PART I
THE PHOTOREARRANGEMENT OF BICYCLO[2.2.2]OCTADIENONES AND RELATED ALCOHOLS

PART II
THE PHOTOISOMERIZATION OF 1(2H)-NAPHTHALENONES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
ROGER K. MURRAY, JR.
1968

This is to certify that the

thesis entitled
PART I
THE PHOTOREARRANGEMENT OF THE BICYCLO[2.2.2]-
OCTADIENONES AND RELATED ALCOHOLS

PART II
THE PHOTOISOMERIZATION OF 1(2H)-NAPHTHALENONES
presented by

Roger K. Murray, Jr.

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Harold Hart
Major professor

Date December 20, 1968

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ABSTRACT

PART I

THE PHOTOREARRANGEMENT OF BICYCLO[2.2.2]OCTADIENONES AND RELATED ALCOHOLS

PART II

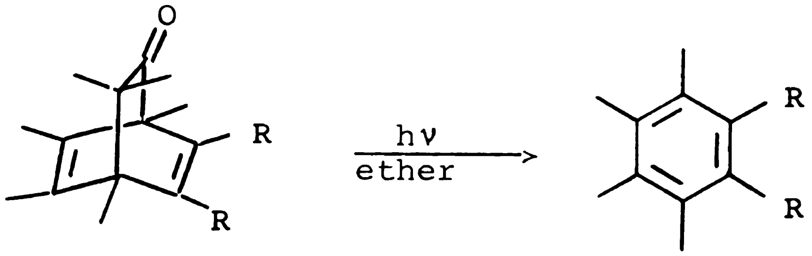
THE PHOTOISOMERIZATION OF 1(2H)-NAPHTHALENONES

By

Roger K. Murray, Jr.

In the first part of this thesis the photochemistry of variously substituted bicyclo[2.2.2]octadienones was investigated.

Irradiation of ether solutions of hexamethylbicyclo-[2.2.2]octadienones 30 and 32 provided high yields of the benzene derivatives 31 and 33, respectively.



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33, R = C_6H_5

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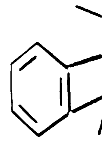

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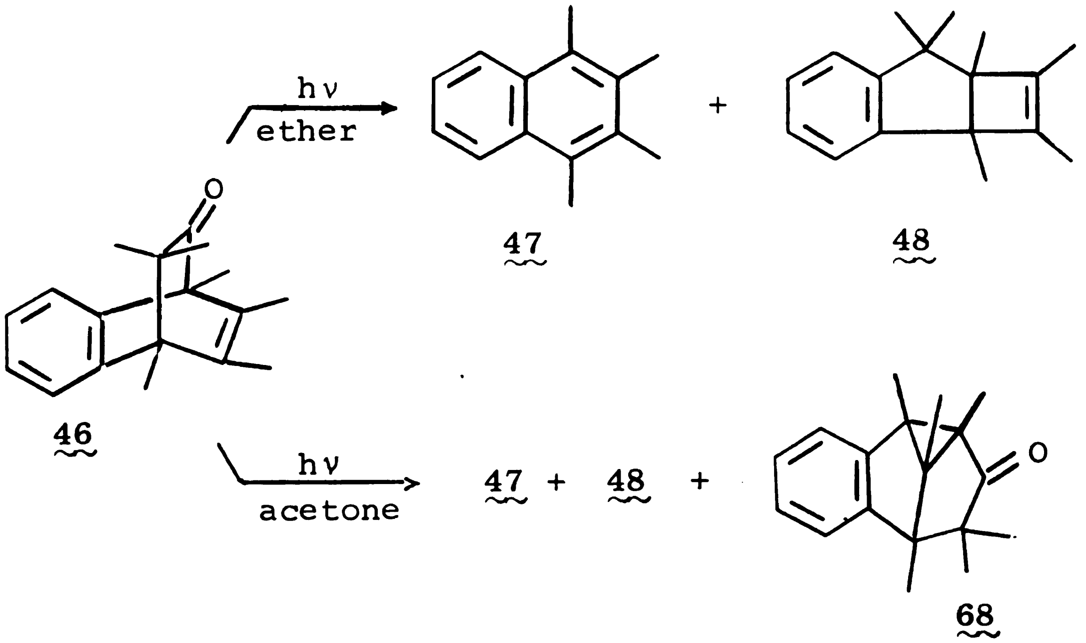
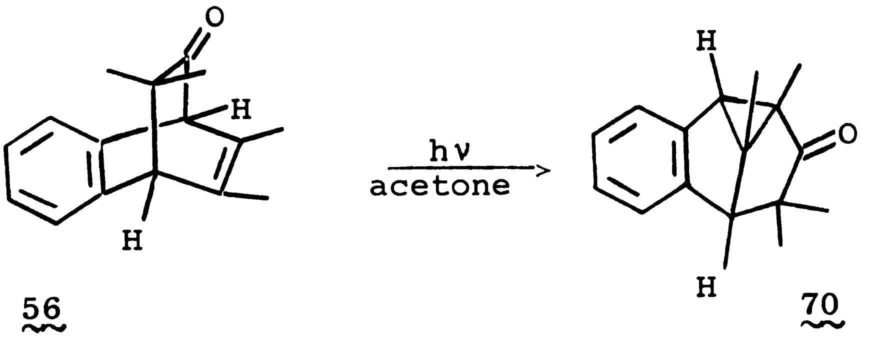
The photoelimination of dimethylketene from **32** proceeded efficiently even at -100°.

Similarly, irradiation of a solution of benzobicyclo[2.2.2]octadienone **46** in ether gave 1,2,3,4-tetramethylnaphthalene, **47**, and a benzobicyclo[3.2.0]heptadiene, **48**. However, acetone-sensitized irradiation of **46** gave not only **47** and **48**, but also ketone **68**. The ketonic product isolated from the acetone-sensitized irradiation of benzobicyclo[2.2.2]octadienone **56** has been identified as **70**. This result





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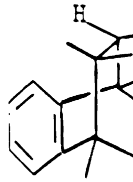

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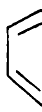
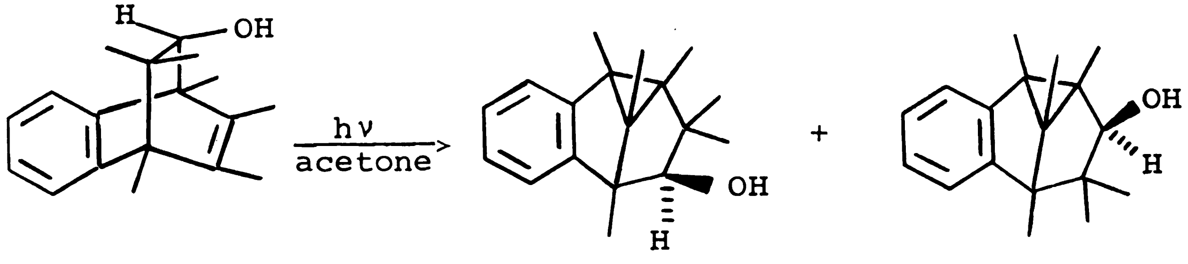


requires that the photoisomerization of **46** to ketone **68** occurs from the triplet *via* 1,2-acyl migration and not by a di-π-methane rearrangement.

A most unusual substituent effect was observed in the photochemistry of *anti*- and *syn*-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols, **90** and **91**, respectively. Acetone-sensitized irradiation of *anti*-alcohol **90** provided a 3:2 mixture of two alcohols, **92** and **93**. These are the products expected from the photoisomerization of **90** *via* a di-π-methane rearrangement. However, similar irradiation of *syn*-alcohol **91** gave only a single alcohol, **99**. Hydrogen bonding or charge transfer interaction with the



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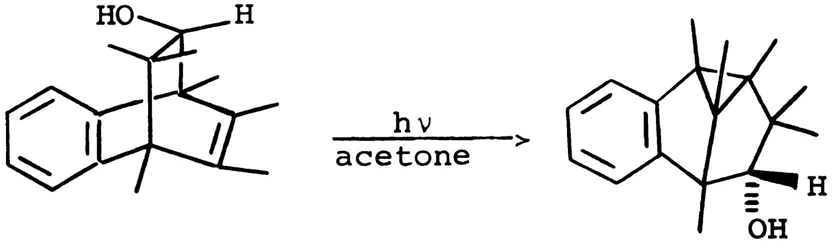

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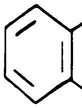

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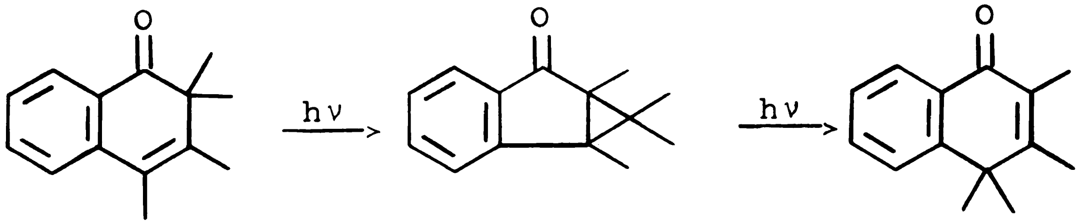
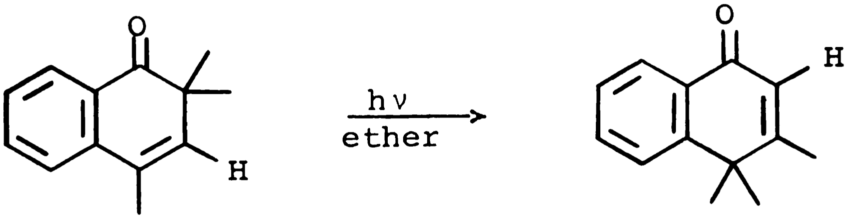
oxygen may be the factors which control the course of this photorearrangement.

A determination of the mechanisms operative in the photoisomerization of naphthalenone 121 to benzobicyclo[3.1.0]hexenone 123 and of 123 to naphthalenone 124 was the purpose of the second part of this thesis.



121 123 124

Irradiation of an ether solution of 2,2,4-trimethyl-1(2H)-naphthalenone, 136, prepared by the oxidation of 1,2,4-trimethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride, provided 3,4,4-trimethyl-1(4H)-naphthalenone, 148. A detailed



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consideration of the mechanisms possible for the photoisomerization of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]-hexenone shows that the isolation of 148 from the photolysis

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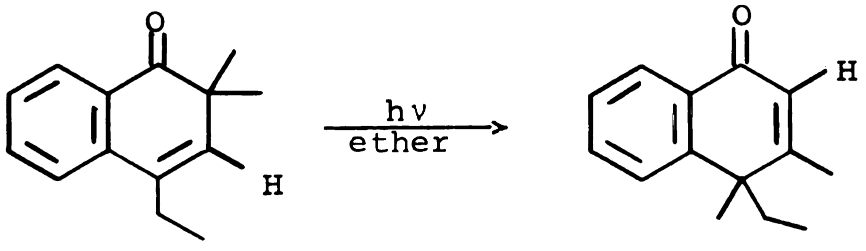
of 136 requires that the photorearrangement of naphthalenone 121 to benzobicycloketone 123 proceeds by a "bond-crossing" mechanism.

Photolysis of a hexane solution of naphthalenone 121 containing dimethyl amine gave 123. Irradiation of a solution of naphthalenone 121 in methanol afforded naphthalenone 124 *via* bicycloketone 123. These results suggest that the "bond-crossing" mechanism for the photoisomerization of 121 to 123 does not involve a ketene intermediate.

Irradiation of an ether solution of 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone, 154, prepared by the oxidation of 4-ethyl-1,2-dimethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride, gave 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone, 156. An examination of the possible mechanisms for the photorearrangement of a benzobicyclo[3.1.0]hexenone to a 1(4H)-naphthalenone shows that the isolation of 156 from the photolysis of 154 requires that the photoisomerization of benzobicycloketone 123 to naphthalenone 124 occurs *via* a 1,2-alkyl migration.



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Roger K. Murray, Jr.

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for the degree of

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Department of Chemistry

1968

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PART I

THE PHOTOREARRANGEMENT OF BICYCLO[2.2.2]OCTADIENONES AND RELATED ALCOHOLS

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INTRODUCTION

During the past decade investigations concerning the interaction of formally nonconjugated chromophores in photochemical transformations have attracted considerable interest. A case in point is the photochemical behavior of monocyclic and bicyclic β,γ-unsaturated ketones.

The ultraviolet spectra (1,2) and optical rotatory dispersion and circular dichroism curves (2-4) of a number of β,γ-unsaturated ketones indicate there is a considerable interaction between the π-electron systems of the β,γ-double bond and the carbonyl group. This interaction can be attributed (1,4) to the overlapping of the nonbonding p-orbital of the oxygen atom with the π-orbitals of the ground state of the β,γ-double bond (which has only slightly different energy) and results in an intensification of the $n \rightarrow \pi^*$ absorption of such unsaturated ketones. For a given geometrical arrangement, the smaller the difference in energy between the $\pi \rightarrow \pi^*$ transition of the carbon-carbon double bond and the $n \rightarrow \pi^*$ transition of the carbonyl, the more intense will be the mixed $n \rightarrow \pi^*$ transition (5). Of course the borrowing of intensity by the $n \rightarrow \pi^*$ transition from the $\pi \rightarrow \pi^*$ transition reduces the intensity of the latter. The chemical consequences of this ele

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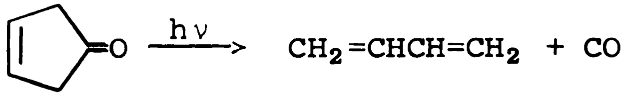
of this electronic interaction are demonstrated in the photochemical reactions of monocyclic and bicyclic β,γ-unsaturated ketones.

Irradiation of the $n \rightarrow \pi^*$ band of 3-cyclopentenones results in decarbonylation and highly efficient conversion to derivatives of 1,3-butadiene. Thus the vapor-phase irradiation of 3-cyclopentenone, 1, provides only 1,3-butadiene and carbon monoxide, with a



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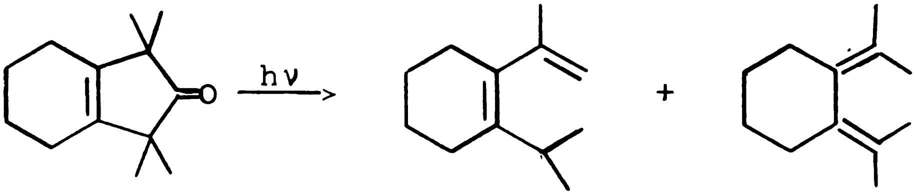
quantum efficiency near unity for the formation of these products and constant over the temperature range of 60-190° (6). Similarly, irradiation of a cyclohexane solution of 2 with the unfiltered radiation of a high-pressure



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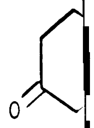
mercury arc gives dienes 3 and 4 (7).

In striking contrast to these results, 3-cyclohexenones have been observed to photochemically rearrange with 1,2-acyl migration to provide isomeric conjugated cyclopropyl ketones. Thus Williams and Ziffer have reported (8) that the irradiation of a t-butyl alcohol solution of 5 through a Pyrex fil



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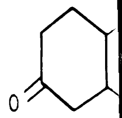

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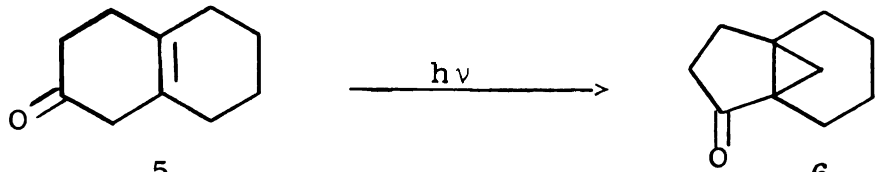
a Pyrex filter affords 6 in greater than 60% yield. Photolysis of (+)-17β-hydroxyoestr-5(10)-en-3-one, 7, under similar conditions gives the single isomer 17β-hydroxy-5α,10α-methylene-A-noroestran-3-one, 8 (9).



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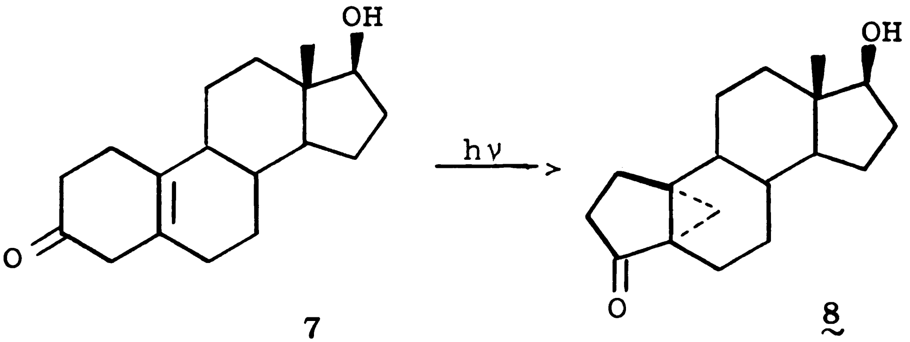

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Recent investigations of the photochemistry of 3-cycloheptenones and 3-cyclooctenones have shown that the principal photochemical transformation of medium-sized monocyclic β,γ-unsaturated ketones involves 1,3-acyl rearrangement and migration of the allylic double bond. This transformation appears to occur <u>via</u> the $n \longrightarrow \pi^*$ singlet state (10-12). Irradiation of an ether solution of 2,2-dimethyl-3-cycloheptenone, 9, through a Corex filter provides 10 as the only volatile photoproduct. This rearrangement is photochemically reversible (10). Paquette (11) and Crandall (12) have also reported that irradiation of

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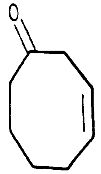

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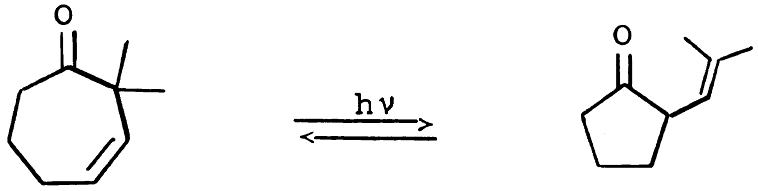

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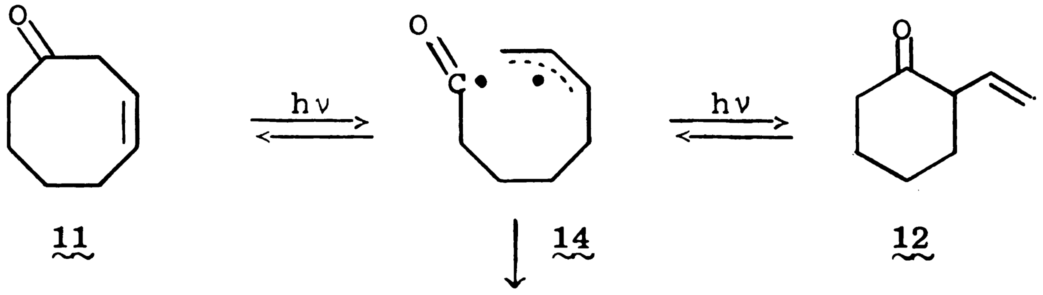
3-cyclooctenone, 11, in a variety of solvents yields 2-vinylcyclohexanone, 12, and 5,7-octadienal, 13, as the main photolysis products. The experimental data (12) re-



11 14 12

$$CH_2 = CHCH = CH(CH_2)_3\overset{O}{\overset{\|}{C}}\text{-}H$$

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quire a photoequilibrium between ketones 11 and 12 and an irreversible process leading to aldehyde 13. Consequently the photorearrangement of 11 has been explained in terms of a primary Norrish type I process leading to the biradical 14, followed by transannular rebonding to provide 12 or hydrogen abstraction to give 13.

Ultraviolet irradiation of *bicyclic* ketones in solution has produced a variety of photochemical reactions (13). However, several recent reports suggest that β,γ-unsaturated bicyclic ketones undergo a general photochemical reaction that involves cleavage of the carbon-carbon bond located

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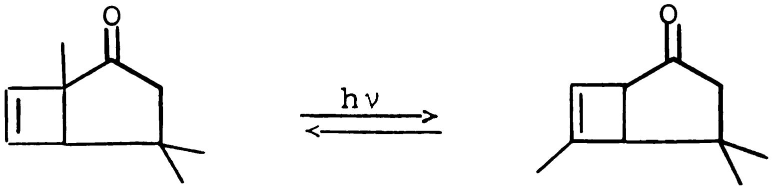
allyl to the double bond and α to the carbonyl with subsequent double bond migration and recyclization. In a classic study Büchi and Burgess found (14) that 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one, 15, and 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one, 16, are interconverted



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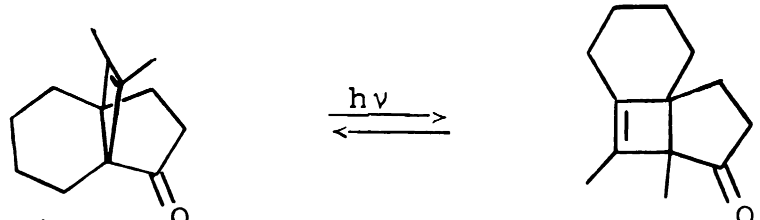
on irradiation with ultraviolet light. Similarly, irradiation of either pure 17 or 18 provides a photostationary



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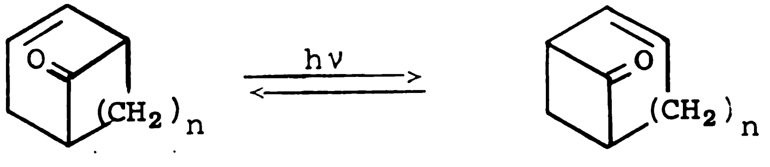
state mixture containing 70% 18 and 30% 17 (15). Erman and Kretschmar have also shown that cyclic enones of type 19 and 20 are interconverted on irradiation with a broad

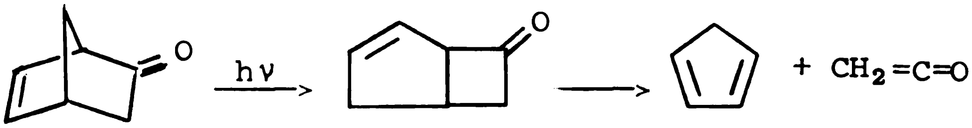


19 20

spectrum mercury arc lamp (16). As a result of these studies, it may be concluded that the product distribution

of the photostationary state cannot be related to the relative thermodynamic stability of the products, but rather is a function of the photochemical properties of the molecules considered (14,16).

In the photochemical rearrangements of other β,γ-unsaturated bicyclic ketones the reverse photorearrangements have not been observed, apparently due to competition from more efficient reactions of the photoproducts. Thus ultraviolet irradiation of dehydronorcamphor, 21, in a variety of solvents provides bicyclo[3.2.0]hept-2-en-7-one, 22, as the initial photoproduct (17). However, upon further irradiation 22 is converted into cyclopentadiene and ketene (17,18). Cookson has also examined the photochemistry of a number of substituted bornenones and found them to photorearrange to isomeric bicyclo[3.2.0]hept-2-en-7-ones, which with longer irradiation dissociate into ketene and the appropriately substituted cyclopentadienes (19).



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Most recently two reports have appeared concerning related systems in which the pi-electrons of more than one β,γ-double bond can interact with the carbonyl group. Kende has found that irradiation of a solution of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one, 23, in acetonitrile giv

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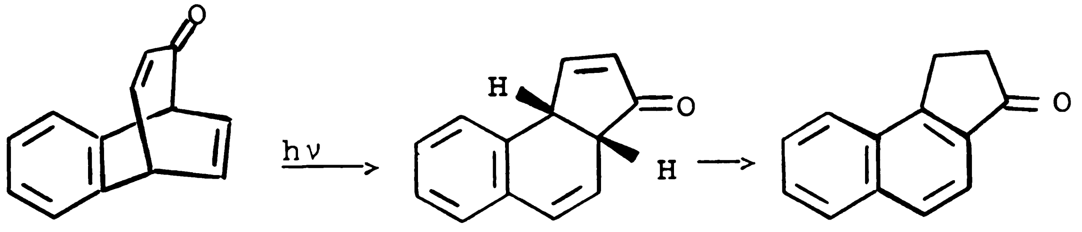
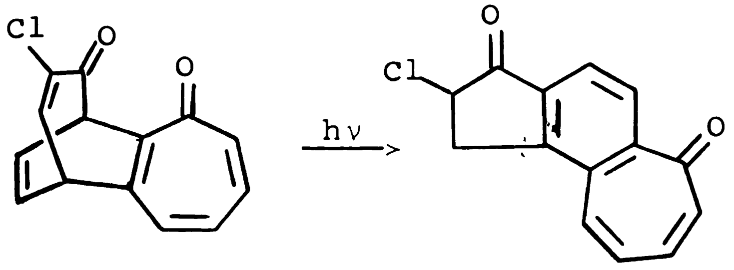


23 25 24

that ketone 24 is not present in the photolysis solution during the irradiation, but can be instantly generated therein by the addition of base. Thus it is proposed that the primary step in the photoisomerization is the rearrangement of 23 to the diolefinic ketone 25, with ultimate isomerization to 24 taking place during the work-up procedure. Similarly, irradiation of 26 gives 27 (21).



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Previous studies in this laboratory (22,23) have provided a number of variously substituted bicyclo[2.2.2]octa-5,7-dien-2-ones, 29, *via* the addition of acetylenic derivatives to the readily available (24) hexamethyl-2,4-cyclohexadienone, 28. Such bicyclo[2.2.2]octadienones as 29 provide a rigid bicyclic system in which the pi-electrons of bot

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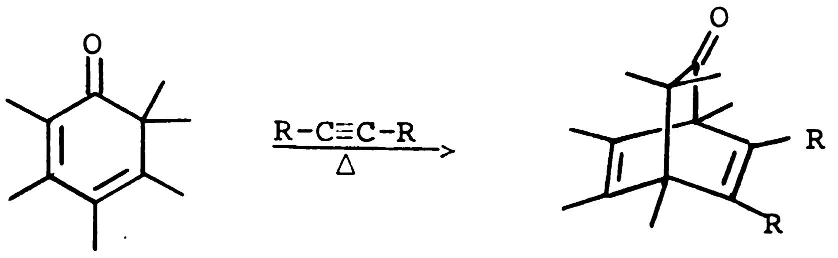
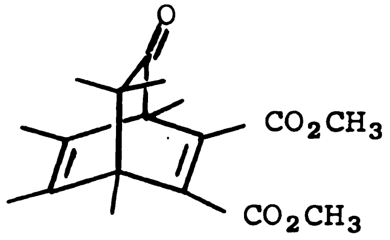


28 **29**

both β,γ-double bonds can interact equally with the carbonyl group. The presence of such interaction is reflected in the enhanced n ⟶ π* absorption maxima (22) in the ultraviolet spectra of **30** and the benzo derivative **46**. Part I



30

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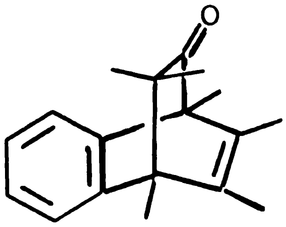


46

λ_{max} 300

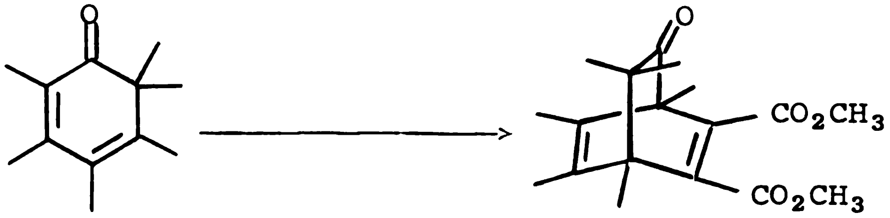
ε 373

of this thesis examines the photochemical consequences of this electronic interaction in variously substituted bicyclo-[2.2.2]octadienones.

RESULTS AND DISCUSSION

A. The Direct Irradiation of 1,3,3,4,7,8-Hexamethyl-5,6-dicarbomethoxybicyclo[2.2.2]octa-5,7-dien-2-one (30) and 1,3,3,4,7,8-Hexamethyl-5,6-diphenylbicyclo[2.2.2]-octa-5,7-dien-2-one (32).

The bicyclo[2.2.2]octa-5,7-dien-2-ones desired for this study were prepared by the addition of acetylenic derivatives to hexamethyl-2,4-cyclohexadienone, 28 (24). As previously reported by Kakihana (22), refluxing 28 and dimethyl acetylenedicarboxylate in xylene gave a high yield of 1,3,3,4,7,8-hexamethyl-5,6-dicarbomethoxybicyclo[2.2.2]octa-5,7-dien-2-one, 30. Similarly, 1,3,3,4,7,8-hexmethyl-5,6-diphenylbicyclo[2.2.2]octa-5,7-dien-2-one, 32, was prepared by heating 28 and diphenyl acetylene at 200°(22).



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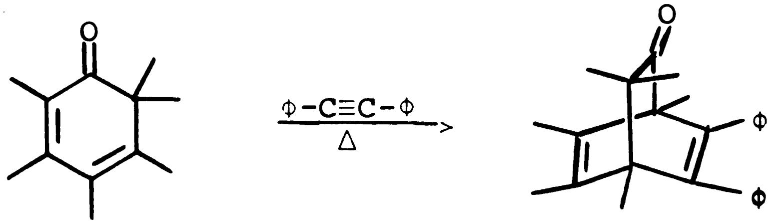
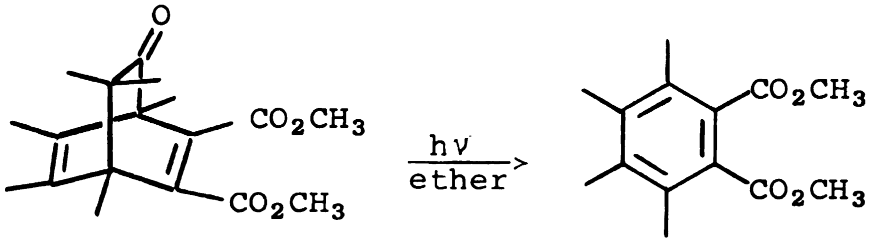


28 32

Irradiation of a 1% ether solution of 30 through a Corex filter with a Hanovia L 450-W lamp proceeded smoothly and efficiently to provide an 80% yield of dimethyl 3,4,5,6-tetramethylphthalate, 31, which was identified by comparison (mp, ir and nmr spectra, R_t) with an authentic sample (22). Irradiation of 32 under identical conditions gave an 83% yield of 3,4,5,6-tetramethyl-1,2-diphenylbenzene, 33, which was also identified by comparison (mp, mixed mp, ir and nmr spectra) with an authentic sample (22). Dimethylketene, 34, formed during the reaction was trapped as isobutyranilide, 35, by the addition of aniline to the crude photolysate.



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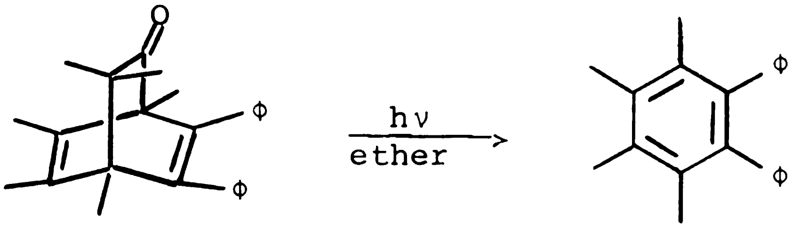

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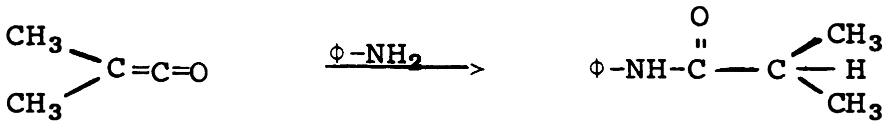

$$(CH_3)_2C{=}C{=}O \xrightarrow{\Phi\text{-}NH_2} \Phi\text{-}NH\text{-}\overset{O}{\overset{\parallel}{C}}\text{—}C(CH_3)_2H$$

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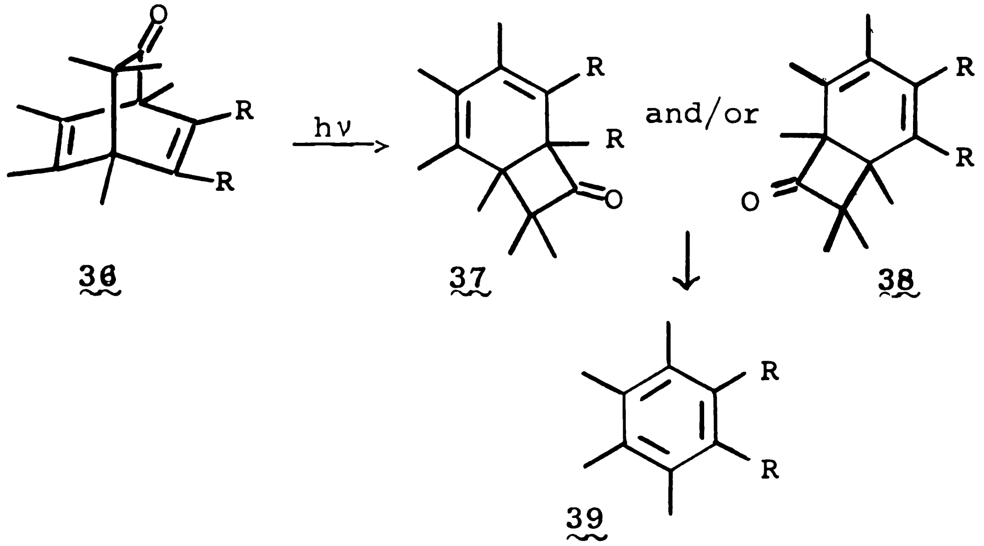
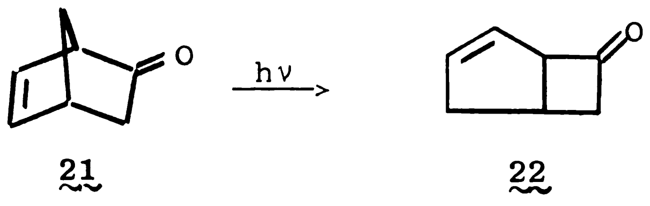
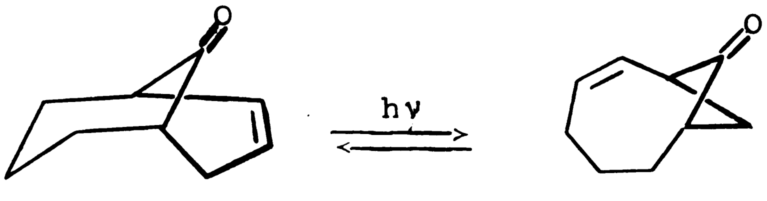
Two alternative mechanisms can be suggested for these conversions: (a) direct photoelimination of dimethylketene from the bicyclo[2.2.2]octadienone in either a concerted or stepwise fashion (The implications of a concerted photoelimination of dimethylketene are discussed in Section B.), or (b) photorearrangement of the bicyclo[2.2.2]octadienone 36 to cyclobutanone 37 and/or 38, which then eliminates dimethylketene to give 39. Path b has ample precedent, for the principal photochemical transformation of bicyclic β,γ-unsaturated ketones involves 1,3-acyl rearrangement and migration of the allylic double bond (16). For example, ultraviolet irradiation of dehydronorcamphor, 21, provides bicyclo[3.2.0]hept-2-en-7-one, 22, as the initial



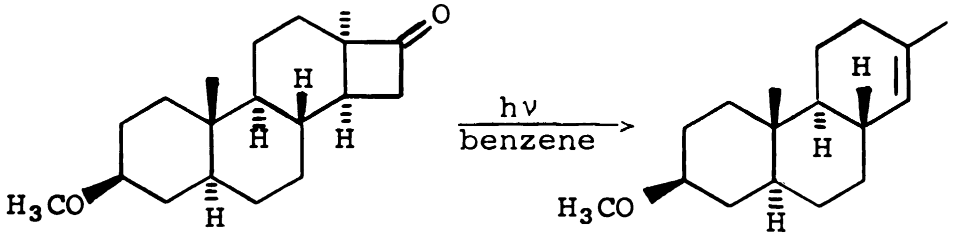


photoproduct (17). Similarly, irradiation of bicyclo[3.3.1]-non-2-en-9-one, **40**, provides a photoequilibrium mixture of **40** (27%) and bicyclo[5.1.1]non-2-en-9-one, **41** (62%) (16).



