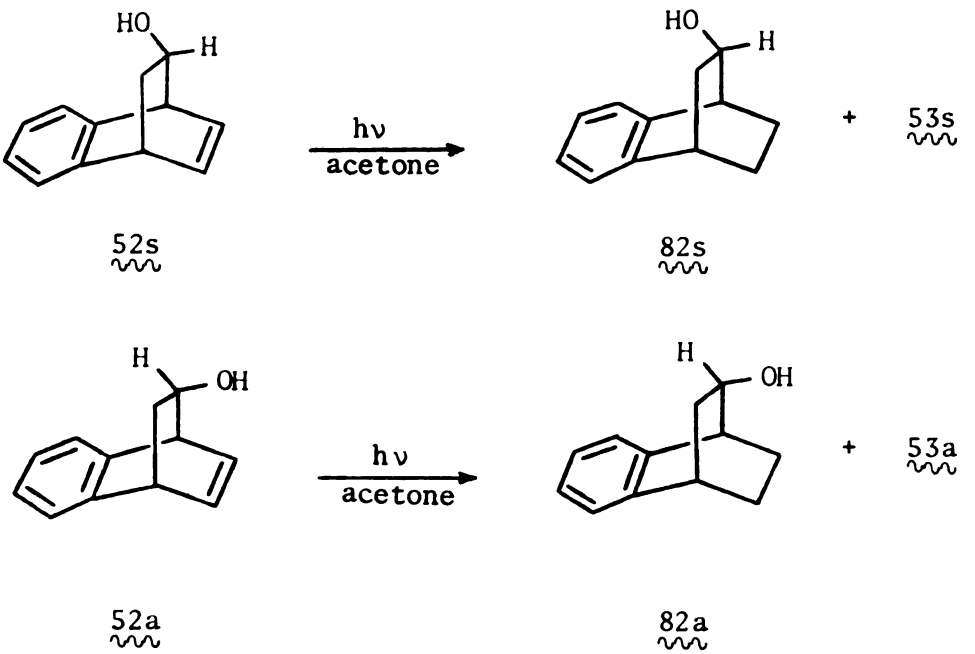
The precise nature of this substituent effect is still not understood, and explanations remain speculative. One possibility would be that the substituent affects the transfer of triplet energy from the acetone sensitizer to the molecule. Such a mechanism would require that the functionality at C_9 direct the excited acetone molecule to transfer its triplet energy asymmetrically to the substrate. This directive effect could be steric in the case of the methyl substituent or both steric and polar in the case of the hydroxyl and acetoxyl substituents.

The sequence of events during electronic energy transfer clearly requires diffusion together of a triplet donor molecule and an acceptor molecule followed by an interaction between the two molecules. The

nature of the interaction is still unclear. However, Schenk[53] has taken the viewpoint that during energy transfer the excited sensitizer interacts with the substrate to form a reactive complex or even a covalent bond. The activated substrate may then undergo isomerization or rearrangement. The sensitizer is eventually excised unharmed. There is no case for which this mechanism has been clearly demonstrated. However, if such a mechanism is operating, steric and polar effects may well influence the energy transfer process. Photolysis of 58s in the presence of a ketone with inherent steric strain such as diisopropyl ketone or other bulkier ketones as sensitizer could give further insight regarding this problem. If, for example, an increase in the ratio of photoproducts 67s to 66s with an increase in the size of the alkyl group in the ketone sensitizer is observed, one would have a strong case for the explanation presented in this thesis. Perhaps a careful kinetic study of the reaction of 58s and 58a using different alkyl ketones as sensitizer would also be fruitful.

The formation of photoreduction products 65s and 65a is not without precedent. The same type of photochemically-induced reduction was observed by Sauers[54] during irradiation of acetone solutions of several norbornene derivatives, and by Kropp[55] during irradiation of alcoholic solutions of several cycloalkenes in the presence of aromatic hydrocarbon photosensitizers such as benzene or toluene. The reductions probably involve the triplets produce *via* energy transfer. Abstraction of hydrogen from acetone would lead to the 1,(2 or 3),4-trihydro-1,4-ethanonaphthalene radicals (58aH• and 58sH•) and acetonyl radicals. In dilute solution, 58aH• and 58sH• can abstract a second hydrogen atom in competition with other radical recombination reactions.

It should be noted that the same type of reduction products were observed during the acetone sensitized irradiation of 52s and 52a. Although 82s was previously detected, it was not characterized.[45] Alcohol 82a was not previously detected (see Part N of Experimental Section).



In conclusion, although the results presented here do not permit a conclusive explanation for the observed regioselectivity of the reactions, it clearly rules out the possibility of a charge transfer complex. At present a steric interaction between the substituent and the sensitizer best explains the observed results.

EXPERIMENTAL

A. General Procedures

Except where otherwise noted, all nmr spectra were measured in $CDCl_3$ or CCl_4 solutions using TMS as an internal standard. The 60 MHz spectra were recorded on a Varian T-60 spectrometer and the 100 MHz spectra were recorded on a Varian HA-100 spectrometer. Infrared spectra were recorded on a Perkin Elmer 237 grating spectrophotometer and calibrated against a polystyrene film. Ultraviolet spectra were obtained with a Unicam SP-800 in 95% ethanol, unless otherwise noted. Mass spectra were obtained from a Hitachi-Perkin Elmer RMU-6 operated by Mrs. Ralph Guile. Melting points were determined with a Thomas-Hoover Melting Point Apparatus and are uncorrected. Varian Aerograph gas chromatographs were used. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

B. 9-Methylene-1,4-dihydro-1,4-ethanonaphthalene (60).

To a 250 ml three-necked flask equipped with a magnetic stirrer, condenser, addition funnel and gas inlet was added 1.47 g (41.0 mmol) of 57% NaH in mineral oil. The flask was flushed with nitrogen and the NaH was washed free of mineral oil with hexane. To the NaH was added 15 ml of DMSO and the solution was heated to 60° in an oil bath until

hydrogen gas evolution ceased. The reaction mixture was cooled to room temperature and to it was added 20.3 g (45.0 mmol) of triphenylmethylphosphonium bromide in 60 ml of DMSO followed by addition of 7.00 g (41 mmol) of 9-oxo-1,4-dihydro-1,4-ethanonaphthalene (59)[45] in 10 ml of DMSO. The reaction mixture was stirred at room temperature for 4 hours, diluted with 500 ml of water and extracted with pentane. The pentane extracts were combined, washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. The pentane was rotary evaporated leaving behind 6.80 g of a clear liquid. Chromatography on silica gel using hexane as the eluent yielded 5.80 g (34.5 mmol, 84.0%) of 60: ir (neat) 3060 (m), 3010 (w), 2960 (m), 2810 (w), 1650 (m), 1475 (m), 1465 (w), 1345 (w), several weak bands from 1300 to 900, 880 (m), 845 (m), 780 (m), 760 (s), 700 cm^{-1} (s); nmr ($CDCl_3$) δ 2.13-2.33 (m, 2H, bridge methylene H's), 3.85-4.13 (m, 1H, bridgehead H), 4.25-4.45 (m, 1H, bridgehead H), 4.63-4.78 (m, 1H, $=CH_2$), 4.93-5.08 (m, 1H, $=CH_2$), 6.43-6.75 (m, 2H, vinyl H's at C-2 and C-3), 7.00-7.23 (m, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel. intensity) 168 (89), 167 (56), 153 (35), 128 (100), 115 (15), 102 (8), 63 (10), 51 (10).

Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19

Found: C, 92.85; H, 7.18

C. *Syn*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s).

In a dry three-necked flask equipped with a condenser, magnetic stirrer, thermometer, nitrogen gas inlet and a pressure-equilibrated funnel were placed 50 ml of a 1.08M solution of B_2H_6 (52.0 mmol) in tetrahydrofuran. The reaction flask was immersed in an ice salt bath and cooled to -5°. From the dropping funnel 11 ml (104 mmol) of

2-methyl-2-butene was added dropwise to the stirred solution over a period of 30 minutes. The disiamylborane was permitted to remain an additional 15 hours at 0-5° under a nitrogen atmosphere, then used for the hydroboration of 9-methylene-1,4-dihydro-1,4-ethanonaphthalene (60).

To a 100-ml three-necked flask equipped with a condenser, magnetic stirrer, thermometer, nitrogen gas inlet and a serum cap was added 2.50 g (14.9 mmol) of 60 in 15 ml of tetrahydrofuran. The flask was immersed in an ice-salt bath, the solution cooled to 0°, and 18.2 ml (14.9 mmol) of disiamylborane in tetrahydrofuran was added dropwise by means of a syringe to the stirred solution. After being stirred for one hour at 0° the reaction mixture was allowed to remain for approximately 3 hr at room temperature. To the reaction mixture was added 5.0 ml of propionic acid, then 30 ml of diglyme. The reflux condenser was substituted by a distillation head and enough tetrahydrofuran was distilled to maintain a reflux temperature of 130°. The reflux condenser was replaced and the residual reaction mixture was refluxed at 130° for 8 hr. The reaction mixture was then diluted with 200 ml of water and extracted with pentane. The pentane extracts were combined, washed with saturated $NaHCO_3$, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. The pentane was evaporated leaving behind a yellowish liquid. Chromatography on silica gel using hexane as the eluent yielded 1.59 g (9.35 mmol, 63.0%) of 58s, a clear liquid: ir (neat) 3040 (m), 3010 (w), 2950 (s), 2860 (m), 1475 (m), 1460 (m), 1380 (w), 1350 (w), several weak bands from 1275-800, 770 (m), 690 cm^{-1} (s); nmr ($CDCl_3$) δ 0.62 (d, 3H, J = 7.0 Hz, methyl), 0.72-1.05 (m, 1H, methine), 1.53-2.08 (m, 2H, methylene), 3.42-3.65 (m, 1H, bridgehead), 3.67-3.92 (m, 1H, bridgehead), 6.27-6.77 (m, 2H, vinyl), 7.13 (broad s, 4H, aromatic); mass spectrum (70 eV) m/e (rel. intensity) 170 (25) 165 (16), 155 (32), 153 (44),

152 (49), 141 (55), 128 (2330), 115 (77), 102 (100), 89 (31), 77 (94), 63 (107), 51 (147); uv (95% ethanol) λ_{max} 270 nm (ε 411), 263 (411), 256 (213, sh), 219 (3730, sh), 203.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29

Found: C, 91.60; H, 8.11

D. Dimethyl 9-methylene-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dicarboxylate (62).

Following the procedure for the synthesis of 60, a solution of sodium methylsulfinyl carbanion was prepared from 4.25 g (0.10 mol) of 57% NaH in mineral oil and 60 ml of dimethyl sulfoxide. To this solution was added 35.7 g (0.10 mol) of triphenylmethylphosphonium bromide in 100 ml of dimethyl sulfoxide. The reaction mixture was stirred for 30 minutes at room temperature.

To a 500-ml three-necked flask equipped with a magnetic stirrer, condenser, addition funnel, and nitrogen gas inlet was added 28.8 g (0.10 mol) of dimethyl 9-oxo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dicarboxylate (61)[48] in 100 ml of dimethyl sulfoxide. By means of a U-tube the ylid solution prepared above was transferred to the addition funnel and added dropwise over a period of 30 minutes to the keto-diester. The reaction mixture was stirred overnight, diluted with 1000 ml of water and extracted with methylene chloride. The methylene chloride extracts were combined, washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the methylene chloride gave a dark-brown oil which on vacuum distillation, bp 135-140° at 0.05 mm Hg, yielded 20.19 g (70.7 mmol, 70.7%) of 62, a clear viscous liquid: ir (neat) 3070 (w), 3015 (m), 2940 (m), 2840 (m), 1725 (doublet, s), 1650 (w),

1480 (m), 1465 (m), 1375 (w), 1310 (m), 1280 (m), 1205 (broad s), 1115 (m), 1030 (s), 895 (m), 875 (w), 765 cm^{-1} (s); nmr ($CDCl_3$) δ 1.85-2.78 (m, 2H, C-10 methylene H's), 3.02-3.30 (m, 1H, C-2 or C-3 methine), 3.60 (broad s, 5H, C-2 or C-3 methine, bridgehead and carboxylate methyl), 3.80 (s, 3H, carboxylate methyl), 3.93-4.08 (m, 1H, bridgehead), 4.68-4.85 (m, 1H, $=CH_2$), 4.93-5.22 (m, 1H, $=CH_2$), 7.23 (s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 286 (3), 255 (3), 227 (3), 195 (3), 167 (9), 164 (4), 145 (13), 143 (13), 142 (100), 141 (32), 128 (7), 115 (7), 113 (10), 59 (3).

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34

Found: C, 71.26; H, 6.40

E. Dimethyl *Anti*-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dicarboxylate (63).

A solution of 62 (6.00 g, 21.0 mmol) in 100 ml of methanol was hydrogenated in the presence of 0.8 g of 10% Pd on charcoal at room temperature and 1 atm of pressure. The reduction was stopped after one equivalent of hydrogen was absorbed. The catalyst was removed by filtration, and the solvent was evaporated leaving 5.50 g (19.3 mmol, 91.5%) of 63 as a clear oil which solidified on standing. Recrystallization from chloroform yielded a white solid mp 70-72°; ir (neat) 3060 (w), 3010 (w), 2940 (m), 2870 (w), 1730 (s), 1480 (w), 1460 (m), 1430 (m), 1375 (w), 1305 (m), 1280 (m), 1235 (s), 1195 (s), 1120 (w), 1080 (m), 1025 (m), 945 (w), 920 (w), 865 (w), 795 (w), 760 cm^{-1} (m); nmr ($CDCl_3$) δ 1.03 (d, 3H, J = 6.5 Hz, C-9 methyl), 1.15-1.98 (m, 3H, C-9 methine and methylene), 2.87-3.10 (m, 1H, C-2 or C-3 methine), 3.37-3.53 (m, 3H, C-2 or C-3 methine and bridgeheads), 3.58 (s, 3H, carboxylate methyl), 3.78 (s, 3H,

carboxylate methyl), 7.20 (s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel. intensity) 288 (22), 256 (26), 228 (21), 213 (9), 186 (61), 169 (26), 155 (45), 143 (69), 128 (100), 114 (57), 87 (11), 77 (9), 59 (25).

Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99

Found: C, 70.90; H, 7.11

F. *Anti*-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dicarboxylic Acid (64).

A solution of 80 ml of approximately 20% aqueous sodium hydroxide was placed in a 250-ml Erlenmeyer flask and to it was added 5.50 g (19.3 mmol) of diester 63. The mixture was then heated to boiling for 1.5 hr during which time the diester completely dissolved. After the solution had been boiled vigorously for 30 minutes, it was cooled to room temperature and concentrated hydrochloric acid was added with stirring until the solution was acidic to litmus paper. The white solid which precipitated after cooling was filtered, washed with water and dried. The yield of dicarboxylic acid 64, mp 179-183° (recrystallized from methanol) was 5.00 g (19.1 mmol, 98.5%): ir (KBr) 3650-2300 (s), 2950 (m), 2870 (m), 1700 (s), 1485 (w), 1470 (w), 1420 (m), 1310 (m), 1290 (m), 1260 (s), 1225 (m), 1085 (w), 925 (m, broad), 775 (m), 755 cm^{-1} (m); nmr (acetone-d_6) δ 1.25 (d, 3H, J = 7.0 Hz, methyl), 1.30-1.85 (m, 3H, C-9 methine and methylenes), 2.82-3.02 (m, 1H, carboxylic methine), 3.17-3.73 (m, 3H, carboxylic methine and bridgeheads), 7.20 (s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 260 (40), 242 (9), 214 (19), 172 (38), 153 (94), 129 (100), 118 (23), 115 (18), 100 (16), 91 (7), 89 (4), 77 (11), 72 (11), 57 (18).

Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20

Found: C, 69.23; H, 6.20

G. *Anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58a).

A solution of 5.0 g (19.1 mmol) of 64 in a mixture of 150 ml of pyridine, 3 ml of triethylamine and 50 ml of water was placed in a rectangular jar which contained two Pt electrodes (5 x 7.5 cm) separated by 4.5 cm, a water cooling coil and a nitrogen dispersion tube. A constant unfiltered DC potential (110 V) was placed on the electrodes; the initial current was 800 mA. After 15 hr of electrolysis the current had decreased to 200 mA and the solution was black. The solvents were evaporated *in vacuo* and the black residue was extracted with hot pentane. The pentane extracts were combined, washed successively with 15% hydrochloric acid, saturated $NaHCO_3$, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent yielded 0.842 g (4.96 mmol, 26%) of 58a. Column chromatography on alumina using hexane as the eluent yielded a clear liquid: ir (neat) 3040 (m), 3010 (w), 2950 (s), 2860 (m), 1475 (m), 1375 (w), 1350 (w), several weak bands from 1275-900, 775 (w), 755 (s), 705 cm^{-1} (s); nmr ($CDCl_3$) δ 0.98 (d, 4H, methyl superimposed on C-9 methine, J = 6.5 Hz), 1.48-2.00 (m, 2H, methylene H's), 3.57-3.97 (m, 2H, bridgehead H's), 6.37-6.75 (m, 2H, vinyl H's), 7.15 (broad s, 4H, aromatic H's); uv (95% ethanol) and mass spectra are identical with those of 58s.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29

Found: C, 91.50; H, 8.27

H. Irradiation of *Syn*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s).

A solution of 285 mg (1.68 mmol) of 58s in 470 ml of acetone was photolyzed through pyrex with a 450-W Hanovia lamp, while a slow stream of nitrogen passed through the solution. The progress of the reaction was followed by vpc. After 3.5 hr the acetone was evaporated and the residue was extracted with pentane. The mixture was analyzed by vpc (5 ft x 0.125 in., 10% FFAP on chromosorb W, AW-DMCS 80/100, 128°, N_2 flow rate 30 ml/min). Three products [retention times in minutes, % yield versus a calibrated internal standard (pentadecane)] were observed: 65s (10.0, 22.7%), 66s (20.2 10.8%), 67s (24.0, 63.8%). The products were isolated by preparative scale vpc (10 ft x 0.25 in., 20% FFAP on chromosorb W P/G 30/60, 150°, He flow rate 40 ml/min).

Syn-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (65s): ir (neat) 3060 (w), 3025 (w), 3010 (w), 2925 (s), 2850 (m), 1480 (m), 1450 (m), 1375 (w), several weak bands from 1350 to 840, 760 cm^{-1} (s); nmr ($CDCl_3$) δ 0.58 (d, 3H, J = 6.5 Hz, methyl partially superimposed on C-9 methine), 0.60-1.07 (m, 1H, C-9 methine), 1.15-2.28 (m, 6H, methylene H's), 2.60-2.77 (m, 1H, bridgehead), 2.83-3.05 (m, 1H, bridgehead), 7.20 (s, 4H aromatic H's); mass spectrum (70 eV) m/e (rel. intensity) 172 (33), 143 (14), 130 (100), 115 (20), 102 (3.5), 77 (6), 63 (5), 51 (6).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36

Found: C, 90.92; H, 9.37

Syn-7-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (66s): ir (neat) 3040 (m), 3020 (m), 2930 (s), 2860 (m), 1480 (s), 1465 (m), 1380 (w), several weak bands from 1350 to 850, 810 (m), 775 (m), 760 (s), 745 (m), 725 cm^{-1} (w); HA-100 nmr ($CDCl_3$) δ 0.48 (d, 3H, J = 7.5 Hz, methyl), 1.39 (d, 1H, J = 11.0 Hz, *syn*-H at C-6), 1.76-1.98 (m, 1H,

cyclopropyl H adj. to methyl), 2.16-2.34 (m, 1H, benzylic cyclopropyl H), 2.46-2.77 (m, 2H, C-7 methine and *anti*-H at C-6), 2.78-2.99 (m, 1H, cyclopropyl methine), 3.43-3.60 (m, 1H, benzylic methine), 6.73-7.17 (m, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel. intensity) 170 (32), 169 (8), 155 (68), 141 (16), 128 (100), 115 (58), 102 (7), 91 (9), 89 (6), 77 (12), 65 (8), 63 (8), 55 (22). Double resonance was performed; only those bands which were affected are included. Irradiation of the doublet at δ 0.48 partially collapsed the multiplet at δ 2.46-2.77; 3.43-3.60 irradiated, 2.78-2.99 and 2.46-2.77 partially collapsed; 2.16-2.34 irradiated, 2.78-2.99 and 1.76-1.98 partially collapsed; 2.46-2.77 irradiated, 3.43-3.60, 1.76-1.98, 1.39 and 0.48 collapsed.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29

Found: C, 91.68; H, 8.33

Syn-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67s): ir (neat) 3040 (m), 3020 (m), 2930 (s), 2860 (m), 1480 (s), 1465 (m), 1380 (w), several weak bands from 1350 to 825, 790 (w), 775 (w), 755 (s), 720 cm^{-1} (w); HA-100 nmr ($CDCl_3$) δ 0.51-0.91 (m, 1H, *syn*-H at C-7), 0.74 (d, 3H, J = 7.0 Hz, methyl superimposed on *syn*-H at C-7), 1.60-1.93 (m, 2H, cyclopropyl H adj. to methylene and *anti*-H at C-7), 2.12-2.38 (m, 1H, benzylic cyclopropyl H), 2.44-2.95 (m, 2H, cyclopropyl methine and C-6 methine), 3.17-3.33 (m, 1H, benzylic methine), 6.85-7.37 (m, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel. intensity) 170 (27), 169 (5), 155 (4), 141 (12), 128 (100), 115 (32), 102 (5), 91 (3), 89 (4), 77 (6), 63 (7), 55 (9). Double resonance was performed; only those bands which were affected are included. Irradiation of the doublet at δ 0.74 partially collapsed the multiplet at δ 2.44-2.95 and 1.60-1.93; 1.60-1.93 irradiated, 2.12-2.38, 2.44-2.95 and 0.51-0.91 partially collapsed;

2.12-2.38 irradiated, 2.44-2.95 and 1.60-1.93 partially collapsed; 2.44-2.95 irradiated, 3.17-3.33, 2.13-2.38 and 1.60-1.93 partially collapsed; 3.17-3.33 irradiated 2.44-2.95 partially collapsed.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29

Found: C, 91.91; H, 8.23

I. Irradiation of *Anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58a).

A solution of 258 mg (1.56 mmol) of 58a in 470 ml of acetone was irradiated for 3.5 hr in the same manner as 58s. The mixture was analyzed by vpc (5 ft x 0.125 in., 10% FFAP on chromosorb W, AW-DMCS 80/100, 125°, N_2 flow rate 30 ml/min). Two products [retention time in minutes, % yield versus a calibrated internal standard (pentadecane)] were observed: 65a (16.2, 11.7%), 67a (24.8, 81.8%). The products were isolated by preparative scale vpc (10 ft x 0.25 in., 20% FFAP on chromosorb W P/G 30/60, 150°, He flow rate 40 ml/min).

Anti-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (65a): ir (neat) 3060 (w), 3040 (w), 3020 (w), 2940 (s), 2860 (m), 1480 (m), 1465 (w), 1455 (w), 1380 (w), several weak bands from 1350 to 800, 765 (s), 750 cm^{-1} (w); nmr ($CDCl_3$) δ 1.10 (d, 4H, J = 6.5 Hz, methyl superimposed on C-9 methine), 1.16-2.20 (m, 6H, methylene H's), 2.52-2.68 (m, 1H, bridgehead), 2.73-2.93 (m, 1H, bridgehead), 6.98 (s, 4H, aromatic H's); mass spectrum (70 eV) is identical to 65s.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36

Found: C, 90.86; H, 9.43

Anti-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67a): ir (neat) 3060 (w), 3040 (w), 2940 (m), 2920 (m), 2860 (w), 1475 (m), 1460 (m), 1375 (w), several weak intensity bands from 1310-810, 800 (m), 775 (m),

760 cm^{-1} (s); HA-100 nmr ($CDCl_3$) δ 1.08 d, 3H J = 7.0 Hz, methyl), 1.25-2.16 (m, 4H), 2.26-2.48 (m, 1H), 2.70-2.93 (m, 1H), 3.17 (d, 0.5H, J = 5.5 Hz), 3.46-3.60 (m, 0.5H), 6.92-7.37 (m, 4H, aromatic H's); mass spectrum (70 eV) is identical to 67s. A 270 MHz nmr (Bruker) was determined and double resonance was performed;[50] the results are given in Table IV and shown in the Appendix section (Figures 10 and 11).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29

Found: C, 91.56; H, 8.20

J. *Syn*-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (65s).

A solution of 58s (100 mg, 0.588 mmol) in 4 ml of MeOH was hydrogenated in the presence of 10 mg of 10% Pd on charcoal at room temperature and 1 atm of pressure. The reduction was stopped after 1 equivalent of hydrogen was absorbed. The catalyst was removed by filtration, and the solvent was evaporated, leaving behind 91 mg (5.29 mmol, 90%) of 65s which was not purified. The nmr and ir spectra were identical to those of the product obtained from irradiation of *syn*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s).

K. *Anti*-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (65a).

Hydrogenation of 58a (98.2 mg, 0.588 mmol), as described for 58s (*vide supra*), gave 82.1 mg (0.477 mmol, 81.2%) of 65a. The nmr and ir spectra were identical to those of the product obtained from irradiation of *anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58a).

L. 7-Methylene-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (69).

Following the procedure given for 60, 69 was prepared in 70% yield from 0.395 g (6.90 mmol) of 57% NaH in mineral oil, 2.46 g (6.90 mmol) of triphenylmethylphosphonium bromide, and 1.17 g (6.90 mmol) of 3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-7-one (68)[49] in dimethyl sulfoxide. Chromatography of the crude product on alumina using hexane as the eluent yielded 0.810 g (4.83 mmol, 70.0%) of 69, a clear liquid which solidified on standing: mp 55-56°; ir (neat) 3060 (m), 3030 (m), 2970 (w), 2930 (m), 2875 (w), 2810 (w), 1650 (m), 1475 (s), 1455 (m), 1425 (w), 1310 (w), several weak bands from 1200 to 925, 875 (s), 800 (m), 720 cm^{-1} (s); nmr (CCl_4) δ 1.97-2.67 (m, 3H, methylene H's and cyclopropyl H adj. to double bond), 2.80-3.28 (m, 2H, benzylic cyclopropyl H and cyclopropyl methine, 3.48-3.75 (m, 1H, benzyl methine), 4.73-4.97 (m, 2H, vinyl H's), 6.83-7.28 (m, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel. intensity) 168 (100), 167 (96), 153 (62), 152 (39), 141 (10), 128 (58), 115 (21) 102 (8), 83 (21), 77 (8), 76 (10), 63 (7), 51 (7).

Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19
Found: C, 92.87; H, 7.08

M. *Syn*-7-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (66s).

To a dry 15-ml three-necked flask equipped with a condenser, serum cap, magnetic stirrer, and nitrogen gas inlet was added 3 ml of freshly distilled tetrahydrofuran. The flask was immersed in an ice-salt bath, cooled to approximately 0° and 1.10 ml (1.19 mmol) of 1.08M B_2H_6 in tetrahydrofuran was added by means of a syringe followed

by the addition of 200 mg (1.19 mmol) of 69 in 3 ml of tetrahydrofuran. After being stirred for 0.5 hr at 0°, the reaction mixture was allowed to remain for 2 hours at room temperature. To the reaction mixture was added 1.0 ml of propionic acid followed by 7 ml of diglyme. The tetrahydrofuran was distilled and the reaction mixture was heated at 130° for 8 hours. The mixture was then diluted with 100 ml of water and extracted with pentane. The pentane extracts were combined, washed with saturated $NaHCO_3$, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Chromatography on alumina using hexane as the eluent yielded 0.122 g (0.718 mmoles, 60.5%) of 66s. The nmr and ir were identical to those of the product obtained from irradiation of *syn*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s).

N. 3,4-Benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-6-one (70).

A solution of 1.15 g (6.70 mmol) of a mixture of *syn* and *anti*-9-hydroxy-1,4-ethanonaphthalene (52s and 52a)[45] in 470 ml of acetone was flushed with nitrogen for 20 minutes and photolyzed through pyrex with a 450-W Hanovia lamp, while a slow stream of nitrogen passed through the solution. The progress of the reaction was followed by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW-DMCS 80/100, 190, N_2 flow rate 15 ml/min). After the mixture was irradiated for 3 hr the vpc trace showed complete disappearance of starting material and the formation of four products in a ratio of 2:1:14:7 with retention times of 12.8, 17.0, 18.0 and 23.7 minutes. Comparison of retention time by spiking, indicated that the products with retention times of 12.8 and 17.0 minutes correspond to *syn* and *anti*-9-hydroxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (82s and 82a, obtained by catalytic

hydrogenation of 52s and 52a) and products with retention time of 18.0 and 23.7 minutes correspond to alcohols 53s and 53a. The photolysis was repeated three times, the products combined and the solvent evaporated leaving behind a dark yellow oil which was oxidized as described below.

Chromium trioxide, 20 g (0.20 mol), was added to a mechanically stirred solution of 32 g (0.40 mol) of pyridine in 500 ml of methylene chloride at 0°. The flask was stoppered with a drying tube containing drierite, and the deep burgundy solution was allowed to warm to room temperature and stirred for 0.5 hr. At the end of this period, a solution of the alcohols obtained above in 15 ml of methylene chloride was added in one portion. A tarry black deposit separated immediately. After being stirred for one additional hour at room temperature, the solution was decanted from the residue. The residue salts were washed with methylene chloride, the organic solutions were combined and washed successively with 5% NaOH, 5% HCl, saturated $NaHCO_3$, saturated NaCl solution and dried over anhydrous $MgSO_4$. The methylene chloride was rotary evaporated leaving 3.73 g of a yellow oil. Chromatography on a 4.5 ft x 1 in column packed with silica gel using 10% ether in hexane as the eluent afforded 0.300 g (1.76 mmol, 6.6%) of a clear oil which was crystallized from hexane to give white crystals of 9-oxo-1,4-dihydro-1,4-ethanonaphthalene, mp 54-56° (lit.[56] mp 56.5-58°), 0.283 g (1.65 mmol, 6.2%) of 9-oxo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene which was crystallized from hexane to give white crystals, mp 33-34 (lit.[56] mp 30-31°), and 2.50 g (14.7 mmol, 55%) of white crystals which were recrystallized from hexane to give pure ketone 70[45], mp 57-59°.

O. *Syn*-6-hydroxyl-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (71).

To a 50-ml three-necked flask equipped with a condenser, serum cap, magnetic stirrer and nitrogen gas inlet was added 0.500 g (2.94 mmol) of 3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-6-one (70) in 20 ml of tetrahydrofuran. The solution was cooled to approximately 0° there was added, by means of a syringe, 2.33 ml (3.50 mmol) of a 1.50M solution of methyllithium in ether. The reaction mixture was stirred under N_2 atm at room temperature for 3 hr, then quenched with saturated NH_4Cl solution and extracted with ether. The ether extracts were combined, washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent yielded 0.529 g (2.84 mmol, 97%) of a yellowish oil which solidified on standing. Recrystallization from cold pentane gave a white solid, 71: mp 52-53°; ir (CCl_4) 3575 (m), 3450 (m, broad), 3040 (s), 2980 (s), 2950 (s), 2870 (m), 1475 (s), 1460 (m), 1445 (m), 1380 (s), 1355 (s), 1300 (m), 1215 (s), 1150 (s, broad), 100 (w), 955 cm^{-1} (m). The band at 3575 cm^{-1} did not change in relative intensity as a function of the concentration of 71 in CCl_4, whereas the intensity of the band at 3450 cm^{-1} decreased drastically with a decrease in concentration of 71. Nmr ($CDCl_3$) δ 0.95 (d, 1H, J = 11.5 Hz, *syn* C-7 H), 1.50 (s, 3H, methyl), 1.57-1.98 (m, 3H, hydroxyl H superimposed on *anti* C-7 H and cyclopropyl H adj. to methylene), 2.18-2.53 (m, 1H, benzylic cyclopropyl H), 2.58-2.92 (m, 1H, cyclopropyl methine), 3.00-3.17 (m, 1H, benzylic H), 6.83-7.22 (m, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 186 (10), 168 (16), 167 (12), 153 (10), 143 (25), 128 (100), 115 (14), 101 (4), 71 (12), 43 (42).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58

Found: C, 83.77; H, 7.50

P. *Syn*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67s).

To a solution of 154 mg (0.83 mmol) of alcohol 71 in 10 ml of anhydrous benzene, cooled to approximately 5°, was added 130 mg (1.66 mmol) of pyridine followed by 0.10 ml (160 mg, 1.35 mmol) of thionyl chloride. The mixture was stirred at approximately 5° for 15 minutes then added to ice-water. The organic layer was separated and the aqueous layer was extracted with benzene. The benzene extracts were combined and washed successively with cold 15% HCl, saturated $NaHCO_3$, saturated NaCl solution and dried over anhydrous $MgSO_4$. The benzene was evaporated leaving behind 145 mg (0.71 mmol, 85.4%) of chloride 72 which was not purified further. The infrared spectrum (neat) showed no ν_{O-H} band at 3450 cm^{-1}, but the appearance of a ν_{C-Cl} band at 900 cm^{-1}.

