THE PREPARATION AND PHOTOCHEMISTRY OF 2,2,3,4-TETRAMETHYL-1(2H)-NAPHTHALENONE

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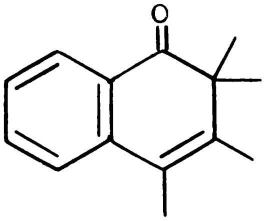
ABSTRACT

THE PREPARATION AND PHOTOCHEMISTRY OF 2,2,3,4-TETRAMETHYL-1(2H)-NAPHTHALENONE

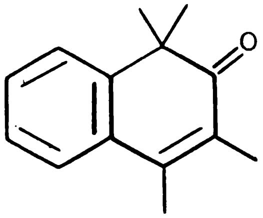
by Roger K. Murray, Jr.

The purpose of this investigation was 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.

The oxidation of 1,2,3,4-tetramethylnaphthalene with peroxytrifluoroacetic acid - boron fluoride etherate in methylene chloride at -12^0 gave: 2,2,3,4-tetramethyl-1(2H)-naphthalenone (I), 1,1,3,4-tetramethyl-2(1H)-naphthalenone (II), and 2,2,4,4-tetramethyl-1,3-dioxotetralin (III) in the ratio of 61:21:18. The overall yield of products was 50%. The proposed oxidation mechanism readily accounts for these products.



I



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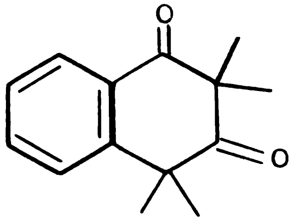
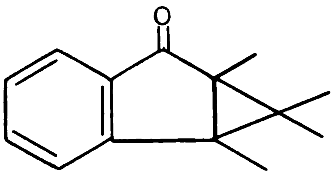


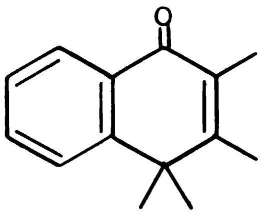
III

Irradiation of naphthalenone I in ether provided 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one (IV) as the primary photoproduct. Further irradiation of

naphthalenone I in ether gave a moderate yield of 2,3,4,4-tetramethyl-1(4H)-naphthalenone (V).



IV



V

Naphthalenone V was recovered unchanged from irradiation in ether, but photolysis in methanol led to a steady decrease in its concentration. However, no volatile products could be detected by vpc.

3,4-Benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one (IV) photolyzed rapidly in ether to afford V. Naphthalenone V was also the major photoproduct when benzobicyclic-ketone IV was irradiated in acid-free methanol, but an unidentified product (VI) was also detected. The photochemical relationship of VI and naphthalenone V has not yet been established.

Irradiation of 1,1,3,4-tetramethyl-2(1H)-naphthalenone (II) in ether or methanol led to a decrease in the concentration of naphthalenone II, but no volatile products were detected by vpc.

Control experiments demonstrated that none of the photochemically interesting compounds studied were reactive in the dark with the solvents in which they were irradiated.

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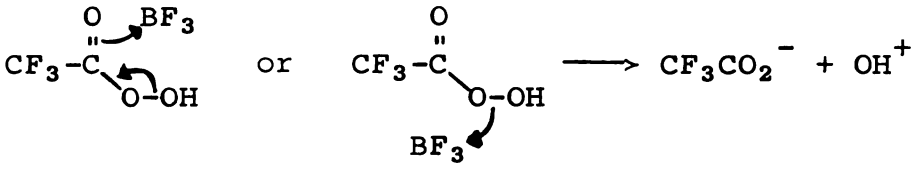
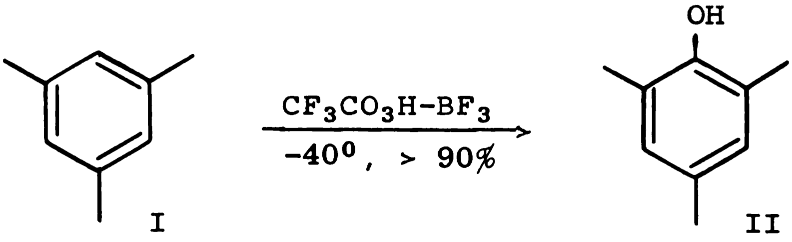
INTRODUCTION