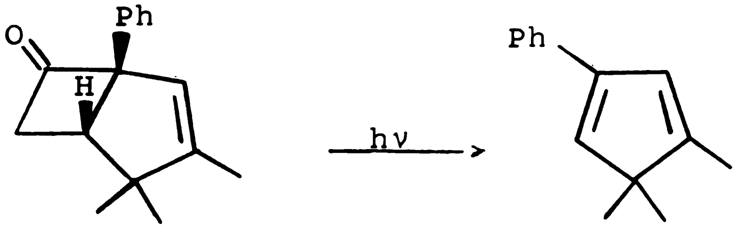
40 **41**

The photoelimination of ketene from a cyclobutanone (step 2 of path b) has also been reported. Thus the principal photoprocess observed in the irradiation of a benzene solution of **42** is the photoelimination of ketene and the formation of **43** (25). Similarly, irradiation of 1-phenyl-3,4,4-



42 **43**

trimethylbicyclo[3.2.0]hept-2-en-7-one, **44**, gave cyclopentadiene **45** and ketene.



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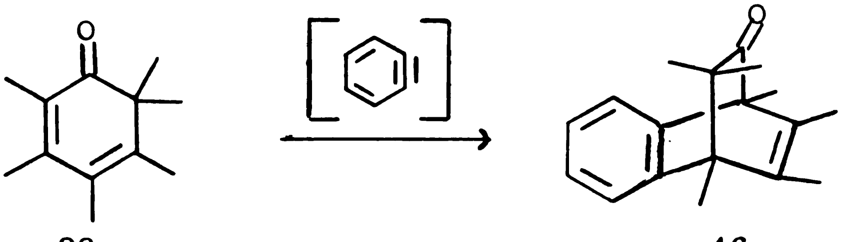
A low temperature study of the photolysis of the diphenylbicyclo[2.2.2]octadienone **32** was carried out in an attempt to help differentiate between the two alternative mechanisms. The apparatus used in this study was designed by Dr. John Griffiths of this laboratory. A solution of **32** in 2-methyltetrahydrofuran was irradiated for short intervals at -100° in a sodium chloride cavity cell. Monitoring the photolysis by infrared showed the immediate appearance of a sharp intense absorption at 2135 cm^{-1} which increased in intensity as the irradiation was continued. The intensity of the carbonyl absorption of **32** decreased during the irradiation. The absorption at 2135 cm^{-1} is attributed to the formation of dimethyl ketene, **34**. Ketene intermediates detected in a similar manner by Hart and Griffiths (26) and Chapman and Lassila (27) show infrared absorptions in the region 2145-2050 cm^{-1}.

These observations are consistent with path a , *i.e.*, the direct photoelimination of dimethylketene from the bicyclo[2.2.2]octadienone. For path b to be plausible, the elimination of dimethylketene from the cyclobutanone intermediates **37** and/or **38** must be efficient at -100°.

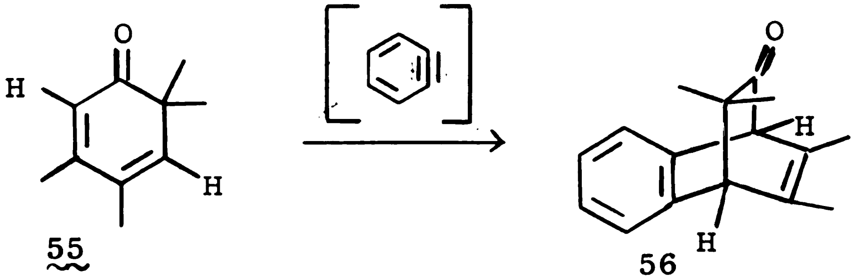
B. The Direct Irradiation of 1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (46) and 3,3,7,8-Tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (56)

As previously reported (23,28), 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one, **46**, was prepared by the reaction of benzyne with hexamethyl-2,4-cyclohexadienone, 28 (24). Similarly, the reaction of benzyne with



28 46

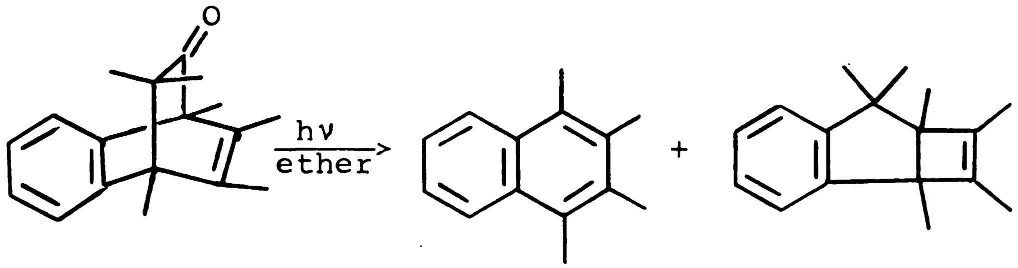
3,4,6,6-tetramethyl-2,4-cyclohexadienone, 55, (29) gives 3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one, 56 (22). The direct irradiation of 46 and 56 was



55 56

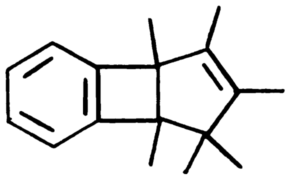
investigated in order to study the influence on the photochemistry of the bicyclo[2.2.2]octadienones when one of the two carbon-carbon double bonds of the bicyclo[2.2.2]-octadienone system belonged to a fused aromatic ring.

Irradiation of a 1% ether solution of 46 through a Corex filter with a Hanovia L 450-W lamp, when allowed to proceed to 86% conversion of 46, provided an 82% yield of 1,2,3,4-tetramethylnaphthalene, 47, and a 13% yield of 1,4,4,5,6,7-hexamethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, 48. 1,2,3,4-tetramethyl naphthalene was identified



46 47 48

by comparison with an authentic sample. The elemental analysis and mass spectrum (parent peak at m/e 226) of 48 indicated that it was formed by the elimination of carbon monoxide from 46. The nmr spectrum of 48 consisted of singlets at τ 8.95 (3H), 8.83 (3H) and 8.75 (6H), quartets at τ 8.53 and 8.50 (3H each, J = 1.2 Hz), and a singlet at τ 3.05 (4H, aromatic protons). Structures 49 and 50 are also consistent with these data. However, examination of



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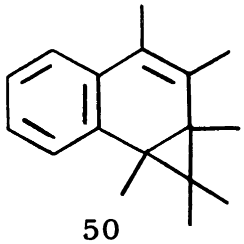

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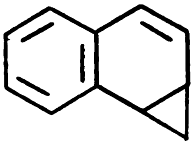
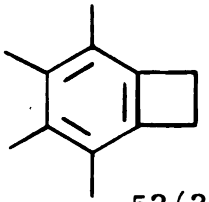
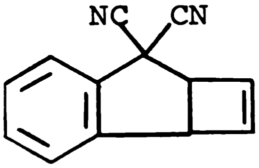
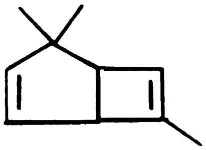
Table I indicates that these compounds can be differentiated by their ultraviolet spectra. As benzonorcaradiene, 51, is structurally analogous to 50, and 4,4-dicyano-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, 54, is similarly related to 48, the ultraviolet spectra of 51 and 54 should provide good models for the expected ultraviolet spectra of 50 and 48, respectively. Previously reported bicyclo[3.2.0]hepta-2,6-dienes show only end absorption in the ultraviolet region.

Table I. The ultraviolet spectra of some bicyclic dienes.

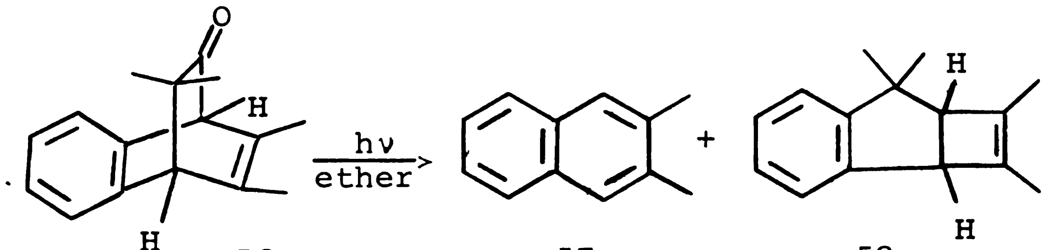
 51(31) λ_{max}, mμ (log ε)	 53(32) λ_{max}, mμ (ε)	 54(33) λ_{max}, mμ (ε)
306 (3.02)	282 (580)	273 (570)
274 (3.81)	278 (580)	266 (550)
221 (4.32)	273 (580)	260 (370)
	228 (2860)	214 (8000)

For example, 52 (30) has λ_{max} 210 mμ (ε 2640). Thus the ultraviolet spectrum of a benzocyclobutene such as 53 should be a good model for that of 49. The ultraviolet spectrum of the olefinic product from the irradiation of 46 has maxima at 274 (ε 1910), 267 (ε 1980) and 211 mμ (ε 8580) with shoulders at 262 (ε 1470) and 230 mμ (ε 4860). This spectrum is nearly identical to that of 54 and hence 48 is assigned the structure of a 2,3-benzobicyclo[3.2.0]hepta-2,6-diene.



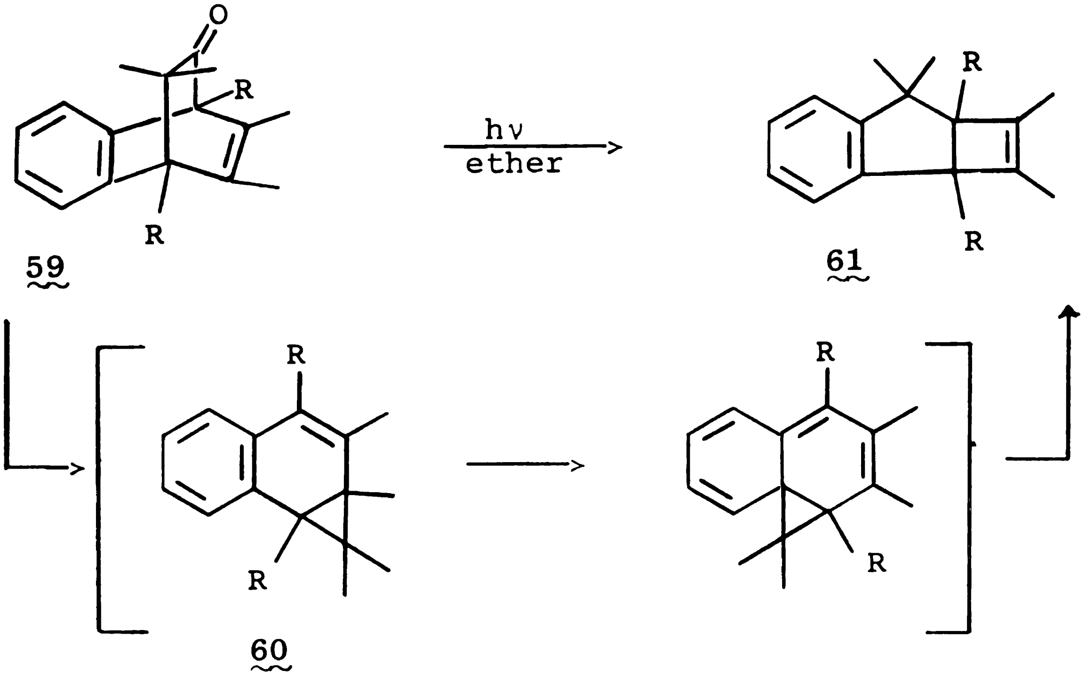
52

Irradiation of a 1% ether solution of 56 through a Corex filter with a Hanovia L 450-w lamp afforded a 70% yield of 2,3-dimethylnaphthalene, 57, and an 8% yield of 4,4,6,7-tetramethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, 58. 2,3-Dimethylnaphthalene was identified by comparison with an authentic sample. Compound 58 analyzed well for the formula $C_{15}H_{18}$. The nmr spectrum of this clear oil consisted of three-proton singlets at τ 8.90 and 8.70, overlapping quartets at τ 8.43 and 8.41 (6H together, J = 1.2 Hz), broad (h_w = 4.5 cycles) one-proton singlets at τ 7.13 and 6.31 and a singlet at τ 3.04 (4H, aromatic protons). The ultraviolet spectrum of 58 in 95% ethanol showed maxima at 273 (ε 1560), 266 (ε 1450), 260 (ε 1020) and 228 mμ (ε 2230) with shoulders at 253 (ε 620) and 213 mμ (ε 1920).



56 57 58

The formation of 61 from 59 can be accounted for by the initial formation of the benzonorcaradiene 60 which then photochemically rearranges to provide 61. An analogous photorearrangement of the type 60 ⟶ 61 has been observed by Ciganek in the photoisomerization of 7,7-dicyano-2,3-benzonorcaradiene, 62, to give 54 (33). Either the



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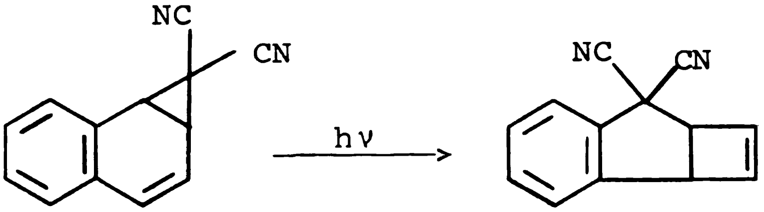

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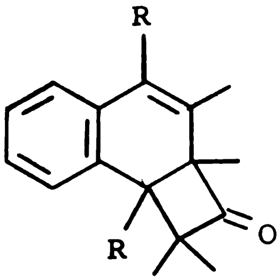
photochemical elimination of carbon monoxide from an intermediate cyclobutanone as 63, or the elimination of carbon monoxide from the diradical species 64 or 65, followed by appropriate rebonding, would account for the formation of 60. The photodecarbonylation of cyclobutanones has ample precedent in the reports of Srinivasan (34), Quinkert (25), and



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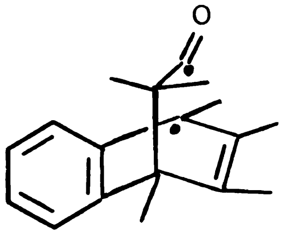

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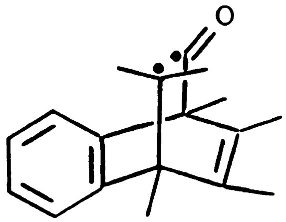

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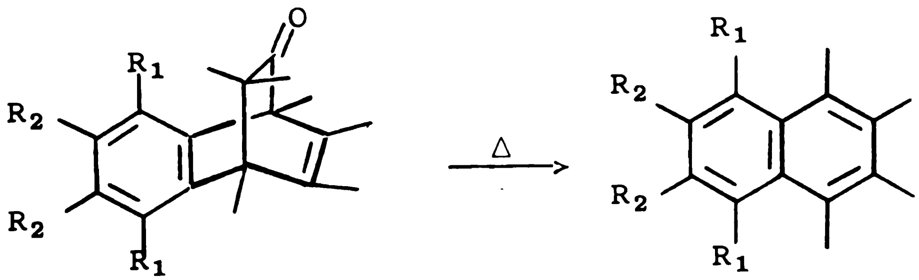
Turro (35).

The conversion of 66 to 67 can also be effected thermally. For example, 66 (R_1 = CH_3; R_2 = H) at 450^0 was converted



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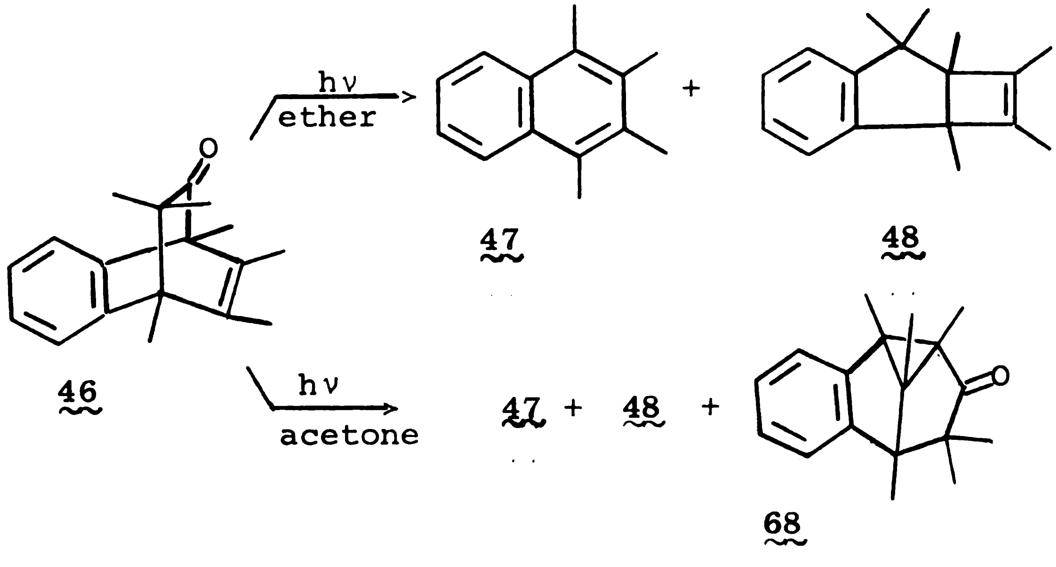
to 67 (R_1 = CH_3; R_2 = H) (17.8%), dimethylketene (17.9%), and 80% of recovered 66 (23). Thus the thermal elimination of dimethyl ketene from 66, a reverse Diels-Alder reaction, proceeds quantitatively, but requires temperatures (450-550^0) which might be considered unusually high, particularly when the aromaticity of the product is taken into account. Thus the ease with which ketenes are formed in the photochemical reverse Diels-Alder reaction 66 —> 67 stands in marked contrast to the high temperatures required for the thermal reaction. If these reactions are considered as concerted reverse 2 + 4 cycloadditions, then these results would be contrary to the expectations of the Woodward-Hoffmann rules (36). Since the photochemical reaction of 66 involves excitation of the carbonyl group, it may be necessary to include the carbon-oxygen double bond in the electron count for predictions concerning cycloadditions involving ketenes. The further observations that ketenes undergo thermal 2 + 2 cycloadditions (37) in a presumably concerted fashion (38) and that ketenes are not reactive as dienophiles in the Diels-Alder reaction (37) suggest that a more detailed theoretical treatment of all cycloadditions involving ketenes is required.

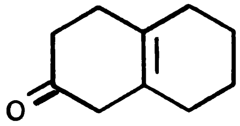
C. The Photosensitized Rearrangements of 1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (46) and 3,3,7,8-Tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (56)

As described in Section B, irradiation of an ether solution of 46 through a Corex filter with a high pressure mercury arc lamp affords 1,2,3,4-tetramethylnaphthalene, 47, (82% yield) and 48 (13%). However, irradiation of 46 with



acetone sensitization under identical conditions provides not only 47 (45% yield) and 48 (6% yield), but also an isomeric ketonic photoproduct 68, mp 100-102°, in 26% yield. From its analysis and spectral properties 68 has been identified as 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-3-one. The ir spectrum of 68 shows an intense carbonyl absorption at 1720 cm^{-1} which is typical of a cyclopropane ring conjugated with a highly substituted five-membered ring ketone (39). The ultraviolet spectrum of 68 has maxima at 278 (ε 1150) and 270 mμ (ε 1370) with a shoulder at 263 mμ (ε 1450) and is indicative of negligible interaction between the carbonyl function and the aromatic ring. The nmr spectrum (CD_3CN) of 68 consists of three-proton singlets at τ 9.44, 8.90, 8.74, 8.68, 8.63 and 8.57 and an aromatic multiplet, τ 2.90-3.22 (4H), and is consistent with the assigned structure.

As discussed in detail in the Introduction, the most common photochemical transformation of medium-sized monocyclic and bicyclic β,γ-unsaturated ketones involves a 1,3-acyl shift and migration of the allylic double bond. However, 3-cyclohexenones have only been observed (8,9) to photochemically rearrange in solution with 1,2-acyl migration to yield conjugated cyclopropyl ketones. Thus irradiation of a t-butyl alcohol solution of 5 through a Pyrex filter gives 6 in greater than 60% yield (8). The multiplicity of this photorearrangement has not been reported.



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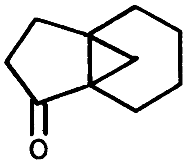

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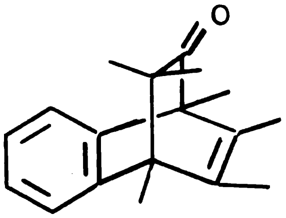
As the formation of benzotricyclic ketone 68 only occurs with acetone sensitization, the photoisomerization 46 ⟶ 68 must proceed <u>via</u> the triplet. Two molecular pathways seem reasonable for the formation of 68 from 46:



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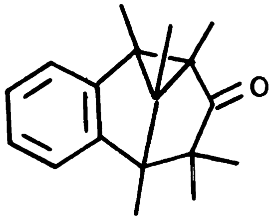

68

(a) acyl migration in 46 from C-1 to C-7 followed by rebonding between C-1 and C-8, analogous to the photorearrangement 5 ⟶ 6, or (b) a regiospecific (40) di-π-methane rearrangement (41) in which only one of the two possible products (68 or 69) which might be formed <u>via</u> benzo-vinyl bridging is observed. A detailed mechanism for the formation of 68 from 46 <u>via</u> a di-π-methane rearrangement (path b) is presented in Figure 1.

Differentiation between these two mechanisms is possible by identification of the ketonic photoproduct formed in the sensitized irradiation of tetramethyl ketone 56, for acyl migration (path a) would provide ketone 70, while a di-π-methane rearrangement (path b) would give 71 and/or 72.

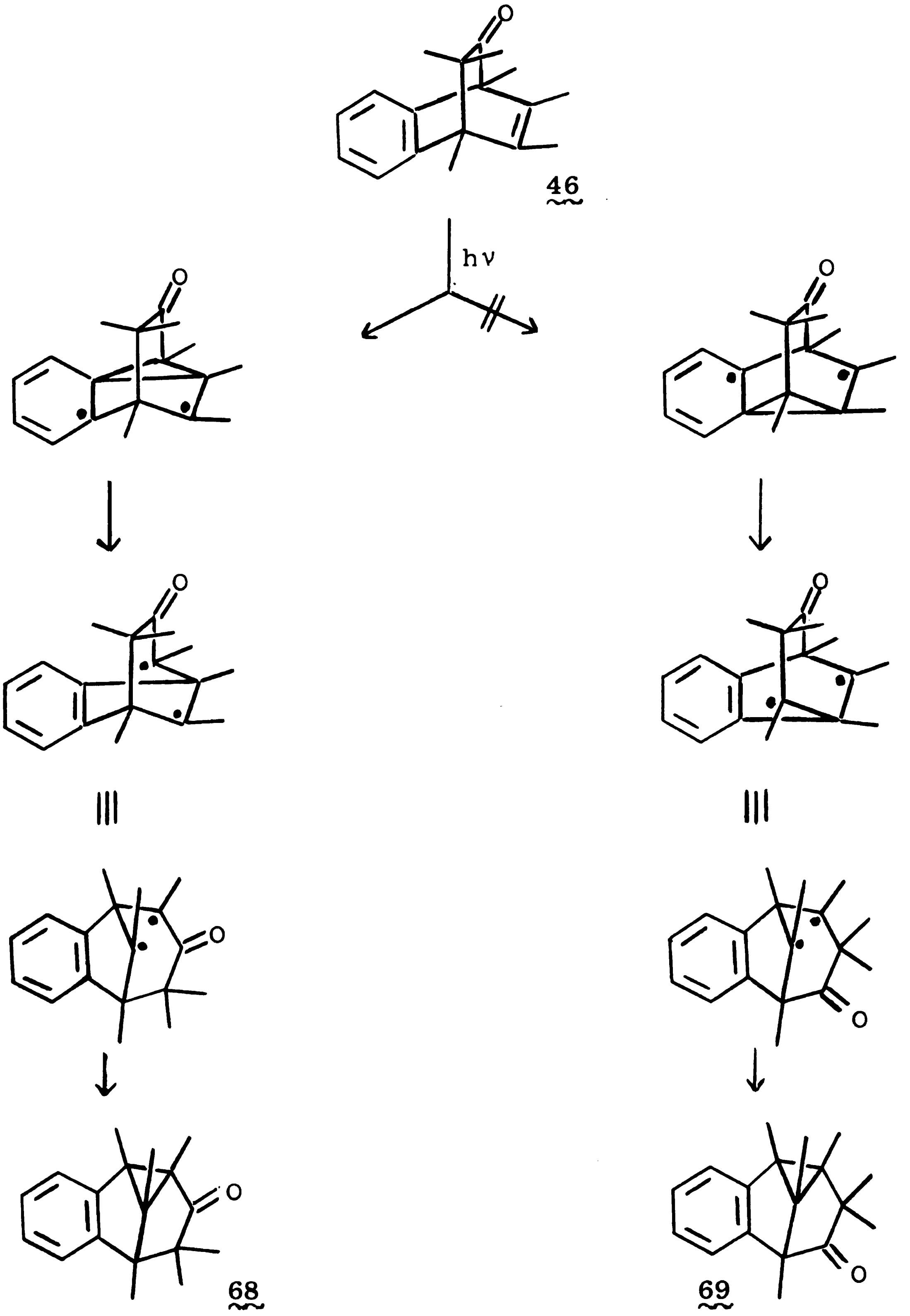

Figure 1. A detailed mechanism for the formation of 68 (or 69) from 46 *via* a di-π-methane photorearrangement.

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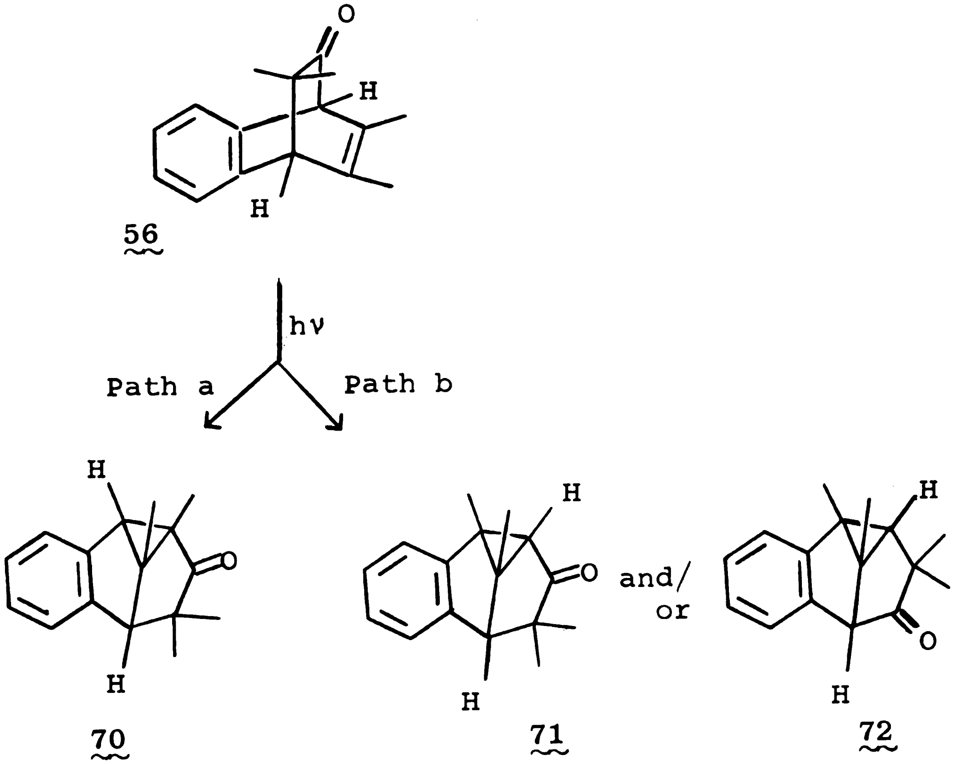
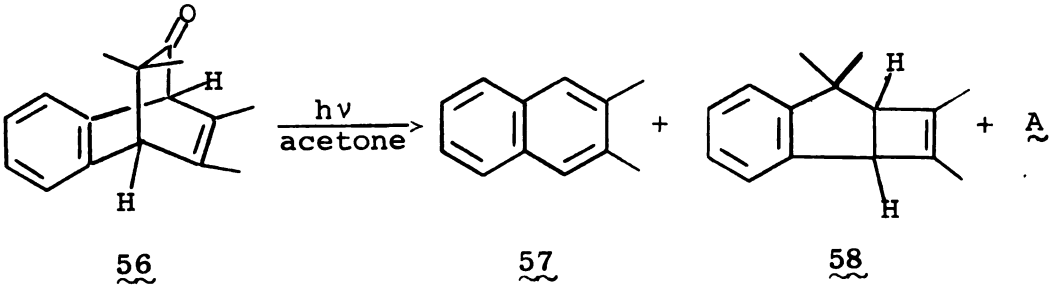
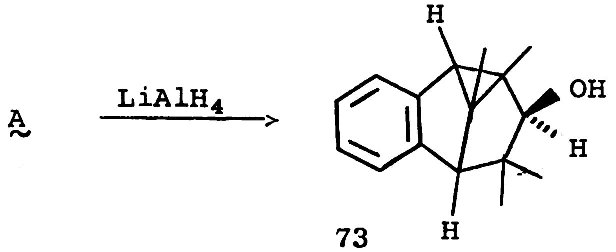


Acetone sensitized irradiation of 56 through a Corex filter with a Hanovia L 450-w lamp provides 2,3-dimethylnaphthalene (66% yield), 58 (6% yield) and an isomeric ketonic product, A, in 9% yield. The ir spectrum of this



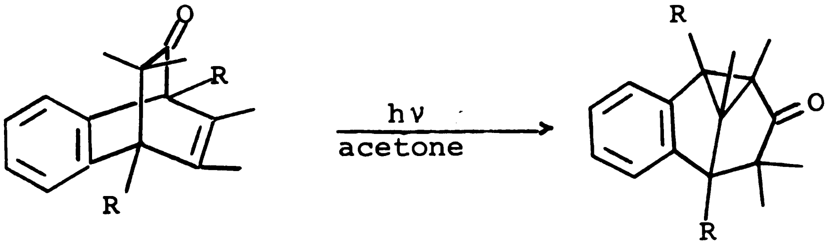
clear oil shows a strong carbonyl absorption at 1721 cm^{-1} and its ultraviolet spectrum has maxima at 279 (ε 660) and 271 mμ (ε 840) with a shoulder at 263 mμ (ε 930). The nmr spectrum of **A** consists of three-proton singlets at τ 9.38, 8.79, 8.65 and 8.44, sharp one-proton singlets at τ 7.80 and 6.97 and an aromatic multiplet, τ 2.81-3.10 (4H).

Reduction of ketone **A** with lithium aluminum hydride yields alcohol **73**, which has been identified as 1,2,4,4-tetramethyl-6,7-benzotricyclo[$3.3.0.0^{2,8}$]oct-6-en-*anti*-3-ol.



73

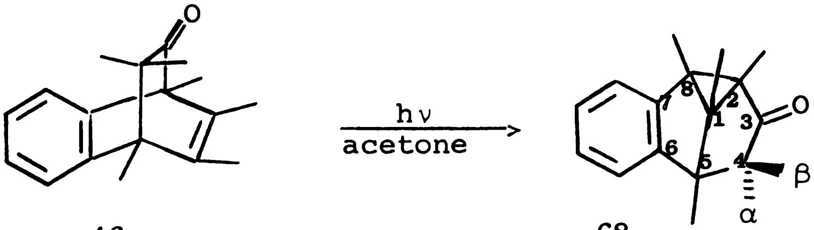
A characteristic infrared absorption (28,42) at 3644 cm^{-1} defines the stereochemistry of the hydroxyl group as being *anti* to the benzene ring. The nmr spectrum of **73** consists of three-proton singlets at τ 9.22, 8.95, 8.80 and 8.57, sharp one-proton singlets at τ 8.20, 7.30 and 6.92, and an aromatic multiplet, τ 2.90-3.13 (4H). Consequently, the nmr spectrum of **73** requires a reduction product in which there are no protons on adjacent carbon atoms. Thus **A**, the precursor of **73**, must be ketone **70**, 1,2,4,4-tetramethyl-6,7-benzotricyclo[$3.3.0.0^{2,8}$]oct-6-en-3-one. The identification of **A** as ketone **70** requires that the photochemical formation of **75** from **74** occurs from the triplet



74 **75**

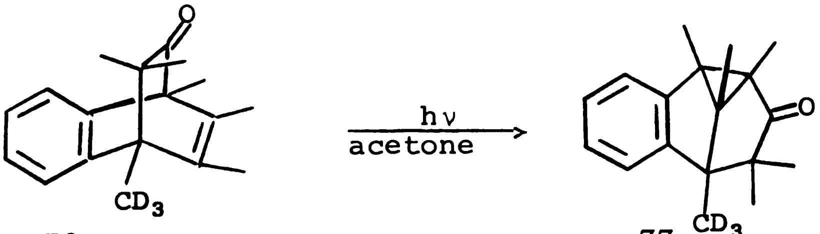
via 1,2-acyl migration (path a).