To a 145 mg sample (0.709 mmol) of chloride 72 prepared as above, placed in a dry test tube, was added 254 mg (0.850 mmol) of tri-n-butyltin hydride and 3.0 ml of a 5.0 mm solution of azobisisobutyronitrile in toluene. The mixture was flushed with nitrogen, the test tube sealed with a serum cap and irradiated at room temperature in a Rayonet-Chamber with 3500 A° lamps for 6 hours. The mixture was analyzed by vpc (5 ft x 0.125 in., 10% FFAP on chromosorb W, AW-DMCS 80/100, 125°, N_2 flow rate 30 ml/min) and showed a main product with the same retention time as 67s. Thick-layer chromatography on alumina using hexane as the eluent yielded 40 mg of starting chloride and 75 mg (0.44 mmol, 85%) of 67s. The nmr and ir spectra were identical to those of the product obtained from irradiation of *syn*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s).

Q. Hydrogenation of *Anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]-oct-3-ene (67a).

A solution of 67a (34 mg, 0.20 mmol) in 4 ml of methanol was hydrogenated in the presence of 7 mg of 10% Pd on charcoal. The reduction was stopped after one equivalent of hydrogen was absorbed. The catalyst was removed by filtration and the solvent was evaporated, leaving 30 mg (0.17 mmol, 87%) of a clear liquid. Analysis of the crude product by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW-DMCS 80/100, 125°, N_2 flow rate 30 ml/min) showed only one product. Preparative gas chromatography (5 ft x 0.25 in, 20% SE-30 on chromosorb W, 30/60, 130°, He flow rate 30 ml/min) afforded the pure *anti*-6-methyl-3,4-benzobicyclo[3.2.0]oct-3-ene (73b); ir (CCl_4) 3060 (w), 3010 (w), 2940 (s), 2860 (m), 1490 (m), 1460 (m), 1380 (w), several weak intensity bands from 1350-825 cm^{-1}; nmr ($CDCl_3$) δ 1.00 (d, 3H, J = 7.0 Hz, methyl), 1.08-2.25 (m, 5H), 2.26-3.25 (m, 4H), 6.68-7.08 (m, 4H, aromatic H's). The nmr spectrum also showed a small doublet at δ 1.17, J = 7.0 Hz, and a multiplet at δ 6.95-7.10 which probably correspond to traces (5-10%) of an isomer of 73b. The mass spectrum (70 eV) m/e (rel intensity): 172 (24), 157 (1.5), 143 (6), 129 (100), 117 (4), 116 (10), 115 (15), 91 (4), 89 (2), 77 (4), 63 (3), 51 (4).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36
Found: C, 90.80; H, 9.36

R. *Anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-7-one (74)

In a dry three-necked flask equipped with a condenser, magnetic stirrer, nitrogen gas inlet and a serum cap was added 424 mg (2.63 mmol)

of hexamethyldisilazane in 7 ml of dry tetrahydrofuran. The flask was immersed in an ice-salt bath, the solution was cooled to approximately 0°, and 1.17 ml of 2.06M n-butyllithium in hexane was added dropwise by means of a syringe to the stirred solution. After the mixture was stirred for 2 hr at 0°, 406 mg (2.39 mmol) of ketone 68[49] in 4 ml of tetrahydrofuran was added and stirring was continued for 0.5 hr. To the reaction mixture was then added 0.5 ml of methyl iodide. Stirring in the cold was continued for 1 hr followed by stirring at room temperature for 8 hr. The solution was diluted with 100 ml of water and extracted with ether. The ether extracts were combined, washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was evaporated leaving 412 mg (2.24 mmol, 98%) of a yellowish oil. Column chromatography on alumina using 15% ether in hexane as the eluent yielded pure 74: ir (neat) 3040 (m), 2960 (s), 2920 (m), 2860 (m), 1720 (s), 1480 (m), 1465 (m), 1380 (w), several medium intensity bands from 1350-850, 830 (s), 820 (s), 770 cm^{-1} (s); nmr ($CDCl_3$) δ 1.32 (d, 3H, J = 7.0 Hz, methyl), 1.90-2.43 (m, 2H, C-6 methine and cyclopropyl H adj to carbonyl), 2.68-3.02 (m, 1H, benzylic cyclopropyl H), 3.12-3.50 (m, 2H, benzylic and cyclopropyl methines) 6.80-7.28 (m, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 184 (7), 169 (3), 155 (5), 141 (18), 128 (100), 115 (12), 100 (3), 91 (1.5), 89 (2), 77 (5), 63 (5), 51 (5).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57
Found: C, 84.61; H, 6.54

S. *Anti*-6-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene-7-one (75).

Hydrogenation of 74 (235 mg, 1.28 mmol), as described for 67a

(*vide supra*), gave 209 mg (1.12 mmol, 87.8%) of a clear liquid. Analysis of the crude product by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW-DMCS, 80/100, 185°, N_2 flow rate 30 ml/min) showed only one product. Preparative thick-layer chromatography on alumina using 10% ether in hexane afforded pure 75: ir (neat) 3065 (w), 3015 (w), 2960 (m), 2930 (s), 2840 (w), 1735 (s), 1480 (m), 1460 (m), 1410 (w), 1380 (w), 1175 (m), several weak bands from 1150-800, 760 cm^{-1} (s); nmr ($CDCl_3$) δ 1.33 (d, 3H, J = 7.0 Hz, methyl), 2.10-3.47 (m, 7H), 7.08 (s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 186 (73), 171 (10), 157 (15), 143 (16), 129 (100), 115 (57), 91 (10), 89 (6), 77 (10), 65 (10), 63 (10), 57 (18).

T. *Anti*-6-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene (73a).

A solution of 150 mg (0.807 mmol) of ketone 75, 2.5 ml of hydrazine hydrate, and 2.0 g of KOH in 15 ml of triethylene glycol was refluxed for 30 hr. The reaction mixture was then cooled, added to 100 ml of 15% HCl and extracted with ether. The ether extracts were combined and washed successively with saturated $NaHCO_3$, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent yielded 111 mg (0.646 mmol, 80%) of a light yellow liquid. Analysis of the crude product by vpc (5 ft x 0.125 in, 3% SE-30 on chromosorb W, 80/100, 120°, N_2 flow rate 30 ml/min) showed only one product. Preparative thick-layer chromatography on alumina using pentane as the eluent afforded pure 73a: ir (neat) 3065 (w), 3015 (w), 2940 (s), 2860 (m), 1480 (m), 1465 (m), 1380 (w), several weak bands from 1350-775, 750 (s); nmr ($CDCl_3$) δ 1.15 (d, 3H, J = 7.0 Hz, methyl), 1.22-2.23 (m, 5H), 2.37-3.22 (m, 4H), 6.98 (s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 172 (43),

143 (8), 129 (100), 117 (12), 116 (54), 115 (32), 91 (5), 89 (3), 77 (5), 63 (5), 51 (5).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36
Found: C, 90.74; H, 9.20

U. 3,4-Benzobicyclo[3.3.0]oct-3-ene-6-one (76).

Hydrogenation of 3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-6-one (70) (292 mg, 1.72 mmol), as described for 67a (*vide supra*), gave 256 mg (1.49 mmol, 86.5%) of a clear oil. Analysis of the crude reaction mixture by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW-DMCS 80/100, 190°, N_2 flow rate 30 ml/min) showed two main products in a ratio of 1:3 with retention times of 6.2 and 7.6 minutes, respectively. These two products were separated by preparative thick-layer chromatography on neutral alumina using 15% ether in hexane as the eluent to give 48 mg of an unidentified product and 129 mg (0.750 mmol, 43.6%) of 76. The 2,4-dinitrophenylhydrazone of 76 was prepared[57] which after crystallization from chloroform-methanol (50:50) gave orange crystals mp 190-192° (lit.[52] mp 195°). The infrared spectrum (neat) of 76 showed bands at 3040 (w), 2990 (w), 2995 (m), 2880 (w), 1740 (s), 1490 (m), 1460 (m), 1440 (w), 1405 (w), 1170 (s), 1130 (m), 1050 (w), 1030 (m), 875 (m), 760 (s), 730 cm^{-1} (m); nmr ($CDCl_3$) δ 1.67-2.37 (m, 4H), 2.45-2.92 (m, 2H), 3.00-3.47 (m, 2H), 6.98 (s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 172 (36), 151 (5), 143 (5), 141 (11), 129 (100), 128 (98), 116 (19), 115 (20), 104 (4), 102 (4), 91 (4), 89 (3), 77 (7), 51 (8).

V. *Anti*-7-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene-6-one (77).

Methylation of ketone 76 (129 mg, 0.745 mmol) as described for the preparation of 74 (*vide supra*), yielded 110 mg of a pale yellow oil. Preparative thick-layer chromatography on neutral alumina using 10% ether in hexane as the eluent afforded 30 mg of unreacted starting material and 65 mg (0.347 mmol, 67.4%) of 77, a clear oil: ir (neat) 3060 (w), 3010 (w), 2950 (s), 2925 (s), 2860 (m), 1740 (s), 1490 (m), 1460 (m), 1435 (w), 1380 (w), 1175 (m), 1130 (m), 1120 (w), 1005 (m), 875 (m), 790 (m), 765 (m), 740 cm^{-1} (m); nmr ($CDCl_3$) δ 1.20 (d, 3H, J = 7.0 Hz, methyl), 1.65-2.90 (m, 5H), 3.05-3.43 (m, 2H), 7.00 (s, 4H, aromatic H's); mass spectrum (70 eV) is identical to that of 75.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58
Found: C, 83.75; H, 7.65

W. *Anti*-7-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene (78).

Wolff-Kishner reduction of 77 (50 mg, 0.269 mmol) as described for the preparation of 73a (*vide supra*), gave a yellowish oil which on analysis by vpc (5 ft x 0.125 in, 3% SE-30 on chromosorb W, 80/100, 125°, N_2 flow rate 30 ml/min) showed one product. Preparative thick-layer chromatography on neutral alumina using pentane as the eluent yielded 34 mg (0.198 mmol, 74%) of 78. The infrared spectrum (neat) showed bands at 3060 (w), 3010 (w), 2940 (s), 2860 (m), 1490 (m), 1460 (m), 1380 (w), several weak bands from 1350-800, 780 (m), 760 (m), 730 cm^{-1} (m); nmr ($CDCl_3$) δ 1.00 (d, 3H, J = 7.0 Hz, methyl), 1.15-2.48 (m, 6H), 2.65-3.22 (m), 3H), 6.90 (br s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 172 923), 155 (3), 143 (4), 141 (3),

129 (100), 115 (13), 91 (4), 89 (2), 77 (4).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36

Found: C, 90.58; H, 9.51

X. *Syn*-7-hydroxy-*anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]-oct-3-ene (79).

To a 25-ml three-necked flask equipped with a condenser, magnetic stirrer, nitrogen gas inlet and serum cap was added 0.4 g of lithium aluminum hydride and 15 ml of anhydrous ether. The suspension was cooled in an ice-bath and to it was added, dropwise by means of a syringe, 275 mg (1.49 mmol) of ketone 74 in 3 ml of ether. After the mixture was stirred at room temperature for 2 hr, the excess lithium aluminum hydride was destroyed by adding, dropwise, 2 ml of saturated NH_4Cl solution. The white precipitate which formed after 0.5 hr stirring was filtered and the filtrate was dried over anhydrous $MgSO_4$. Evaporation of the ether afforded 235 mg (1.26 mmol, 85.0%) of alcohol 79. Analysis of the crude reaction mixture by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW-DMCS 80/100, 200°, N_2 flow rate 30 ml/min) and tlc (neutral alumina, 20% ether in hexane as the eluent) showed only one product which was used for the following reaction without further purification.

Purification of a small sample of alcohol 79 by thick-layer chromatography on neutral alumina using 20% ether in hexane as the eluent gave a clear oil which failed to crystallize on standing or in cold pentane: ir (CCl_4) 3640 (m), 3590 (m), 3440 (br, s), 3060 (w), 3035 (m), 3010 (w), 2950 (s), 2920 (s), 2860 (m), 1480 (s), 1460 (m), 1055 (br, s), several weak bands from 875-780, 760 (s), 745 cm^{-1} (s). The bands at

3640 and 3590 cm^{-1} did not change in relative intensity as a function of the concentration of 79 in CCl_4, whereas the intensity of the band at 3440 cm^{-1} decreased drastically with a decrease in concentration of 79; nmr ($CDCl_3$) δ 1.12 (d, 3H, J = 7.0 Hz, methyl), 1.55-3.08 (m, 5H), 3.22 (d, 1H, J = 5.0 Hz), 3.57 (d, 1H, J = 5.0 Hz), 6.75-7.20 (m, 4H aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 186 (7), 172 (12), 168 (22), 141 (16), 128 (100), 115 (30), 104 (10), 91 (6), 89 (5), 76 (15), 46 (15).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58

Found: C, 83.81; H, 7.62

Y. *Anti*-6-methyl-3,4-benzobicyclo[3.2.1]oct-3-ene-7-one (80).

Hydrogenation of 79 (100 mg, 0.538 mmol), as described for 67a (*vide supra*), gave a clear liquid which on analysis by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW-DMCS 80/100, 200, N_2 flow rate 30 ml/min) showed no starting material but showed the formation of two products. The mixture was not analyzed further.

The crude hydrogenation product was dissolved in 5 ml of acetone and placed in a 25-ml round-bottomed flask equipped with a magnetic stirrer. The stirred solution was cooled in an ice-water bath to 10°, and Jones' reagent (2.67 M) was added dropwise until the orange color of the reagent persisted for about 15 minutes. The excess oxidizing agent was destroyed by the addition of 0.5 ml of isopropyl alcohol. The mixture was decanted into a separatory funnel, the residual green salts were washed with 5 ml of acetone and the washing added to the main acetone solution. The acetone solution was diluted with 100 ml of water and extracted with ether. The ether extracts were combined

and washed successively with saturated $NaHCO_3$, water, saturated NaCl solution and dried ($MgSO_4$). Evaporation of the ether yielded 75 mg (0.40 mmol, 75%) of a light yellow oil. Analysis of the crude product by vpc (5 ft x 0.125 in, 10% FFAP on chromosorb W, AW-DMCS 80/100, 180°, N_2 flow rate 30 ml/min) and tlc (neutral alumina, 10% ether in pentane as the eluent) showed two products in a 3:1 ratio with vpc retention times of 6.5 and 7.5 minutes respectively. Preparative thick-layer chromatography on neutral alumina using 10% ether in pentane as the eluent yielded 15 mg (0.081 mmol, 15%) of 75, identified by its nmr spectrum, and 50 mg (0.269 mmol, 50%) of 80: ir (neat) 3050 (w), 3005 (w), 2945 (s), 2860 (m), 1740 (s), 1485 (m), 1470 (m), 1455 (m), 1430 (w), 1370 (w), several medium intensity bands from 1300-850, 760 (s), 745 (s), 720 cm^{-1} (m); nmr ($CDCl_3$) δ 1.17 (d, 3H, J = 7.0 Hz, methyl), 1.82-2.82 (m, 4H), 2.87-3.08 (m, 3H), 6.97 (s, 4H, aromatic H's); mass spectrum (70 eV) m/e (rel intensity) 186 (55), 171 (8.0), 157 (11), 143 (12), 129 (100), 115 (27), 102 (4), 91 (6), 89 (3), 77 (8).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58

Found: C, 83.90; H, 7.52

Z. *Anti*-6-methyl-3,4-benzobicyclo[3.2.0]oct-3-ene (73b).

Wolff-Kishner reduction of 80 (45 mg, 0.242 mmol), as described for the preparation of 73a (*vide supra*), gave a pale yellow liquid which on analysis by vpc (5 ft x 0.125 in, 3% SE-30 on chromosorb W, 80/100, 125°, N_2 flow rate 30 ml/min) showed two products in approximately 2:3 ratio with retention times of 8.0 and 8.7 minutes, respectively. Comparison of retention times on 3% SE-30, 10% FFAP, 5% TCEP and 20% DEGS columns (5 ft x 0.125 in columns on chromosorb W, 80/100, 125°,

N_2 flow rate 30 ml/min) showed that the product with a retention time of 8.0 minutes had the same retention times as the product obtained from the catalytic hydrogenation of photoproduct 67s, and the product with a retention time of 8.7 minutes had the same retention times as the product obtained from catalytic hydrogenation of photoproduct 67a. The two components were separated by preparative vpc (10 ft x 0.25 in, 10% FFAP on chromosorb W, 30/60, 140°, He flow rate 15 ml/min). The minor product (with a retention time of 8.0 minutes) had an nmr spectrum identical to that of 81, obtained from the hydrogenation of photoproduct 67s, but lacked the small doublet at δ 0.88 and the multiplet at δ 6.95-7.02. The major product (with a retention time of 8.7 minutes) had an ir spectrum identical to the product obtained from the hydrogenation of photoproduct 67a. The nmr spectrum was also identical to that of the dihydro photoproduct 67a, but lacked the small doublet at δ 1.17 and the multiplet at δ 6.95-7.10.