Organic peracids have long been recognized as sources of electrophilic (positive) hydroxyl useful for the oxidation of certain aromatic hydrocarbons (1). An especially good source of positive hydroxyl has been peroxytrifluoroacetic acid, as the trifluoroacetate ion is a good leaving group (2). However, the use of this peracid in oxidations often led to low conversions. It was proposed (3) that a Lewis acid might facilitate the decomposition of peroxytrifluoroacetic acid under mild conditions through coordination with one of the oxygens not used ultimately as an oxidant.



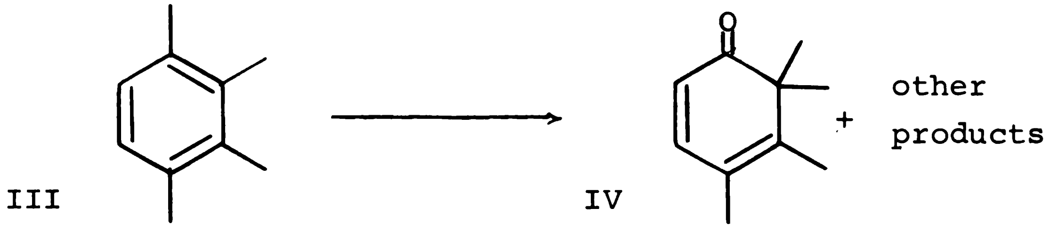
$$CF_3\text{-}\overset{\overset{O\,\rightarrow\,BF_3}{\|}}{C}\text{-}O\text{-}OH \quad \text{or} \quad CF_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{BF_3}{\downarrow}}{O}\text{-}OH \longrightarrow CF_3CO_2^- + OH^+$$

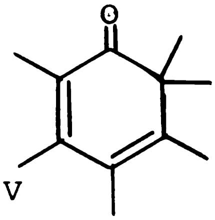
The use of peroxytrifluoroacetic acid in the presence of boron fluoride proved effective in the hydroxylation of certain aromatic hydrocarbons. The yield of phenol was especially good if positions _ortho_ or _para_ to the entering hydroxyl group were blocked to retard further oxidation. Thus mesitylene, I, was converted to mesitol, II, in good yield with efficient use of the peracid even at -40°, and isodurene was converted to isodurenol in 65% yield (4).



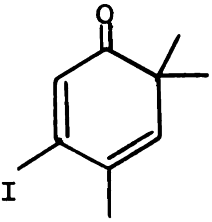
When the oxidation was applied to prehnitene, III, (4) several products were obtained in addition to the expected prehnitol.

Although obtained in very low yield, the isolation of 4,5,6,6-tetramethyl-2,4-cyclohexadienone, IV, in this reaction was especially interesting. The product was accounted for by attack of the electrophilic oxidant at C-1 of the hydrocarbon, followed by a Wagner-Meerwein methyl migration and loss of a proton. The supposition, that if the original hydrocarbon were entirely alkylated the dominant reaction path would be conversion to dienone, was realized in the peroxytrifluoroacetic acid-boron fluoride oxidation of hexamethylbenzene to hexamethyl-2,4-cyclohexadienone, V, (5). The major products from the oxidation





V



VI

of pentamethylbenzene are also dienones (6); even the oxidation of durene proceeded to give over 50% of dienone VI (7).

The photochemistry of 2,4-cyclohexadienones has generated considerable attention (8,9,10). Barton and Quinkert elucidated three types of photochemical transformations of 2,4-cyclohexadienones having blocked *ortho*-positions (11): (a) ring fission to a *cis*-diene ketene; (b) acetoxyl group migration from C-6 to C-5, if unsubstituted, with concomitant aromatization to a phenol; and (c) expulsion of an acetoxyl group from C-6, followed by aromatization to a phenol. These alternatives are depicted in Figure 1.