Having determined the mechanism for the photorearrangement **46** —> **68**, the correct nmr assignments for the



46 **68**

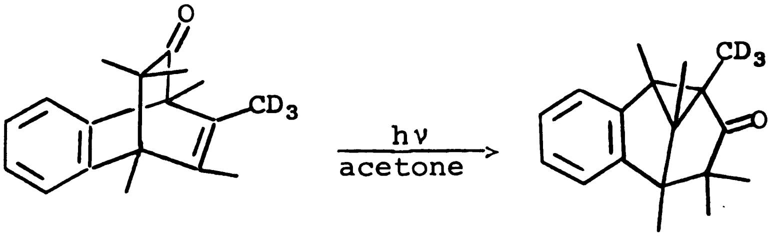
methyl groups of **68** can be determined by examination of the ketone photoproducts from suitably labeled benzobicyclo[2.2.2]octadienones. The labeled benzobicyclo[2.2.2]octadienones were prepared as previously described (28). Acetone sensitized irradiation of **76** provided ketone **77**. The



76 **77**

nmr spectrum (CD_3CN) of **77** was identical with that of **68** except for the absence in **77** of the signal at τ 8.57

present in 68. Similarly, acetone sensitized irradiation of 78 gave ketone 79. The nmr spectrum (CCl_4) of 79 was



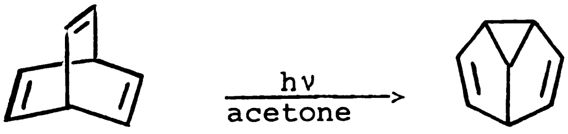
78

79

essentially identical with that of 68 except for the absence in 79 of the signal at τ 8.74 present in 68. Thus the nmr assignments of the signals in 68 are as follows: τ 9.44 (3H, α methyl at C-4), 8.90 (3H, β methyl at C-4), 8.74 (3H, methyl at C-2), and 8.57 (3H, methyl at C-5). The three-proton singlets at τ 8.68 and 8.63 are tentatively assigned to the methyls at C-1 and C-8, respectively.

D. The Photosensitized Rearrangements of 1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols (90 and 91)

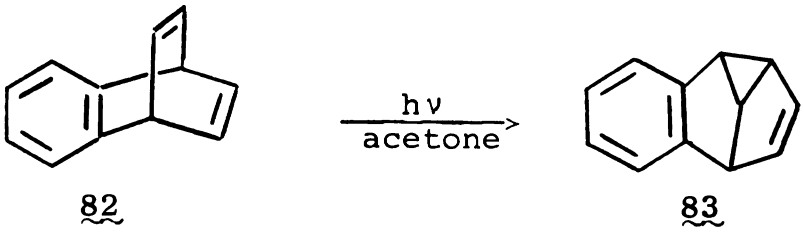
The photochemical conversion of a divinylmethane moiety into a vinylcyclopropane group has recently been suggested by Zimmerman (41) to be a general type of excited-state transformation. An example of this reaction is the photoisomerization of barrelene, 80, to give semibullvalene, 81

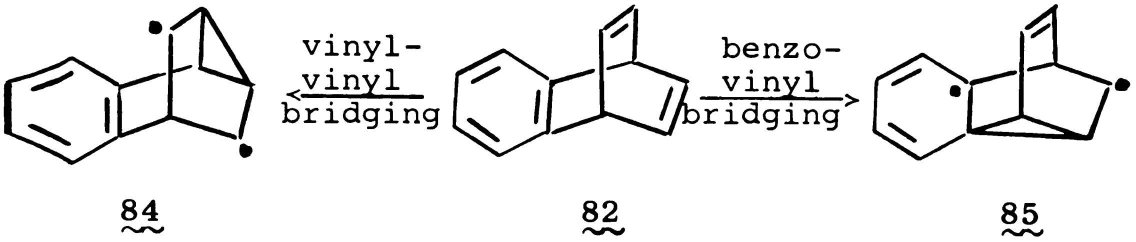


80

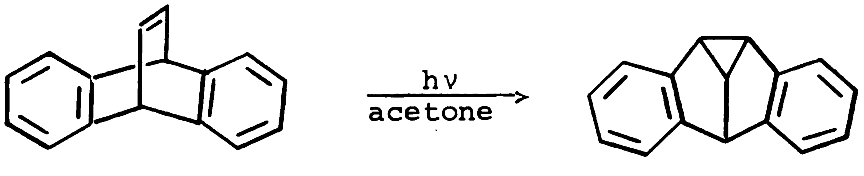
81

(41,43,44). Several recent reports have described the photosensitized rearrangement of benzobarrelene, 82 (45,46) and substituted benzobarrelenes (44,47) to provide appropriately substituted benzosemibullvalenes, 83. Rationalization of this isomerization by a di-π-methane rearrangement indicates that two types of bonding are possible as initial excited-state processes. Vinyl-vinyl bridging in 82 would lead to intermediate 84, whereas, benzo-vinyl bridging would give 85. Zimmerman has investigated this problem in detail and has reported (45) that the photosensitized rearrangement 82 ⟶ 83 proceeds by vinyl-vinyl bridging, not benzo-vinyl bridging.



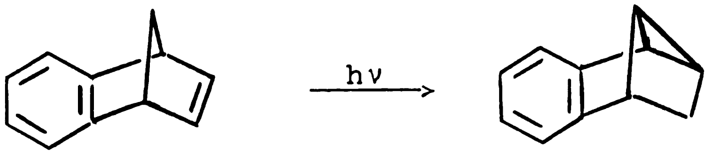


However, di-π-methane rearrangements which do involve benzo-vinyl bridging have been observed, for example, irradiation of an acetone solution of dibenzobarrelene, 86, affords dibenzosemibullvalene, 87, in high yield (46,48).



86 87

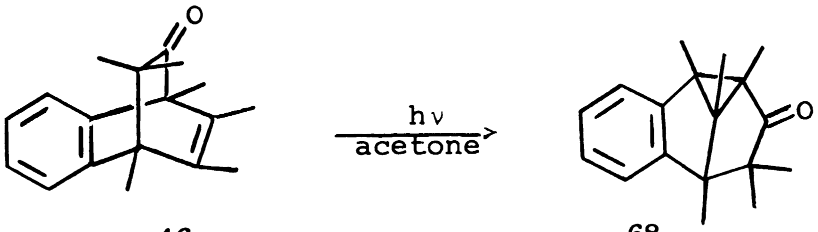
Similarly, the photoisomerization of benzonorbornadiene, 88, to tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-triene, 89, can be readily explained by benzo-vinyl bridging in a



88 89

di-π-methane rearrangement.

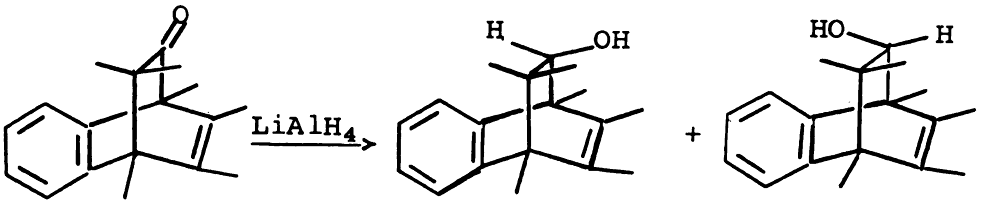
As discussed in Section C, the photo-sensitized rearrangement 46 —> 68 occurs from the triplet via a 1,2-acyl migration and not by a di-π-methane rearrangement. However,



46 68

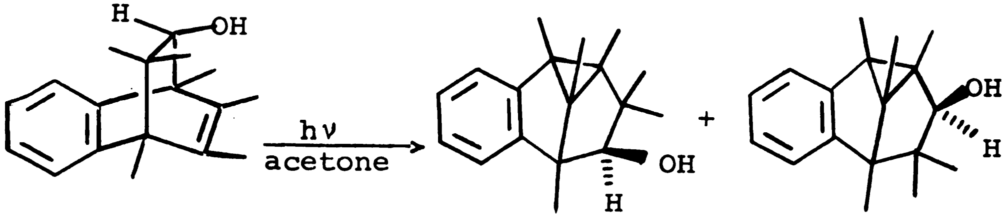
if the carbonyl chromophore in 46 were replaced by a non-absorbing substituent, there was ample precedent that the resulting benzobicyclo[2.2.2]octadiene might photochemically react by a di-π-methane rearrangement.

Reduction of ketone 46 with lithium aluminum hydride gave a 37:63 mixture of the epimeric alcohols 90 and 91, which were separated as previously described (28).



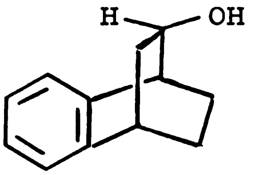
46 90 91

Irradiation of 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-*anti*-2-ol, 90, with acetone sensitization through a Corex filter with a Hanovia L 450-w lamp, when allowed to proceed to 85% conversion, provided a 73% yield of a 3:2 mixture of two alcohols, 92 and 93. Alcohol 92, mp 81-83^0, has been identified as 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-*anti*-4-ol.

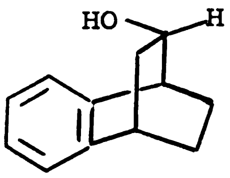


90 92 93

Alcohol 92 shows a sharp absorption in the ir at 3638 cm^{-1} which defines the stereochemistry of the hydroxyl group as being *anti* to the benzene ring. In comparison, *anti*-5,6-benzobicyclo[2.2.2]octen-2-ol, 94, shows a strong band at 3620 cm^{-1} in the infrared, whereas *syn*-5,6-benzobicyclo[2.2.2]octen-2-ol, 95, has a strong absorption at 3586 cm^{-1} (42). The shift in the hydroxyl band of the *syn* alcohol has been attributed to an internal hydrogen bonding of the alcohol function with the aromatic ring. Similar effects have been reported in the infrared spectra of the *syn*-and *anti*-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols, 90 and 91 (28).



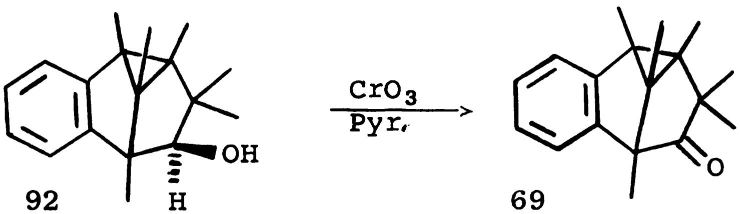
94



95

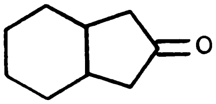
The nmr spectrum of 92 consists of three-proton singlets at τ 9.88, 9.03, 8.95, 8.83, 8.67 and 8.63, a one-proton singlet at τ 6.78 and an aromatic multiplet, τ 2.94-3.04 (4H).

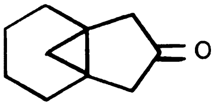
Oxidation of 92 with chromium trioxide-pyridine gave a ketonic product, mp 87-88.5^0, isomeric with 46, which has been identified by its analysis, spectral properties and reactivity as 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-one, 69. The infrared spectrum of 69

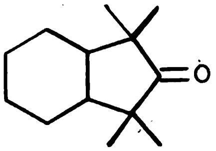


92 69

has an intense carbonyl absorption at 1725 cm^{-1}. The carbonyl absorptions of a series of related model ketones, 96 (49), 97 (7) and 98 (7) are presented below. If the substituent effects are assumed to be cumulative, then the


96
1744 cm^{-1}


97
1742 cm^{-1}

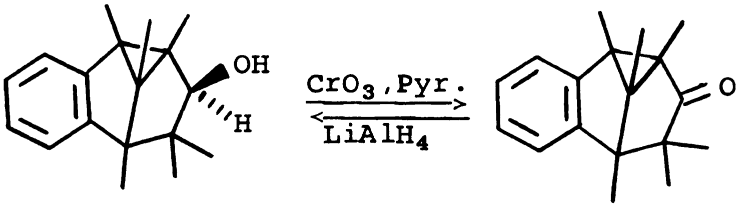

98
1727 cm^{-1}

$$\therefore \; 1744-2-17 = 1725 \text{ cm}^{-1}$$

value of 1725 cm^{-1} is exactly what would be expected for the carbonyl absorption of such a highly substituted bicyclo-[3.1.0]hexan-3-one as 69. The ultraviolet spectrum of 69 has a maximum at 292 mμ (ε 1290) with shoulders at 313 (ε 800), 301 (ε 1230) and 247 mμ (ε 2980). The enhancement of the $n \longrightarrow \pi^*$ transition in 69 is typical of other twisted β,γ-unsaturated ketones (1,2,17). The nmr spectrum of ketone 69 contains three-proton singlets at τ 9.50, 9.00, 8.80, 8.77, 8.58 and 8.50, and an aromatic multiplet, τ 2.92-3.08 (4H) and is consistent with the assigned structure.

Alcohol 93, mp 90-92°, also formed in the photoisomerization of the anti alcohol 90, has been identified as 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-anti-3-ol. Alcohol 93 shows a sharp absorption in the infrared at 3642 cm^{-1} which defines the stereochemistry of the hydroxyl substituent as being anti to the benzene ring (42). The nmr spectrum of 93 has three-proton singlets at τ 9.33, 9.13, 8.90, 8.85, 8.80 and 8.67, a one-proton singlet at τ 7.08 and an aromatic multiplet, τ 2.94-3.20 (4H).

Oxidation of alcohol 93 with chromium trioxide-pyridine gave ketone 68. A discussion of the spectral characteristics of 68 appears in Section C. Reduction of 68 with lithium aluminum hydride provided only the anti-alcohol 93.



93 68

Thus hydride attack on ketone 68 occurs exclusively syn to the benzene ring. Apparently hydride attack on ketone 68 anti to the benzene ring is sterically more hindered.

The formation of alcohols 92 and 93 in the acetone sensitized irradiation of anti alcohol 90 can readily be explained by a di-π-methane photorearrangement. As alcohol 90 is unsymmetric with respect to the di-π-methane moiety, two different benzo-vinyl bridgings are possible. As can be seen in Figure 2, initial bridging of C-6 and C-7 (path a) provides alcohol 93, whereas bridging C-5 and C-8 (path b) gives 92.

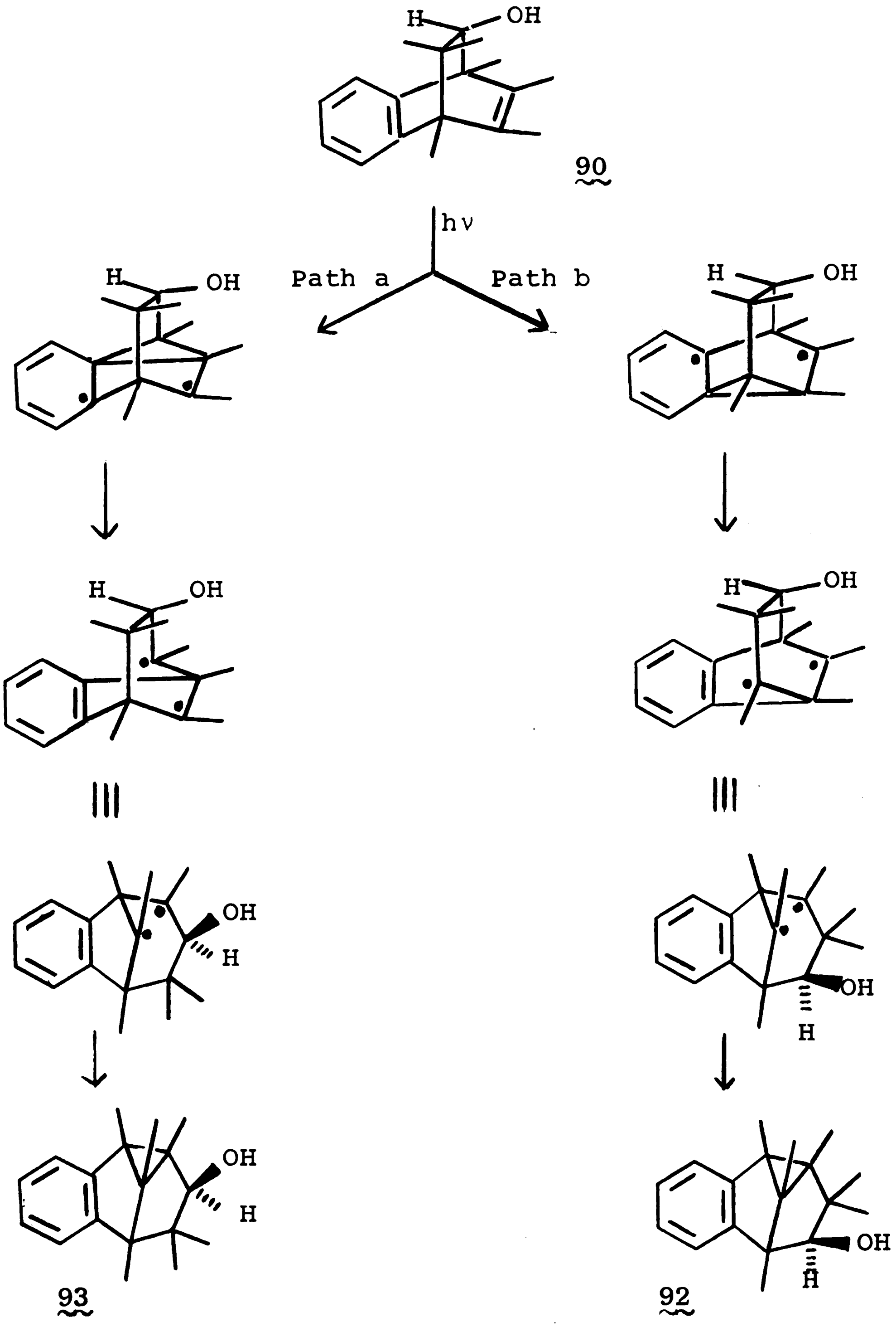
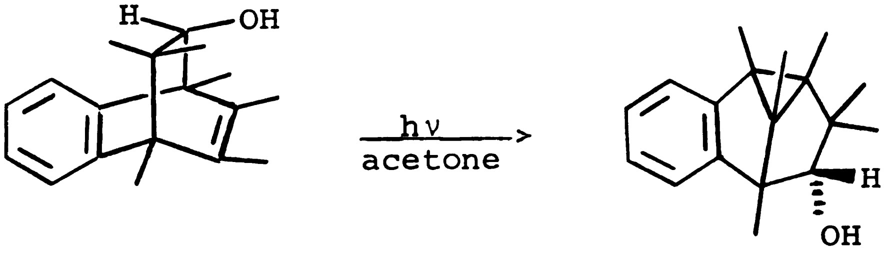


Figure 2. A detailed mechanism for the formation of 92 and 93 from 90 *via* a di-π-methane photorearrangement.

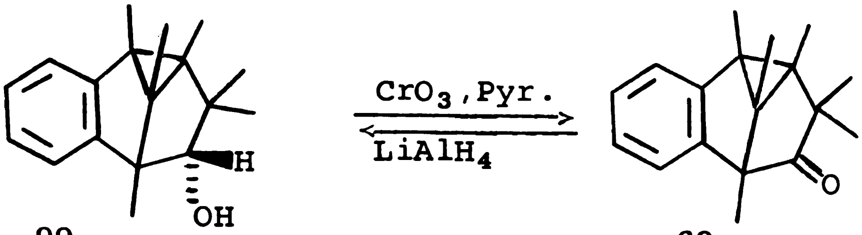
However, in marked contrast with the anti-alcohol 90, identical irradiation of 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-syn-2-ol, 91, provided only a single alcohol, 99. Irradiation to only 18% conversion of 91 gave a 97% yield of 99, whereas at 80% conversion, the yield of 99 was 68%. Alcohol 99, mp 72-73^0, has been identified as 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo-[3.3.0.0^{2,8}]oct-6-en-syn-4-ol. The infrared spectrum of 99



91 99

has a sharp absorption at 3580 cm^{-1} which determines the stereochemistry of the hydroxyl group as being syn to the benzene ring (42). The nmr spectrum of 99 consists of three-proton singlets at τ 10.00, 9.02, 8.93, 8.83, 8.67 and 8.62, a broad one-proton signal, τ 6.53-6.73, and an aromatic multiplet, τ 2.88-3.13 (4H).

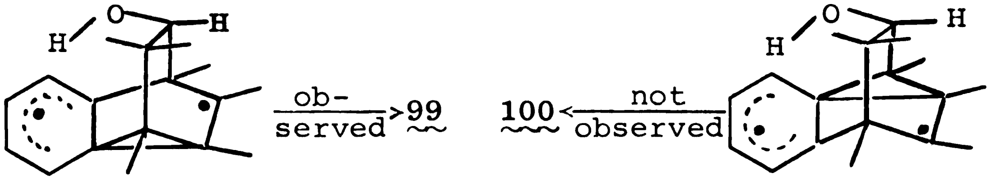
Oxidation of alcohol 99 with chromium trioxide-pyridine gave ketone 69, while reduction of 69 with lithium aluminum hydride provided only the syn-alcohol 99. Therefore



99 69

hydride attack on ketone 69 occurs exclusively *anti* to the benzene ring.

As alcohol 91 is unsymmetric with respect to its di-π-methane moiety, two different benzo-vinyl bridgings are possible. As shown in Figure 3, initial bridging of C-5 and C-8 (path a) would provide 99, whereas bridging C-6 and C-7 would give 100. However, acetone-sensitized irradiation of the *syn*-alcohol 91 affords only a single product, 99. No 100 was formed. The regiospecificity (40) in this rearrangement indicates a strong preference for intermediate 101 *vis-a-vis* 102. No such preference is observed in the



101

102

photorearrangement of the *anti*-alcohol 90. Possible factors which may contribute to the preference of 101 over 102 may be: (1) internal hydrogen bonding between the alcohol substituent and the π-electron system of the benzene ring, or (2) a charge-transfer interaction between the oxygen atom of the alcohol function and the π-electron system of the fused aromatic ring.

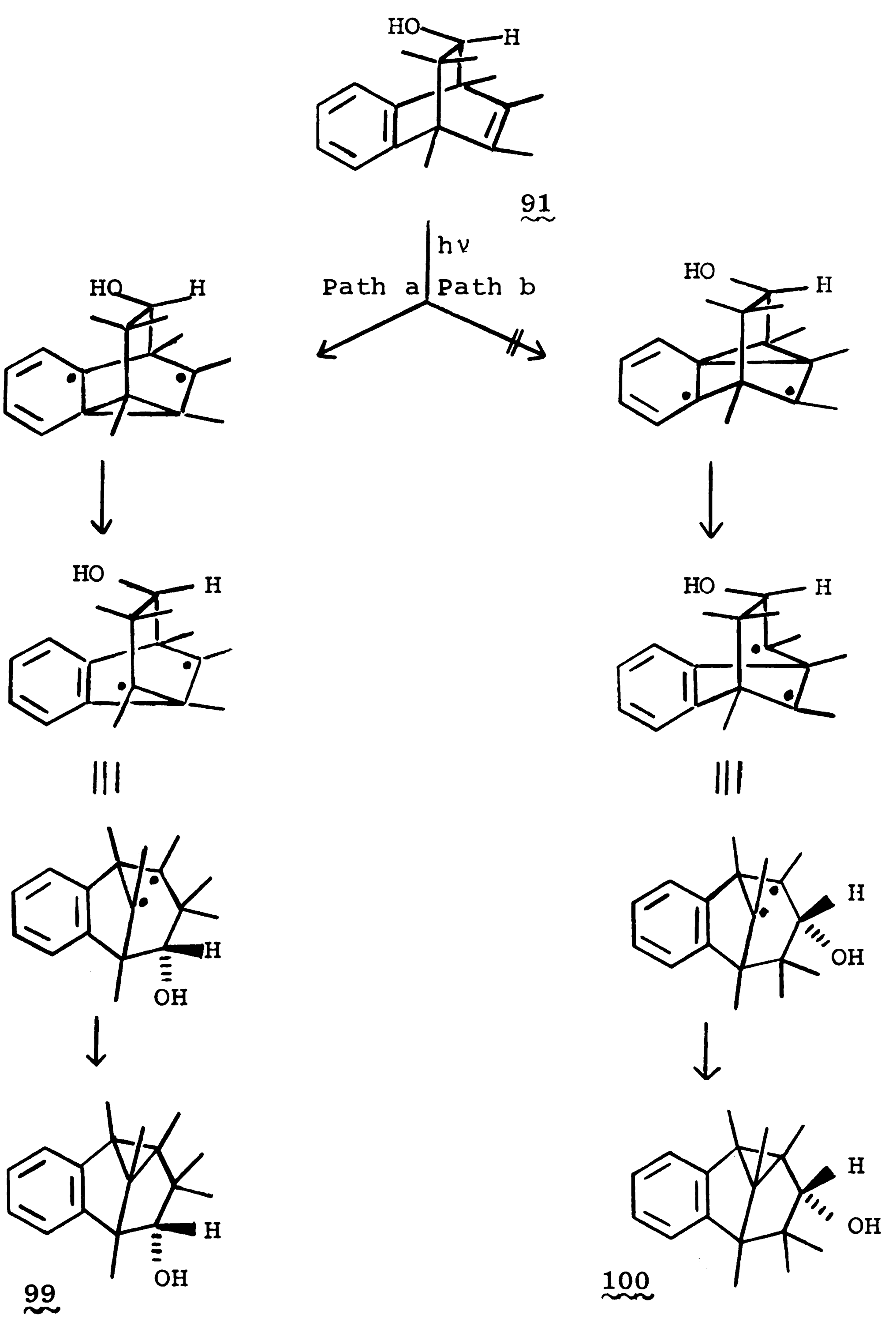


Figure 3. A detailed mechanism for the formation of 99 (or 100) from 91 *via* a di-π-methane photorearrangement.

EXPERIMENTAL

A. General Procedures

All ultraviolet spectra were measured with a Unicam Model SP-800 spectrophotometer. The infrared spectra were obtained on a Unicam Model SP-200 infrared spectrometer or a Perkin-Elmer Model 237B grating infrared spectrophotometer and all ir spectra were calibrated (polystyrene). The nmr spectra were measured with a Varian A-60 or a J.E.O.L. C-60H spectrometer using tetramethylsilane as an internal reference. The mass spectra were carried out by Mr. M. Petschel of this laboratory with a Consolidated Electrodynamic Corp. 21-103C instrument operating at an ionizing potential of 70v. Melting points were obtained with an Electrothermal melting point apparatus and are uncorrected. Elemental analyses are by Spang Microanalytical Laboratories, Ann Arbor, Michigan or Clark Microanalytical Laboratory, Urbana, Illinois.

B. General Photolysis Procedures

All irradiations were conducted with a 450-watt Hanovia Type L mercury lamp with the light filtered through a Corex glass sleeve. The solution to be irradiated was placed in a quartz test tube, sealed with a serum cap and attached to the outside of a Hanovia quartz immersion well, 2-3 cm from the center of the mercury arc. This apparatus was then placed in a water bath, which maintained the temperature of the solution during irradiation between 15 and 20^0.

The photolyses were monitored by withdrawal of small aliquots at various time intervals and examination of these by vapor phase chromatography (vpc). After the irradiations were completed, the solvent was removed at reduced pressure and a suitable internal standard was added to the crude reaction mixture. Analysis by vpc (using appropriate calibration curves) and/or nmr integration provided the reported yields. The vpc calibration curves were obtained by analysis of carefully prepared standard solutions of the reactants, products and standard. The specific method employed to determine the yield is noted in each experiment.

For each successful irradiation experiment reported, a control reaction was carried out in which a solution identical to that irradiated was prepared, sealed with a serum cap in a quartz test tube and stored in the dark. After two weeks the solvent was evaporated and ir and nmr spectra of the residue were obtained. Spectra identical to those of the starting material resulted in all cases. No "dark" reactions were detected in vpc analysis of the residues.

C. Irradiation of 1,3,3,4,7,8-Hexamethyl-5,6-dicarbomethoxybicyclo[2.2.2]octa-5,7-dien-2-one (**30**) in Diethyl Ether

A solution of 102 mg of **30** (22) in 10 ml of diethyl ether was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (10' x 1/4" SE-30 column; 220°; 50 ml/min of He) indicated the formation of a single photoproduct. The photoproduct was purified by vpc (above conditions) and was shown to be identical in all respects (mp: 126-127°; nmr spectrum (CCl_4): sharp singlets at τ 7.82 (12H) and 6.28 (6H); ir spectrum; R_t) with an authentic sample of dimethyl 3,4,5,6-tetramethylphthalate (**31**) previously prepared in this laboratory (22). Irradiation of an identical solution under the above conditions for two hours provided an 80% yield (vpc, p-dibromobenzene as standard) of **31**.

D. Irradiation of 1,3,3,4,7,8-Hexamethyl-5,6-diphenylbicyclo[2.2.2]octa-5,7-dien-2-one (**32**) in Diethyl Ether

A solution of 130 mg of **32** (22) in 10 ml of diethyl ether was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (5' x 1/8" SE-30 column, 280°, 90 ml/min of He) indicated the formation of a single photoproduct. Monitoring the photolysis by uv revealed a sharp decrease in the shoulder absorption of **32** at 300-310 mμ. The uv spectrum remained constant after three hours irradiation. The photoproduct was purified by chromatography on silica gel (pentane eluant) and was shown to be identical in all respects (mp: 125-127°; nmr spectrum (CCl_4): six-proton singlets at τ 8.04 and 7.73 and a broad aromatic multiplet, τ 3.03-3.23 (10H); ir spectrum) with an authentic sample of 3,4,5,6-tetramethyl-1,2-diphenylbenzene (33) previously prepared in this laboratory (22). Irradiation of an identical solution under the above conditions for three hours provided an 83% yield (vpc, hexamethylbenzene as standard; nmr, methylene bromide as standard) of 33.

Similarly, a solution of 101 mg (2.8×10^{-4} mole) of 32 in 10 ml of diethyl ether was sealed in a quartz test tube and irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp for four hours. Upon completion of the irradiation, the solution was treated with 48 mg (5.6×10^{-4} mole) of aniline. After evaporation of the solvent, the photosylate residue was chromatographed on silica gel. Elution with pentane provided 65 mg of 33, and further elution with methylene chloride-ethanol (1:1) gave 35 mg of a solid, mp 100-102°. This material proved to be identical (mixed mp and ir spectrum) with an authentic sample of isobutyranilide (35).

E. A Low Temperature Study of the Photolysis of 1,3,3,4,7,8-Hexamethyl-5,6-diphenylbicyclo[2.2.2]octa-5,7-dien-2-one (32)

The apparatus used in this experiment was designed by Dr. John Griffiths of this laboratory. This apparatus consisted of a lead block (designed to hold liquid nitrogen) into which a sodium chloride cavity cell (0.2 mm pathlength) could be set via a hole suitably drilled in the block. The metal block was insulated by a close fitting styrofoam box. When the reservoir was filled with liquid nitrogen, the cell was cooled to an equilibrium temperature of $-100^0 \pm 10^0$C. Suitable aperatures were placed in the metal block and the styrofoam box which permitted ir measurements and irradiation of the cell to be made. Icing of the cavity cell windows was minimized by passing a vigorous stream of very dry nitrogen over the cell windows throughout the experiment.

A solution of 20 mg of 32 in one ml of 2-methyltetrahydrofuran was sealed in the cavity cell inside the styrofoam block and cooled to -100^0 with liquid nitrogen. The ir spectrum of the solution was then recorded, using a similar pathlength cell containing 2-methyltetrahydrofuran as reference. The ir spectrum showed the strong carbonyl absorption of 32 at 1705 cm^{-1}. A parallel beam of radiation from an enclosed 450-watt Hanovia Type L mercury lamp was filtered through Corex and diverted into the cavity cell. Examination of the ir spectrum after irradiation for five minutes indicated a decrease in the intensity of the absorption at 1705 cm^{-1} and the appearance of a sharp intense absorption at 2135 cm^{-1}, which is attributed to the formation of dimethyl ketene, 34. Examination of the ir spectra after total irradiation periods of 10 min, 25 min, 40 min, and 60 min showed a progressive decrease in the absorption at 1705 cm^{-1} and an increase in the intensity of the absorption at 2135 cm^{-1}. When the solution was warmed to room temperature, the dimethyl ketene absorption band at 2135 cm^{-1} gradually disappeared.

F. Photolysis of 1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (46) in Diethyl Ether

A solution of 100 mg of 46 (23,28) in 10 ml of diethyl ether was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (10' x 1/4" SE-30 column; 220°; 50 ml/min of He) indicated the formation of two photoproducts. The photoproducts were purified by vpc (above conditions). The compound with longer R_t was shown to be identical in all respects (mp: 105-107°; nmr spectrum (CCl_4): six-proton singlets at τ 7.62 and 7.43 and aromatic multiplets centered at τ 2.72 (2H) and τ 2.10 (2H); ir spectrum) with an authentic sample (prepared by a modification (50) of the method of Hewett (51)) of 1,2,3,4-tetramethylnaphthalene, 47. The compound with the shorter R_t has been identified as 1,4,4,5,6,7-hexamethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, 48. The mass spectrum of this colorless oil showed a parent peak at m/e 226. The ultraviolet spectrum of **48** in 95% ethanol had maxima at 274 (ε 1910), 267 (ε 1980), and 211 mμ (ε 8580) with shoulders at 262 (ε 1470) and 230 mμ (ε 4860). The nmr spectrum (CCl_4) of **48** (Figure 4) consisted of singlets at τ 8.95 (3H), 8.83 (3H) and 8.75 (6H), quartets at τ 8.53 and 8.50 (3H each, J = 1.2 Hz), and a singlet at τ 3.05 (4H, aromatic protons).

Anal. Calcd. for $C_{17}H_{22}$: C, 90.20; H, 9.80

Found: C, 90.25; H, 9.72.

When an identical solution of **46** in diethyl ether was irradiated under the above conditions for six hours, the reaction proceeded with 86% conversion (vpc, p-dibromobenzene as standard) of **46** to give an 82% yield of 1,2,3,4-tetramethylnaphthalene and a 13% yield of **48**.