AA'. Hydrogenation of *Syn*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]-oct-3-ene (67s).

Hydrogenation of 67s (91 mg, 0.535 mmol), as described for 67a (*vide supra*), gave 80.5 mg (0.468 mmol, 87.5%) of a clear liquid. Analysis of the crude reaction mixture by vpc (5 ft x 0.125 in, 3% SE-30 on chromosorb W, 80/100, 125°, N_2 flow rate 30 ml/min) showed only one product with a retention time of 8.0 minutes, 81. The infrared spectrum (neat) showed bands at 3060 (w), 2010 (w), 2930 (s), 2860 (m), 1490 (m), 1460 (m), 1375 (w), several weak intensity bands from 1350 to 810, 760 (m), 730 (m), 720 cm^{-1} (w); nmr ($CDCl_3$) δ 0.63 (d, 3H, J = 7.0 Hz, methyl), 1.77 (br s, 2H), 1.90-3.30 (m, 7H),

6.65-7.07 (s, 4H, aromatic H's). The nmr spectrum also showed a small doublet at δ 0.88, J = 7.0 Hz and a multiplet at δ 6.95-7.02 which probably correspond to a small amount (approximately 15%) of an isomer of 81. Mass spectrum (70 eV) is identical to that of 73b.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36

Found: C, 90.68; H, 9.40

APPENDIX

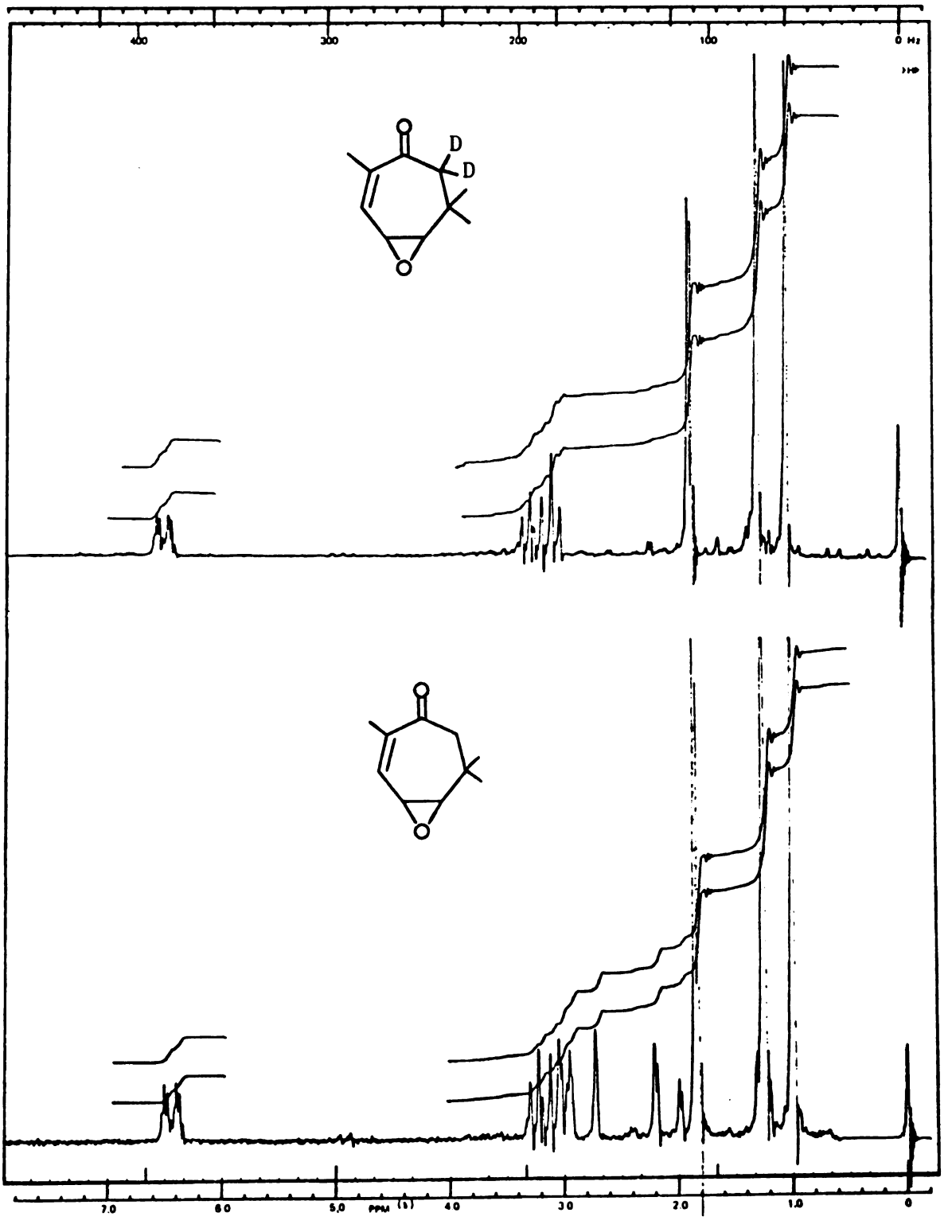


Figure 1. NMR Spectra of 4,5-Epoxy-2,6,6-trimethyl-2-cycloheptenone (26) [bottom] and 7,7-Dideuterio-4,5-epoxy-2,6,6-trimethyl-2-cycloheptenone (26-d_2) [top].

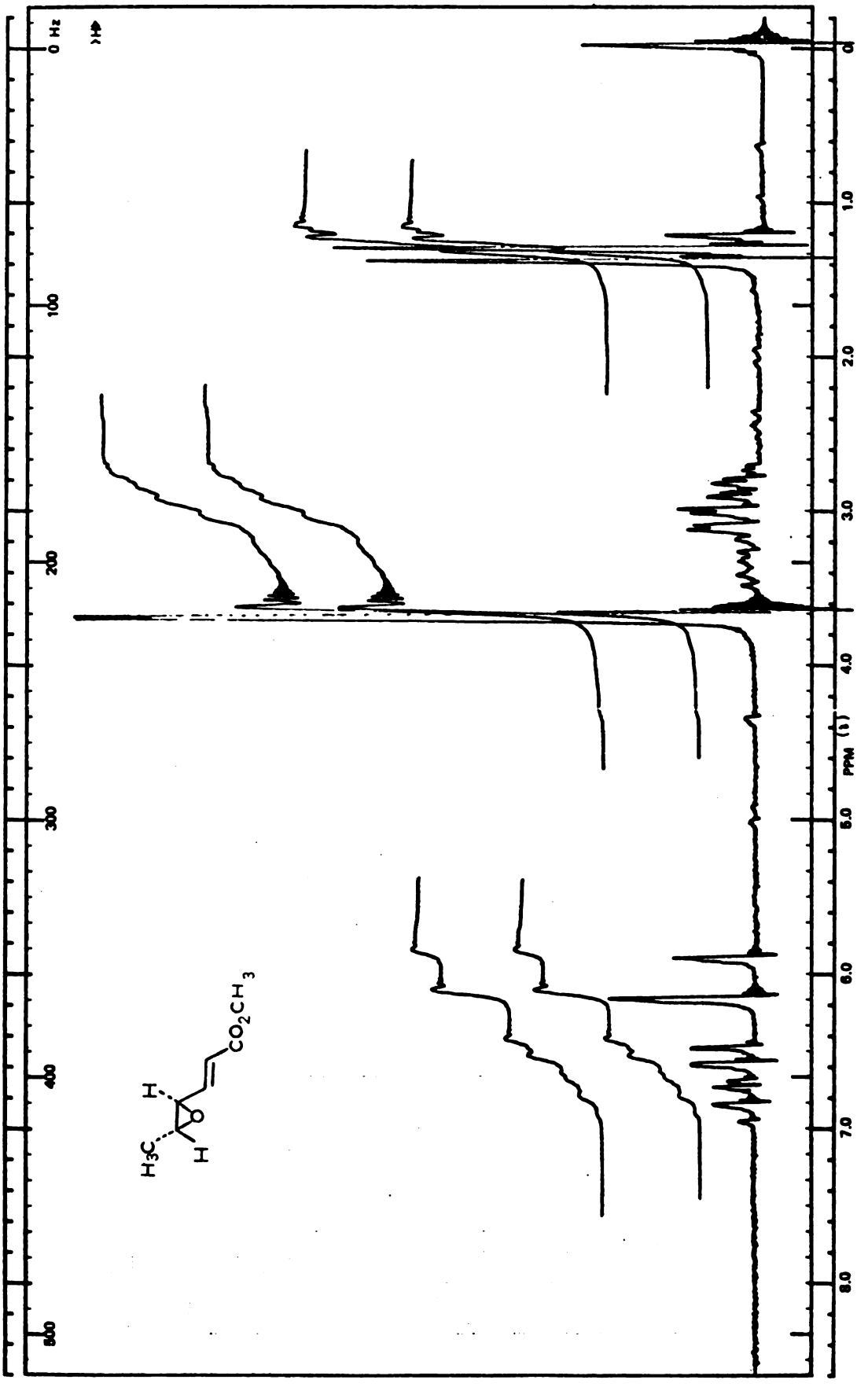


Figure 2. NMR Spectrum of Methyl 4,5-Epoxy-2-hexenoate (29).

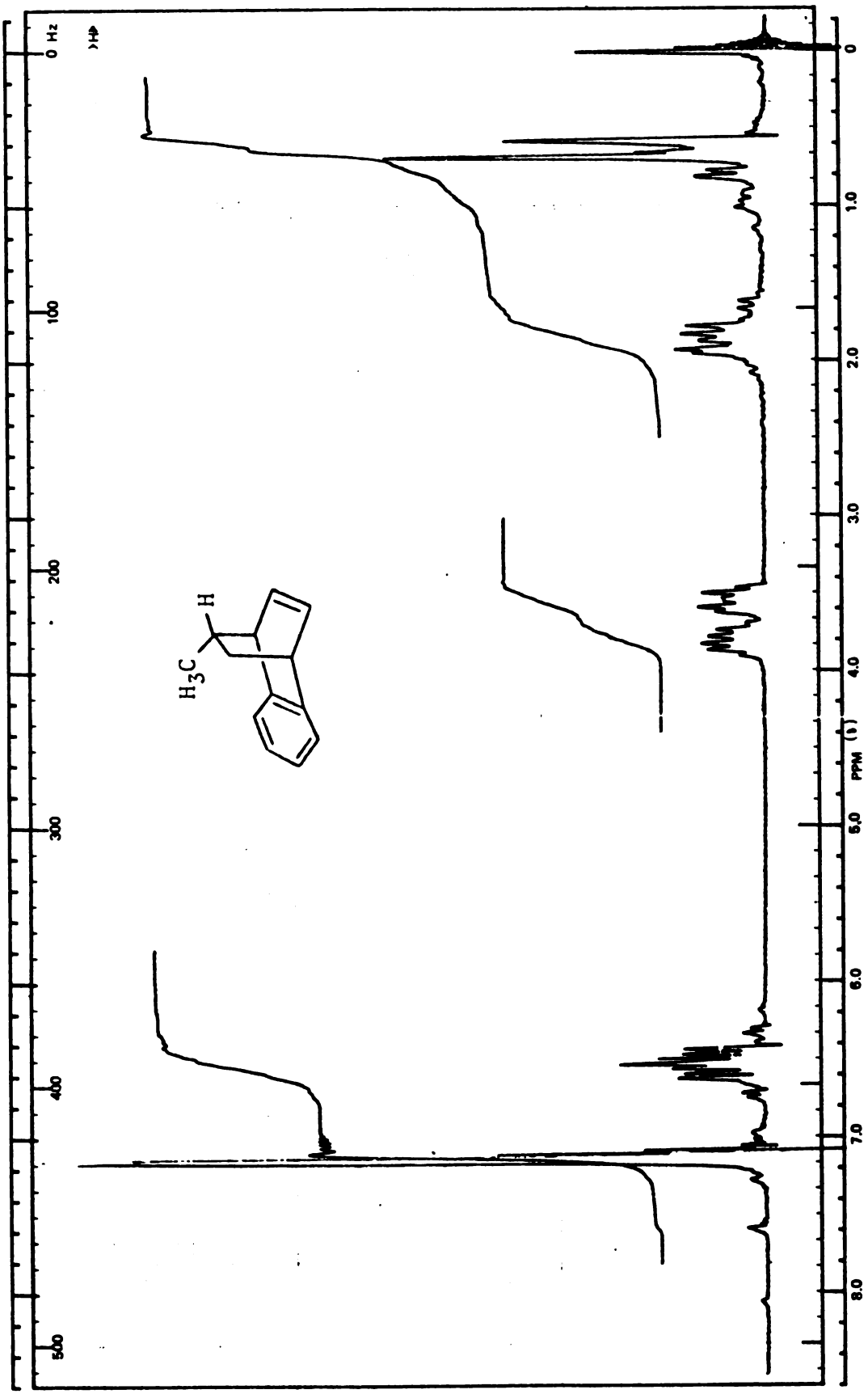


Figure 3. NMR Spectrum of *Syn*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58s).

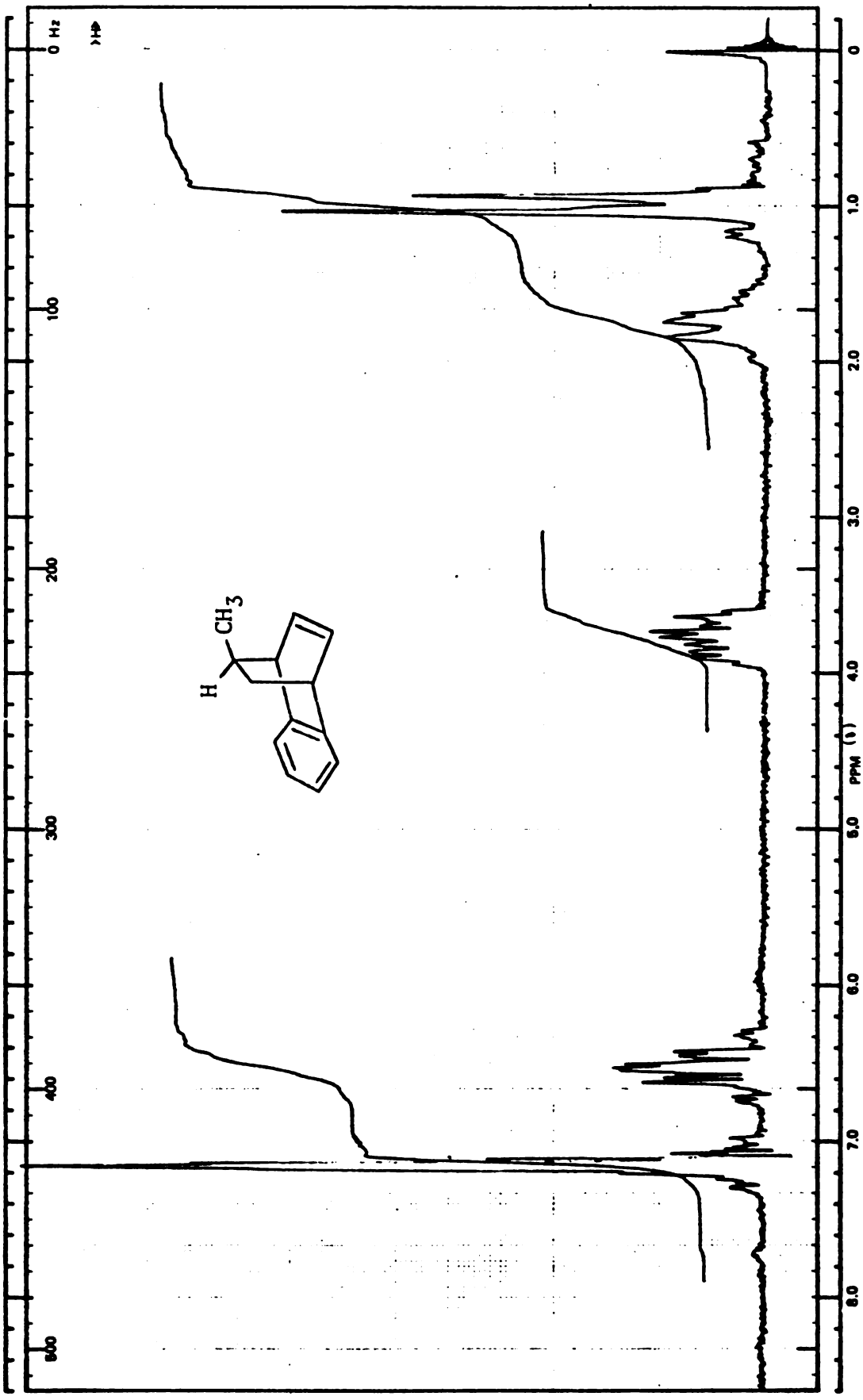


Figure 4. NMR Spectrum of *Anti*-9-methyl-1,4-dihydro-1,4-ethanonaphthalene (58a).