The most important rearrangement process is ring fission of a 2,4-cyclohexadienone, A, to afford a *cis*-diene ketene, B, followed by isomerization to the *trans*-diene ketene, C, which can then react with an available nucleophile, D, to provide the observed product, E or F. The ease with which this reaction proceeds depends on the number and positions of the substituents in the cyclohexadienone molecule, and on the nucleophilic character of H-X.

If the substituents of the intermediate diene ketene do not cause mutual steric hindrance, then a weakly nucleophilic reactant H-X is sufficient to lead to products via C. Thus the irradiation of 6-acetoxy-6-methyl-2,4-cyclohexadienone (A; R^2 = OAc, R' = Me, $R^3 = R^4$ = H) in ether containing water gives the corresponding unsaturated acid (E; R^2 = OAc, R' = Me, $R^3 = R^4$ = H). However, if mutual repulsions exist so that the desired *trans*-diene ketene has

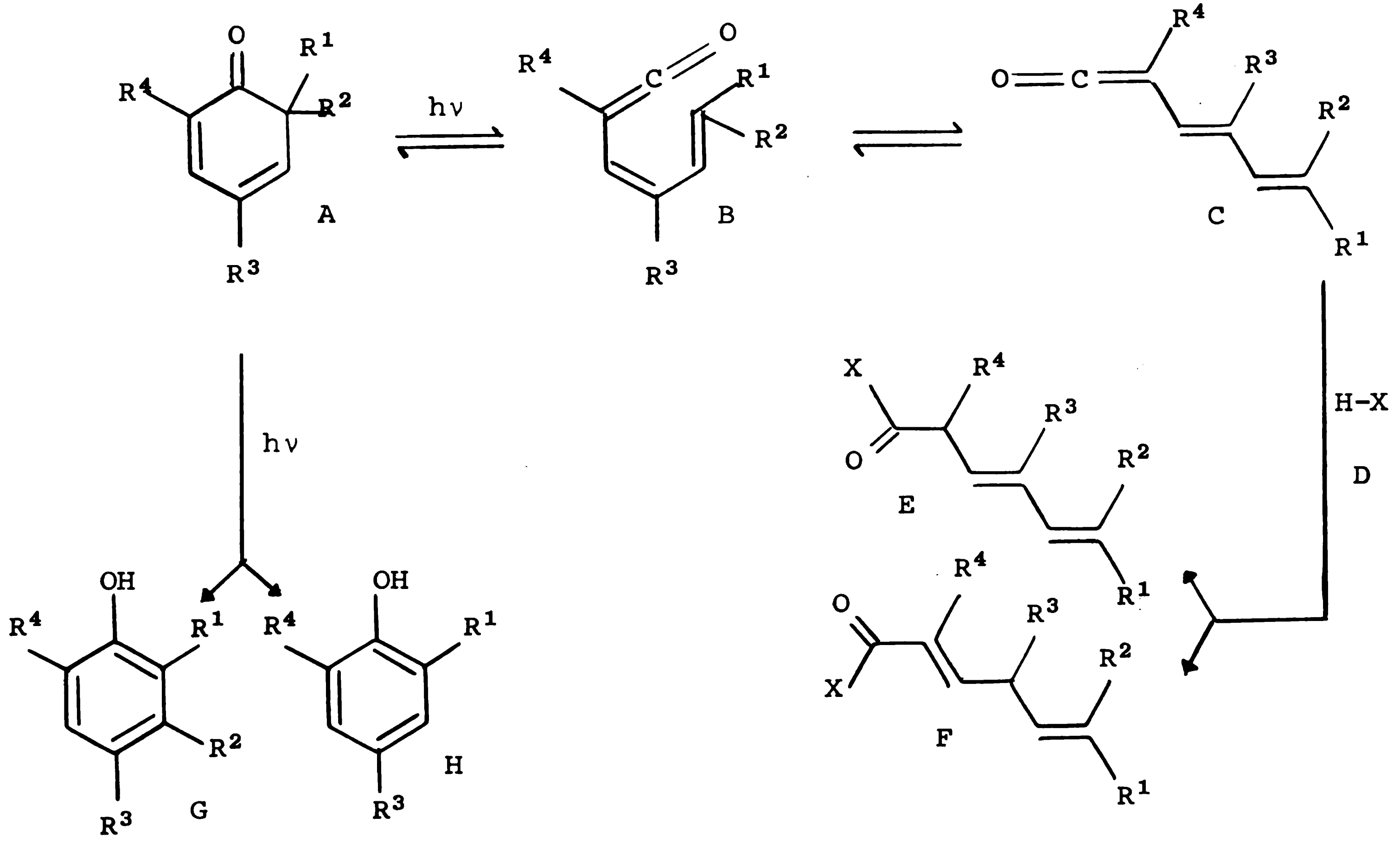
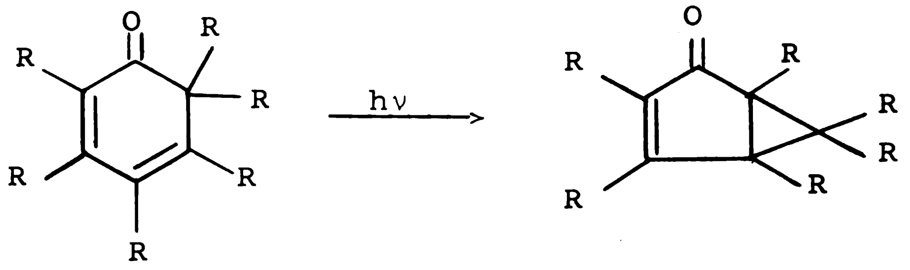