G. Photolysis of 4-Methyl-d_3-1,3,3,7,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (103) in Diethyl Ether

Irradiation of a solution of 150 mg of **103** (28) in 11 ml of diethyl ether through a Corex filter with a 450-watt Hanovia Type L mercury lamp for eight hours provided a mixture of two photoproducts which were separated by vpc (10' x 1/4" SE-30 column; 220°; 50 ml/min of He). The nmr spectrum (CCl_4) of the compound with the shorter R_t consisted of singlets at τ 8.96 (3H) and 8.76 (6H), a multiplet at τ 8.53-8.50 (6H) and a singlet at τ 3.03 (4H, aromatic protons). Thus the nmr spectrum of this

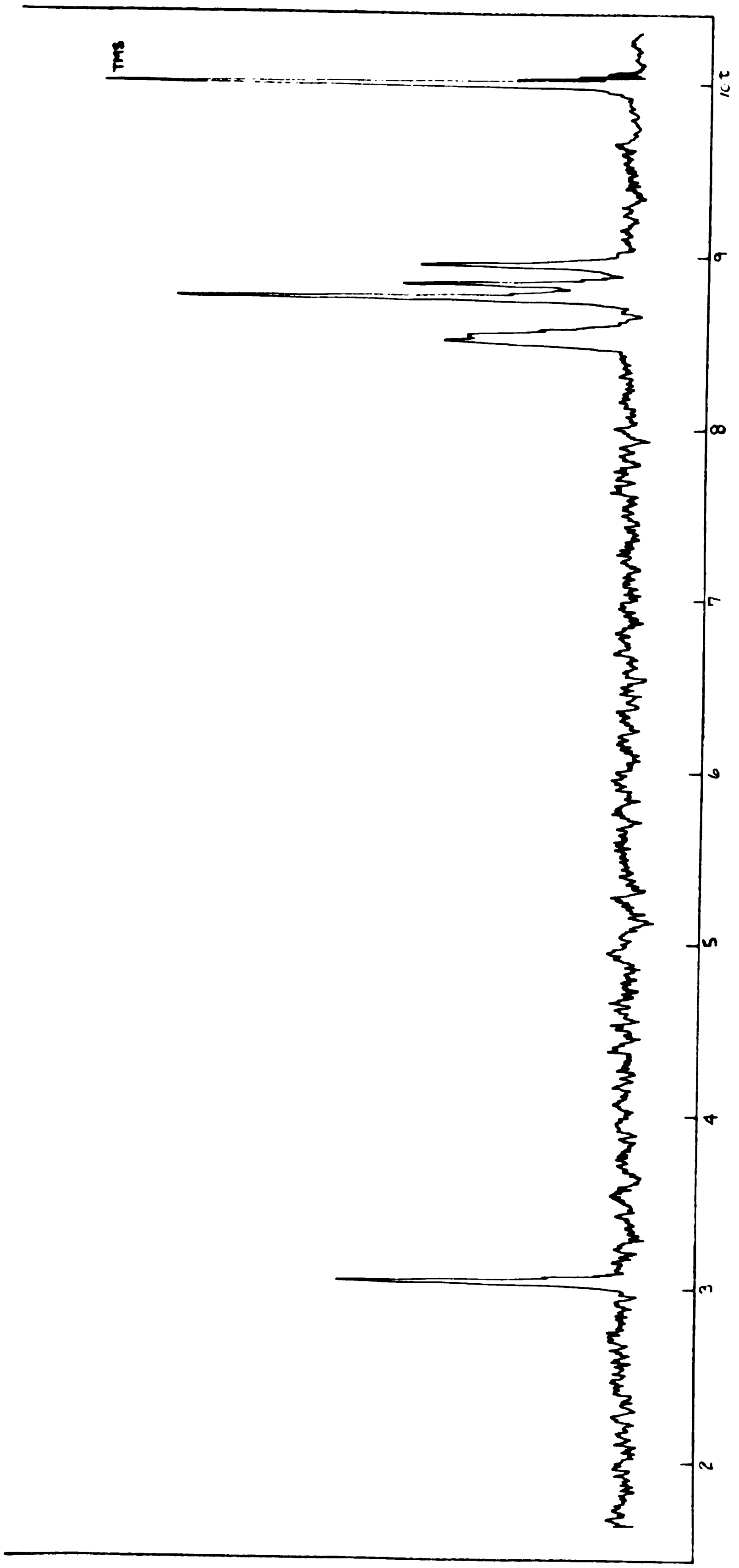


Figure 4. Nmr spectrum (CCl_4) of 1,4,4,5,6,7-hexamethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (48).

photoproduct is essentially identical with that of unlabeled 48 except for the absence here of the peak at τ 8.83 in 48.

H. Photolysis of 7-Methyl-d_3-1,3,3,4,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (104) in Diethyl Ether

Irradiation of a solution of 124 mg of 104 (28) in 10 ml of diethyl ether through a Corex filter with a 450-watt Hanovia Type L mercury lamp for eight hours gave a mixture of two photoproducts which were separated by vpc (10' x 1/4" SE-30 column; 220^0; 50 ml/min of He). The nmr spectrum (CCl_4) of the compound with the shorter R_t consisted of singlets at τ 8.94 (3H), 8.84 (3H), 8.72 (6H), 8.50 (3H) and 3.06 (4H). Examination of the nmr spectrum at a sweep width of 50 cycles confirmed the signal at τ 8.50 to be a singlet. Thus the quartets at τ 8.53 and 8.50 (3H each, J = 1.2 Hz) of unlabeled 48 have been replaced here with a singlet at τ 8.50.

I. Irradiation of 3,3,7,8-Tetramethyl-5,6-benzobicyclo-[2.2.2]octa-5,7-dien-2-one (56) in Diethyl Ether

A solution of 100 mg of 56 (22) in 10 ml of diethyl ether was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (10' x 1/4" SE-30 column; 220^0; 60 ml/min of He) indicated the formation of two photoproducts. The photoproducts were purified by vpc (above conditions). The compound with longer R_t was shown to be identical in all respects (mp: 105-108°; mixed mp; ir and nmr spectra) with an authentic sample (Aldrich Chemical Co., recrystallized twice from ethanol) of 2,3-dimethylnaphthalene, **57**. The compound with the shorter R_t has been identified as *4,4,6,7-tetramethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene*, **58**. The ultraviolet spectrum of this clear oil in 95% ethanol showed maxima at 273 (ε 1560), 266 (ε 1450), 260 (ε 1020) and 228 mμ (ε 2230) with shoulders at 253 (ε 620) and 213 mμ (ε 1920). The nmr spectrum (CCl_4) of **58** (Figure 5) consisted of three-proton singlets at τ 8.90 and 8.70, overlapping quartets at τ 8.43 and 8.41 (6H together, J = 1.2 Hz), broad (h_w = 4.5 cycles) one-proton singlets at τ 7.13 and 6.31 and a singlet at τ 3.04 (4H, aromatic protons).

Anal. Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15

Found: C, 90.77; H, 9.21.

When a solution of 70 mg of **56** in 7 ml of diethyl ether was irradiated under the above conditions for four hours, the reaction gave a 70% yield (vpc, *p*-dibromobenzene as standard; nmr, methylene bromide as standard) of 2,3-dimethylnaphthalene and an 8% yield of **58**.

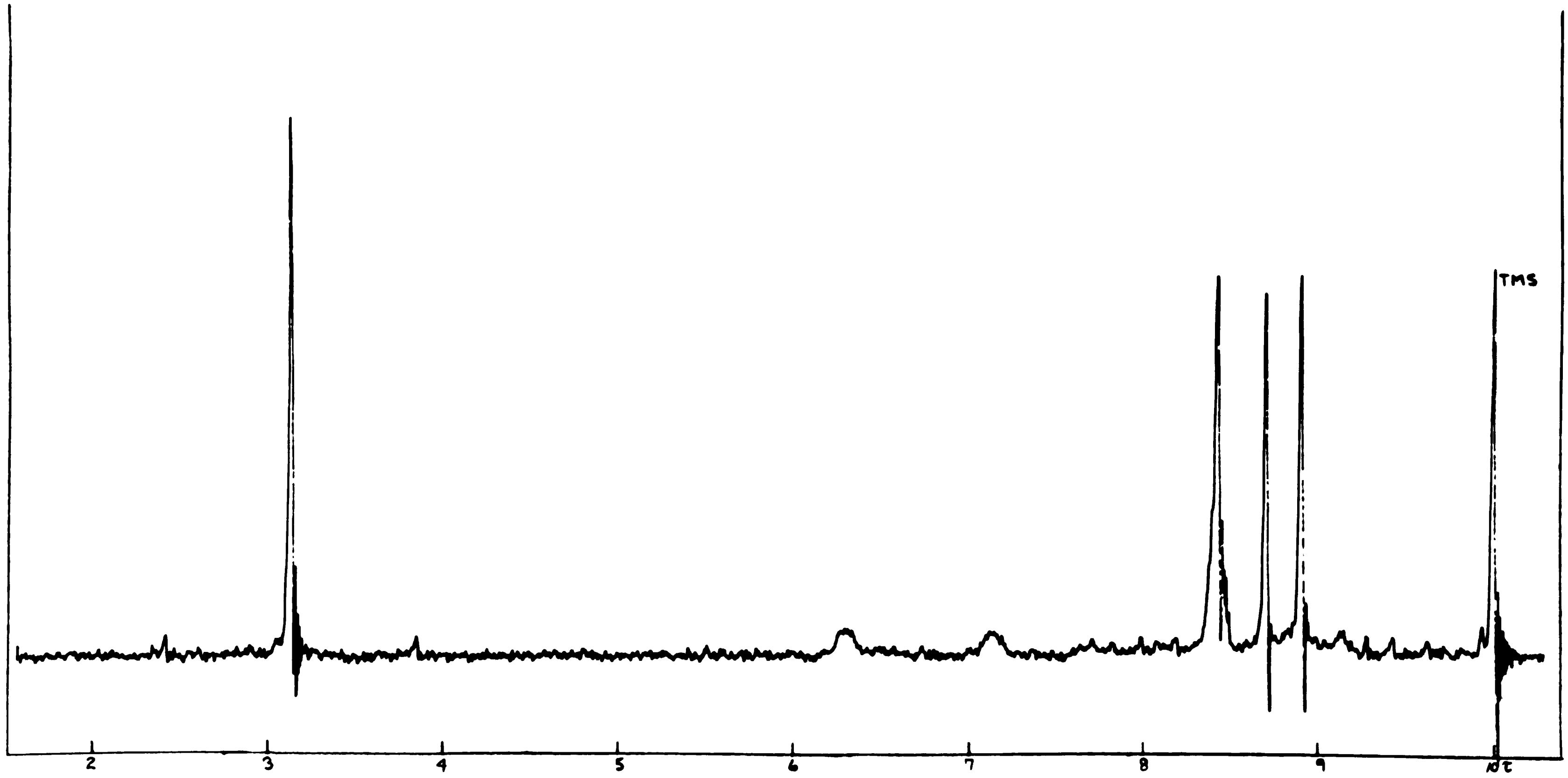


Figure 5. Nmr spectrum (CCl_4) of 4,4,6,7-tetramethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (58).

J. Irradiation of 1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (46) in Acetone

A solution of 110 mg of 46 (23,28) in 10 ml of acetone was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (10' x 1/4" SE-30 column; 220°; 50 ml/min of He) indicated the formation of three photoproducts. The photoproducts were purified by vpc (above conditions). The main product (intermediate R_t) was shown to be identical in all respects (mp, ir and nmr spectra, R_t) with an authentic sample (prepared by a modification (50) of the method of Hewett (51)) of 1,2,3,4-tetramethylnaphthalene, 47. The compound with the shortest R_t was identified (R_t, ir and nmr spectra) as 1,4,4,5,6,7-hexamethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, 48 (see Section F for spectral characteristics and analysis). The compound with the longest R_t has been identified as 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo$[3.3.0.0^{2,8}]$oct-6-en-3-one, 68. This white solid, mp 100-102°, showed an intense absorption in the ir (CCl_4) at 1720 cm^{-1} ($\nu_{C=O}$) and its ultraviolet spectrum (95% ethanol) had maxima at 278 (ε 1150) and 270 mμ (ε 1370) with a shoulder at 263 mμ (ε 1450). The nmr spectrum of 68 in CCl_4 (Figure 6) consisted of three-proton singlets at τ 9.44, 8.94, 8.74 and 8.69, a six-proton singlet at τ 8.60 and an aromatic multiplet, τ 2.85-3.14 (4H); while the nmr spectrum of 68 in CD_3CN showed three-proton singlets at τ 9.44, 8.90, 8.74, 8.68, 8.63 and 8.57 and an aromatic multiplet, τ 2.90-3.22 (4H).

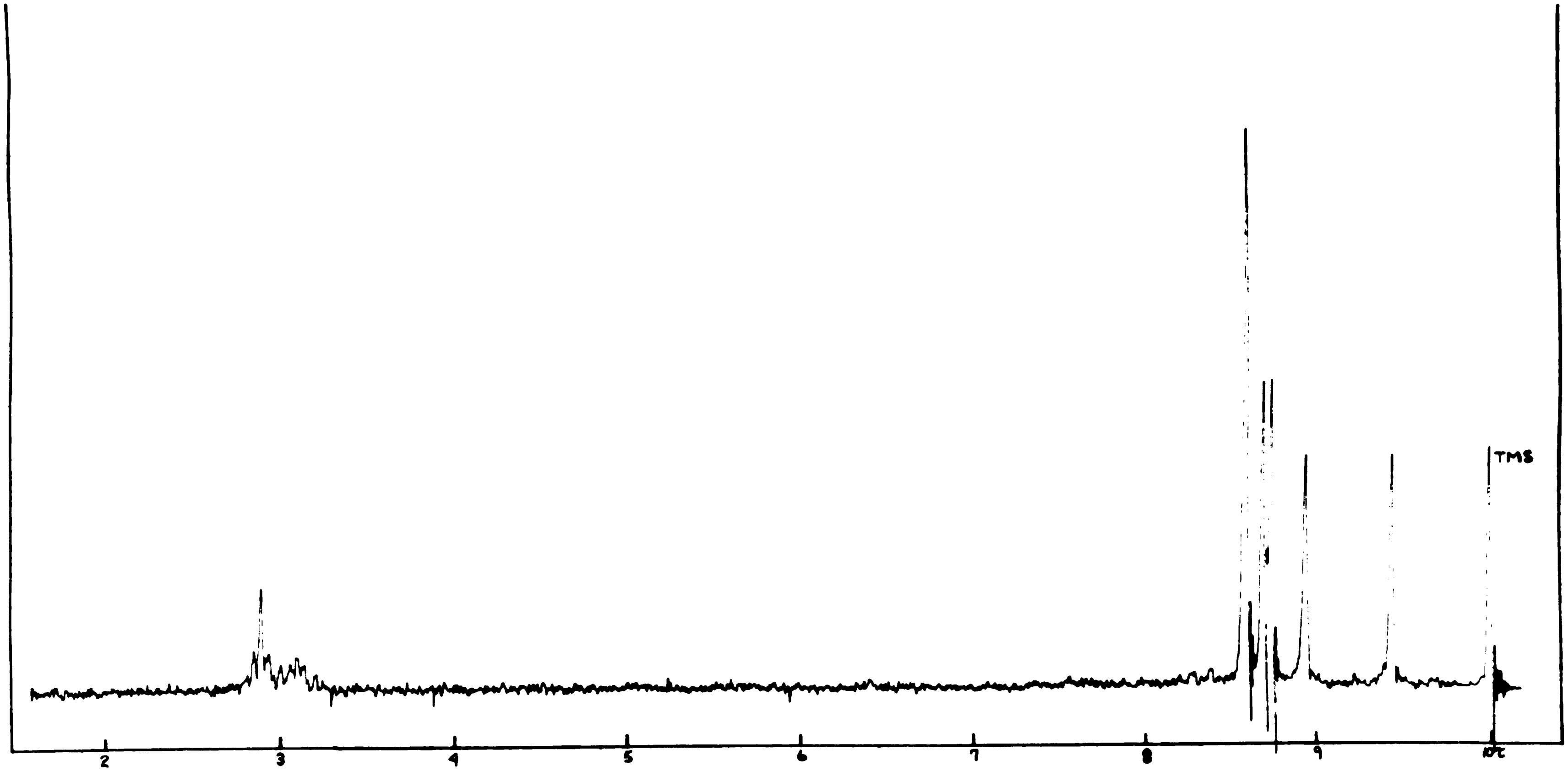


Figure 6. Nmr spectrum (CCl_4) of 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-en-3-one (68).

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72

Found : C, 84.65; H, 8.54.

Irradiation of a solution of 101 mg of 46 in 10 ml of acetone under the above conditions for nine hours proceeded with 91% conversion of 46 and gave a 45% yield (vpc, *p*-dibromobenzene as standard; nmr, methylene bromide as standard) of 1,2,3,4-tetramethylnaphthalene, a 6% yield of 48 , and a 26% yield of the ketonic product 68.

K. Irradiation of 4-Methyl-d_3-1,3,3,7,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (76) in Acetone

Irradiation of a solution of 105 mg of 76 (28) in 10 ml of acetone through a Corex filter with a 450-watt Hanovia Type L mercury lamp for 9.5 hours afforded a mixture of three photoproducts which were separated by vpc (10' x 1/4" SE-30 column; 220°; 50 ml/min of He). The nmr spectrum (CCl_4) of the compound with the longest R_t (the ketonic photoproduct) showed singlets at τ 9.44 (3H), 8.95 (3H), 8.75 (3H), 8.70 (3H) and 8.60 (3H) and a multiplet τ 2.86-3.15 (4H, aromatic protons). Comparison of this nmr spectrum with that of unlabeled 68 shows that the six-proton singlet at τ 8.60 in 68 now integrates for only three protons. The nmr spectrum of this labeled ketonic photoproduct n CD_3CN consisted of three-proton singlets at τ 9.44, 8.90, .74, 8.68 and 8.62 and an aromatic multiplet, τ 2.75-3.06 4H). Thus this nmr spectrum of the labeled ketonic photo-roduct differs from that of unlabeled 68 (in CD_3CN) in the bsence here of the peak at τ 8.57 in 68.

L. Irradiation of 7-Methyl-d_3-1,3,3,4,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (78) in Acetone

Photolysis of a solution of 100 mg of 78 (28)in 12 ml of acetone through a Corex filter with a 450-watt Hanovia Type L mercury lamp for nine hours provided a mixture of three photoproducts which were separated by vpc (10' x 1/4" SE-30 column; 220°; 50 ml/min of He). The nmr spectrum (CCl_4) of the compound with the longest R_t (the ketonic photoproduct) has singlets at τ 9.44 (3H), 8.95 (3H), 8.70 (3H), 8.60 (6H) and a multiplet τ 2.88-3.20 (4H, aromatic protons). Thus the three-proton singlet at τ 8.75 present in the nmr spectrum of unlabeled 68 is absent here.

M. Irradiation of 3,3,7,8-Tetramethyl-5,6-benzobicyclo-[2.2.2]octa-5,7-dien-2-one (56) in Acetone

A solution of 120 mg of 56 (22) in 10 ml of acetone was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (10' x 1/4" SE-30 column; 220°; 60 ml/min of He) indicated the formation of three photoproducts. The photoproducts were separated and purified by vpc (above conditions). The main product (intermediate R_t) was shown to
e identical in all respects (mp, ir and nmr spectra, R_t)
ith an authentic sample (Aldrich Chemical Co., recrystal-
ized twice from ethanol) of 2,3-dimethylnaphthalene, 57.
he compound with the shortest R_t was identified (R_t, ir

spectrum) as 4,4,6,7-tetramethyl-2,3-benzobicyclo[3.2.0]-hepta-2,6-diene, 58 (see Section I for spectral characteristics and analysis). The compound with the longest R_t has been identified as 1,2,4,4-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-3-one, 70. The ir spectrum (CCl_4) of this clear oil showed a strong absorption at 1721 cm^{-1} ($\nu_{C=O}$) and its ultraviolet spectrum (95% ethanol) had maxima at 279 (ε 660) and 271 mμ (ε 840) with a shoulder at 263 mμ (ε 930). The nmr spectrum of 70 in CCl_4 (Figure 7) consisted of three-proton singlets at τ 9.38, 8.79, 8.65 and 8.44, sharp one-proton singlets at τ 7.80 and 6.97 and an aromatic multiplet, τ 2.81-3.10 (4H).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02

Found: C, 84.76; H, 8.05.

Irradiation of a solution of 71 mg of 56 in 7 ml of acetone under the above conditions for four hours proceeded with 96% conversion of 56 and gave a 66% yield (nmr, methylene bromide as standard) of 2,3-dimethylnaphthalene, a 6% yield of 58, and a 9% yield of the ketonic product 70.

N. Reduction of 1,2,4,4-Tetramethyl-6,7-benzotricyclo-[3.3.0.0^{2,8}]oct-6-en-3-one (70) with Lithium Aluminum Hydride

A solution of 52 mg of 70 in 10 ml of dry tetrahydrofuran was added during 15 min to a suspension of 364 mg of lithium aluminum hydride in 20 ml of dry, vigorously stirred, refluxing tetrahydrofuran. The mixture was stirred at

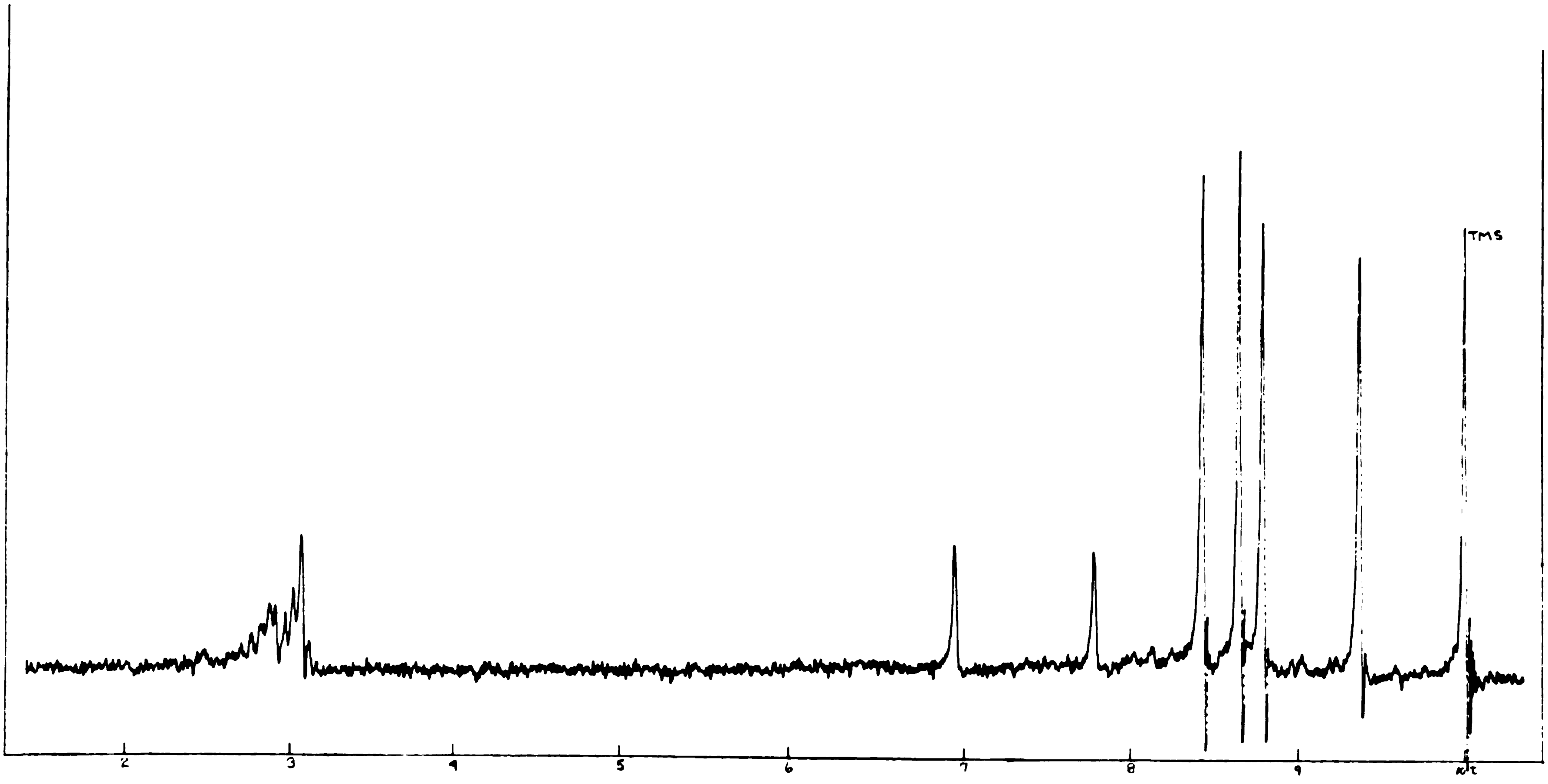


Figure 7. Nmr spectrum (CCl_4) of 1,2,4,4-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (70).

reflux for an additional three hours, then cooled in an ice bath, and small pieces of ice were added to hydrolyze the excess lithium aluminum hydride. To this mixture was added 8 ml of water. The resulting mixture was extracted with ether (3 x 20 ml) and the separated ether layer was dried over anhydrous magnesium sulfate. Evaporation of the ether solution provided an oil which when examined by vpc (10' x 1/4" FFAP column; 210°; 60 ml/min of He) showed a single reduction product. This compound was purified by vpc (above conditions) and has been identified as 1,2,4,4-tetramethyl-6,7-benzotricyclo[$3.3.0.0^{2,8}$]oct-6-en-*anti*-3-ol, (**73**). The ir spectrum (CCl_4) of this clear oil showed a sharp absorption at 3644 cm^{-1} (ν_{O-H}). The nmr spectrum of **73** in CCl_4 (Figure 8) had three-proton singlets at τ 9.22, 8.95, 8.80 and 8.57, sharp one-proton singlets at τ 8.20, 7.30 and 6.92 and an aromatic multiplet, τ 2.90-3.13 (4H).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83

Found: C, 83.94; H, 8.90.

O. Irradiation of 1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo-[2.2.2]octa-5,7-dien-*anti*-2-ol (**90**) in Acetone

A solution of 80 mg of **90** (28) in 8 ml of acetone was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (10' x 1/4" FFAP column; 220°; 100 ml/min of He) indicated the formation of two photoproducts. The photoproducts were separated and purified by vpc (above conditions). The compound with

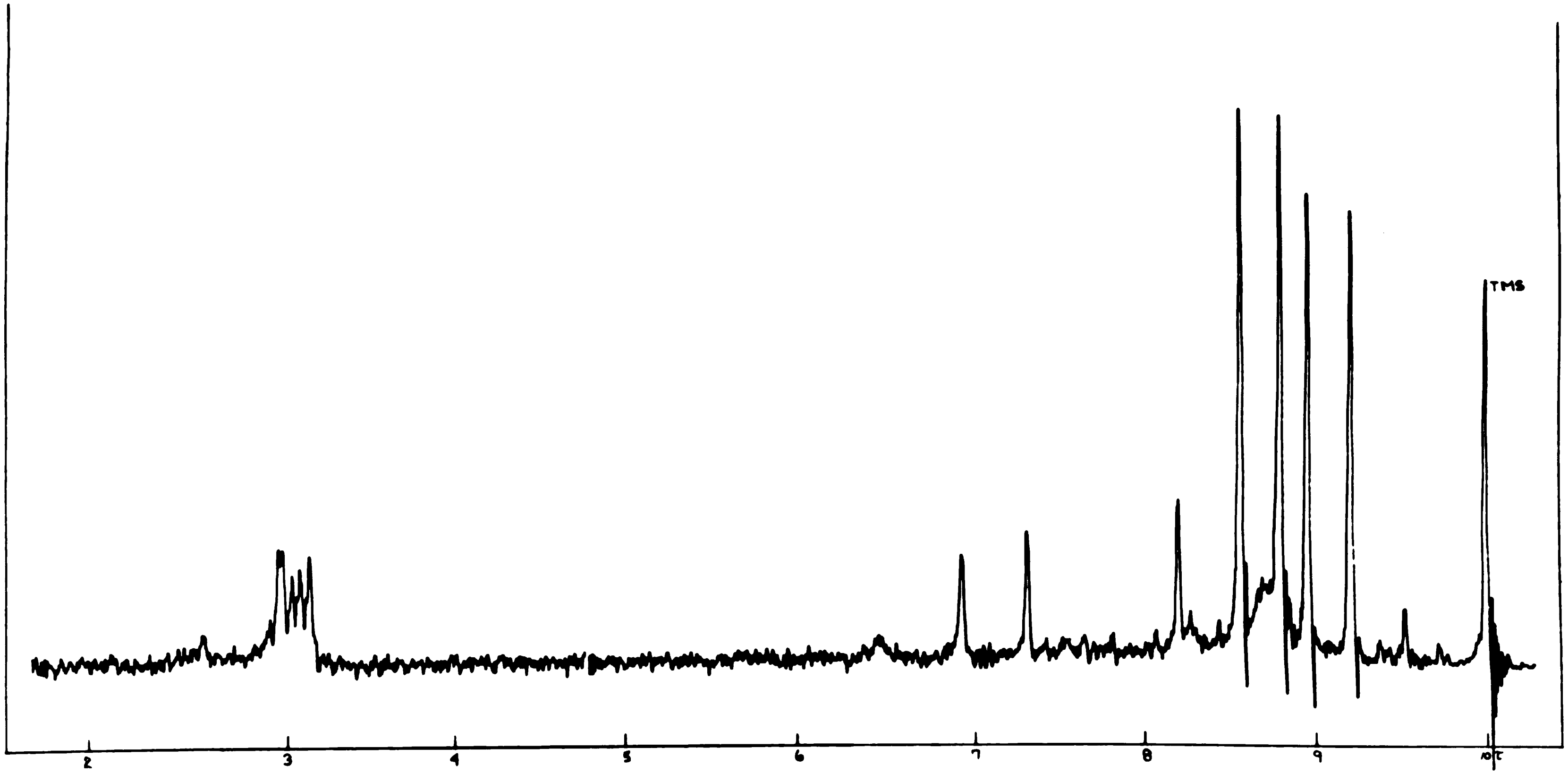


Figure 8. Nmr spectrum (CCl_4) of 1,2,4,4-tetramethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]-oct-6-en-anti-3-ol (73).

the shorter R_t has been identified as *1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-anti-4-ol*, **92**. This white solid, mp 81-83^0, showed a sharp absorption in the ir (CCl_4) at 3638 cm^{-1} (ν_{O-H}). The nmr spectrum of **92** in CCl_4 (Figure 9) consisted of three-proton singlets at τ 9.88, 9.03, 8.95, 8.83, 8.67 and 8.63, a one-proton singlet at τ 6.78 and an aromatic multiplet, τ 2.94-3.04 (4H).

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44

Found: C, 84.16; H, 9.33.

The compound with the longer R_t has been identified as *1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-anti-3-ol*, **93**. This white solid, mp 90-92^0, showed a sharp absorption in the infrared (CCl_4) at 3642 cm^{-1}. The nmr spectrum of **93** in CCl_4 (Figure 10) had three-proton singlets at τ 9.33, 9.13, 8.90, 8.85, 8.80 and 8.67, a one-proton singlet at τ 7.08 and an aromatic multiplet, τ 2.94-3.20 (4H).

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44

Found: C, 84.08; H, 9.26.

When a solution of 70 mg of **90** in 10 ml of acetone was irradiated under the above conditions for two hours, the reaction proceeded with 85% conversion (nmr, hexamethylbenzene as standard) of **90** and gave a 44% yield of **92** and a 29% yield of **93**.

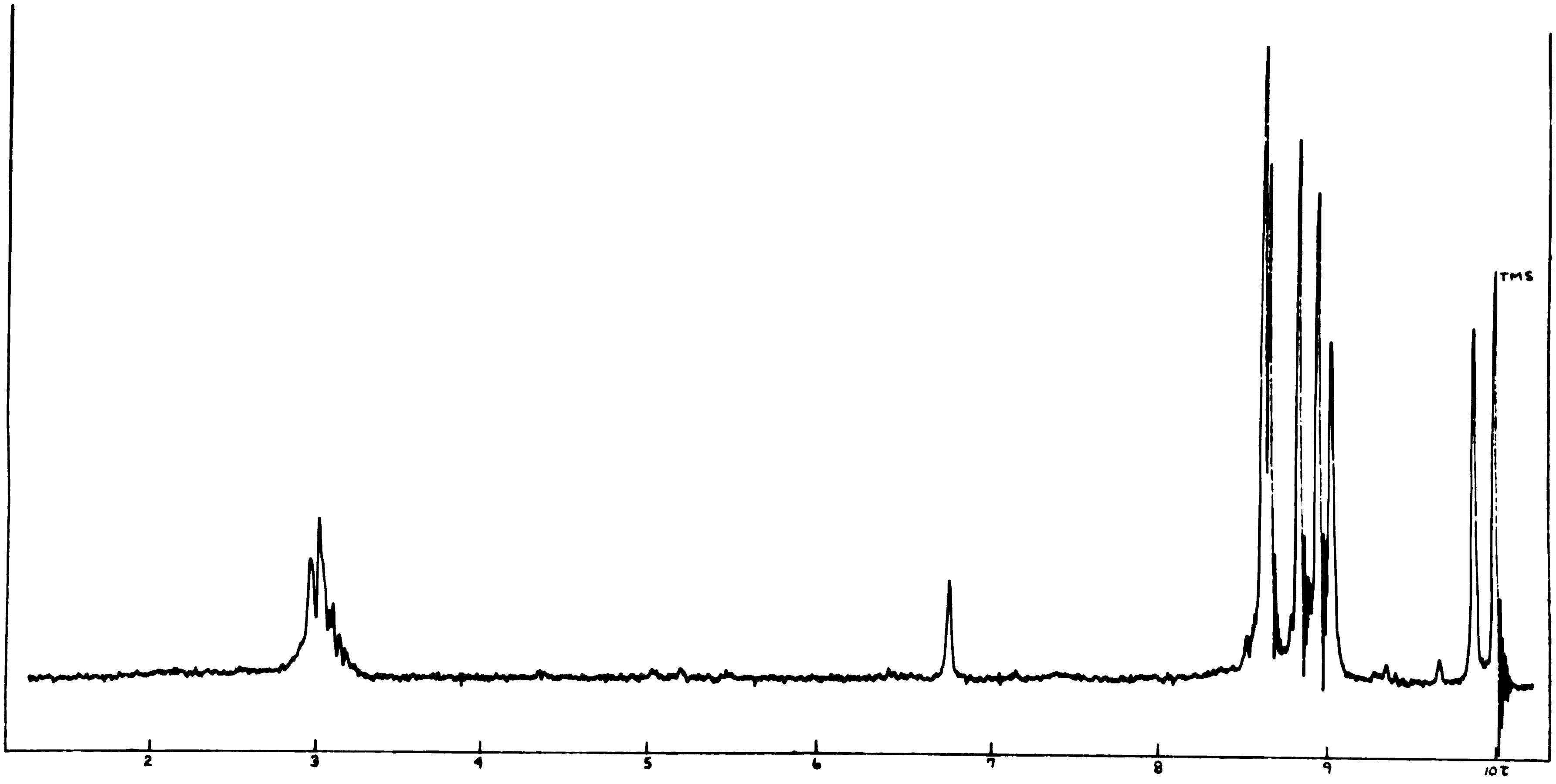


Figure 9. Nmr spectrum (CCl_4) of 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-anti-4-ol (92).