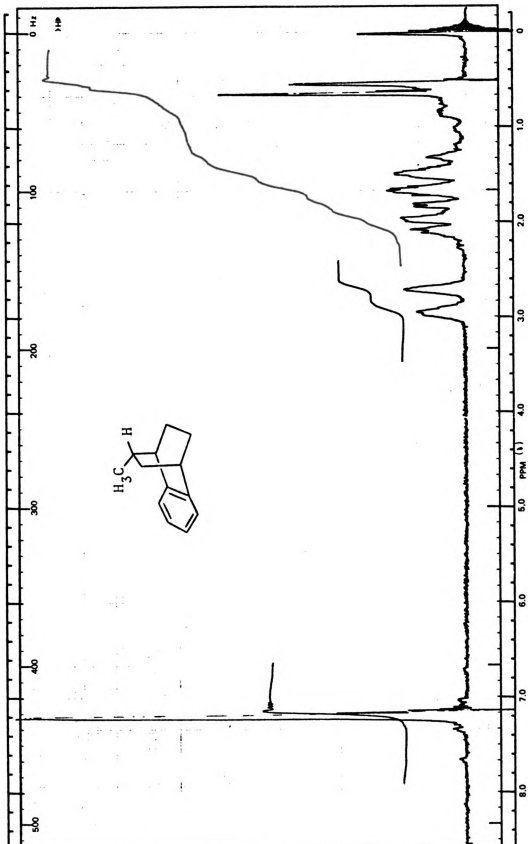


Figure 5. NMR Spectrum of *Syn*-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (65s).

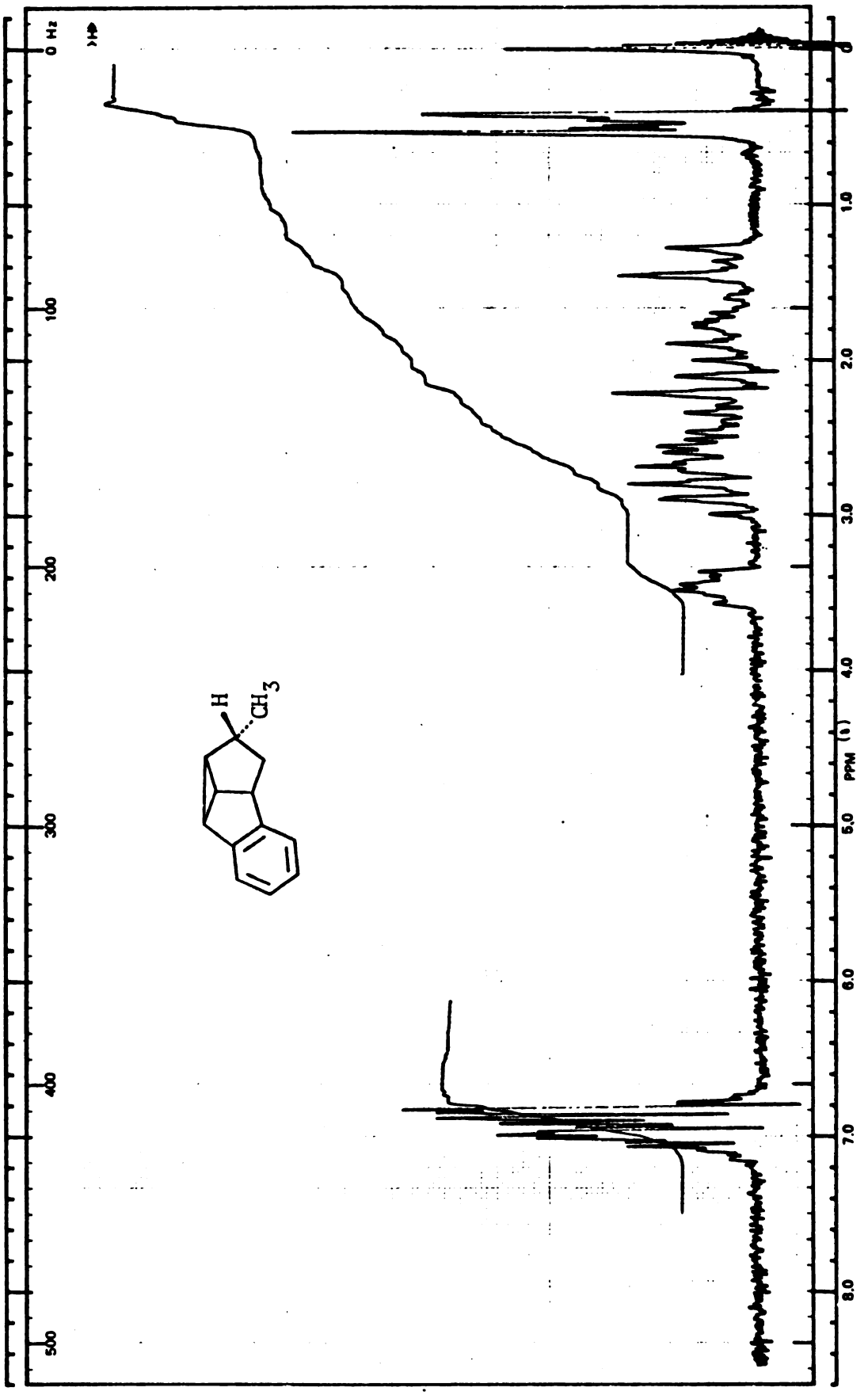


Figure 6. NMR Spectrum of *Syn*-7-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (66s).

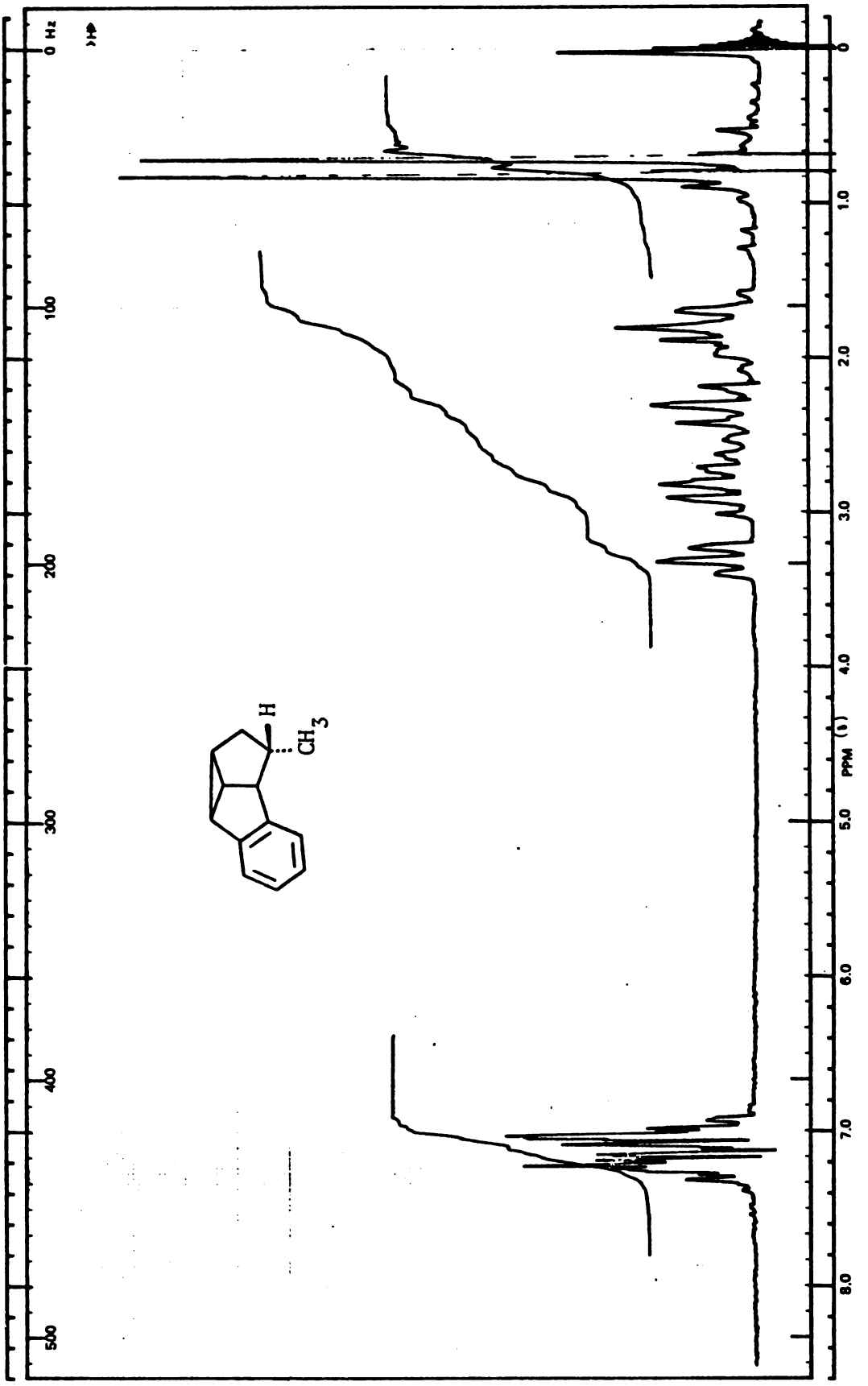


Figure 7. NMR Spectrum of *Syn*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67s).

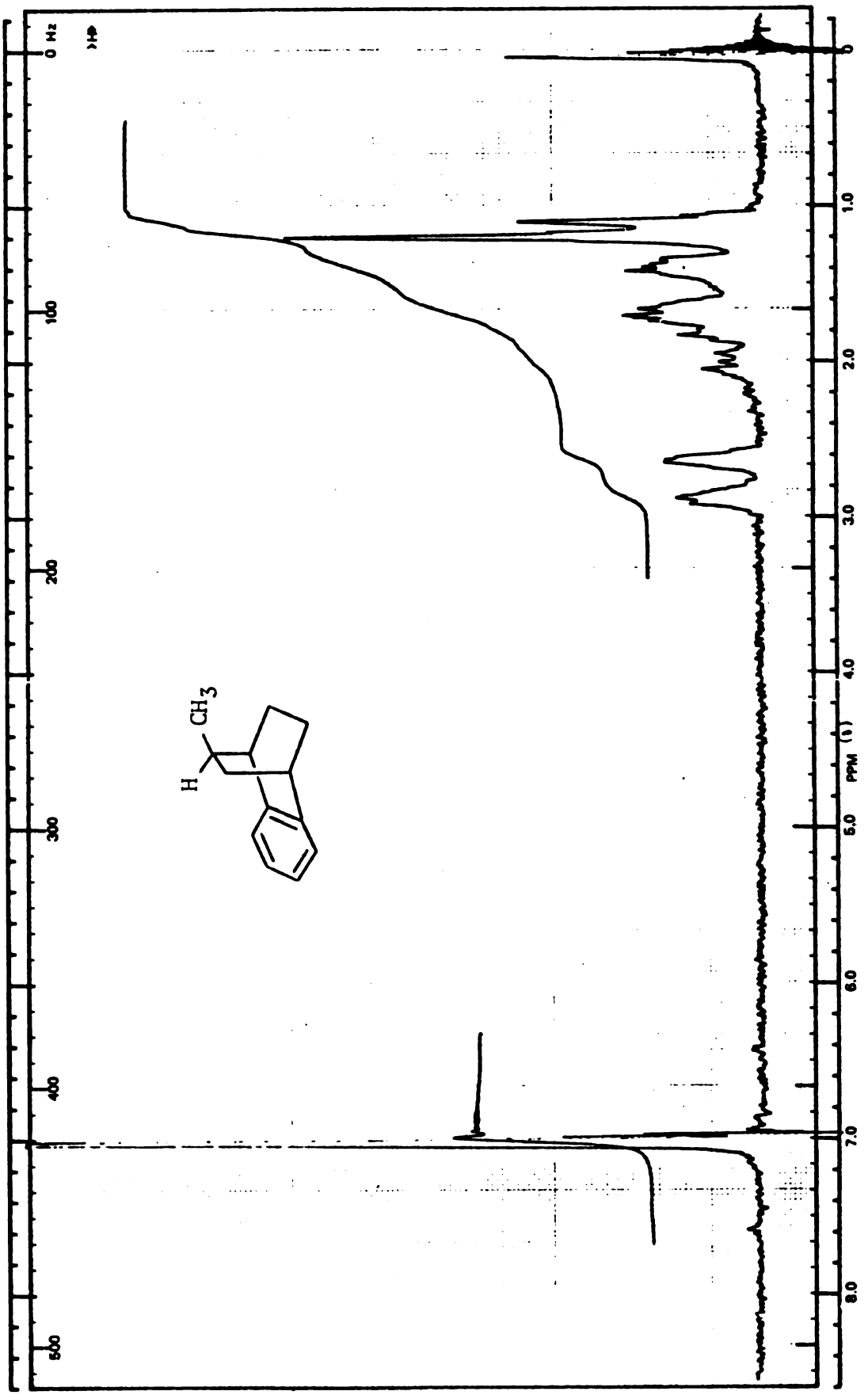


Figure 8. NMR Spectrum of *Anti*-9-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (65a)

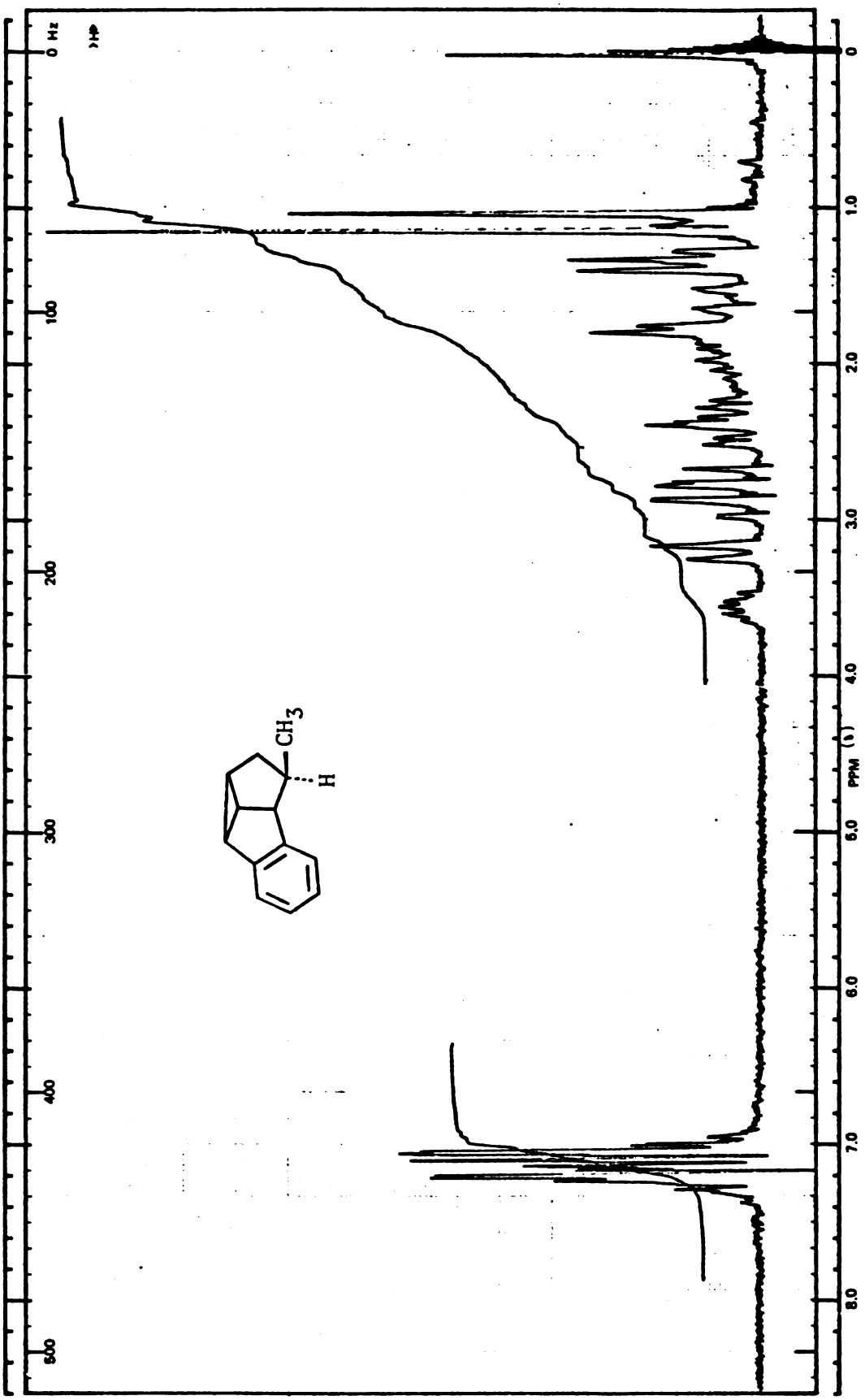


Figure 9. NMR Spectrum of *Anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67a).