Figure 1. Possible courses for the photochemical reaction of 2,4-cyclohexadienones having blocked ortho-positions. [Reproduced from G. Quinkert, Angew. Chem., Intern. Ed. Engl., 4, 213 (1065).]

unfavorable interactions between the substituents, then the *trans*-form, C, is destabilized relative to the *cis*-diene ketene, B, and the rate of the back reaction to give the cyclohexadienone, A, is increased. In this case the formation of the acid derivatives will only predominate if a strong nucleophile (e.g., a primary amine) is used.

Recyclization of the *cis*-diene ketene permits slower processes to become important, namely the formation of phenols, either by a dienone/phenol photo-rearrangement to give G, or by homolytic photo-dissociation followed by abstraction of hydrogen from the solvent to give H. The dienone/phenol photo-rearrangement requires R^2 to be a nucleophilic group. Thus irradiation of 2,4,6-trimethyl-6-acetoxy-2,4-cyclohexadienone (A; R^2 = OAc, R' = R^3 = R^4 = Me) in dry ether, or in the presence of water or aniline gave 3-acetoxy mesitol (G; R^2 = OAc, R^1 = R^3 = R^4 = Me), whereas the analogous compound (A; R^2 = allyl, R^1 = R^3 = R^4 = Me) did not undergo such a rearrangement. The migration of the acetoxyl group to an adjacent carbon is a typical example of neighboring group participation. Expulsion of an acetoxyl group from C-6, followed by aromatization to a phenol, is demonstrated in the irradiation of 6-acetoxy-6-methyl-2,4-cyclohexadienone (A; R^2 = OAc, R^1 = Me, R^3 = R^4 = H) in anhydrous ether to give *o*-cresol (H; R^1 = Me, R^3 = R^4 = H).