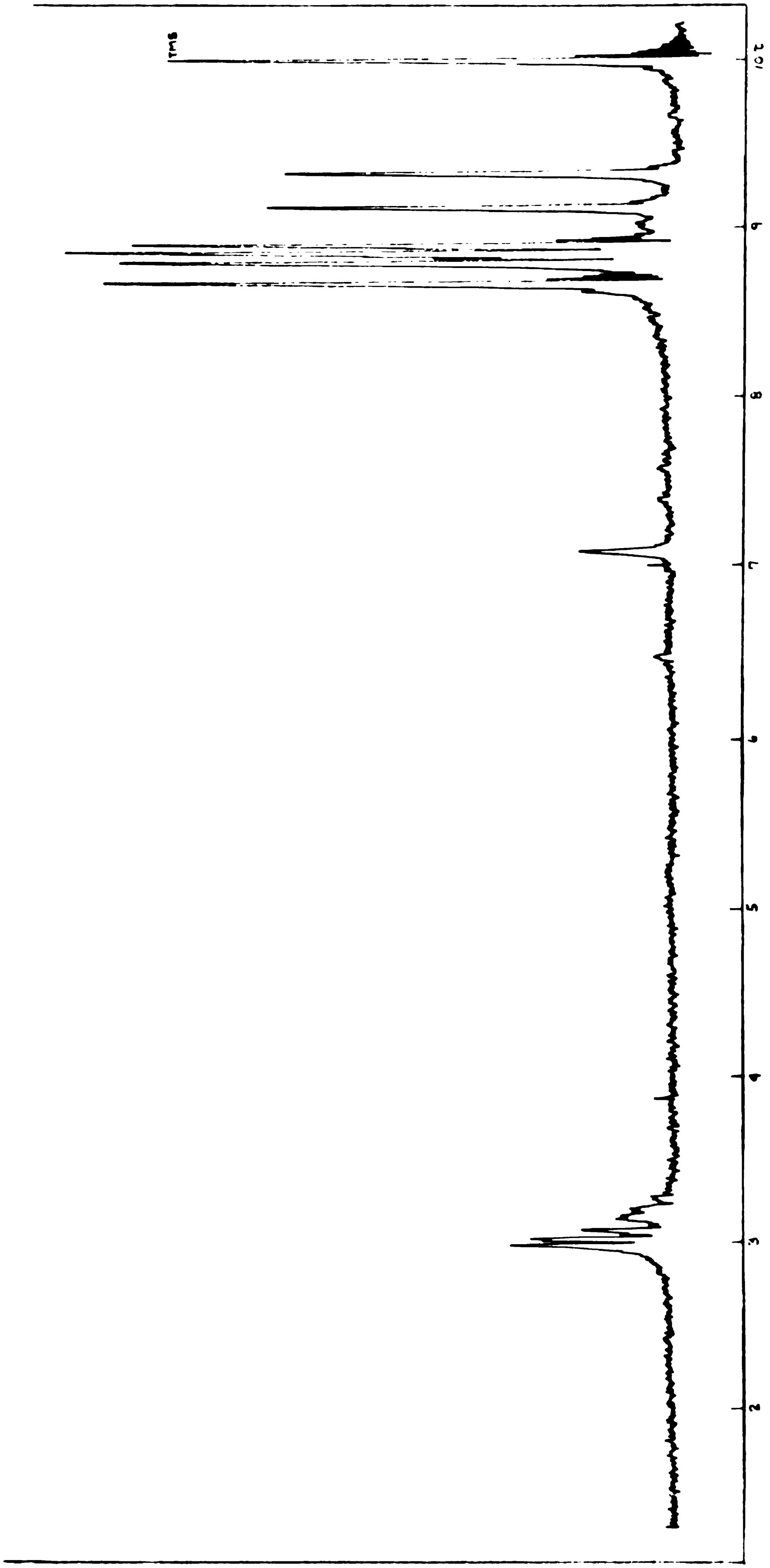


Figure 10. Nmr spectrum (CCl$_4$) of 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-*anti*-3-ol (**93**).

P. Oxidation of 1,2,3,3,5,8-Hexamethyl-6,7-benzotricyclo-[3.3.0.$0^{2,8}$]oct-6-en-*anti*-4-ol (92) with Chromium Trioxide-Pyridine

A solution of 30 mg of 92 in pyridine (1.0 ml) was added to the ice-cooled complex (52) prepared from chromium trioxide (385 mg) and pyridine (1.5 ml) and the mixture was left at room temperature for 46 hrs. Methanol (0.8 ml) and water (3.0 ml) were then added to the mixture and the result was extracted with ether (3 x 15 ml). The organic layer was dried over anhydrous magnesium sulfate and then evaporated to provide 30 mg of a white solid. This residue was purified by vpc (10' x 1/4" FFAP column; 220^{0}; 100 ml/min of He) and afforded a single white solid which was identified (mp, mixed mp, ir spectrum, R_t) as 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-en-4-one, 69 (see Section T for spectral characteristics and analysis).

Q. Oxidation of 1,2,4,4,5,8-Hexamethyl-6,7-benzotricyclo-[3.3.0.$0^{2,8}$]oct-6-en-*anti*-3-ol (93) with Chromium Trioxide-Pyridine

A solution of 19 mg of 93 in pyridine (1.0 ml) was added to the ice-cooled complex (52) prepared from chromium trioxide (385 mg) and pyridine (1.5 ml) and the mixture was left at room temperature for 41 hrs. Methanol (0.8 ml) and water (3.0 ml) were then added to the mixture and the result was extracted with ether (3 x 15 ml). The organic layer was dried over anhydrous magnesium sulfate and then evaporated to provide 18 mg of an off-white solid which was identified (mp, mixed mp, ir spectrum, R_t) as 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-en-3-one, **68** (see Section J for spectral characteristics and analysis).

R. Reduction of 1,2,4,4,5,8-Hexamethyl-6,7-benzotricyclo-[3.3.0.$0^{2,8}$]oct-6-en-3-one (**68**) with Lithium Aluminum Hydride

A solution of 150 mg of **68** in 10 ml of dry tetrahydrofuran was added in 10 min to a suspension of 600 mg of lithium aluminum hydride in 15 ml of dry, vigorously stirred, refluxing tetrahydrofuran. The mixture was stirred at reflux for an additional 15 hrs, then cooled in an ice bath, and small pieces of ice were added to hydrolyze the excess lithium aluminum hydride. To this mixture was added 8 ml of water. The resulting mixture was extracted with ether (3 x 20 ml) and the separated ether layer was dried over anhydrous magnesium sulfate. Evaporation of the ether solution provided a solid which when examined by vpc (10'x 1/4" FFAP column; 220°; 100 ml/min of He) showed a single reduction product. This compound was purified by vpc (above conditions) and has been identified (mp, mixed mp, ir and nmr spectra) as 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.$0^{2,8}$]oct-6-en-*anti*-3-ol, **93** (see Section O for spectral characteristics and analysis).

S. Irradiation of 1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-*syn*-2-ol (91) in Acetone

A solution of 120 mg of 91 (28) in 10 ml of acetone was irradiated through a Corex filter with a 450-watt Hanovia Type L mercury lamp. Monitoring the photolysis by vpc (10' x 1/4" FFAP column; 220°; 100 ml/min of He) indicated the formation of a single photoproduct. This compound was purified by vpc (above conditions) and has been identified as 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-*syn*-4-ol, 99. This white solid, mp 72-73°, showed a sharp absorption in the infrared (CCl_4) at 3580 cm^{-1} (ν_{O-H}). The nmr spectrum of 99 in CCl_4 (Figure 11) had three-proton singlets at τ 10.00, 9.02, 8.93, 8.83, 8.67 and 8.62, a broad one-proton signal at τ 6.53-6.73 and an aromatic multiplet, τ 2.88-3.13 (4H).

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44

Found: C, 84.33; H, 9.27.

When a solution of 67 mg of 91 in 7 ml of acetone was irradiated under the same conditions for ten min, the reaction proceeded with 18% conversion (nmr, hexamethylbenzene as standard) of 91 and gave a 97% yield of 99. When a solution of 70 mg of 91 in 10 ml of acetone was irradiated under the same conditions for 45 min, the reaction proceeded with 80% conversion (vpc, hexamethylbenzene as standard; nmr, hexamethylbenzene as standard) of 91 and gave a 68% yield of 99.

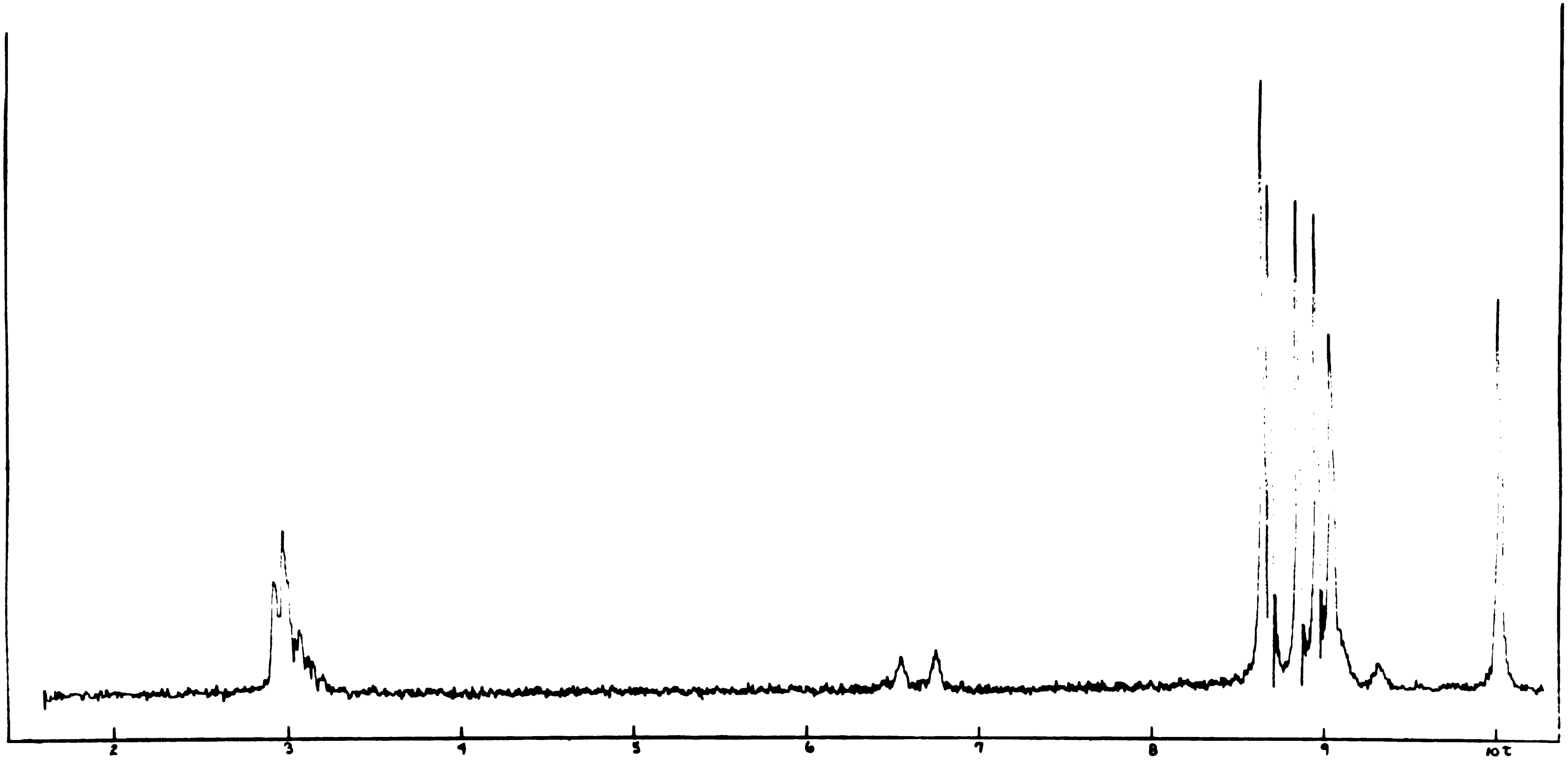


Figure 11, Nmr spectrum (CCl_4, no TMS) of 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo-[3.3.0.0^{2,8}]oct-6-en-_syn_-4-ol (99).

Oxidation of 1,2,3,3,5,8-Hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-*syn*-4-ol (99) with Chromium Trioxide-Pyridine

A solution of 71 mg of 99 in 2.0 ml of pyridine was added to the ice-cooled complex (52) prepared from chromium trioxide (770 mg) and pyridine (3.0 ml) and the mixture was left at room temperature for 48 hrs. Methanol (1.6 ml) and water (6.0 ml) were then added to the mixture and the result was extracted with ether (3 x 15 ml). The organic layer was dried over anhydrous magnesium sulfate and then evaporated to provide an off-white solid which when examined by vpc (10' x 1/4" FFAP column; 220°; 100 ml/min of He) indicated the presence of a single product. This compound was purified by vpc (above conditions) and has been identified as 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-4-one, 69. This white solid, mp 87-88.5°, showed an intense absorption in the ir (CCl_4) at 1725 cm^{-1} ($\nu_{C=O}$) and its ultraviolet spectrum (95% ethanol) has a maximum at 292 mμ (ε 1290) with shoulders at 313 (ε 800), 301 (ε 1230) and 247 mμ (ε 2980). The nmr spectrum of 69 in CCl_4 (Figure 12) consisted of three-proton singlets at τ 9.50, 9.00, 8.80, 8.77, 8.58 and 8.50 and an aromatic multiplet, τ 2.92-3.08 (4H).

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72

Found: C, 84.73; H, 8.59.

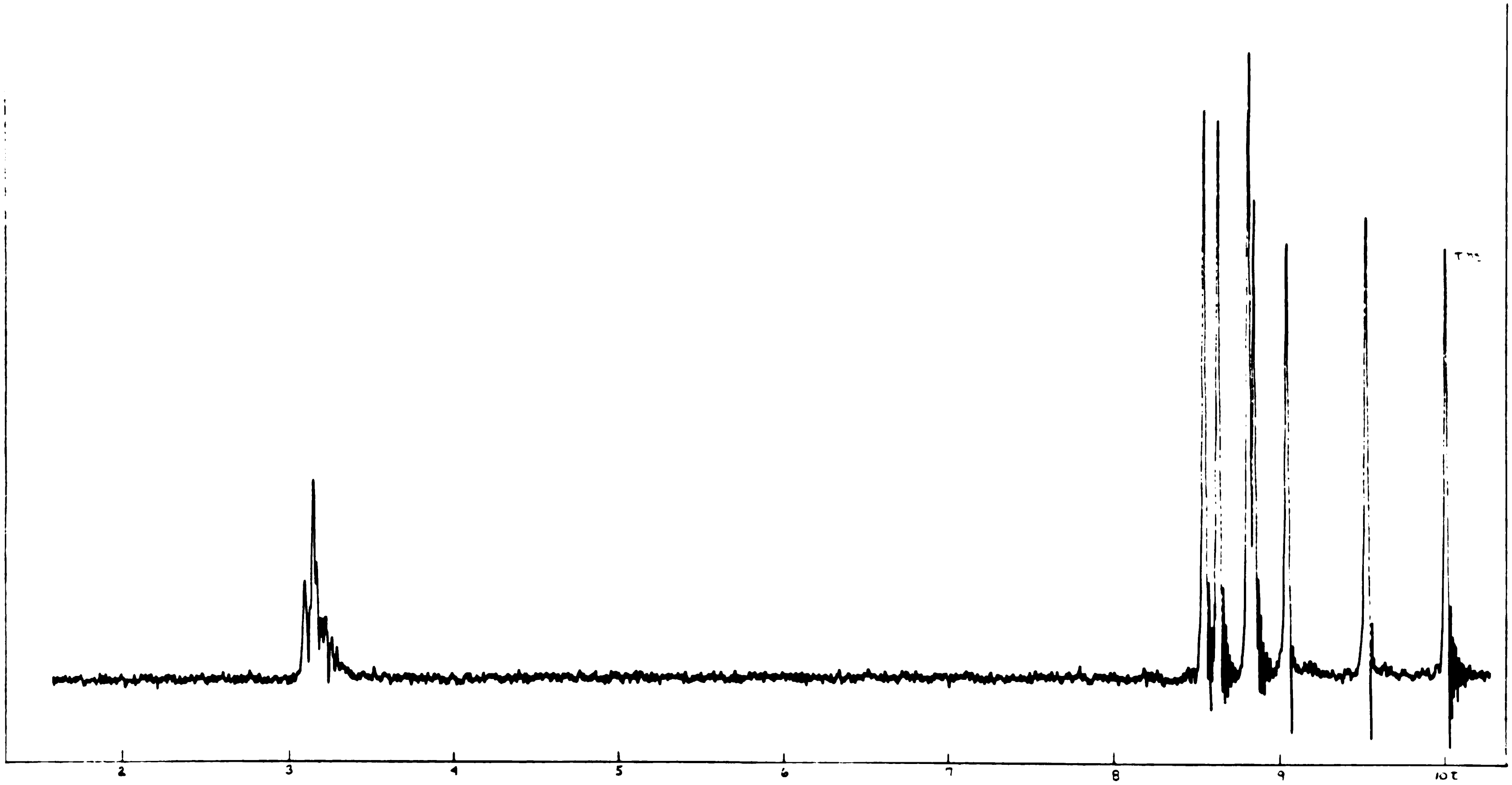


Figure 12. Nmr spectrum (CCl_4) of 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-4-one (69).

Reduction of 1,2,3,3,5,8-Hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-one (69) with Lithium Aluminum Hydride

A solution of 32 mg of 69 in 2 ml of dry tetrahydrofuran was added to a suspension of 474 mg of lithium aluminum hydride in 4 ml of dry, refluxing tetrahydrofuran. The mixture was refluxed for 27 hrs, then cooled in an ice bath, and small pieces of ice were added to hydrolyze the excess lithium aluminum hydride. To this mixture was added 10 ml of water. The resulting mixture was extracted with ether (3 x 20 ml) and the separated ether layer was dried over anhydrous magnesium sulfate. Evaporation of the ether solution provided a solid which when examined by vpc (10' x 1/4" FFAP column; 220^0; 100 ml/min of He) indicated a single reduction product. The compound was purified by vpc (above conditions) and has been identified (mp, ir spectrum, R_t) as 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-syn-4-ol, 99 (see Section S for spectral characteristics and analysis).

SUMMARY

1. Irradiation of an ether solution of 1,3,3,4,7,8-hexamethyl-5,6-dicarbomethoxybicyclo[2.2.2]octa-5,7-dien-2-one (30) provided an 80% yield of dimethyl 3,4,5,6-tetramethylphthalate (31). Irradiation of 1,3,3,4,7,8-hexamethyl-5,6-diphenylbicyclo[2.2.2]octa-5,7-dien-2-one (32) under identical conditions gave an 83% yield of 3,4,5,6-tetramethyl-1,2-diphenylbenzene (33).

2. When a solution of 32 in 2-methyltetrahydrofuran was irradiated for short intervals at -100^0 in a sodium chloride cavity cell, the formation of dimethylketene was detected spectroscopically (infrared).

3. Irradiation of an ether solution of 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (46) afforded an 82% yield of 1,2,3,4-tetramethylnaphthalene (47) and a 13% yield of 1,4,4,5,6,7-hexamethyl-2,3-benzobicyclo-[3.2.0]hepta-2,6-diene (48). Irradiation of 3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (56) under identical conditions gave a 70% yield of 2,3-dimethylnaphthalene (57) and an 8% yield of 4,4,6,7-tetramethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (58).

4. Irradiation of **46** with acetone sensitization provided not only a 45% yield of **47** and a 6% yield of **48**, but also a 26% yield of 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo-[3.3.0.0^{2,8}]oct-6-en-3-one (**68**). Similarly, acetone-sensitized irradiation of **56** gave a 66% yield of **57**, a 6% yield of **58**, and a 9% yield of 1,2,4,4-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (**70**).

5. The photoisomerization of **46** to **68** and of **56** to **70** was shown to occur from the triplet state of the ketones *via* 1,2-acyl migrations.

6. Acetone-sensitized irradiation of 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-*anti*-2-ol (**90**) afforded a 73% yield of a 3:2 mixture of 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-*anti*-4-ol (**92**) and 1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]-oct-6-en-*anti*-3-ol (**93**). However, acetone-sensitized irradiation of 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]-octa-5,7-dien-*syn*-2-ol (**91**) provided the single photoisomer 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-*syn*-4-ol (**99**).

7. Oxidation of the *syn* alcohol **99** or the *anti* alcohol **92** with chromium trioxide-pyridine gave 1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-one (**69**). However, reduction of ketone **69** with lithium aluminum hydride afforded only the *syn* alcohol **99**.

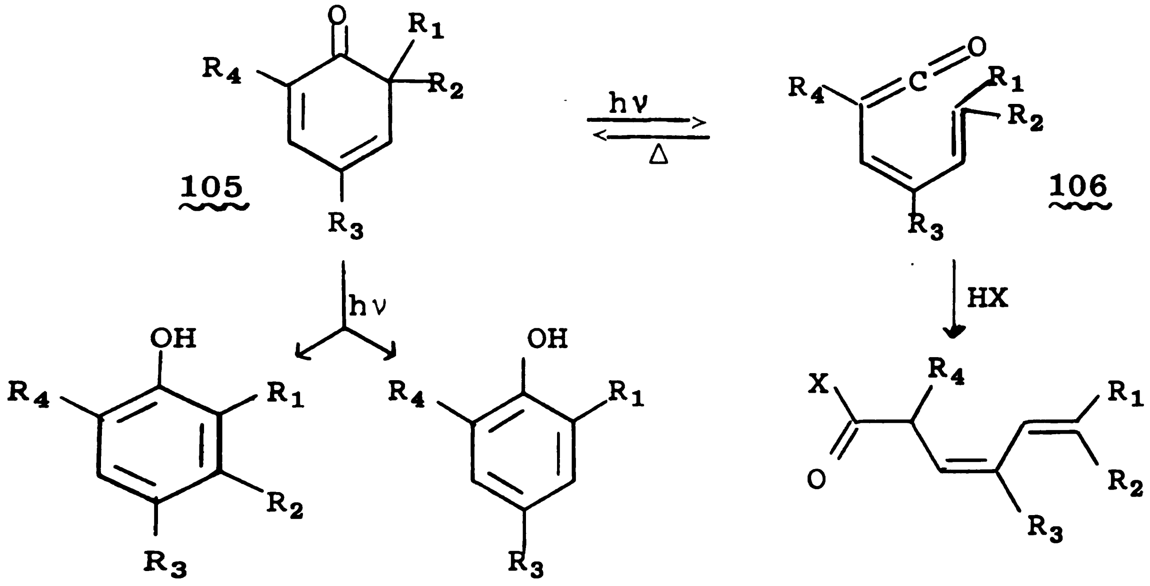
8. Oxidation of *anti* alcohol **93** with chromium trioxide-pyridine provided ketone **68**. Reduction of ketone **68** with lithium aluminum hydride only gave *anti* alcohol **93**.

PART II

THE PHOTOISOMERIZATION OF 1(2H)-NAPHTHALENONES

INTRODUCTION

The photochemistry of 2,4-cyclohexadienones has attracted considerable attention since 1960, and has been the subject of several reviews (13,61-63). In a pioneering study, Barton and Quinkert (64) elucidated three types of photochemical transformations of 2,4-cyclohexadienones having blocked *ortho*-positions. They found that the most common process in the photochemistry of 2,4-cyclohexadienones is ring fission of **105** to provide a *cis*-diene ketene, **106**. Collins and Hart (65) established that it is this *cis*-diene ketene that subsequently reacts with an available nucleophile to give the observed product, **107**. The ease with which this reaction proceeds depends on the

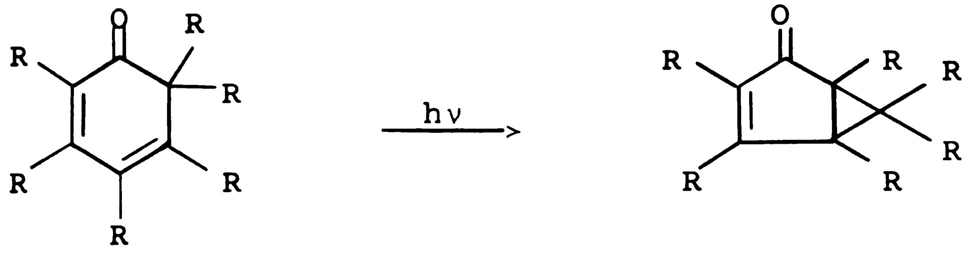


105 **106**

108 **109** **107**

number and positions of the substituents in the 2,4-cyclohexadienone and on the nucleophilic character of HX. In the absence of a strong nucleophile the reaction may fail, and recyclization of the *cis*-diene ketene permits minor (and presumably slower) processes to become important, namely the formation of phenols, either by a dienone/phenol photorearrangement to give **108**, or by homolytic photodissociation, followed by hydrogen abstraction from the solvent, to yield **109**. The dienone/phenol photorearrangement requires R_2 to be a nucleophilic group. Thus irradiation of 2,4,6-trimethyl-6-acetoxy-2,4-cyclohexadienone (**105**: R_2 = OAc; R_1 = R_3 = R_4 = Me) in dry ether, or in the presence of water or aniline gave 3-acetoxy mesitol (**108**: R_2 = OAc, R_1 = R_3 = R_4 = Me), whereas an analogous compound (**105**: R_2 = allyl, R_1 = R_3 = R_4 = Me) did not undergo such a rearrangement.

Recently Hart and his co-workers have reported that certain alkyl-substituted 2,4-cyclohexadienones undergo specific photoisomerization to bicyclo[3.1.0]hexenones to the complete exclusion of ring-opened products, even with alcohols as solvent. Thus hexamethyl- and hexaethyl-2,4-cyclohexadienones (**28** and **110**, respectively) are photoisomerized to bicyclo[3.1.0]hexenones **111** and **112**, respectively (24,66). However, this photorearrangement is sensitive to the position and number of alkyl substituents in the



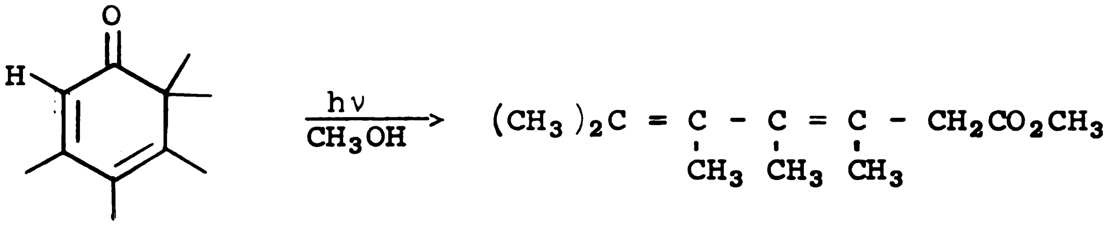
28, R = CH_3

110, R = CH_2CH_3

111, R = CH_3

112, R = CH_2CH_3

cyclohexadienone. For example, although pentamethylcyclohexadienone 113 is photochemically inert in ether, irradiation of 113 in methanol gave 114 (67), the ring-opened product expected from a *cis*-diene ketene intermediate. However, irradiation of the isomeric pentamethyl cyclohexa-

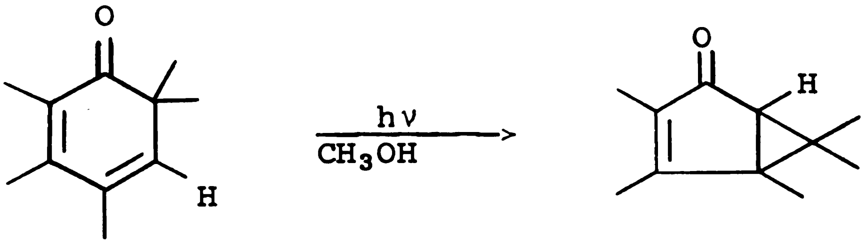


$$(CH_3)_2C = \underset{CH_3}{C} - \underset{CH_3}{C} = \underset{CH_3}{C} - CH_2CO_2CH_3$$

113

114

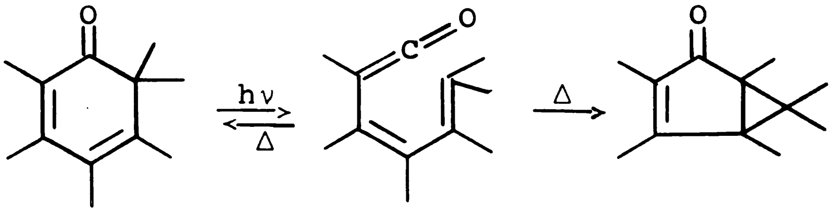
dienone 115 in ether or methanol provided 116 exclusively (67).



115

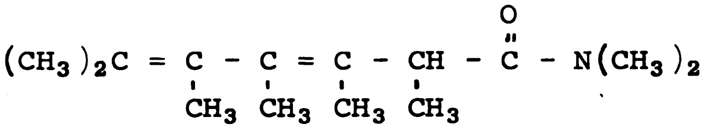
116

Griffiths and Hart (26) have now shown that in all these cases the only photochemical reaction is ring opening to a ketene and that all other processes, including isomerization to a bicyclo[3.1.0]hexenone, are thermal. The *cis*-diene ketene intermediate, **117**, was detected spectroscopically at low temperatures and could be trapped, even at room temperature, by the inclusion of a strong nucleophile in the photolysis solution. Thus irradiation of **28** in alcohol or hexane with dimethylamine present provided amide **118** in high yield (26). Similar observations have been made by



28 **117** **111**

$\downarrow (CH_3)_2NH$

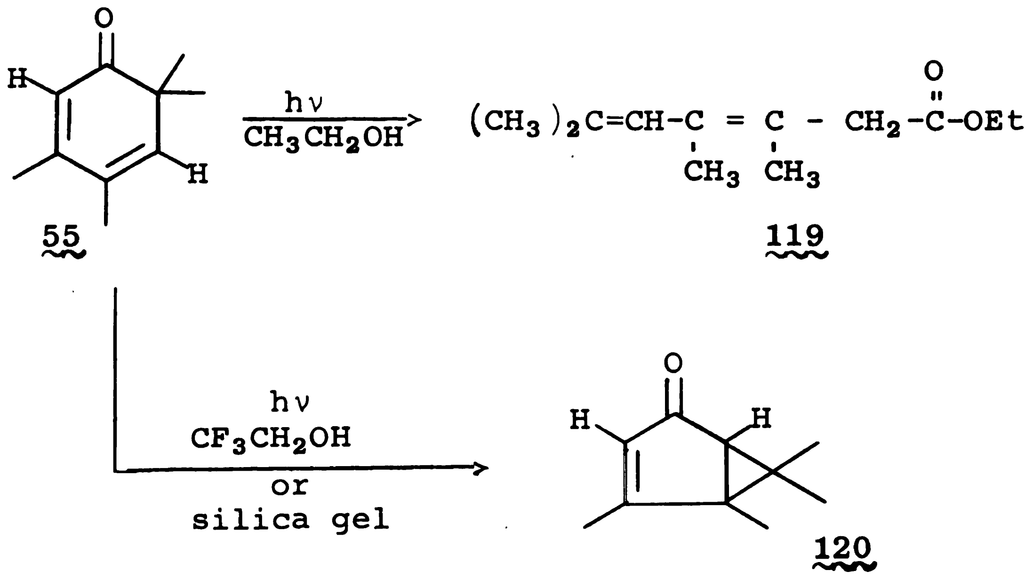


$$(CH_3)_2C = \underset{CH_3}{C} - \underset{CH_3}{C} = \underset{CH_3}{C} - \underset{CH_3}{CH} - \overset{O}{\overset{\|}{C}} - N(CH_3)_2$$

118

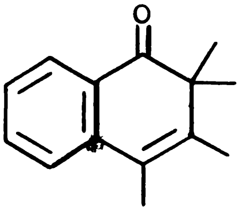
Perst and Dimroth (68) in a report concerning the photochemistry of 2,4,6-triphenyl-*o*-quinolesters. Further studies by Griffiths and Hart (26,69) suggest that the photochemical cleavage of the 1,6-bond in 2,4-cyclohexadienones to form *cis*-diene ketenes occurs efficiently (but not necessarily exclusively) from the n,π^* singlet state of the dienone.

Most recently it has been established by Hart and Griffiths (69) that the photoisomerization of a 2,4-cyclohexadienone to a bicyclo[3.1.0]hexenone can be effected directly, *i.e.*, without the intermediacy of a ketene. For example, although 3,4,6,6-tetramethyl-2,4-cyclohexadienone, **55**, is photochemically inert in non-nucleophilic solvents (29), and gave only ketene-derived ethyl 3,4,6-trimethylhepta-3,5-dienoate, **119**, when irradiated in ethanol (29), it was readily photoisomerized in trifluoroethanol or on silica gel to the isomeric bicyclic ketone **120**. The



authors suggest that the photoisomerization proceeds from the first π,π^* singlet state of the dienone. Thus the major requirement necessary to effect this photoisomerization directly is that the dienone be sufficiently perturbed by medium effects to bring about inversion of the n,π^* and first π,π^* singlet states.