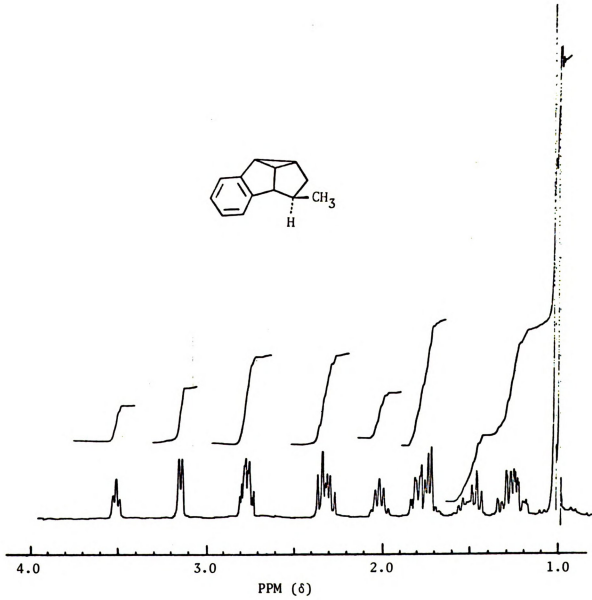


Figure 10. 270 MHz NMR Spectrum of *Anti*-6-methyl-3,4-benzotricyclo-[3.3.0.$0^{2,8}$]oct-3-ene (67a).

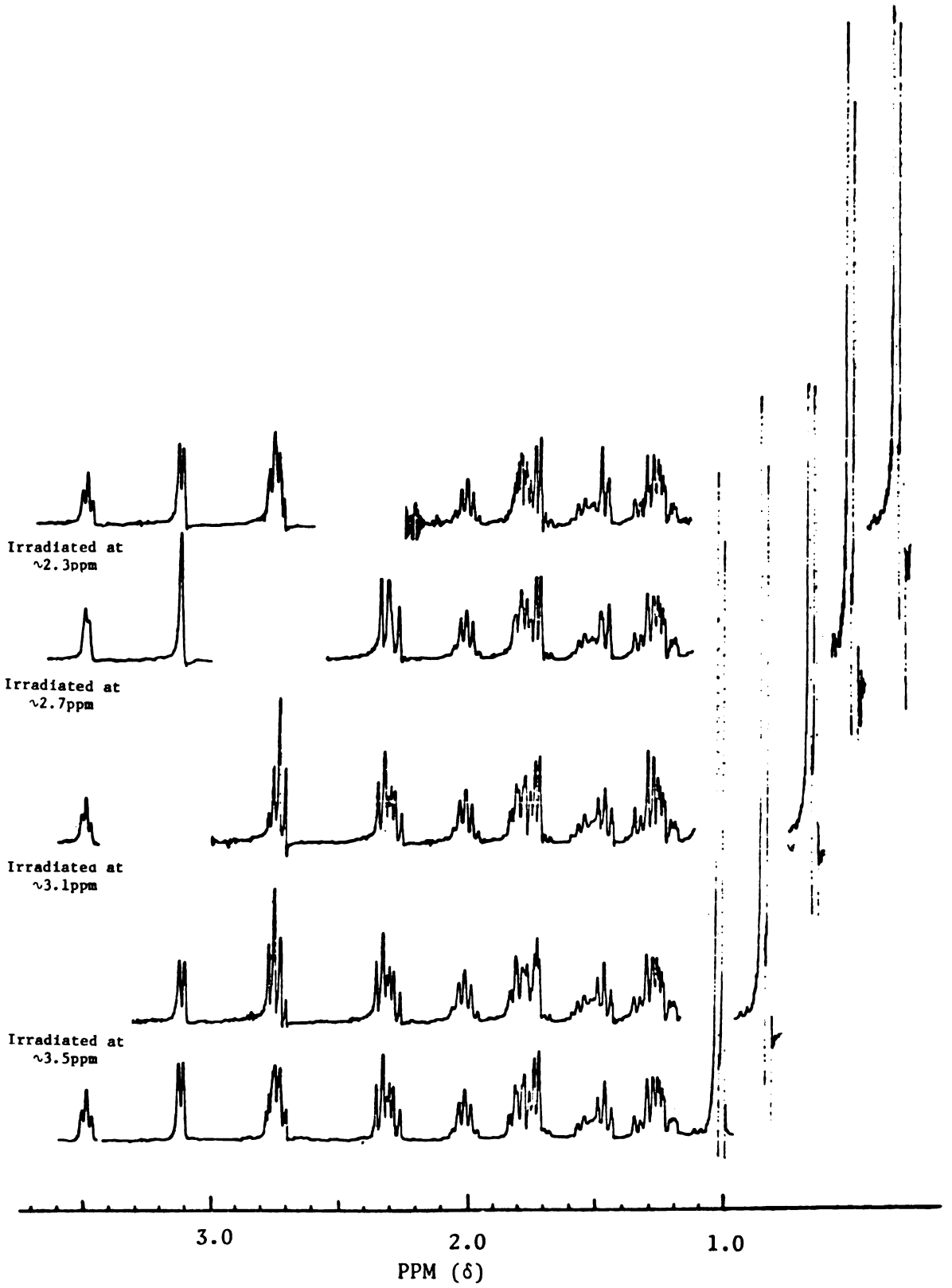


Figure 11. Double Irradiation of *Anti*-6-methyl-3,4-benzotricyclo-[3.3.0.$0^{2,8}$]oct-3-ene (67a).

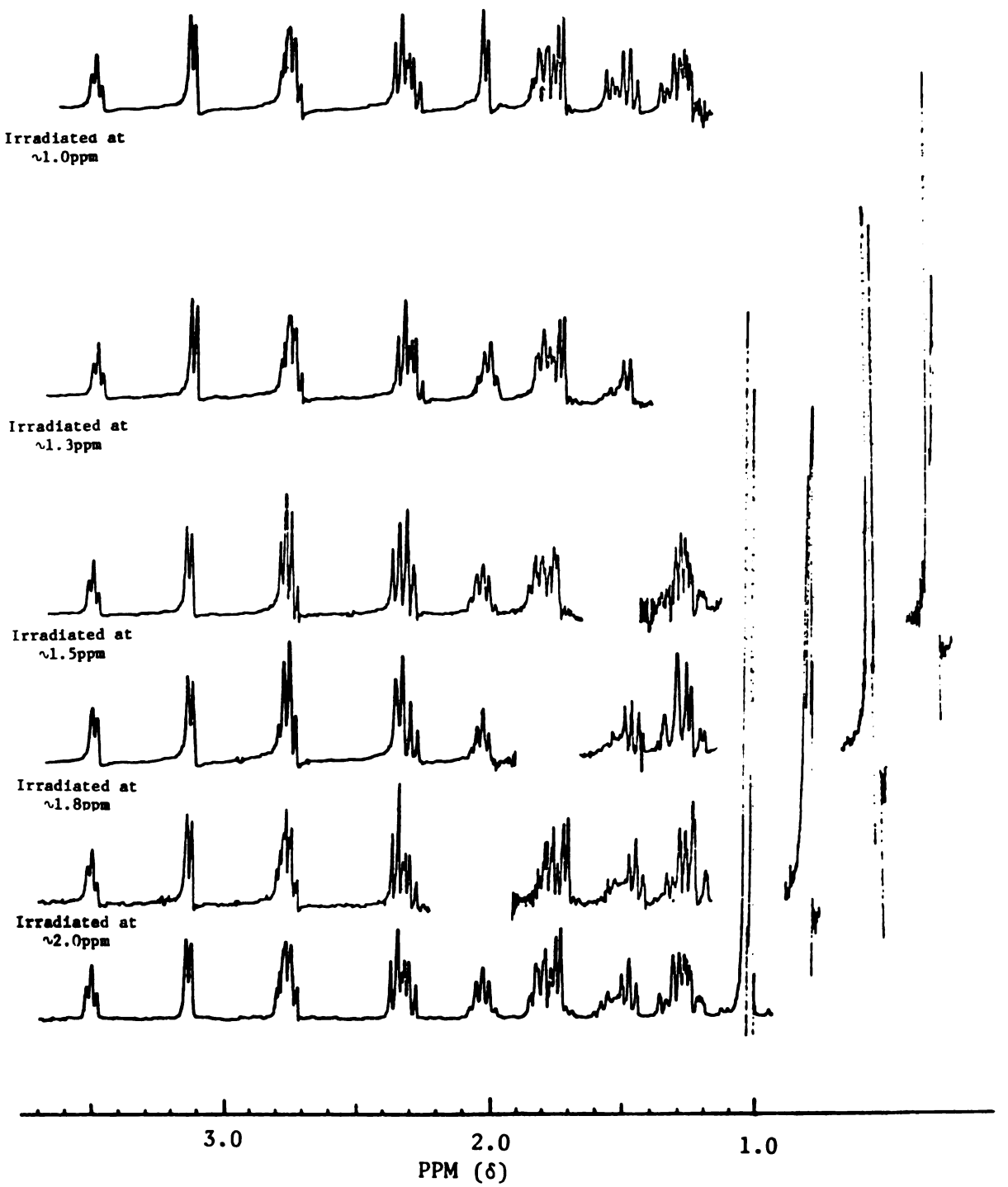


Figure 11 (continued). Double Irradiation of *Anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (67a).

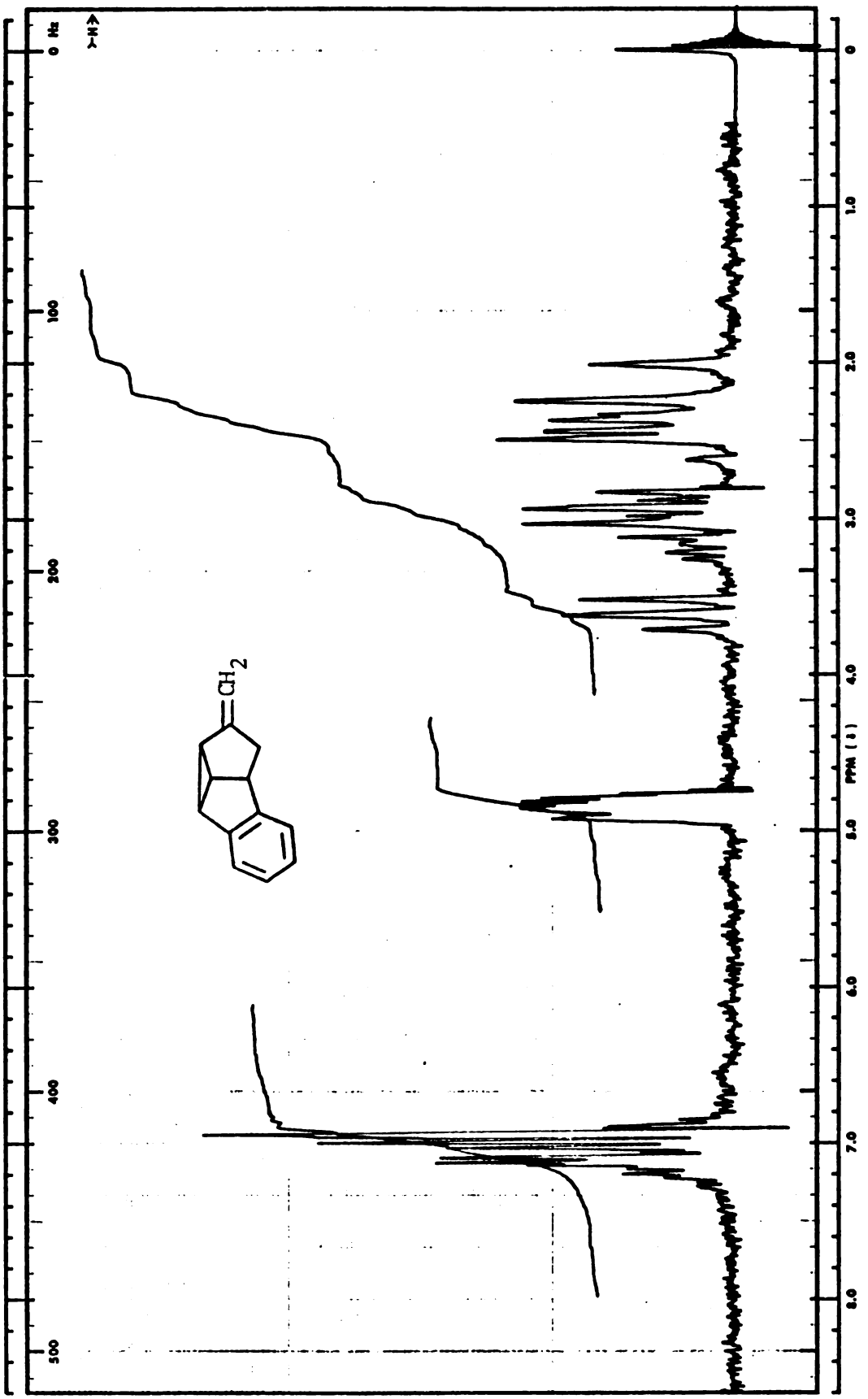


Figure 12. NMR Spectrum of 7-Methylene-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (69).

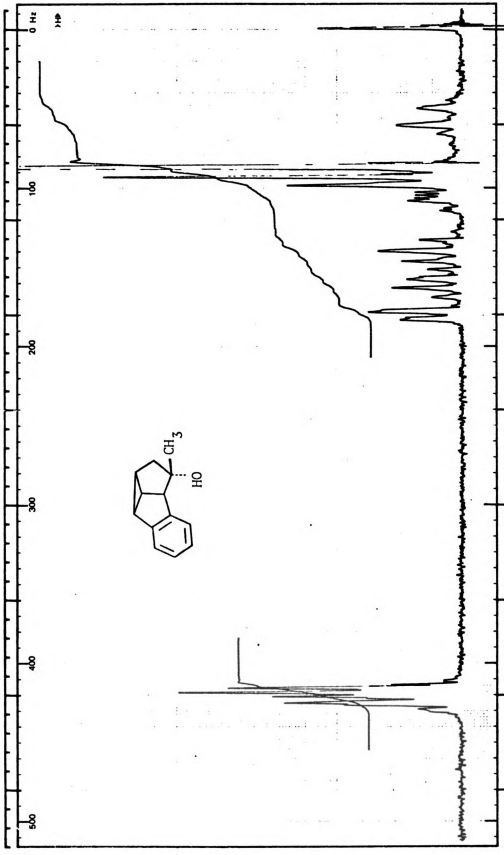


Figure 13. NMR Spectrum of *Syn*-6-hydroxyl-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (71).