A novel photochemical path has recently been discovered for highly substituted 2,4-cyclohexadienones. Irradiation of a 1% ether solution of hexamethyl-2,4-cyclohexadienone, V, (12) or hexaethyl-2,4-cyclohexadienone, VII, (5) in Pyrex produced photo-rearrangement to the corresponding bicyclo[3.1.0]hexane derivatives, VIII and IX. Labeling

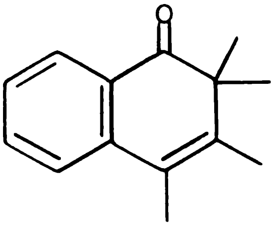


V R = CH_3 VIII R = CH_3

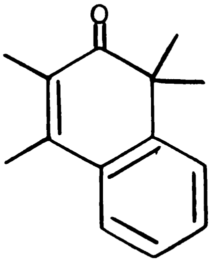
VII R = CH_2CH_3 IX R = CH_2CH_3

experiments established that the product was formed by a "bond-crossing" rather than an alkyl migration mechanism. It was suggested that the trans-diene ketene that would result from V would have an unfavored structure due to the 1,3-methyl interactions present and that conversion to a bicyclic enone would thus be a more favorable energetic process. The authors further stated that some 2,4-cyclohexadienones that appear to give diene-ketenes by a preferred route may do so only because the bicyclic enones initially formed are photochemically reconverted to starting material.

In order to study further the structural requirements for this photo-rearrangement, it was desired to irradiate the benzo-derivatives of hexamethyl-2,4-cyclohexadienone, V, namely tetramethylnaphthalenones X and XI. It was



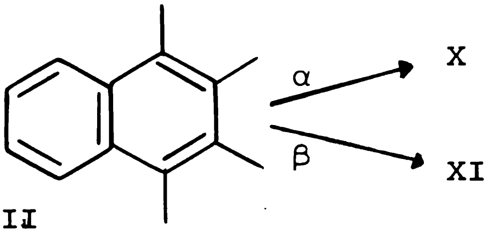
X



XI

anticipated that having one of the two C=C bonds of the cyclohexadienone system belong to a fused aromatic ring might well effect the course of the photochemical reaction.

It was proposed that synthesis of the desired unknown naphthalenones X and XI could be achieved by peroxytrifluoroacetic acid-boron fluoride oxidation of 1,2,3,4-tetramethylnaphthalene, XII. Attack of electrophilic (positive) hydroxyl at an α-methyl-bearing carbon, followed by a Wagner-Meerwein methyl migration to C-2 and loss of a proton, might well afford naphthalenone X. Similarly, attack of positive hydroxyl at a β-methyl-bearing carbon, followed by a methyl migration to C-1 and loss of a proton might provide naphthalenone XI.



XII

The synthesis and photochemistry of tetramethylnaphthalenones X and XI is the subject of this thesis.

RESULTS AND DISCUSSION

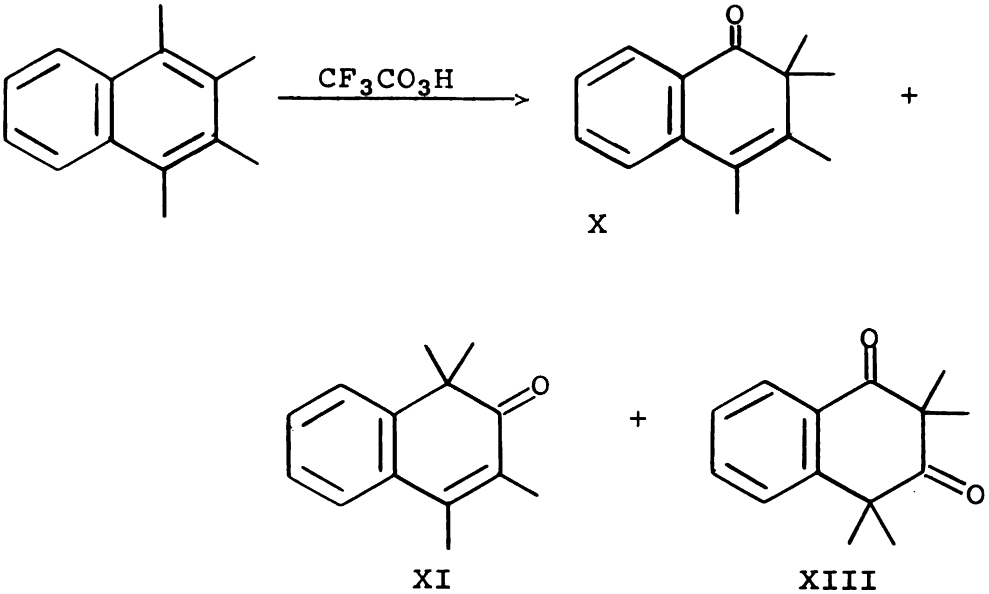
A. The Oxidation of 1,2,3,4-Tetramethylnaphthalene