In order to study the influence on the photochemistry of highly substituted 2,4-cyclohexadienones when one of the two carbon-carbon double bonds of the cyclohexadienone system belongs to a fused aromatic ring, we synthesized naphthalenones 121 and 122 (50,53). As previously reported by us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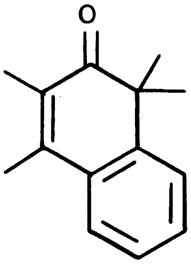
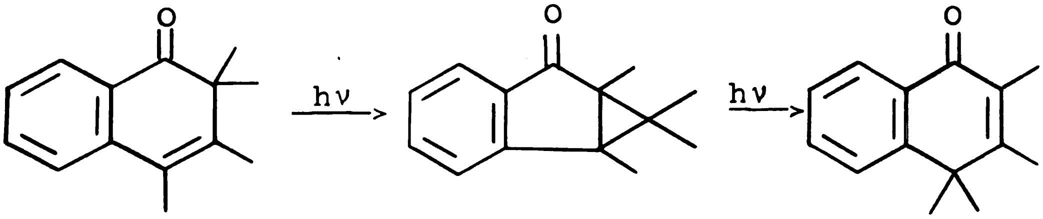

122

(50), no volatile products could be detected from the photolysis of naphthalenone 122 in ether or methanol. However, irradiation of naphthalenone 121 in ether provided the benzobicyclo[3.1.0]hexenone 123 as the primary photoproduct. Further irradiation of 121 in ether gave naphthalenone 124. An investigation of the mechanisms for the



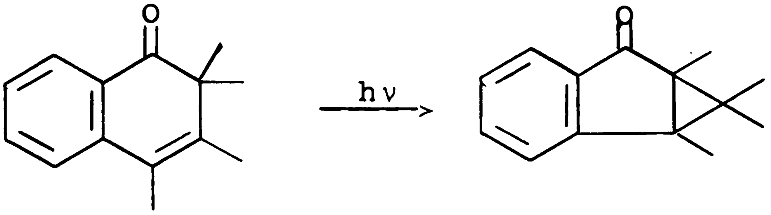
121 123 124

photoisomerizations 121 ——> 123 and 123 ——> 124 is the subject of Part II of this thesis.

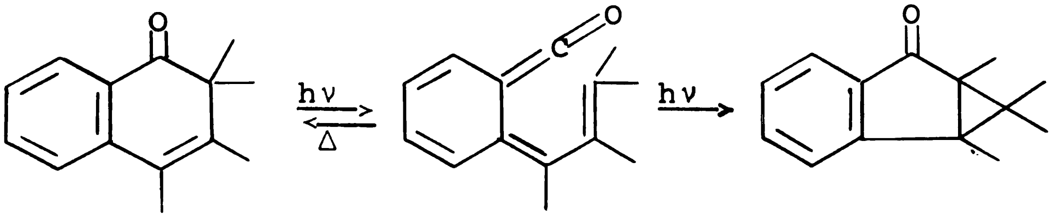
RESULTS AND DISCUSSION

A. Mechanistic Considerations

In view of previous mechanistic photochemical studies of 2,4-cyclohexadienones, three gross mechanisms can be suggested to account for the photoisomerization of 2,2,3,4-tetramethyl-1(2H)-naphthalenone, 121, to 1,5,6,6-tetramethyl-3,4-benzobicyclo[3.1.0]hexen-2-one, 123. One likely mechanism is photochemical cleavage of the 1,2-bond in naphthalenone 121 and electron reorganization to provide the ketene intermediate 125. Such a ketene intermediate could thermally cyclize to the starting naphthalenone 121 or to the observed product, benzobicycloketone 123.



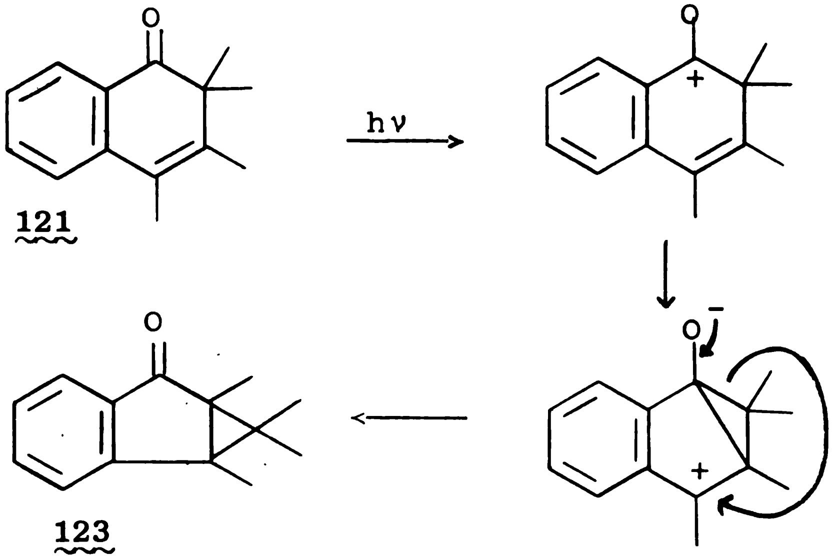
121 123



121 125 123

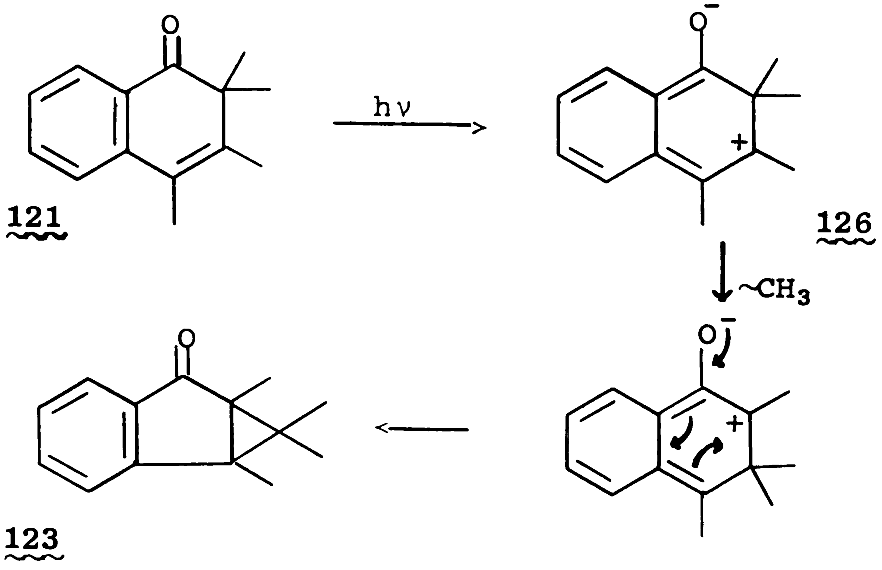
As discussed in the Introduction, Griffiths and Hart (26) have shown that an analogous mechanism is operative in the photoisomerization of 2,4-cyclohexadienones to bicyclo-[3.1.0]hexenones via the n,π* singlet state of the dienone.

The conversion of 121 to 123 can also be formulated as proceeding via a "bond-crossing" mechanism that does not involve the intermediacy of a ketene. Such a mechanism is presented below. Ionic intermediates are used for convenience.

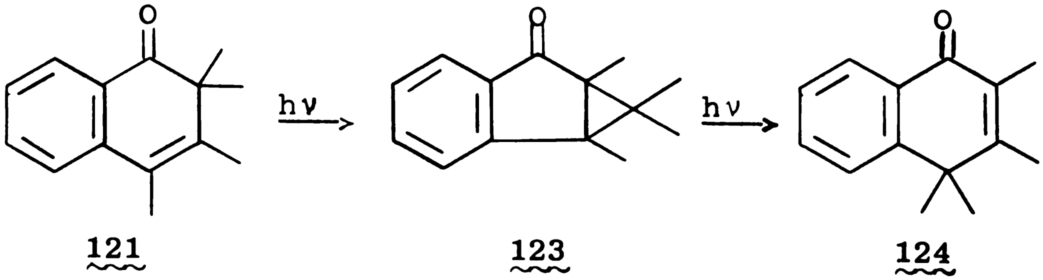


Such a mechanism is tenable, as Griffiths and Hart (69) have found that 2,4-cyclohexadienones can be directly photoisomerized to bicyclo[3.1.0]hexenones via the first π, π* singlet state of the dienone, if the dienone can be sufficiently perturbed by medium effects to cause inversion of the n,π* and first π,π* singlet states.

Finally, the photoisomerization of 121 to 123 can be rationalized by a mechanism involving migration of a methyl group from C-2 to C-3 in intermediate 126, as shown below.

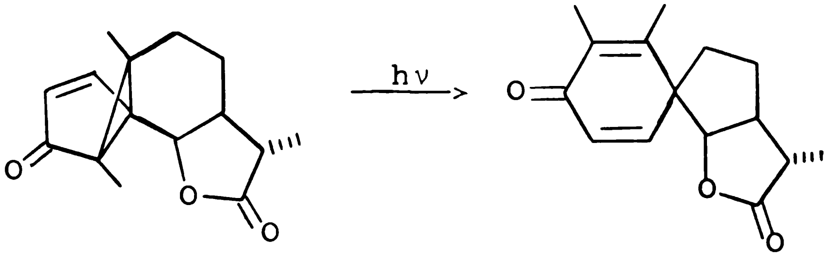


Although the primary photoproduct from the irradiation of naphthalenone 121 in ether is benzobicycloketone 123, continued irradiation of 121 provides naphthalenone 124 (50). Independent irradiation of an approximately



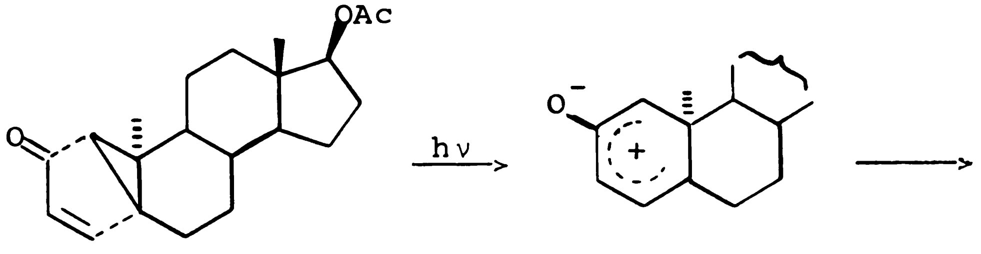
0.5% solution of benzobicyclo[3.1.0]hexenone 123 through a Pyrex filter provided an 80% yield of naphthalenone 124. Thus 123 can be considered as the intermediate in the photoisomerization of naphthalenone 121 to naphthalenone 124.

Although a much more common photochemical reaction is the photorearrangement of 2,5-cyclohexadienones to bicyclo[3.1.0]hexenones (13,63,70), a few cases of photoisomerizations of bicyclo[3.1.0]hexenones to 2,5-cyclohexadienones have been reported. For example, Schuster has shown that irradiation of 127 provides 2,5-cyclohexadienone 128 (77).

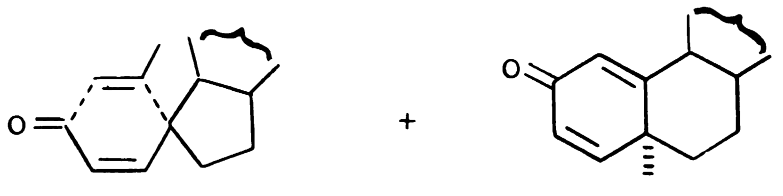


127 128

Similarly, Jeger and his co-workers have reported that irradiation of 129 gives a mixture of 2,5-cyclohexadienones 131 and 132, presumably *via* the ionic intermediate 130 (72).

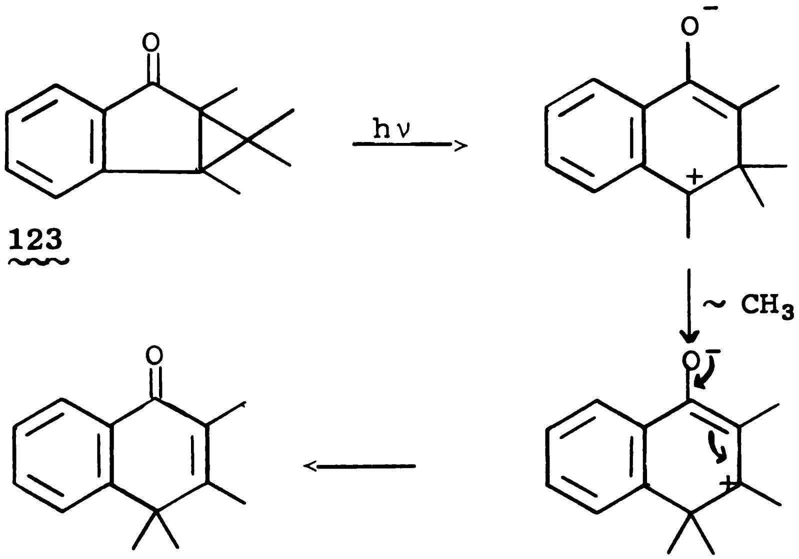


129 130



131 132

In each of these cases the photoisomerization proceeds by an apparent 1,2-methyl migration. As depicted below, an analogous mechanism would account for the photoisomerization of 123 to 124.



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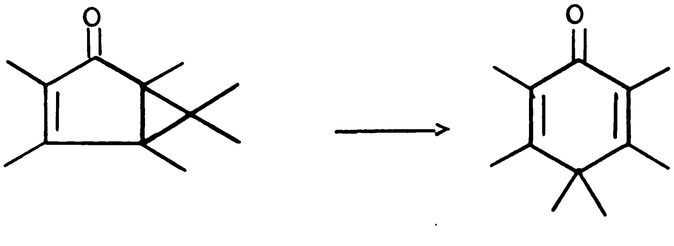
124

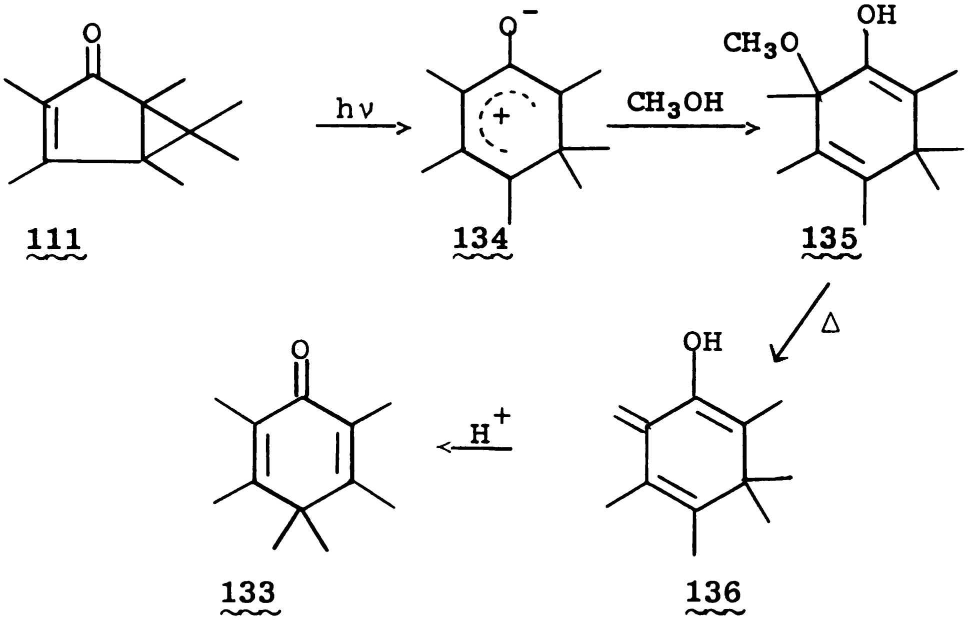
In a preliminary investigation, it was found that irradiation of bicyclo[3.1.0]hexenone 111 in ethanol gives hexamethyl-2,5-cyclohexadienone, 133. However, Hart and



111

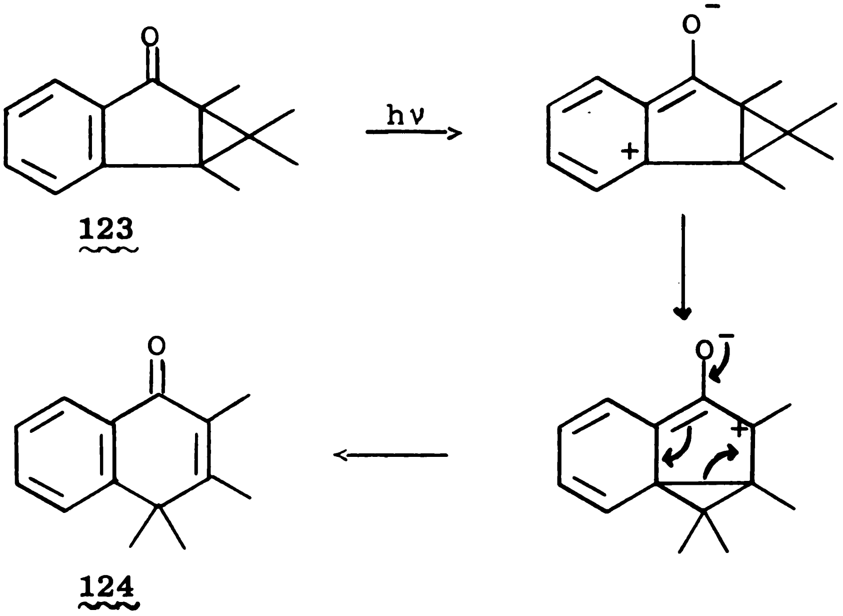
133

Swatton (73) have shown that photolysis of 111 in methanol through Pyrex initially gives methoxyenol 135. This product is considered to result from the trapping of a dipolar intermediate (**134**) by the solvent. Methoxyenol **135** readily



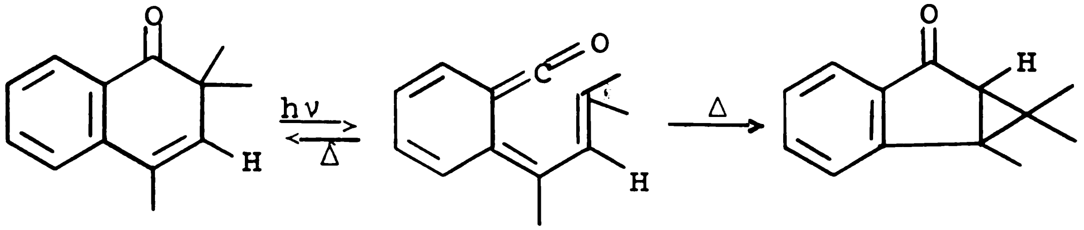
loses methanol (thermally or in acid) to afford the enolic triene **136**, which gives **133** on further treatment with acid. Of course the photoisomerization of benzobicyclo[3.1.0]-hexenone **123** to naphthalenone **124** can be rationalized by a similar mechanism (for details, see Section C). However, it should be noted that the acid-catalyzed rearrangement of **136** to **133** requires a 1,2-methyl migration. Therefore, for the photoisomerization of **123** to **124** to proceed by either of the mechanisms already presented, a 1,2-methyl migration is necessary.

The conversion of **123** to naphthalenone **124** can also be explained by a "bond-crossing" mechanism, as is shown below. In such a mechanism the methyl substituents retain their original positions.



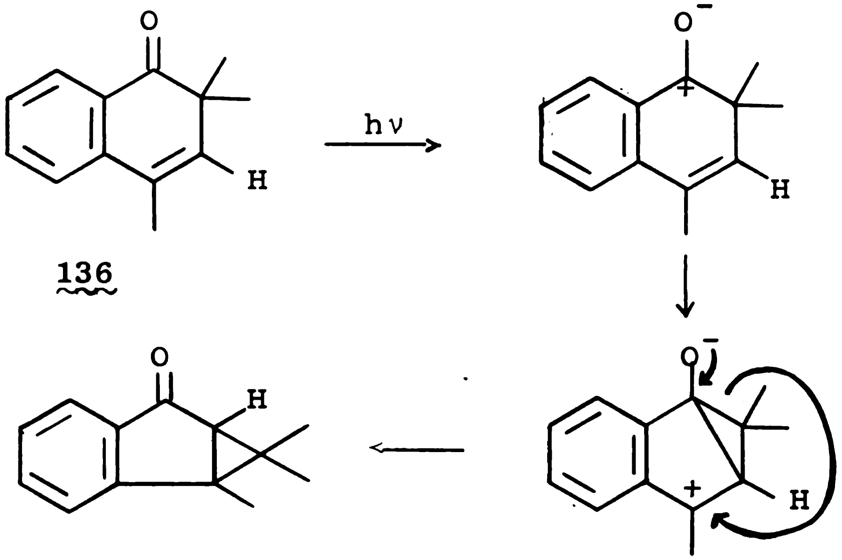
B. The Photorearrangement of 2,2,4-Trimethyl-1(2H)-naphthalenone (**136**)

In Part A three discrete mechanisms were advanced to account for the reported photoisomerization of 2,2,3,4-tetramethyl-1(2H)-naphthalenone, **121**, to 1,5,6,6-tetramethyl-3,4-benzobicyclo[3.1.0]hexen-2-one, **123**. These mechanisms can be differentiated by an examination of the photorearrangement of 2,2,4-trimethyl-1(2H)-naphthalenone, **136**. Photoisomerization of naphthalenone **136** *via* ketene intermediate **137** would be expected to yield benzobicycloketone **138**. The same benzobicycloketone photoproduct would be expected if the rearrangement occurred by a "bond-crossing"



136 **137** **138**

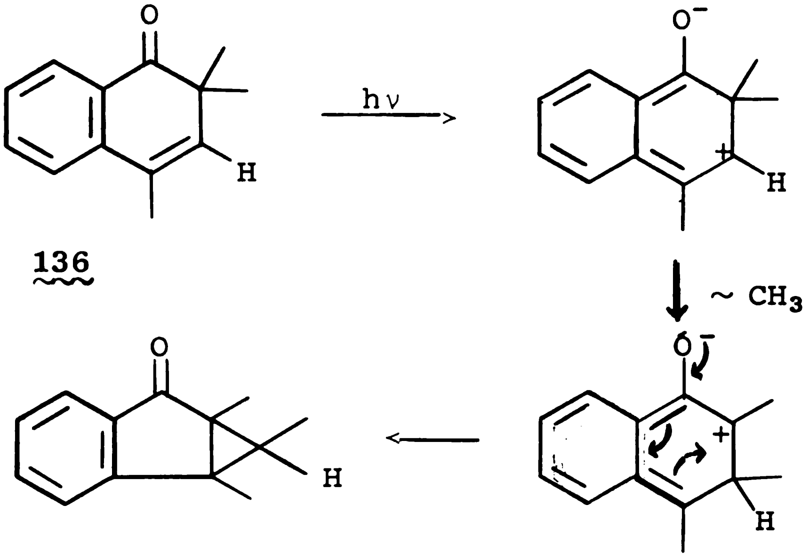
mechanism that did not involve a ketene intermediate, *i.e.*, *via* **139**. However, photoisomerization of **136** by a mechanism



136

138 **139**

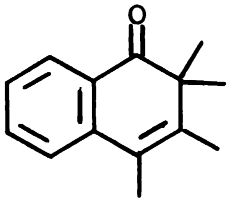
that required a 1,2-methyl migration would give a different photoproduct, benzobicycloketone **140**.



136

140

A reasonable synthesis for the desired naphthalenone **136** appeared to be the electrophilic oxidation of 1,2,4-trimethylnaphthalene. In a series of recent reports (24, 29,67), Hart and his co-workers have shown that oxidation of highly alkyl-substituted benzenes with electrophilic oxidants proceeds with Wagner-Meerwein rearrangement to give the corresponding cyclohexadienones in excellent yields (74). For example, oxidation of hexamethylbenzene with peroxytrifluoroacetic acid-boron fluoride gave a 90% yield of hexamethyl-2,4-cyclohexadienone (24), and the major products from the oxidation of pentamethylbenzene are also dienones (67). Similarly, oxidation of 1,2,3,4-tetramethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride provided naphthalenones **121** and **122** and the tetramethyldioxotetralin **141** in the ratio of 61:21:18 with an overall yield of 50% (50).



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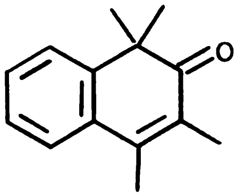

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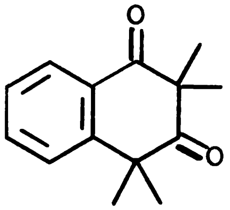
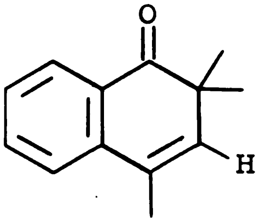


141

1,2,4-Trimethylnaphthalene was prepared <u>via</u> a modification of the method of Hewett (51). 1,2-Dimethylnaphthalene was chloromethylated with paraformaldehyde and hydrogen chloride in acetic acid. Hydrogenolysis of the resulting 1-chloromethyl-3,4-dimethylnaphthalene with lithium aluminum hydride in tetrahydrofuran provided 1,2,4-trimethylnaphthalene (Hewett used catalytic hydrogenolysis).

1,2,4-Trimethylnaphthalene was oxidized at -20^{0} to -10^{0} with a 10% excess of peroxytrifluoroacetic acid in methylene chloride. Boron fluoride etherate was added at a molar rate equal to that of the oxidant. These conditions effected an 83% conversion of 1,2,4-trimethylnaphthalene. The volatile products were separated by distillation and column chromatography and finally purified by vpc. The composition of the distillate consisted of unreacted 1,2,4-trimethylnaphthalene (42%), 2,2,4-trimethyl-1(2H)-naphthalenone, 136, (47%), 1,1,4-trimethyl-2(1H)-naphthalenone, 142, (9%) and an unidentified product (2%). The structures of the products follow from their analyses, spectral properties, and mode of formation.



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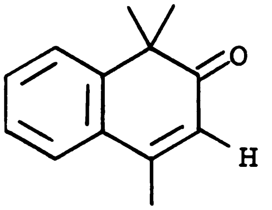


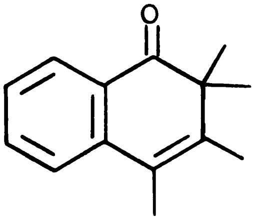
142

Examination of Table II shows that the infrared and ultraviolet spectra of naphthalenone 136 compare very favorably with the data previously reported for tetramethylnaphthalenone 121 (50). The nmr spectrum of 136 consisted of a six-proton singlet at τ 8.78 (gem-dimethyl group), a three-proton doublet (J = 1.5 Hz) at τ 7.89 (allylic methyl split by a neighboring vinyl proton), a one-proton quartet (J = 1.5 Hz) centered at τ 4.15 (vinyl proton split by allylic methyl), and aromatic multiplets, τ 2.30-2.90 and τ 1.85-2.10 (4H together).

Inspection of Table III indicates that the infrared and ultraviolet spectra of naphthalenone 142 also compare favorably with the data previously reported for tetramethylnaphthalenone 122 (50). The nmr spectrum of 142 contained a six-proton singlet at τ 8.62 (gem-dimethyl group), a three-proton doublet (J = 0.9 Hz) at τ 7.68 (allylic methyl split by a neighboring vinyl proton), a broad (h_w = 4.0 cycles) one-proton singlet at τ 4.03 and an aromatic multiplet, τ 2.51-2.86 (4H).

A reasonable mechanism for the formation of the oxidation products is presented in Figure 13. For simplicity

Table II. The infrared and ultraviolet spectra of 1(2H)-naphthalenones **121** and **136**



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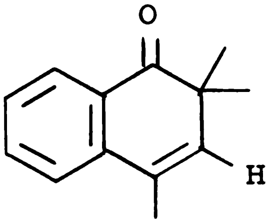
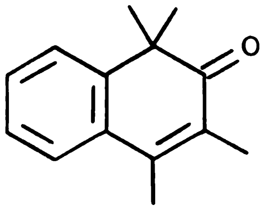


136

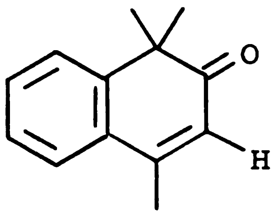
Infrared Spectra (liquid film)	**121**	**136**
$\nu_{C=O}$, cm^{-1}	1674	1673
$\nu_{C=C}$ (conj), cm^{-1}	1633	
$\nu_{C=C}$ (arom), cm^{-1}	1600	1600

Ultraviolet Spectra (95% Ethanol)	λ_{max}, mμ (log ε)	λ_{max}, mμ (log ε)
	340 (3.14)	333 (3.23)
	286 (3.33)	283 (3.35)
	276 (3.49)	274 (3.56)
	268 (3.49)	266 (3.54)
	239 (5.05)	236 (4.53)

Table III. The infrared and ultraviolet spectra of 2(1H)-naphthalenones 122 and 142



122



142

Infrared Spectra 122, liquid film 142, CCl_4 soln.	122	142
$\nu_{C=O}$, cm^{-1}	1652	1660
$\nu_{C=C}$(conj), cm^{-1}	1621	1628
$\nu_{C=C}$(arom), cm^{-1}	1600	1604
Ultraviolet Spectra (95% Ethanol)	λ_{max}, mμ (log ε)	λ_{max}, mμ (log ε)
	308 (3.91)	304 (4.10)
	239 (3.95)	238 (4.09)
	234 (3.97)	234 (4.09)

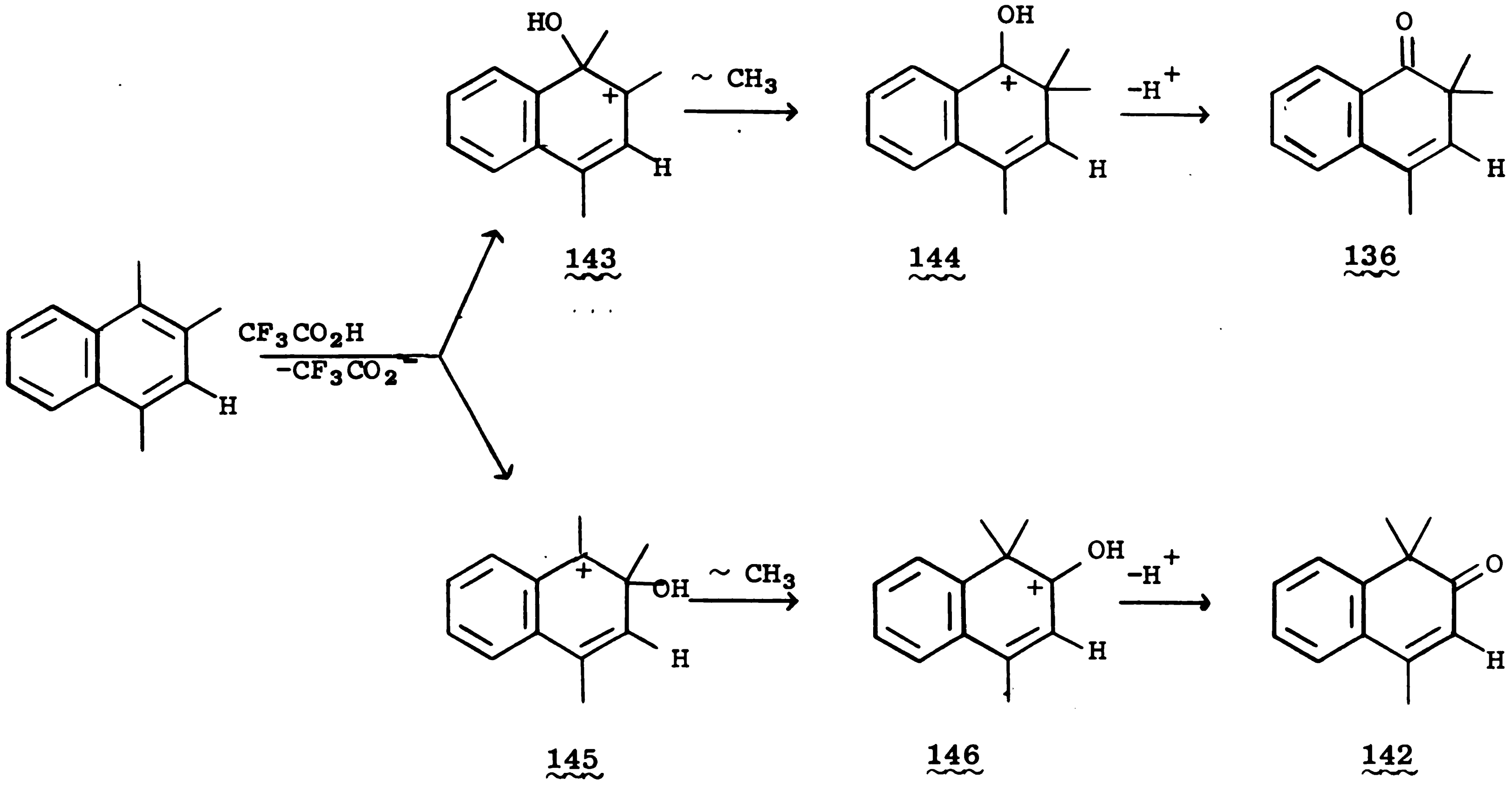
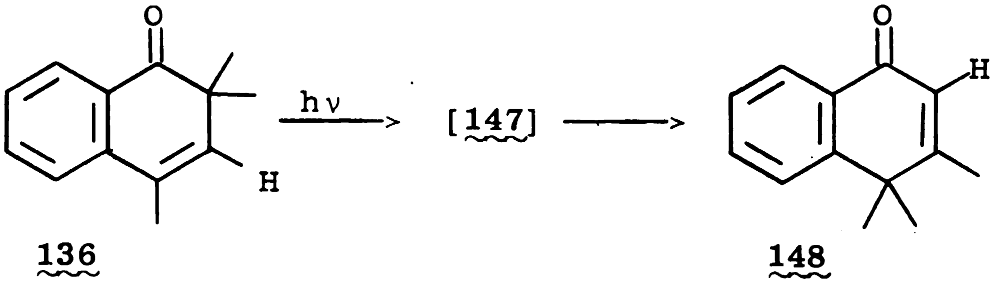


Figure 13. A mechanism for the formation of the oxidation products of 1,2,4-trimethylnaphthalene.

the mechanism is written using OH^+ as the oxidant, although it is recognized that the positive hydroxyl species may have trifluoroacetate or other ligands attached (74). Strong evidence has been presented by Norman and Davidson supporting the intermediacy of an electrophilic, cationic reactant in peroxytrifluoroacetic acid oxidations (75).

Naphthalenone 136 is presumably formed by electrophilic attack of peroxytrifluoroacetic acid at C-1 of 1,2,4-trimethylnaphthalene, leading to the intermediate carbonium ion 143. Wagner-Meerwein migration of a methyl group to C-2 would provide carbonium ion 144, and loss of a proton would give naphthalenone 136. Similarly, the formation of naphthalenone 142 is accounted for by attack of the electrophilic oxidant at C-2 of 1,2,4-trimethylnaphthalene, leading to carbonium ion 145. Migration of a methyl group to C-1 would afford intermediate carbonium ion 146, and loss of a proton would give naphthalenone 142.