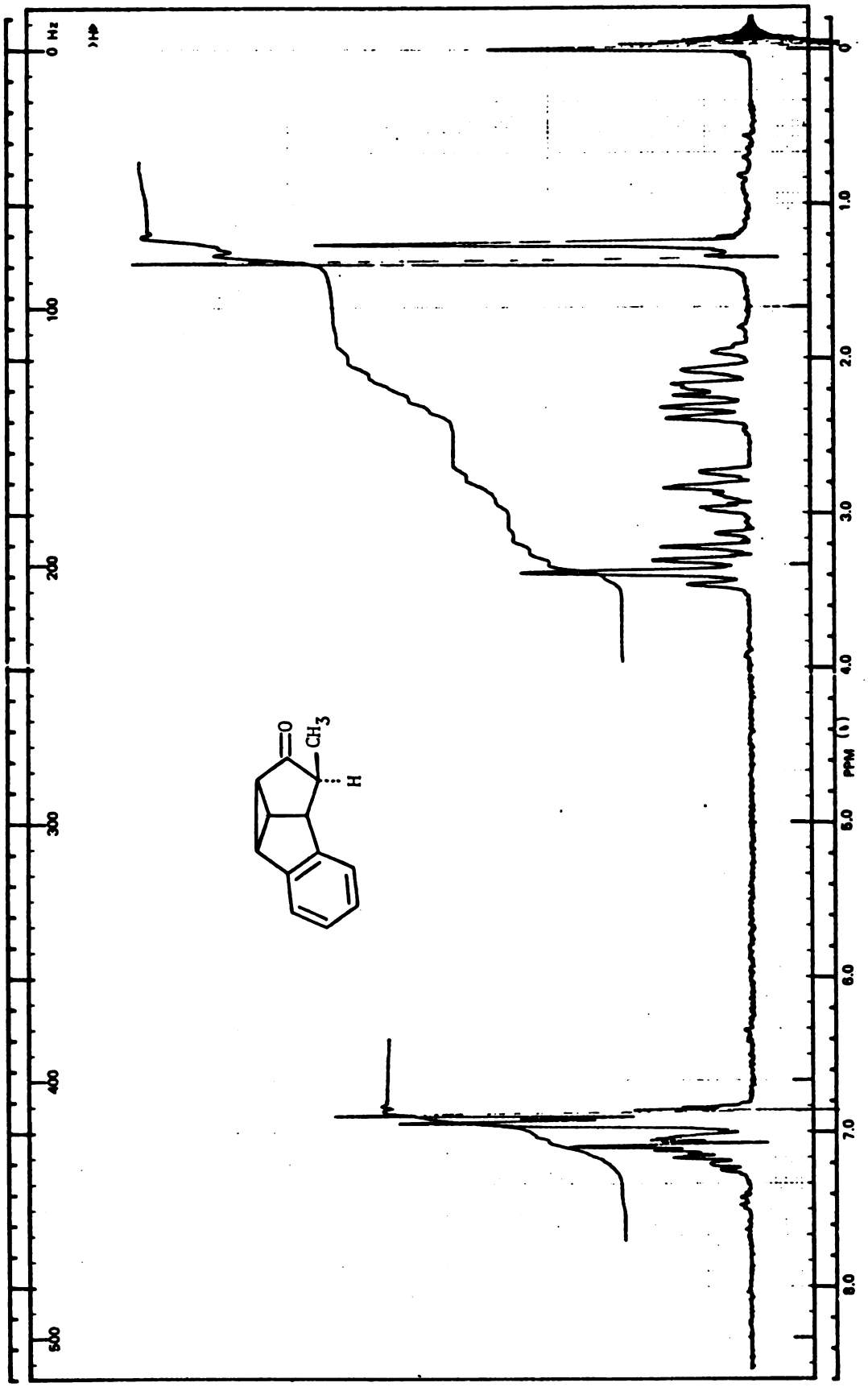


Figure 14. NMR Spectrum of *Anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene-7-one (74).

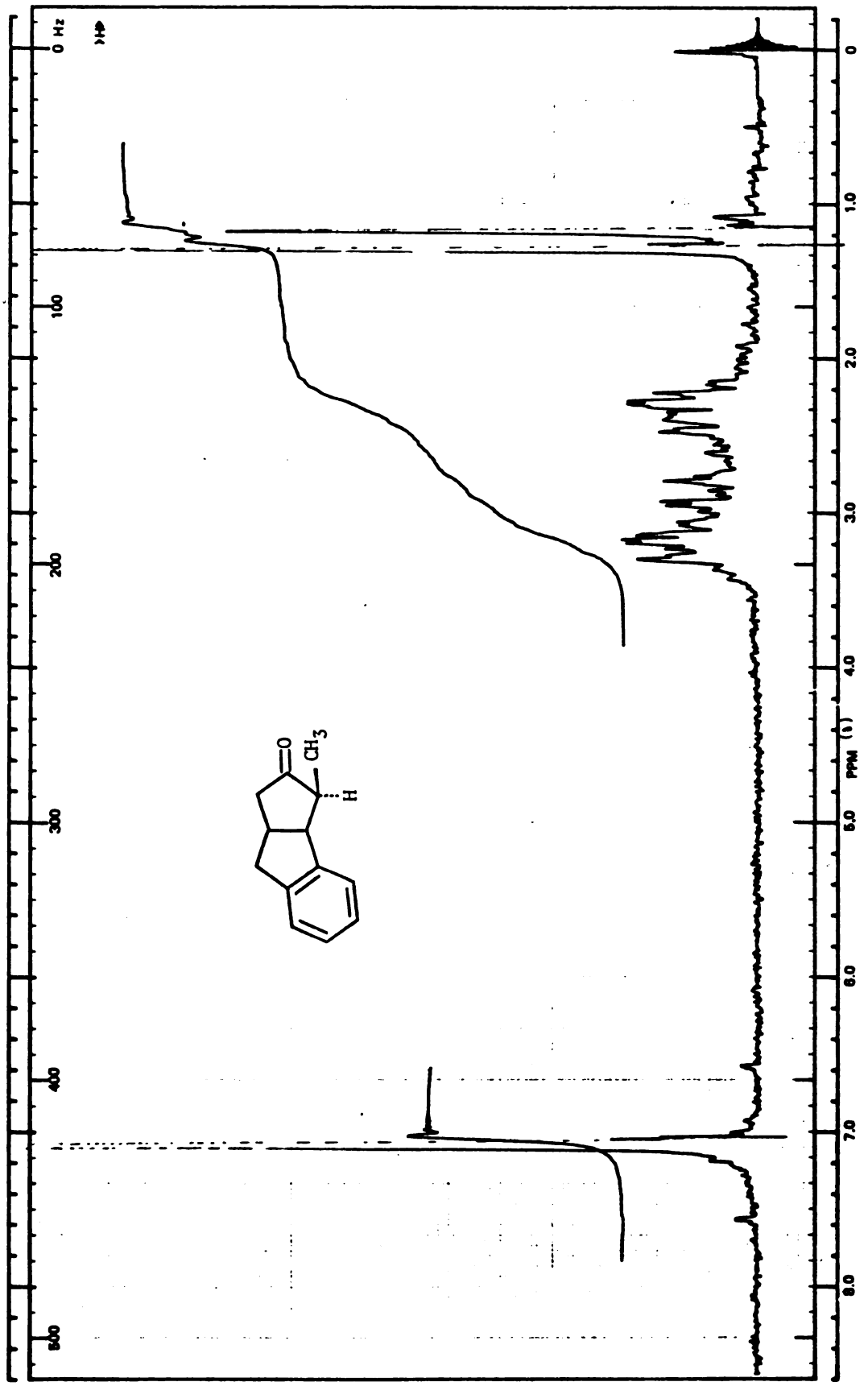


Figure 15. NMR Spectrum of *Anti*-6-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene-7-one (75).

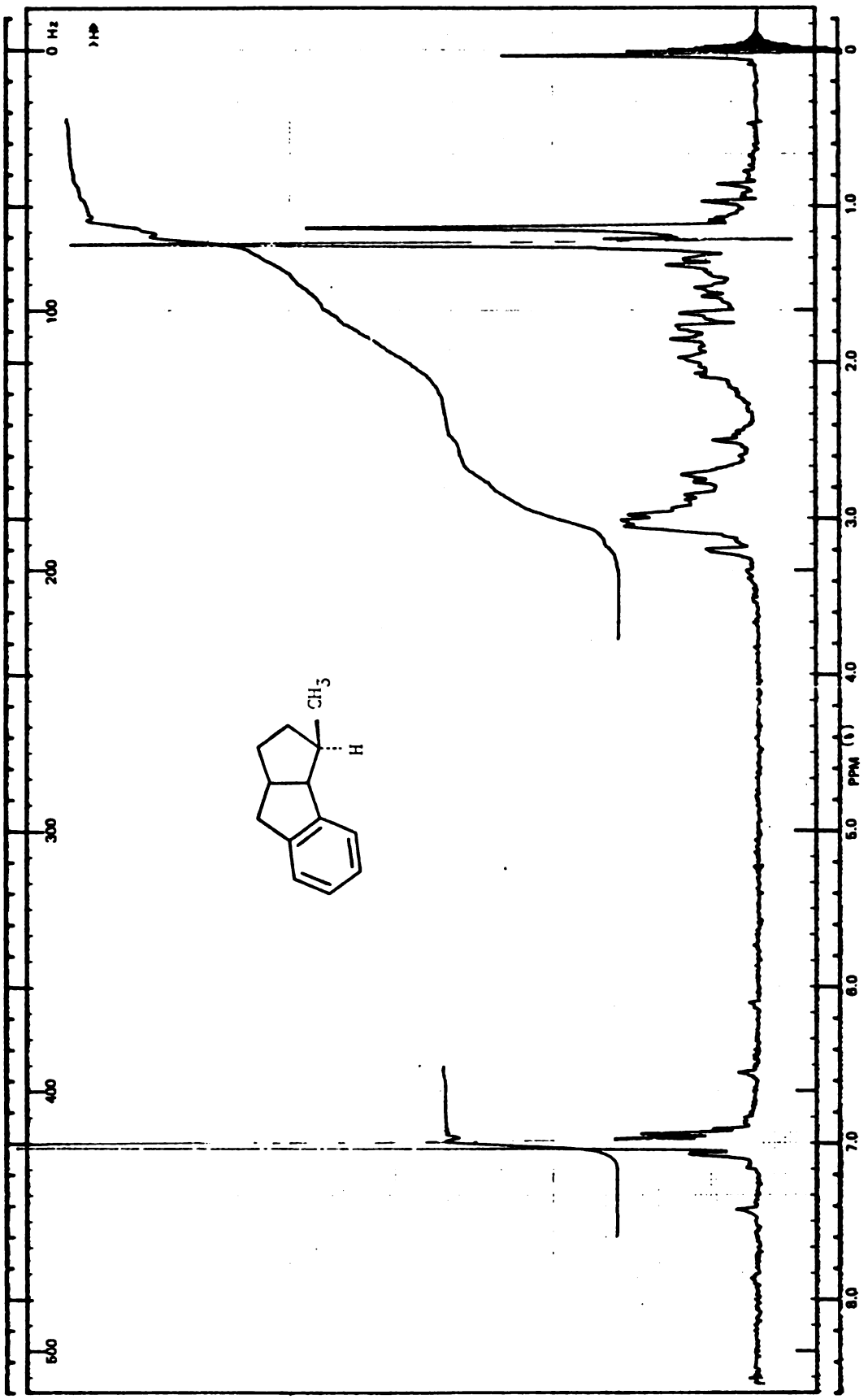


Figure 16. NMR Spectrum of *Anti*-6-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene (73a).

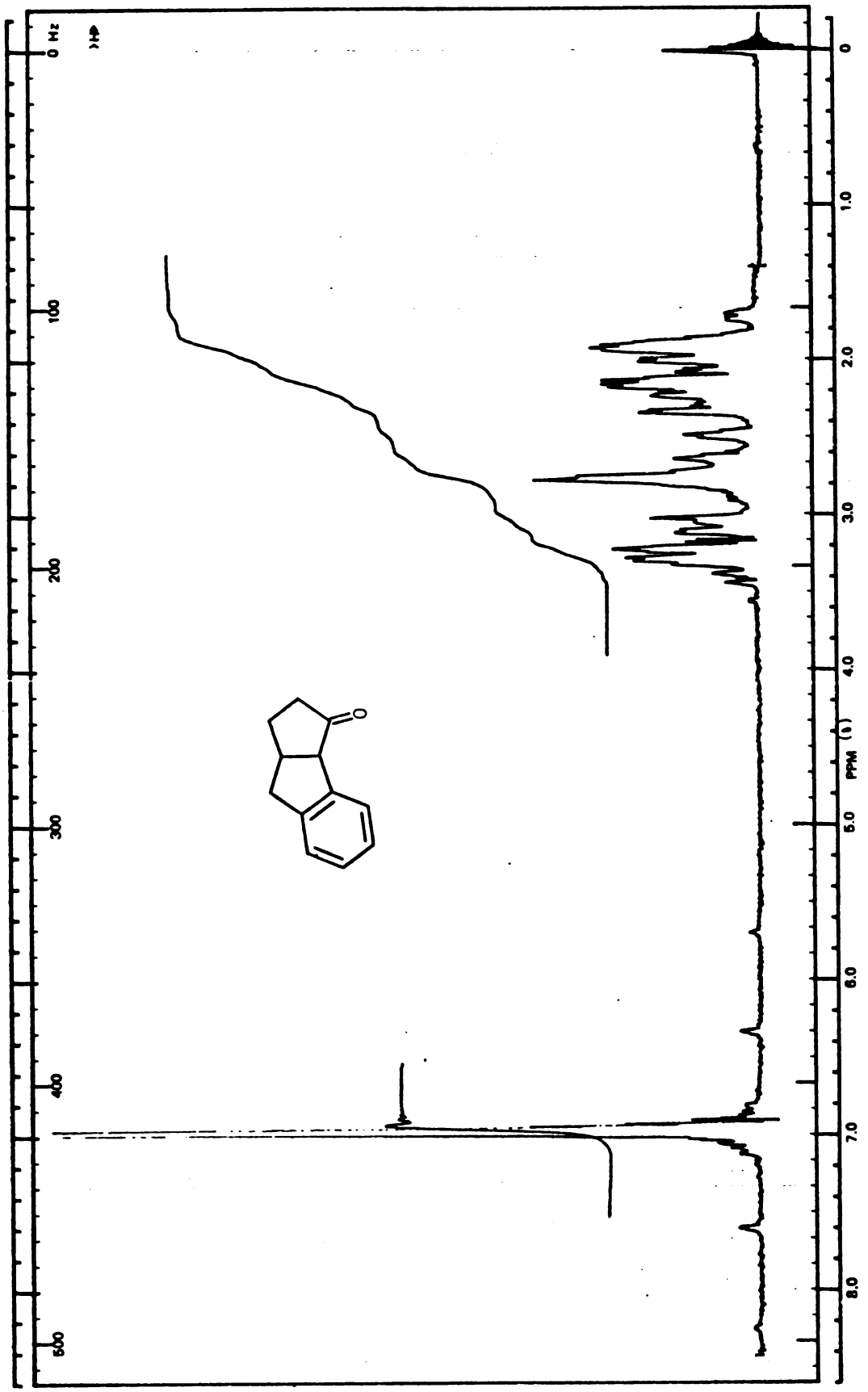


Figure 17. NMR Spectrum of 3,4-Benzobicyclo[3.3.0]oct-3-ene-6-one (76).

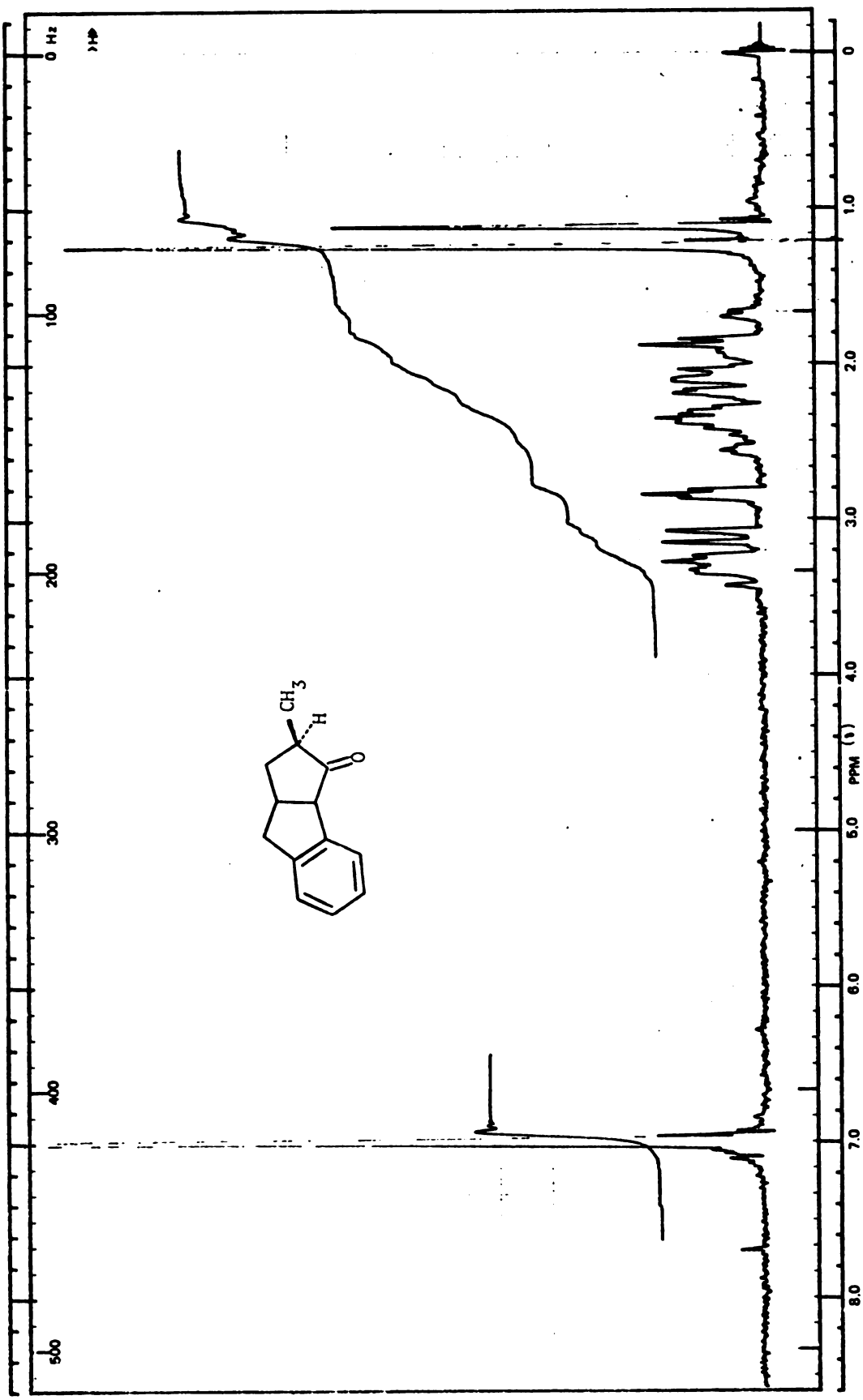


Figure 18. NMR Spectrum of *Anti*-7-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene-6-one (77).

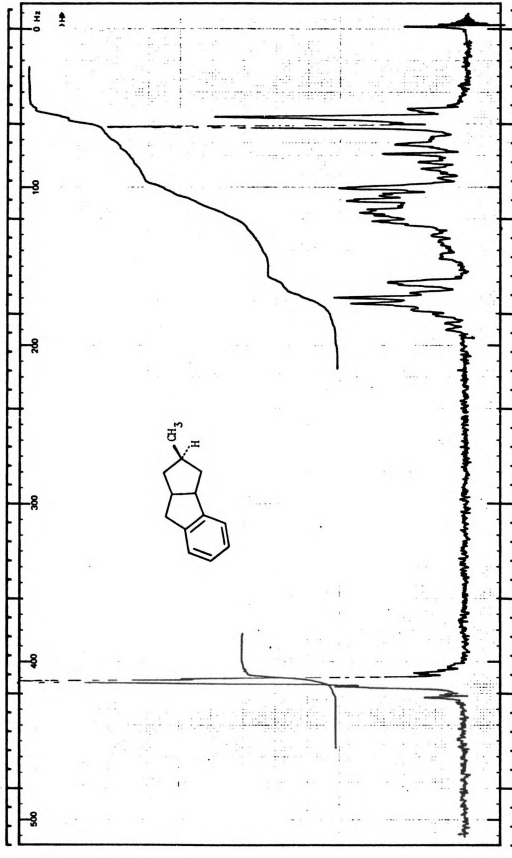


Figure 19. NMR Spectrum of *Anti*-7-methyl-3,4-benzobicyclo[3.3.0]oct-3-ene (78).

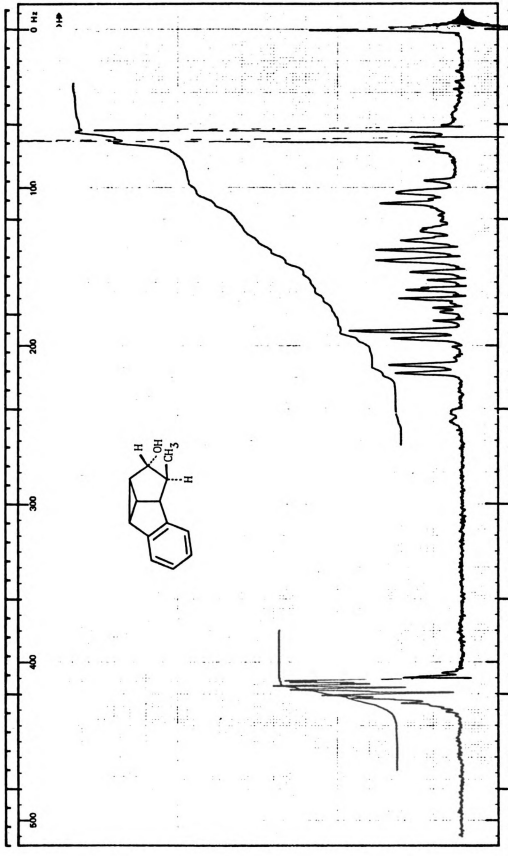


Figure 20. NMR Spectrum of *Syn*-7-hydroxy-*anti*-6-methyl-3,4-benzotricyclo[3.3.0.$0^{2,8}$]oct-3-ene (79).

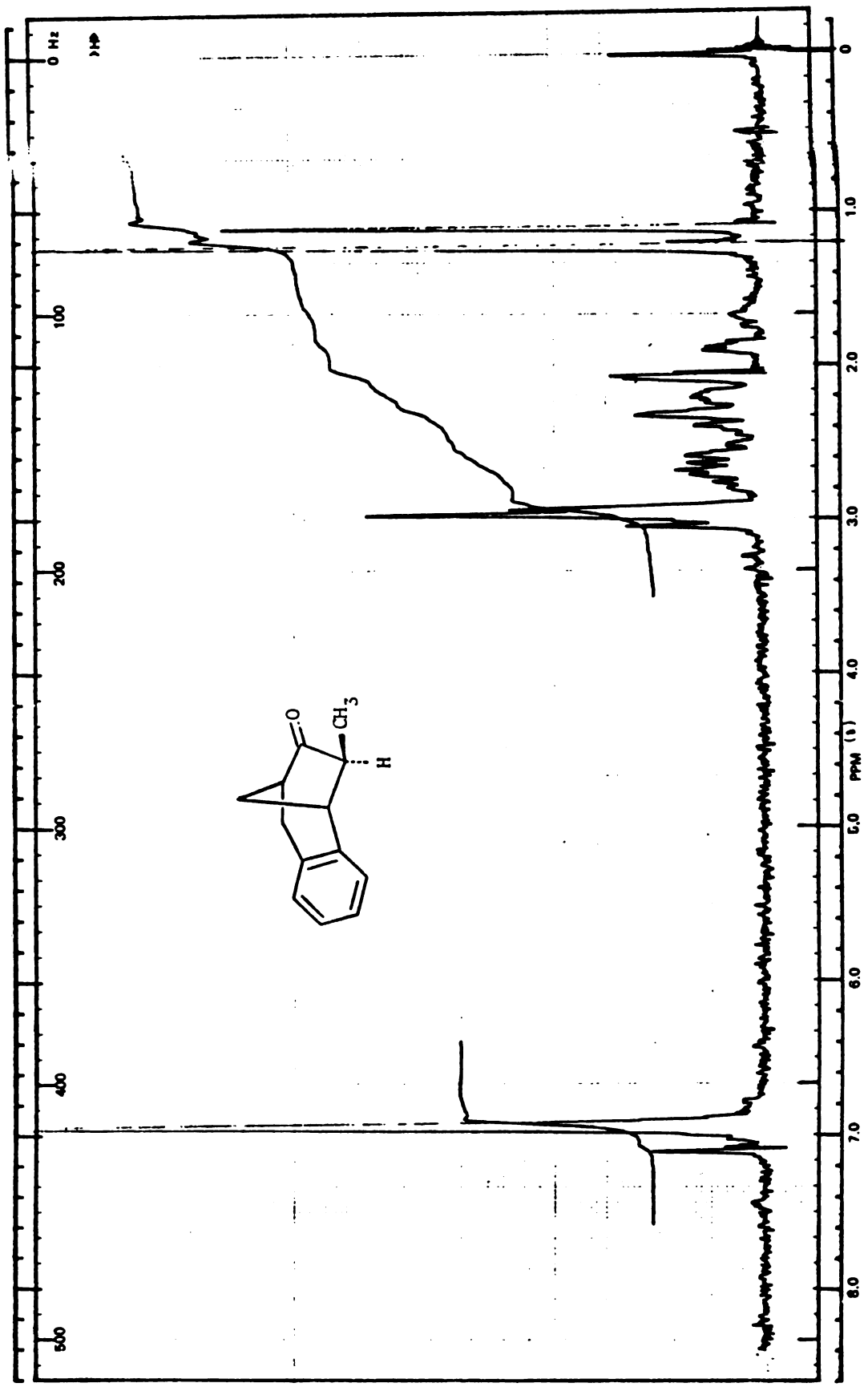


Figure 21. NMR Spectrum of *Anti*-6-methyl-3,4-benzobicyclo[3.2.1]oct-3-ene-7-one (80).

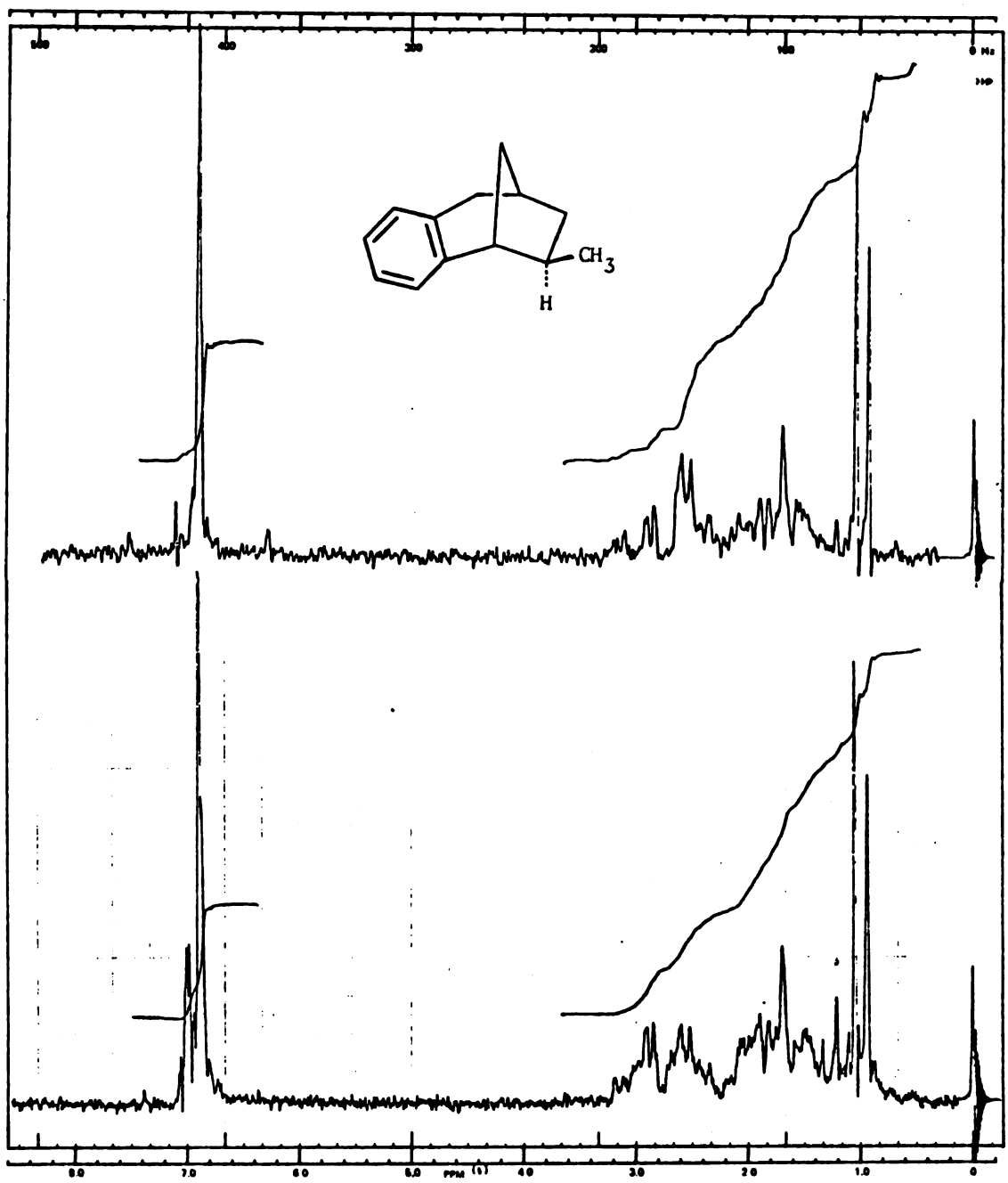


Figure 22. NMR Spectra of *Anti*-6-methyl-3,4-benzobicyclo[3.2.1]oct-3-ene (73b). Top: material obtained from hydrogenation of photoproduct 67a. Bottom: material obtained from Wolf-Kishner reduction of ketone 80.

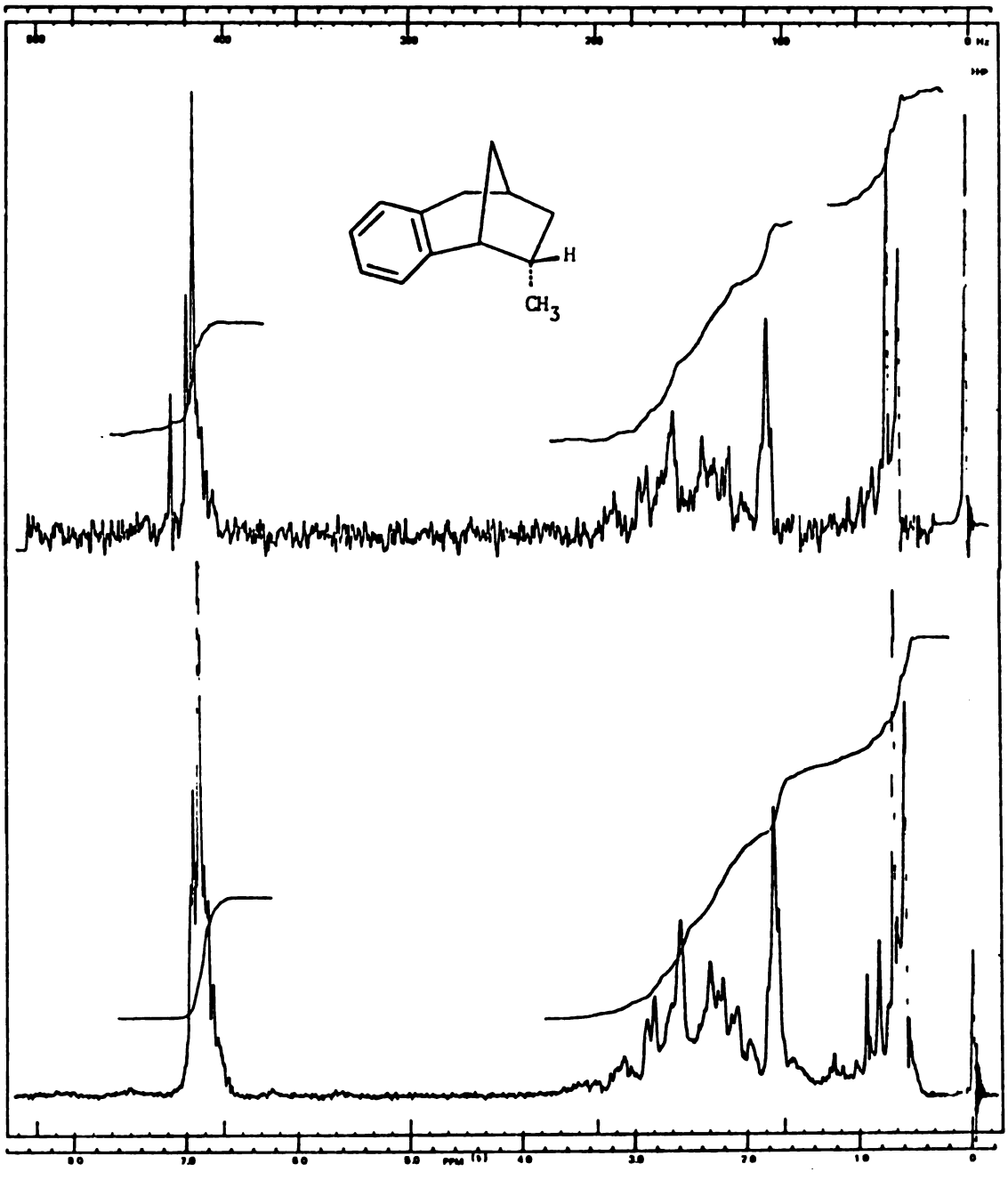


Figure 23. NMR Spectra of *Syn*-6-methyl-3,4-benzobicyclo[3.2.1]oct-3-ene (81). Top: material obtained from hydrogenation of photoproduct 67s. Bottom: material obtained from Wolf-Kishner reduction of ketone 80.

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