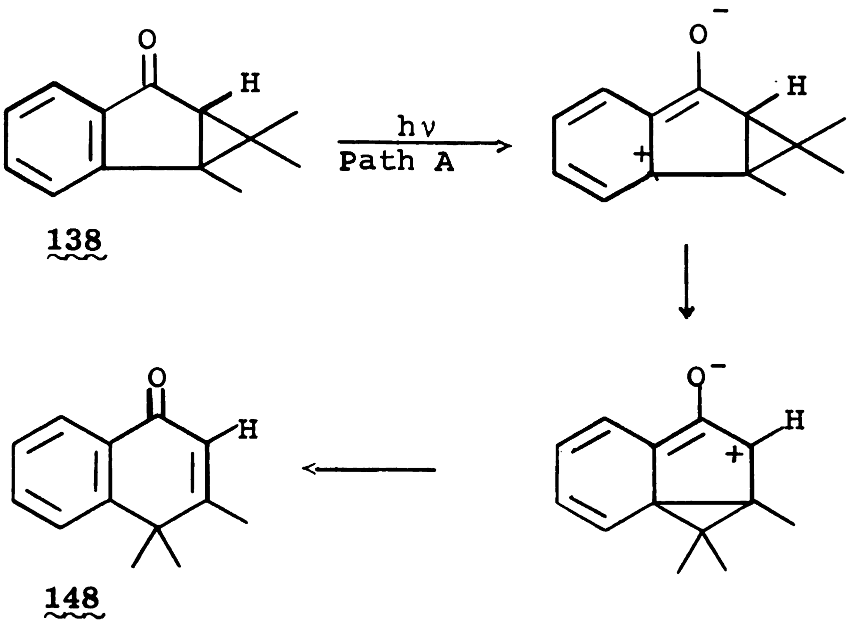
Having successfully prepared naphthalenone 136, the photochemistry of this compound was investigated. The irradiation of a solution of naphthalenone 136 in anhydrous ether through a Pyrex filter with a Hanovia L 450-w lamp was monitored by vpc. Photolysis led to a decrease in the concentration of naphthalenone 136 and the appearance of a photoproduct, 147, that reached a maximum concentration of 11% of the volatiles after three hours irradiation, and then decreased as the photolysis was continued. Another photoproduct, 148, was also detected and the concentration of 148 continued to increase until the photolysis was terminated. After 12 hours irradiation, vpc analysis of the photolysate indicated the volatiles were composed of: naphthalenone 136 (18%), 147 (3%) and 148 (78%). Photoproduct 148 has been identified as 3,4,4-trimethyl-1(4H)-naphthalenone. In view of the known photochemistry of

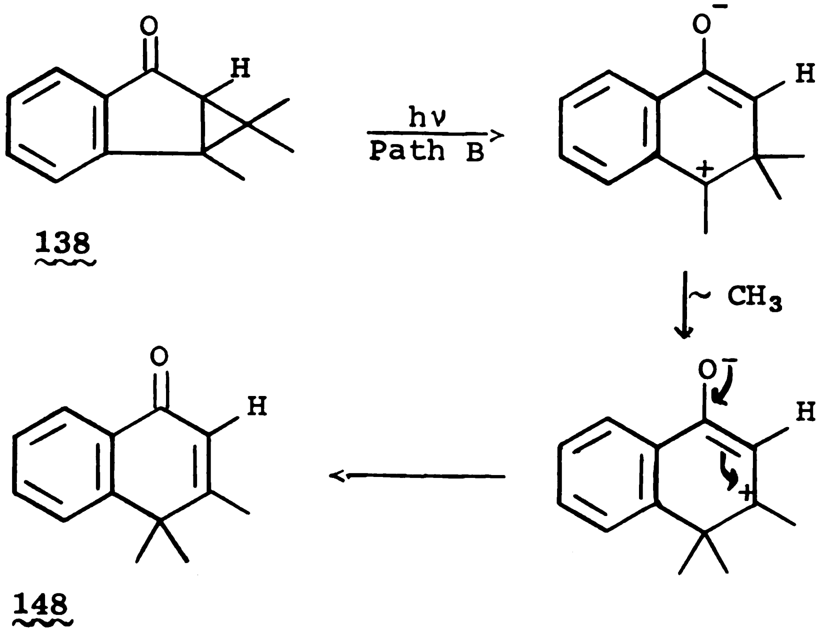


2,2,3,4-tetramethyl-1(2H)-naphthalenone, 121, (described in detail in Section A), photoproduct 147 is presumed to be a benzobicyclo[3.1.0]hexenone. However, it was not trapped, nor was its structure investigated.

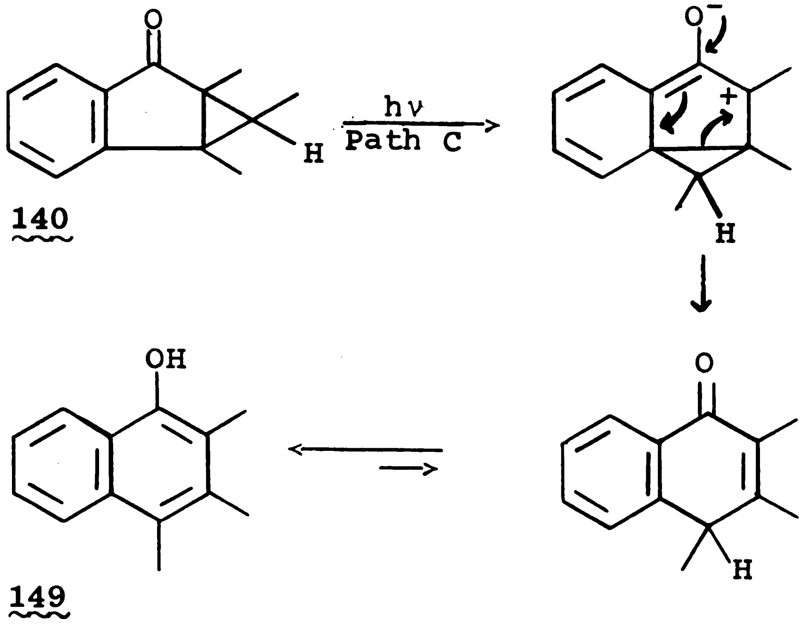
Naphthalenone 148 was an oil that showed conjugated carbonyl and double-bond absorptions in the infrared region at 1660 and 1632 cm^{-1} respectively. The nmr spectrum of 148 consisted of a six-proton singlet at τ 8.52 (*gem*-dimethyl group), a three-proton doublet (J = 1.5 Hz) at τ 7.91 (allylic methyl split by a neighboring vinyl proton), a one-proton quartet (J = 1.5 Hz) centered at τ 3.85 (vinyl proton split by allylic methyl) and aromatic multiplets, τ 2.45-2.85 and τ 1.85-2.10 (4H together). The identity of naphthalenone 148 was firmly established by comparison of the 2,4-DNP derivative of 148 with an authentic sample of the 2,4-dinitrophenylhydrazone of 3,4,4-trimethyl-1(4H)-naphthalenone prepared independently by Huffman and Bethea (57,58).

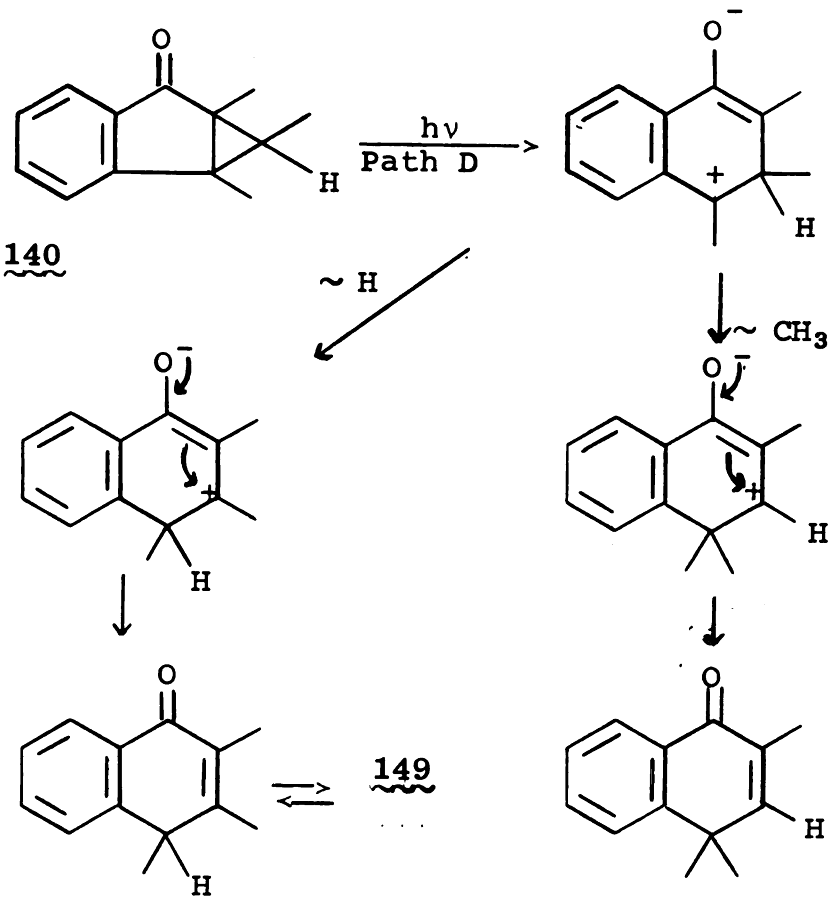
As previously shown, photoisomerization of naphthalenone 136 to a benzobicyclo[3.1.0]hexenone *via* a ketene intermediate or by a "bond-crossing" mechanism that does not involve a ketene intermediate would be expected to yield benzobicycloketone 138. However, the photorearrangement of 136 by a mechanism that requires a 1,2-methyl migration would give benzobicycloketone 140. The photorearrangement of 138 to naphthalenone 148 could also occur by either of two mechanisms, a "bond-crossing" mechanism (Path A) or by a 1,2-methyl migration (Path B). However, photoisomerization of benzobicycloketone 140 to a 1(4H)-naphthalenone





would be expected to ultimately provide 2,3,4-trimethyl-1-naphthol, **149**, by a "bond-crossing" mechanism (Path C) and a mixture of **149** and naphthalenone **150** *via* a mechanism involving a 1,2-methyl migration (Path D).





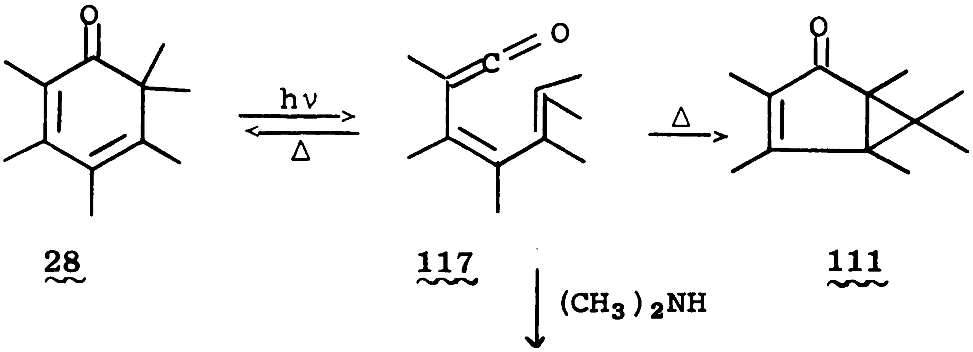
140

149

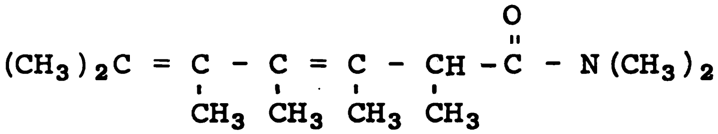
150

As the photoproduct isolated in the photoisomerization of naphthalenone 136 is naphthalenone 148, the intermediate benzobicyclohexenone in the conversion of 136 to 148 must be 5,6,6-trimethyl-3,4-benzobicyclo[3.1.0]hexen-2-one, 138. Therefore the photorearrangement of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]hexenone cannot involve methyl migration, and must occur either <u>via</u> a ketene intermediate or by a "bond-crossing" mechanism that does not involve the intermediacy of a ketene.

Hart and Griffiths were successful in trapping the ketene intermediate 117 in the photoisomerization of hexamethyl-2,4-cyclohexadienone, 28, to ketone 111 (26) by the inclusion of a strong nucleophile in the photolysis solution. Thus irradiation of 28 in alcohol or hexane with dimethylamine present provided amide 118 in high yield. However,

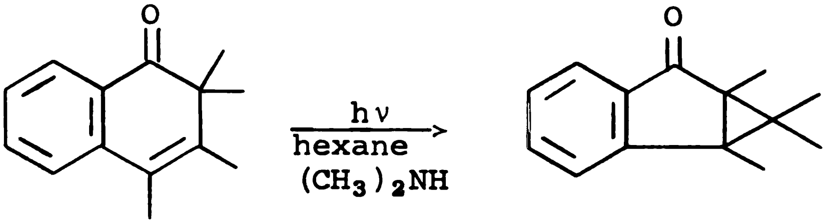


28 117 111


$$(CH_3)_2C=\underset{CH_3}{C}-\underset{CH_3}{C}=\underset{CH_3}{C}-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$$

118

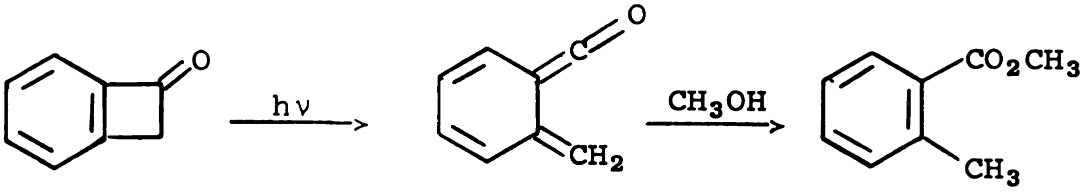
similar irradiation of a hexane solution of tetramethylnaphthalenone 121 with an excess of dimethylamine present was found to give only benzobicycloketone 123. No other



121 123

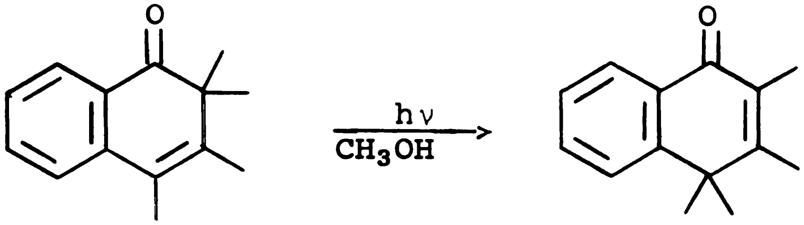
products could be detected by vpc or nmr analysis of the photolysate.

One explanation for this result is that a ketene intermediate is not involved in the photoisomerization of 121 to 123. Contrarily, it can be contended that the reaction does proceed by a ketene intermediate, but due to the strong driving force for rearomatization of the ketene, it thermally cyclizes to 121 or 123 faster than it reacts with an available nucleophile. However, Cava and Spangler have reported trapping a closely related ketene with a weaker nucleophile than dimethylamine (76). Thus benzocyclobutenone, 151, is smoothly converted to methyl *o*-toluate, 153, by irradiation in methanol. The reaction is rationalized as proceeding *via*



151 152 153

ketene 152. In a similar experiment, irradiation of a methanol solution of naphthalenone 121 proceeded *via* benzobicycloketone 123 to provide a high yield of 124. No other

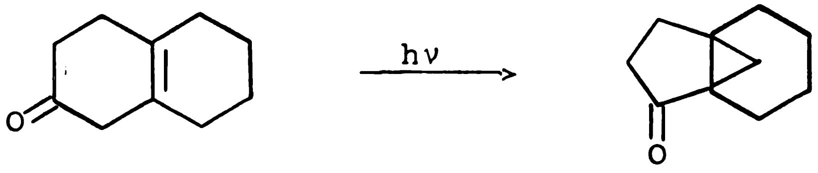


121 124

products were detected by vpc or nmr analysis of the photolysate.

Therefore it is concluded that the photoisomerization of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]hexenone most likely occurs by a "bond-crossing" mechanism that does not involve the intermediacy of a ketene. Hart and Griffiths have recently shown that the photoisomerization of a 2,4-cyclohexadienone to a bicyclo[3.1.0]hexenone from the first π,π^* singlet state of the dienone proceeds by an analogous mechanism.

Throughout this discussion, the photochemistry of 1(2H)-naphthalenones has been compared to that of 2,4-cyclohexadienones. However, if the π electrons of the aromatic ring in 1(2H)-naphthalenones do not influence the photochemistry of these compounds, then the photochemistry of 1(2H)-naphthalenones can be compared to that of 3-cyclohexenones. Williams and Ziffer have shown that the characteristic photoreaction of 3-cyclohexenones in solution is isomerization to bicyclo[3.1.0]hexanones (8,9). For example, irradiation of a t-butyl alcohol solution of 5 through Pyrex provided 6 in good yield. Thus the photo-

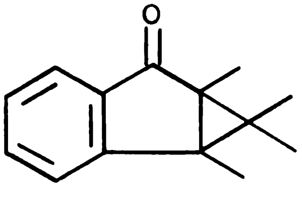


5 6

rearrangement of 3-cyclohexenones is similar to that found for 1(2H)-naphthalenones.

C. The Photorearrangement of 4-Ethyl-2,2-dimethyl-1(2H)-naphthalenone (**154**)

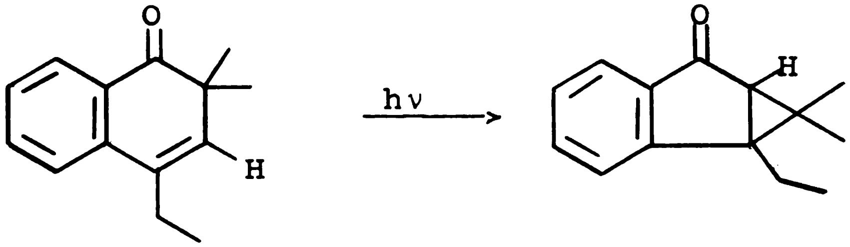
As discussed in detail in Part A, the observed photochemical conversion of benzobicycloketone **123** to naphthalenone **124** can be formulated as proceeding by a 1,2-methyl migration, or the methyls may retain their original positions



123 **124**

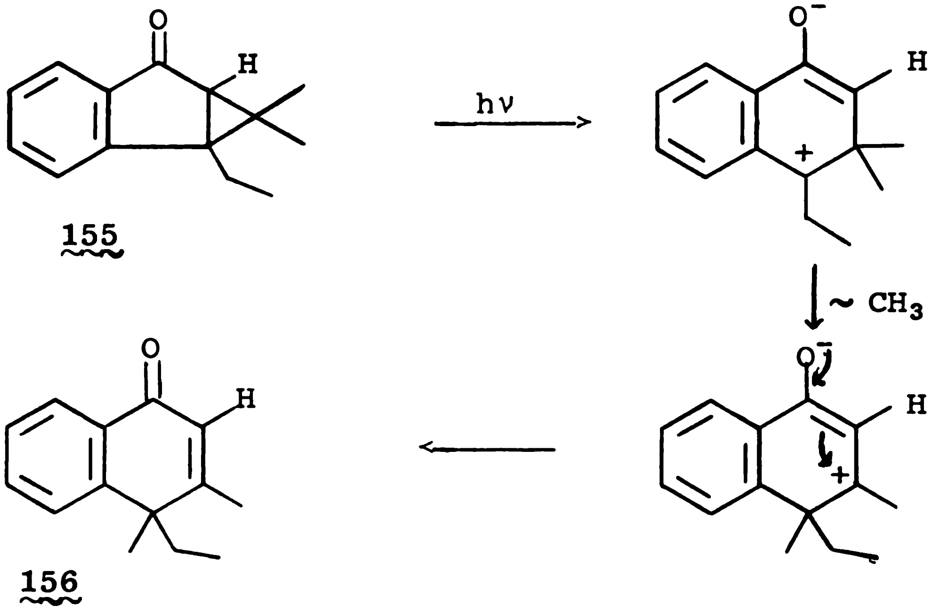
and the rearrangement may be of the "bond-crossing" type. These alternative mechanisms can be differentiated by an examination of the photorearrangement of 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone, **154**.

In Part B it was established that the photoisomerization of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]-hexenone occurs by a "bond-crossing" mechanism. Thus ultraviolet irradiation of naphthalenone **154** will provide ketone **155**. Photoisomerization of **155** by a mechanism that required

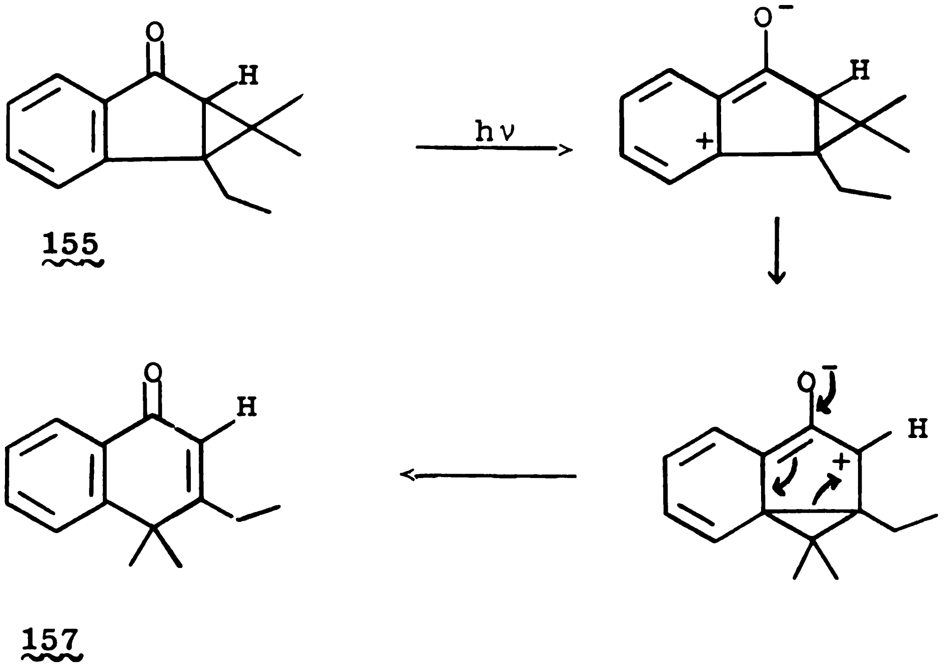


154 **155**

a 1,2-methyl migration would be expected to give naphthalenone 156. However, photorearrangement of 155 by a "bond-

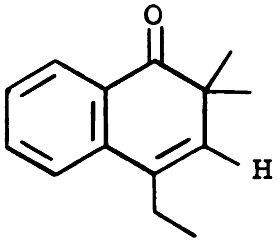


crossing" mechanism would be expected to yield another product, naphthalenone 157.

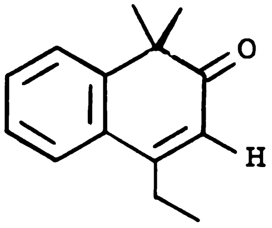


A suitable synthesis for the desired naphthalenone 154 appeared to be the electrophilic oxidation of 4-ethyl-1,2-dimethylnaphthalene, 158. 1,2-Dimethylnaphthalene was acetylated with acetyl chloride-aluminum chloride at 0^{0} (59). Clemmenson reduction of the resulting 1-acetyl-3,4-dimethylnaphthalene provided 4-ethyl-1,2-dimethylnaphthalene.

4-Ethyl-1,2-dimethylnaphthalene was oxidized at -20^{0} to -10^{0} with a 10% excess of peroxytrifluoroacetic acid in methylene chloride. Boron fluoride etherate was added at a molar rate equal to that of the oxidant. These conditions effected a 78% conversion of 4-ethyl-1,2-dimethylnaphthalene. The volatile products were separated by distillation and column chromatography and finally purified by vpc. The composition of the distillate consisted of unreacted 4-ethyl-1,2-dimethylnaphthalene (41%), 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone, 154, (49%), and 4-ethyl-2,2-dimethyl-2(1H)-naphthalenone, 159, (10%). The structures of the products follow from their analyses, spectral properties, and mode of formation.



154

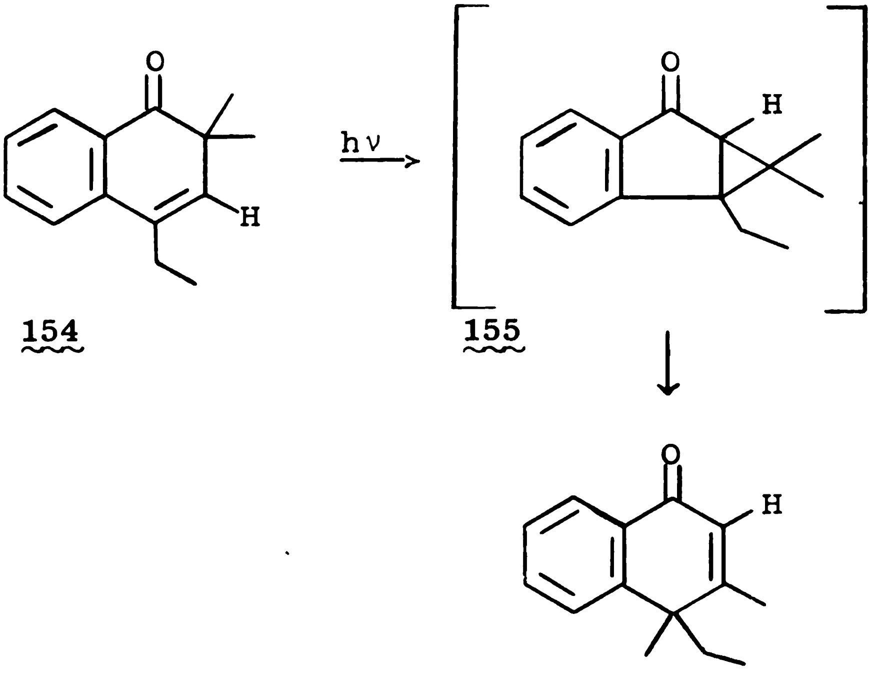


159

Naphthalenone 154 was an oil that showed principal infrared bands (CCl$_4$) at 1675 ($\nu_{C=O}$, conjugated), 1640 (shoulder, $\nu_{C=C}$) and 1600 cm^{-1} ($\nu_{C=C}$, aromatic). The ultraviolet spectrum of 154 in 95% ethanol had maxima at 333 (log ε 3.32), 283 (log ε 3.42), 274 (log ε 3.61), 266 (log ε 3.61) and 236 mμ (log ε 4.74). Inspection of Table II shows that the infrared and ultraviolet spectra of naphthalenone 154 compare favorably with the data previously determined for similarly substituted 1(2H)-naphthalenones. The nmr spectrum of 154 contained a six-proton singlet at τ 8.80, a three-proton triplet (J = 7.8 Hz) centered at τ 8.80, a two-proton quartet (J = 7.8 Hz) centered at τ 7.50, a broad (h_w = 3.3 cycles) one-proton singlet at τ 4.25, and aromatic multiplets, τ 2.55-3.13 (3H) and 2.0-2.2 (1H). The nmr spectrum of 154 is consistent with the assigned structure.

Naphthalenone 159 was also an oil that had infrared bands (CCl_4) at 1660 ($\nu_{C=O}$, conjugated), 1622 ($\nu_{C=C}$, conjugated) and 1602 cm^{-1} ($\nu_{C=C}$, aromatic). The ultraviolet spectrum of 159 in 95% ethanol showed maxima at 303 (log ε 4.11), 237 (log ε 4.10) and 232 mμ (log ε 4.10). The infrared and ultraviolet spectra of naphthalenone 159 compare well with the data previously obtained for similarly substituted 2(1H)-naphthalenones (see Table III). The nmr spectrum of 159 consisted of a three-proton triplet (J = 7.8 Hz) centered at τ 8.69, a six-proton singlet at τ 8.62, a two-proton quartet (J = 7.8 Hz) at τ 7.29, a broad one-proton singlet at τ 4.07, and an aromatic multiplet, τ 2.48-2.95 (4H).

Having prepared the desired naphthalenone 154, the photochemistry of this compound was examined. Irradiation of a solution of naphthalenone 154 in diethyl ether through a Pyrex filter with a Hanovia L 450-w lamp was monitored by vpc. Photolysis produced a decrease in the concentration of naphthalenone 154 and the appearance of a photoproduct that reached a maximum concentration of 15% of the volatiles after five hours irradiation, and then decreased as the photolysis was continued. This photoproduct is tentatively assigned the structure of 5-ethyl-6,6-dimethyl-3,4-benzobicyclo[3.1.0]hexen-2-one, 155. As the irradiation was continued, another photoproduct was also detected and the concentration of this product continued to increase until the photolysis was terminated. The latter compound was isolated and has been identified as 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone, 156.



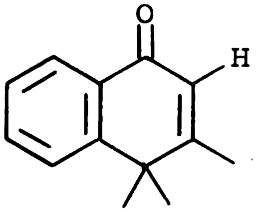
154

155

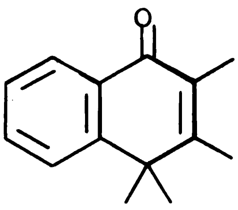
156

After 12 hours irradiation, vpc analysis of the photolysate indicated the volatiles were composed of: naphthalenone 154 (30%), 155 (7%) and 156 (63%). In an attempt to increase the yield of 155, a solution of naphthalenone 154 in trifluoroethanol was irradiated through a uranium glass filter (short wavelength cut-off at about 360 mμ). Vpc analysis of the photolysis solution after brief irradiation showed the volatiles were composed of: naphthalenone 154 (51%), 155 (11%) and naphthalenone 156 (38%). Further irradiation provided an excellent yield of 156.

Naphthalenone 156 was an oil that analyzed well for the empirical formula $C_{14}H_{16}O$. In the infrared region 156 showed conjugated carbonyl and double-bond absorptions at 1660 and 1631 cm^{-1} respectively. The ultraviolet spectrum of 156 in 95% ethanol had a maximum at 252 mμ (log ε 4.17) and a shoulder at 269 mμ (log ε 4.07). The infrared and ultraviolet spectra of 156 compare favorably with data previously reported for similarly substituted 1(4H)-naphthalenones (50,57). The positions of the substituents in naphthalenone 156 were apparent from the nmr spectrum, which consisted of a three-proton triplet (J = 7.8 Hz) centered at τ 9.62, a three-proton singlet at τ 8.55 (C-4 methyl), a two-proton quartet (J = 7.8 Hz).centered at τ 8.05, a three-proton doublet (J = 1.5 Hz) at τ 7.94 (allylic methyl split by a neighboring vinyl proton), a broad (h_W = 3.6 cycles) one-proton singlet at τ 3.79 (vinyl methyl) and aromatic multiplets centered at τ 2.67 (3H) and τ 1.93-2.12 (1H). In the related naphthalenone 148, the allylic methyl appears at τ 7.91. Similarly, in tetramethylnaphthalenone 124 the



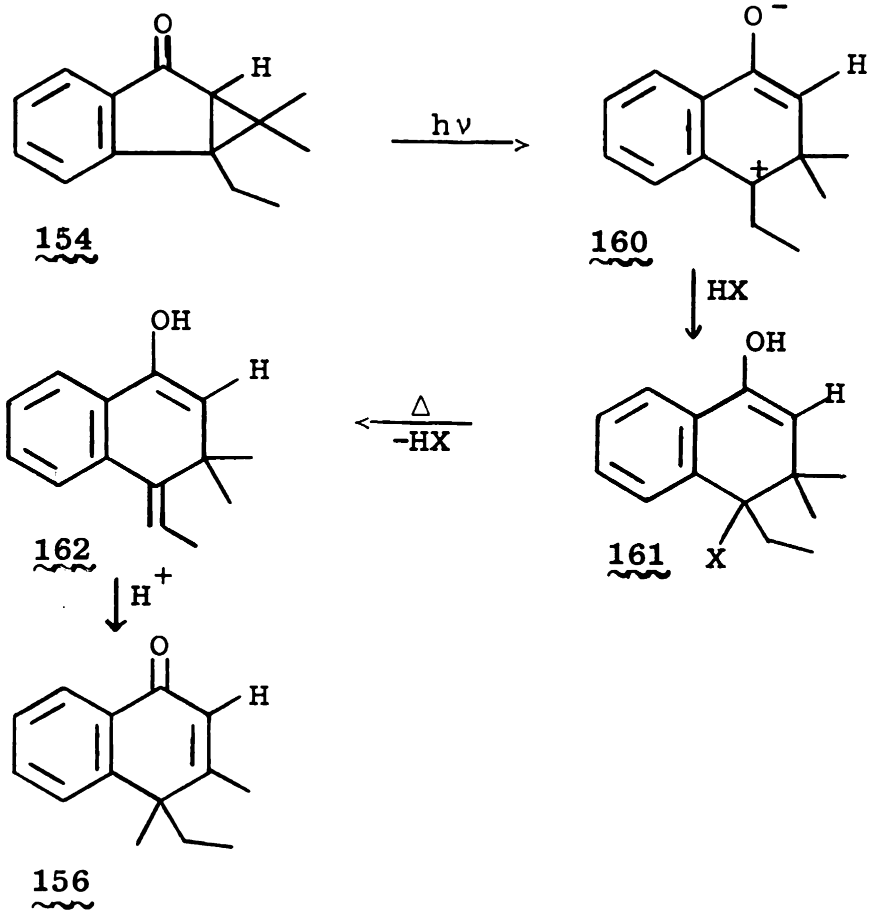
148



124

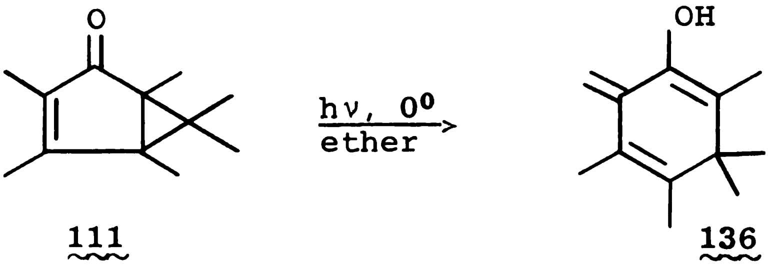
allylic methyls appear at τ 8.02 and 7.93. The signal at τ 7.93 has been assigned to the methyl at C-3, as a methyl attached to the β carbon of a cyclic dienone exhibits a lower field signal (24,71).

Since the photoproduct isolated in the isomerization of naphthalenone 154 is naphthalenone 156, the photorearrangement of a benzobicyclo[3.1.0]hexenone to a 1(4H)-naphthalenone must occur *via* a 1,2-alkyl migration. A few cases have been reported in which the photoisomerization of a bicyclo[3.1.0]hexenone to a 2,5-cyclohexadienone occurs by a 1,2-alkyl migration (72,77). However, the photorearrangement of 154 to 156 can also be rationalized by a mechanism analogous to that eluciated by Hart and Swatton for the conversion of bicyclo[3.1.0]hexenone 111 to hexamethyl-2,5-cyclohexadienone (see Section A). Thus the dipolar intermediate 160, photochemically generated from 155, could be trapped by a suitable nucleophile to give 161. Thermal or acid-catalyzed elimination of the nucleophile from 161 would provide the enolic triene 162, which



could yield 156 on further treatment with acid.

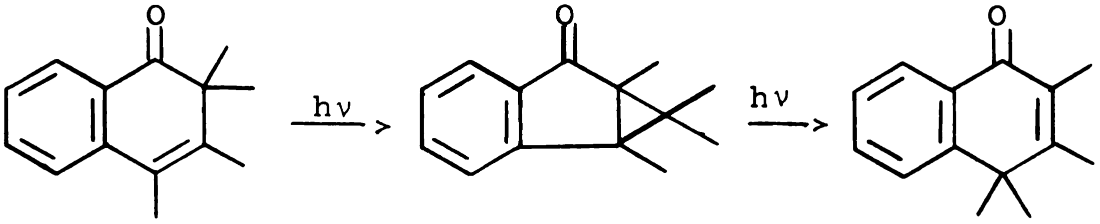
Although Swatton was able to obtain the enolic triene 136 by irradiation of a solution of bicyclo[3.1.0]hexenone 111 in anhydrous ether at 0° (78), no intermediates have



been detected in the photoisomerization of benzobicyclo-[3.1.0]hexenones to 1(4H)-naphthalenones.

D. Conclusion

The goal of Part II of this thesis was to determine the mechanisms for the photoisomerization of 121 to 123 and of 123 to 124.



121 123 124

Having examined the comparable photorearrangement of 2,2,4-trimethyl-1(2H)-naphthalenone, 136, it can be concluded that the photoisomerization of naphthalenone 121 to benzobicycloketone 123 occurs by a "bond-crossing" mechanism that most likely does not involve a ketene intermediate. Furthermore, an investigation of the photorearrangement of 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone, 154, has shown that the photoisomerization of 123 to naphthalenone 124 must proceed *via* a 1,2-alkyl migration.

EXPERIMENTAL

A. Irradiation of 1,5,6,6-Tetramethyl-3,4-benzobicyclo[3.1.0]hexen-2-one (123) in Diethyl Ether

A solution of 44 mg of 123 (50) in 8 ml of diethyl ether was irradiated through a Pyrex filter with a 450-watt Hanovia Type L mercury arc lamp. Monitoring the photolysis by vpc (5' x 1/4" DEGS column; 180°; 100 ml/min of He) indicated the formation of a single photoproduct. This compound was purified by vpc (above conditions) and was shown to be identical [mp: 76-78°; ir spectrum (CCl_4): 1648 ($\nu_{C=O}$, conjugated), 1626 (shoulder, $\nu_{C=C}$, conjugated) and 1605 cm^{-1} ($\nu_{C=C}$, aromatic); nmr spectrum (CCl_4): a six-proton singlet at τ 8.52, broad three-proton singlets at τ 8.02 and 7.93 and an aromatic multiplet centered at τ 2.57 (4H)] with a sample of 2,3,4,4-tetramethyl-1(4H)-naphthalenone, 124, previously prepared in this laboratory (53). The photoisomerization of 123 to 124 proceeded in 80% yield (vpc and nmr, hexamethylbenzene as standard).

B. Preparation of 1,2,4-Trimethylnaphthalene

1. 1-Chloromethyl-3,4-dimethylnaphthalene (51)

To an ice-cold solution of 1,2-dimethylnaphthalene (60.0 g, 0.38 mole) in 200 ml of acetic acid was added 23.3 g of paraformaldehyde. Hydrogen chloride gas was passed through the suspension until a clear solution resulted and the mixture was stirred at room temperature for 16 hrs. The solution was then diluted with water (400 ml) and extracted with benzene (3 x 200 ml). The benzene extract was washed with dilute sodium carbonate (3 x 200 ml) and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled, bp 153-158^0 (1.2 mm) providing 28.5 g (0.14 mole) of 1-chloromethyl-3,4-dimethylnaphthalene, mp 68-71^0 [lit. val. (51) 70-71^0]. The yield was 37%.

2. 1,2,4-Trimethylnaphthalene (51)

A solution of 1-chloromethyl-3,4-dimethylnaphthalene (28.0 g, 0.14 mole) in 200 ml of dry tetrahydrofuran was added over one hr to a suspension of lithium aluminum hydride (4.5 g, 0.14 mole) in 300 ml of dry, stirred, refluxing tetrahydrofuran. The mixture was stirred at reflux for an additional 24 hrs, then cooled in an ice bath, and small pieces of ice were added to hydrolyze the excess lithium aluminum hydride. To this mixture was added 150 ml of 10% HCl and 150 ml of water. The resulting mixture was extracted with ether (4 x 200 ml) and the separated ether layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent provided 32.0 g of an oil which solidified with cooling. Recrystallization of this residue from 95% ethanol gave 12.9 g (0.076 mole) of 1,2,4-trimethylnaphthalene, mp 48-50^0 [lit. val. (51) 49-50^0]. The yield was 55%. The ultraviolet (54) and nmr (55) spectra of 1,2,4-trimethylnaphthalene corresponded to those in the literature.

C. The Oxidation of 1,2,4-Trimethylnaphthalene

A solution of peroxytrifluoroacetic acid (56), prepared from 0.65 ml of 90% hydrogen peroxide (0.024 mole) and 5.55 g (0.026 mole) of trifluoroacetic anhydride in 10 ml of freshly distilled methylene chloride, was cooled to -20^0 and added with stirring over 45 min to a solution of 3.7 g (0.022 mole) of 1,2,4-trimethylnaphthalene in 50 ml of methylene chloride which had previously been cooled via a carbon tetrachloride-dry ice bath to -20^0. Boron trifluoride etherate (7.25 ml of 47% $BF_3 \cdot Et_2O$) was added concurrently with the addition of the peracid. The temperature of the solution was maintained between -10^0 and -20^0 throughout the addition. After further stirring for 45 min at -20^0, the solution was poured into 200 ml of water and the organic layer was separated. The organic layer was washed with water (3 x 100 ml), saturated sodium bicarbonate (3 x 150 ml), and washed with water (3 x 100 ml). The aqueous sodium hydroxide extract and the methylene chloride fraction were investigated separately.

The aqueous base fraction was acidified with dilute hydrochloric acid and extracted with methylene chloride (3 x 100 ml), which yielded on evaporation 0.07 g of a dark viscous oil. Vapor phase chromatography (5' x 1/4" 20% DEGS 60/80 CHROM W column; 180^0; 100 ml/min of He) indicated the presence of several components. This material was not investigated further.

The methylene chloride fraction was dried over anhydrous magnesium sulfate and evaporated to afford a deep red viscous oil. Vacuum distillation of this material at 0.06 mm provided 1.52 g of a yellow liquid, bp $79\text{-}82^0$. The pot residue was 1.18 g of a deep red very viscous material. Vapor phase chromatography (5' x 1/4" DEGS column; 180^0; 100 ml/min of He) of the distillate showed that the crude oil had components with the following retention times: 4.6 min (47%), 5.7 min (42%), 6.1 min (2%) and 9.8 min (9%). The distillate was chromatographed on silica gel in a column measuring 4 x 47 cm. Elution with 1500 ml of pentane provided 0.64 g of 1,2,4-trimethylnaphthalene which was identified by its mp ($49\text{-}51^0$), ir spectrum, and R_t (5.7 min). The conversion of 1,2,4-trimethylnaphthalene in the oxidation was 83%. Elution with 600 ml of methylene chloride provided a yellow oil which was shown to be homogeneous (R_t 4.6 min) by vpc (above conditions). Finally, elution with 350 ml of 95% ethanol provided an oil which vpc analysis indicated was composed of two compounds (R_t 6.1 and 9.8 min). Final purification of all compounds was achieved by vpc. None of the compounds were found to be thermally interconvertible under the vpc column conditions. An insufficient amount of the product with R_t 6.1 min (which composed 2% of the distillate) was obtained to permit identification.

1. Product Identification

a. 2,2,4-Trimethyl-1(2H)-naphthalenone (136). This colorless oil had a R_t of 4.6 min and showed principal infrared bands (liquid film) at 1673 ($\nu_{C=O}$, conjugated) and 1600 cm^{-1} ($\nu_{C=C}$, aromatic), whereas in CCl_4 solution the absorptions appeared at 1681 and 1603 cm^{-1}. The ultraviolet spectrum of 136 in 95% ethanol had maxima at 333 (log ε 3.23), 283 (log ε 3.35), 274 (log ε 3.56), 266 (log ε 3.54) and 236 mμ (log ε 4.53). The nmr spectrum (CCl_4) of 136 consisted of a six-proton singlet at τ 8.78, a three-proton doublet (J = 1.5 Hz) centered at τ 7.89, a one-proton quartet (J = 1.5 Hz) centered at τ 4.15, and aromatic multiplets, τ 2.30-2.90 and τ 1.85-2.10 (4H together).

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

Found: C, 83.71; H, 7.47.

b. 1,1,4-Trimethyl-2(1H)-naphthalenone (142). This oil had a R_t of 9.8 min and showed principal infrared bands (CCl_4) at 1660 ($\nu_{C=O}$, conjugated), 1628 ($\nu_{C=C}$, conjugated) and 1604 cm^{-1} ($\nu_{C=C}$, aromatic). The ultraviolet spectrum of 142 in 95% ethanol had maxima at 304 (log ε 4.10), 238 (log ε 4.09) and 234 mμ (log ε 4.09). The nmr spectrum (CCl_4) of 142 consisted of a six-proton singlet at τ 8.62, a three-proton doublet (J = 0.9 Hz) centered at τ 7.68, a broad (h_w = 4.0 cycles) one-proton singlet at τ 4.03 and an aromatic multiplet, τ 2.51-2.86 (4H).

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

Found: C, 83.69; H, 7.54.

D. Irradiation of 2,2,4-Trimethyl-1(2H)-naphthalenone (136) in Diethyl Ether

A solution of 198 mg of 2,2,4-trimethyl-1(2H)-naphthalenone, 136, in 20 ml of diethyl ether was irradiated through a Pyrex filter with a 450-watt Hanovia Type L mercury arc lamp. Monitoring the photolysis by vpc (5' x 1/4" DEGS column; 180°; 100 ml/min of He) showed a progressive decrease in the concentration of 136 (R_t 4.6 min) and the appearance of two new compounds with retention times of 6.0 min and 18.6 min. The compound with R_t 6.0 min reached a maximum concentration of 11% of the volatiles after three hours irradiation and then decreased, whereas the concentration of the compound with R_t 18.6 min continued to increase as the photolysis was continued. After irradiation for 12 hours, vpc analysis of the photolysate indicated the volatiles were composed of: 136 (18%), a compound with R_t 6.0 min (3%) and a compound with R_t 18.6 min (78%). The compounds were purified by vpc (above conditions). An insufficient amount of the product with R_t 6.0 min was obtained to permit identification. However, the photoproduct with R_t 18.6 min has been identified as 3,4,4-trimethyl-1(4H)-naphthalenone, 148. This colorless oil had major bands in its ir spectrum (CCl_4) at 1660 ($\nu_{C=O}$, conjugated), 1632 ($\nu_{C=C}$, conjugated) and 1605 cm^{-1} ($\nu_{C=C}$, aromatic). The nmr spectrum (CCl_4) of 148 consisted of a six-proton singlet at τ 8.52, a three-proton doublet (J = 1.5 Hz) centered at τ 7.91, a one-proton quartet (J = 1.5 Hz) centered at τ 3.85, and aromatic multiplets, τ 2.45-2.85 and τ 1.85-2.10 (4H together). Reaction of ketone 148 with 2,4-dinitrophenylhydrazine provided the 2,4-dinitrophenylhydrazone of 148, which was recrystallized from ethanol-ethyl acetate to give deep violet crystals, mp 245-247^{0} (lit. val. (57) 243-245^{0}). A mixture of the 2,4-DNP adduct of the photoproduct and an authentic sample (58) of the 2,4-dinitrophenylhydrazone of 148 also melted at 245-247^{0}.

E. Irradiation of 2,2,3,4-Tetramethyl-1(2H)-naphthalenone (121) in Hexane-Dimethyl Amine

A solution of 114 mg (5.7 x 10^{-4} mole) of 121 and 64 mg (1.4 x 10^{-3} mole) of dimethyl amine in 10 ml of hexane was irradiated through a Pyrex filter with a 450-watt Hanovia Type L mercury arc lamp. The photolysis was monitored by vpc (5' x 1/4" DEGS column; 180^{0}; 100 ml/min of He). Examination by vpc of the photolysis solution after 30 min irradiation indicated a decrease in the concentration of ketone

121 (R_t 7.0 min) and the appearance of a photoproduct with R_t 3.6 min. Continued irradiation caused a progressive decrease in the concentration of 121 and a corresponding increase in the concentration of the photoproduct. Vpc examination of the photolysis solution after 3 hours irradiation only showed the presence of compounds with retention times of 3.6 min (45%) and 7.0 min (55%). The nmr spectrum (CCl_4) of the crude photolysate after three hours irradiation only had singlets at τ 9.27, 8.84, 8.73, and 8.50, in addition to the signals for unreacted 2,2,3,4-tetramethyl-1(2H)-naphthalenone, 121. The photoproduct was purified by vpc (above conditions) and has been identified by its ir spectrum (CCl_4): 1699 cm^{-1} ($\nu_{C=O}$), nmr spectrum (CCl_4): three-proton singlets at τ 9.27, 8.84, 8.73, and 8.50 and an aromatic multiplet centered at τ 2.60 (4H), and R_t as 1,5,6,6-tetramethyl-3,4-benzobicyclo[3.1.0]hexen-2-one, 123 (50).

F. Irradiation of 2,2,3,4-Tetramethyl-1(2H)-naphthalenone (121) in Methanol

A solution of 80 mg of 121 in 8 ml of methanol was irradiated through a Pyrex filter with a 450-watt Hanovia Type L mercury lamp. The photolysis was monitored by vpc (5' x 1/4" DEGS column; 180°; 100 ml/min of He). Examination of the photolysis solution by vpc after 10 min irradiation showed a significant decrease in the concentration of the ketone 121 (R_t 7.0 min) and the appearance of a photoproduct with R_t 3.6 min. After irradiation for one hour, analysis by vpc indicated the presence of only a single photoproduct with R_t 11.5 min. The nmr spectrum (CCl_4) of the crude photolysate (after irradiation for one hour) had a sharp singlet at τ 8.52, broad singlets at τ 8.02 and 7.92 and a complex aromatic multiplet centered at τ 2.60. The photoproduct with R_t 11.5 min was purified by vpc (above conditions) and has been identified by its mp: 76-78^0 and infrared spectrum as 2,3,4,4-tetramethyl-1(4H)-naphthalenone, 124 (53).

G. Preparation of 4-Ethyl-1,2-dimethylnaphthalene (158)

1. 1-Acetyl-3,4-dimethylnaphthalene (59)

Anhydrous aluminum chloride (106.8 g) was added to an ice-cooled solution of 1,2-dimethylnaphthalene (62.4 g) in carbon disulfide (450 ml). Acetyl chloride (32.0 g) was then added dropwise to the ice-cooled mixture. After the initial evolution of hydrogen chloride had subsided, the reaction mixture was refluxed for 3 hrs and then left at room temperature for 16 hours. Most of the carbon disulfide was evaporated and the residue was poured onto a mixture of ice and hydrochloric acid. A dark oil resulted that was extracted with benzene (4 l). The benzene solution was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent provided a dark green oil that was vacuum distilled, bp 140-143^0 at 0.35 mm, to give 31.6 g of 1-acetyl-3,4-dimethylnaphthalene [lit. val. (59) bp:

142-143° at 0.45 mm]. Examination of the distillate by vpc (5' x 1/4" SE-30 column; 230°; 40 ml/min of He) showed that the 1-acetyl-3,4-dimethylnaphthalene obtained was > 95% pure. The slight contaminant may be 3-acetyl-1,2-dimethylnaphthalene.

2. 4-Ethyl-1,2-dimethylnaphthalene (158)

1-Acetyl-3,4-dimethylnaphthalene (20.0 g) was refluxed for 27 hrs with a mixture of amalgamated zinc (70.0 g), concentrated hydrochloric acid (70 ml), methanol (100 ml) and benzene (50 ml). While the mixture was refluxing, three additional 10 ml portions of hydrochloric acid were added. The mixture was cooled and extracted with benzene (3 x 150 ml). The benzene solution was dried over anhydrous magnesium sulfate and evaporated to provide an oil. Vacuum distillation of this oil at 0.9 mm provided 11.2 g of 4-ethyl-1,2-dimethylnaphthalene, 158, bp 130-131° [lit. val. (60) bp: 136° at 1 mm]. Examination of the distillate by vpc (5' x 1/4" SE-30 column; 220°; 50 ml/min of He) showed that the 4-ethyl-1,2-dimethylnaphthalene obtained was > 97% pure. The ultraviolet maxima of 158 correspond exactly to those in the literature: $\lambda_{max}^{95\%EtOH}$ 325, 290 and 232 mμ (60). The nmr spectrum of 158 in CCl_4 consisted of a three-proton triplet (J = 7.5 Hz) centered at τ 8.73, three-proton singlets at τ 7.68 and 7.58, a two-proton quartet (J = 7.5 Hz) centered at τ 7.09, a one-proton singlet at τ 3.12, and aromatic multiplets, τ 2.75-2.92 (2H) and 2.15-2.31 (2H).

H. The Oxidation of 4-Ethyl-1,2-dimethylnaphthalene (158)

A solution of peroxytrifluoroacetic acid (56), prepared from 1.53 ml of 90% hydrogen peroxide (0.055 mole) and 12.7 g (0.06 mole) of trifluoroacetic anhydride in 20 ml of freshly distilled methylene chloride, was cooled to 0° and added with stirring over 50 min to a solution of 9.2 g (0.05 mole) of 4-ethyl-1,2-dimethylnaphthalene in 125 ml of methylene chloride which had previously been cooled *via* a carbon tetrachloride-dry ice bath to -20°. Boron trifluoride etherate (16.6 ml of 47% $BF_3 \cdot Et_2O$) was added concurrently with the addition of the peracid. The temperature of the solution was maintained between -10° and -20° throughout the addition. After further stirring for one hour at -20°, the solution was poured into 300 ml of water and the organic layer was separated. The organic layer was washed with water (2 x 200 ml), saturated sodium bicarbonate (3 x 100 ml), extracted with 10% aqueous sodium hydroxide (3 x 300 ml), and washed with water (3 x 300 ml).

The methylene chloride fraction was dried over anhydrous magnesium sulfate and evaporated to afford a deep red viscous oil. Vacuum distillation of this material at 0.3 mm provided 5.1 g of a yellow oil, bp 113-115°. The pot residue was 4.0 g of a black viscous material. Vapor phase chromatography (5' x 1/4" DEGS column; 180°; 100 ml/min of He) of the distillate showed that the crude oil had components with the following retention times: 4.1 min (49%), 5.4 min (41%), and 8.9 min (10%). The distillate was chromatographed on silica gel in a column measuring 4 x 45 cm. Elution with 1000 ml of pentane provided 2.05 g of 4-ethyl-1,2-dimethylnaphthalene which was identified by its ir spectrum and R_t (5.4 min). The conversion of 4-ethyl-1,2-dimethylnaphthalene in the oxidation was 78%. Elution with 600 ml of methylene chloride provided an oil which vpc analysis (above conditions) showed had two components with retention times of 4.1 min (90%) and 8.9 min (10%). Finally, elution with 500 ml of a 1:1 mixture of methylene chloride-95% ethanol afforded an oil which was shown to be homogeneous (R_t 8.9 min) by vpc (above conditions). Final purification of all compounds was achieved by vpc. Neither of the compounds was found to be thermally interconvertible under the vpc column conditions.

1. Product Identification

a. 4-Ethyl-2,2-dimethyl-1(2H)-naphthalenone (154). This oil had a R_t of 4.1 min and showed principal infrared bands (CCl_4) at 1675 ($\nu_{C=O}$, conjugated), 1640 (shoulder, $\nu_{C=C}$) and 1600 cm^{-1} ($\nu_{C=C}$, aromatic). The ultraviolet spectrum of 154 in 95% ethanol had maxima at 333 (log ε 3.32), 283 (log ε 3.42), 274 (log ε 3.61), 266 (log ε 3.61) and 236 mμ (log ε 4.74). The nmr spectrum (CCl_4) of 154 consisted of a six-proton singlet at τ 8.80, a three-proton triplet (J = 7.8 Hz) centered at τ 8.80, a two-proton quartet (J = 7.8 Hz) centered at τ 7.50, a broad (h_w = 3.3 cycles) one-proton singlet at τ 4.25, and aromatic multiplets, τ 2.55-3.13 (3H) and 2.0-2.2 (1H).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05

Found: C, 83.85; H, 8.02.

b. 4-Ethyl-1,1-dimethyl-2(1H)-naphthalenone (159).

This oil had a R_t of 8.9 min and showed principal infrared bands (CCl_4) at 1660 ($\nu_{C=O}$, conjugated), 1622 ($\nu_{C=C}$, conjugated) and 1602 cm^{-1} ($\nu_{C=C}$, aromatic). The ultraviolet spectrum of 159 in 95% ethanol had maxima at 303 (log ε 4.11), 237 (log ε 4.10) and 232 mμ (log ε 4.10). The nmr spectrum (CCl_4) of 159 consisted of a three-proton triplet ($J = 7.8$ Hz) centered at τ 8.69, a six-proton singlet at τ 8.62, a two-proton quartet ($J = 7.8$ Hz) at τ 7.29, a broad one-proton singlet at τ 4.07, and an aromatic multiplet, τ 2.48-2.95 (4H).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05

Found: C, 83.87; H, 8.01.

I. Irradiation of 4-Ethyl-2,2-dimethyl-1(2H)-naphthalenone (154) in Diethyl Ether

A solution of 167 mg of 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone, 154, in 17 ml of diethyl ether was irradiated through a Pyrex filter with a 450-watt Hanovia Type L mercury arc lamp. Monitoring the photolysis by vpc (5' x 1/4" DEGS column; 180°; 100 ml/min of He) showed a progressive decrease in the concentration of 154 (R_t 4.2 min) and the appearance of two new compounds with retention times of 5.4 min and 15.5 min. The compound with R_t 5.4 min reached a maximum concentration of 15% of the volatiles after

5 hours irradiation and then decreased, whereas the concentration of the compound with R_t 15.5 min continued to increase as the photolysis was continued. After irradiation for 16 hours, vpc analysis of the photolysate indicated the volatiles were composed of: 154 (30%), a compound with R_t 5.4 min (7%) and a compound with R_t 15.5 min (63%). The compounds were purified by vpc (above conditions). An insufficient amount of the product with R_t 5.4 min was obtained to permit identification. However, the photoproduct with R_t 15.5 min has been identified as 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone, 156. This colorless oil had major bands in its ir spectrum (CCl_4) at 1660 ($\nu_{C=O}$, conjugated), 1631 ($\nu_{C=C}$, conjugated) and 1604 cm^{-1} ($\nu_{C=C}$, aromatic). The ultraviolet spectrum of 156 in 95% ethanol had a maximum at 252 mμ (log ε 4.17) and a shoulder at 269 mμ (log ε 4.07). The nmr spectrum (CCl_4) of 156 consisted of a three-proton triplet (J = 7.8 Hz) centered at τ 9.62, a three-proton singlet at τ 8.55, a two-proton quartet (J = 7.8 Hz) centered at τ 8.05, a three-proton doublet (J = 1.5 Hz) centered at τ 7.94, a broad (h_w = 3.6 cycles) one-proton singlet at τ 3.79 and aromatic multiplets centered at τ 2.67 (3H) and τ 1.93-2.12 (1H).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05

Found: C, 84.02; H, 8.09.

J. Irradiation of 4-Ethyl-2,2-dimethyl-1(2H)-naphthalenone (154) in Trifluoroethanol

A solution of 50 mg of 154 in 5 ml of trifluoroethanol was irradiated through a uranium glass filter (short wavelength cut-off at about 360 mμ) with a 450-watt Hanovia Type L mercury arc lamp. Vapor phase chromatography (5' x 1/4" DEGS column; 180°; 100 ml/min of He) of the photolysis solution after 15 min irradiation showed that the photolysate had components with the following retention times: 4.1 min, 154, (51%), 5.4 min (11%), and 15.3 min (38%). Examination of the photolysate by vpc after irradiation for one hour indicated the presence of a single component with R_t 15.3 min. The photoproduct was purified by vpc and has been identified by its infrared spectrum and R_t as 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone, 156.

Similarly, irradiation of a solution of 110 mg of 154 in 11 ml of trifluoroethanol through a Pyrex filter with a 450-watt Hanovia Type L mercury arc lamp for two hours proceeded with complete conversion and provided a 90% yield (nmr, hexamethylbenzene as standard) of 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone, 156.

SUMMARY

1. Irradiation of an ether solution of 1,5,6,6-tetramethyl-3,4-benzobicyclo[3.1.0]hexen-2-one (123) [previously shown to be the primary photoproduct in the irradiation of 2,2,3,4-tetramethyl-1(2H)-naphthalenone (121)] provided an 80% yield of 2,3,4,4-tetramethyl-1(4H)-naphthalenone (124).

2. Oxidation of 1,2,4-trimethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride afforded 2,2,4-trimethyl-1(2H)-naphthalenone (136), 1,1,4-trimethyl-2(1H)-naphthalenone (142), and an unidentified product in the ratio 81:16:3. The over-all yield was 22%, based on 83% conversion of 1,2,4-trimethylnaphthalene.

3. Irradiation of an ether solution of naphthalenone 136 gave 3,4,4-trimethyl-1(4H)-naphthalenone (148). A detailed consideration of the possible mechanisms for the photoisomerization of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]hexenone shows that the isolation of 148 from the photolysis of 136 requires that the photorearrangement of naphthalenone 121 to benzobicycloketone 123 proceeds by a "bond-crossing" mechanism.

4. Irradiation of a hexane solution of naphthalenone **121** containing dimethyl amine gave benzobicycloketone **123**. Photolysis of a solution of naphthalenone **121** in methanol provided naphthalenone **124** *via* bicycloketone **123**. These results suggest that the "bond-crossing" mechanism for the photoisomerization of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]hexenone does not involve a ketene intermediate.

5. Oxidation of 4-ethyl-1,2-dimethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride provided 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone (**154**) and 4-ethyl-1,1-dimethyl-2(1H)-naphthalenone (**159**) in the ratio of 5:1. The over-all yield was 31%, based on 78% conversion of 4-ethyl-1,2-dimethylnaphthalene.

6. Irradiation of an ether solution of naphthalenone **154** gave 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone (**156**). An examination of the possible mechanisms for the photorearrangement of a benzobicyclo[3.1.0]hexenone to a 1(4H)-naphthalenone shows that the isolation of naphthalenone **156** from the irradiation of **154** requires that the photoisomerization of benzobicycloketone **123** to naphthalenone **124** occurs *via* a 1,2-alkyl migration.

LITERATURE CITED

1. Labhart, H. and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).

2. Bays, D. E., R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., Sect. B*, 215 (1967).

3. Mislow, K., M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962).

4. Moscowitz, A., K. Mislow, M. A. W. Glass and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

5. Cookson, R. C. and S. MacKenzie, *Proc. Chem. Soc.*, 423 (1961).

6. Hess, L. D. and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **89**, 1973 (1967).

7. Starr, J. E. and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

8. Williams, J. R. and H. Ziffer, *Chem. Comm.*, 194 (1967).

9. Williams, J. R. and H. Ziffer, *Chem. Comm.*, 469 (1967).

10. Paquette, L. A., R. F. Eizember, and O. Cox, *J. Am. Chem. Soc.*, **90**, 5153 (1968).

11. Paquette, L. A. and R. F. Eizember, *J. Am. Chem. Soc.*, **89**, 6205 (1967).

12. Crandall, J. K., J. P. Arrington, and J. Hen, *J. Am. Chem. Soc.*, **89**, 6208 (1967).

13. Chapman, O. L. in "Advances in Photochemistry", edited by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York, 1963, Vol. 1, p. 323.

14. Büchi, G. and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).

15. Cargill, R. L., M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965).

16. Erman, W. F. and H. C. Kretschmar, *J. Am. Chem. Soc*., **89**, 3842 (1967).

17. Schuster, D. I., M. Axelrod and J. Auerbach, *Tetrahedron Letters*, 1911 (1963).

18. Schenck, G. O. and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

19. Bays, D. E. and R. C. Cookson, *J. Chem. Soc.*, *Sect. B*, 226 (1967).

20. Ciabattoni, J., J. E. Crowley and A. S. Kende, *J. Am. Chem. Soc.*, **89**, 2778 (1967).

21. Mukai, T., H. Tsuruta, A. Takeshita and H. Watanabe, *Tetrahedron Letters*, 4065 (1968).

22. Kakihana, T., M. S. Thesis, Michigan State University, 1966.

23. Oku, A., T. Kakihana, and H. Hart, *J. Am. Chem. Soc*., **89**, 4554 (1967).

24. Hart, H., P. M. Collins and A. J. Waring, *J. Am. Chem. Soc*., **88**, 1005 (1966).

25. Quinkert, G., G. Cimbollek and G. Buhr, *Tetrahedron Letters*, 4573 (1966).

26. Griffiths, J. and H. Hart, *J. Am. Chem. Soc*., **90**, 3297 (1968).

27. Chapman, O. L. and J. D. Lassila, *J. Am. Chem. Soc*., **90**, 2449 (1968).

28. Gripper Gray, A. C. and H. Hart, *J. Am. Chem. Soc*., **90**, 2569 (1968).

29. Hart, H. and R. M. Lange, *J. Org. Chem*., **31**, 3776 (1966).

30. Jones, L. B. and V. K. Jones, *J. Am. Chem. Soc*., **89**, 1880 (1967).

31. Doering, W. von E. and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

32. Hart, H., J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem*., **31**, 2244 (1966).

33. Ciganek, E., *J. Am. Chem. Soc*., **89**, 1458 (1967).

34. Srinivasan, R., *J. Am. Chem. Soc.*, **81**, 5541 (1959).

35. Turro, N. J. and R. M. Southam, *Tetrahedron Letters*, 545 (1967).

36. Hoffmann, R. and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

37. Ulrich, H., "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, 1967, Chapter II.

38. Montaigne, R. and L. Ghosez, *Angew. Chem. Internat. Edit.*, **7**, 221 (1968).

39. Norin, T., *Acta Chem. Scand.*, **15**, 1676 (1961).

40. Hassner, A., *J. Org. Chem.*, **33**, 2684 (1968).

41. Zimmerman, H. E., R. W. Binkley, R. S. Givens and M. A. Sherwin, *J. Am. Chem. Soc.*, **89**, 3932 (1967).

42. Kitahonoki, K. and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

43. Zimmerman, H. E. and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966).

44. Liu, R. S. H., *J. Am. Chem. Soc.*, **90**, 215 (1968).

45. Zimmerman, H. E., R. S. Givens and R. M. Pagni, *J. Am. Chem. Soc.*, **90**, 4191, 6096 (1968).

46. Rabideau, P. W., J. B. Hamilton, and L. Friedman, *J. Am. Chem. Soc.*, **90**, 4465 (1968).

47. Brewer, J. P. N. and H. Heaney, *Chem. Comm.*, 811 (1967).

48. Ciganek, E., *J. Am. Chem. Soc.*, **88**, 2882 (1966).

49. Moriconi, E. S., J. P. St. George and W. F. Forbes, *Can. J. Chem.*, **44**, 759 (1966).

50. Hart, H. and R. K. Murray, Jr., *J. Org. Chem.*, **32**, 2448 (1967).

51. Hewett, C. L., *J. Chem. Soc.*, 293 (1940).

52. Poos, G. I., G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

53. Murray, R. K., Jr., M. S. Thesis, Michigan State University, 1966.

54. Heilbronner, E., U. Fröhlicher and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949).

55. Yew, F. F., R. J. Kurland and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).

56. Emmons, W. D., *J. Am. Chem. Soc.*, **76**, 3468 (1954).

57. Huffman, J. W. and T. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965).

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59. Plattner, Pl. A. and A. Ronco, *Helv. Chim. Acta*, **27**, 400 (1944).

60. Cocker, W., L. O. Hopkins, L. Mabrouk, J. McCormick,, and T. B. H. McMurry, *J. Chem. Soc.*, 2230 (1960).

61. de Mayo, P. and S. T. Reid, *Quart. Rev.*, **15**, 393 (1961).

62. Quinkert, G., *Angew. Chem. Internat. Edn.*, **4**, 211 (1965).

63. Kropp, P. J. in "Organic Photochemistry", edited by O. L. Chapman, Marcel Dekker, Inc., New York, 1967, Vol. 1, p. 1.

64. Barton, D. H. R. and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

65. Collins, P. M. and Hart, H., *J. Chem. Soc.*, *Sect. C*, 1197 (1967).

66. Hart, H. and A. J. Waring, *Tetrahedron Letters*, 325 (1965).

67. Collins, P. M. and H. Hart, *J. Chem. Soc.*, *Sect. C*, 895 (1967).

68. Perst, H. and K. Dimroth, *Tetrahedron*, **24**, 5385 (1968).

69. Griffiths, J. and H. Hart, *J. Am. Chem. Soc.*, **90**, 5296 (1968).

70. Schaffner, K. in "Advances in Photochemistry", edited by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York, 1966, Vol. 4, p. 81.

71. Kropp, P. J., *J. Am. Chem. Soc.*, **86**, 4053 (1964).

72. Frei, J., C. Ganter, D. Kägi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

73. Hart, H. and D. W. Swatton, *J. Am. Chem. Soc*., **89**, 1874 (1967).

74. Hart, H., C. A. Buehler and A. J. Waring in "Selective Oxidation Processes", Advances in Chemistry Series, American Chemical Society, Washington, D.C., 1965, p. 1.

75. Davidson, A. J. and R. O. C. Norman, *J. Chem. Soc.*, 5404 (1964).

76. Cava, M. P. and R. J. Spangler, *J. Am. Chem. Soc*., **89**, 4551 (1967).

77. Schuster, D. I. and A. C. Fabian, *Tetrahedron Letters*, 4093 (1966).

78. Swatton, D. W., Ph.D. Thesis, Michigan State University, 1967.