1,2,3,4-Tetramethylnaphthalene was prepared via a modification of the method of Hewett (13), although several other syntheses of the compound have been reported (14-17). 2,3-Dimethylnaphthalene was added to a solution of paraformaldehyde in acetic acid through which hydrogen chloride gas had been passed. Hydrogenolysis of the resulting 1-chloromethyl-2,3-dimethylnaphthalene by reaction with a suspension of lithium aluminum hydride in tetrahydrofuran provided 1,2,3-trimethylnaphthalene. Repetition of the chloromethylation and hydrogenolysis afforded a moderate yield of 1,2,3,4-tetramethylnaphthalene.

1,2,3,4-Tetramethylnaphthalene was oxidized at -16^0 to -12^0 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 the tetramethylnaphthalene. The volatile products were separated by distillation and purified by vpc. The composition of the volatile material was determined by vpc and is calculated on an 83% conversion of tetramethylnaphthalene. The products were assigned the following structures, based on evidence which will be presented:

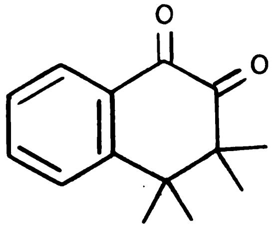
2,2,3,4-tetramethyl-1(2H)-naphthalenone (X) 61%,

1,1,3,4-tetramethyl-2(1H)-naphthalenone (XI) 21%,
2,2,4,4-tetramethyl-1,3-dioxotetralin (XIII) 18%.

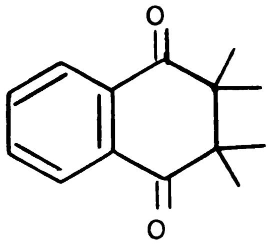


Compound XIII analyzed well for the formula $C_{14}H_{16}O_2$. The mass spectrum indicated a parent peak at m/e 216 showing this to be the molecular formula. The infrared spectrum of XIII had carbonyl absorptions at 1712 and 1683 cm^{-1} (liquid film) and only aromatic C=C stretching vibrations, while the uv spectrum had maxima at 289 mμ (log ε 3.12) and 248 mμ (log ε 3.83) in 95% ethanol. The nmr spectrum of XIII consisted of six-proton singlets at τ 8.67 and 8.52 (gem-dimethyl groups) and a complex multiplet for four protons at τ 2.63 (aromatic protons).

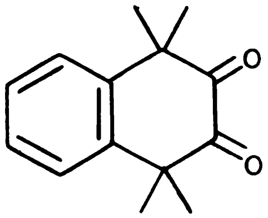
These data suggested a tetramethyldioxotetralin of which there are four isomers, XIII - XVI. The 1,4- and 2,3-dioxoisomers XV and XVI were eliminated as rapid flipping of the non-aromatic ring would make the gem-dimethyl groups



XIV

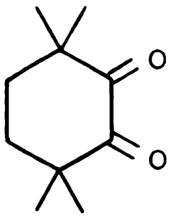


XV

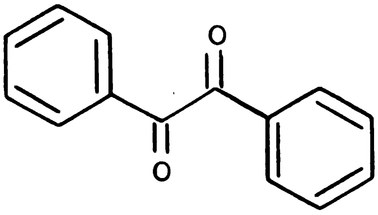


XVI

equivalent in each compound leading to a single peak in the nmr spectrum. The 1,2-dioxoisomer XIV was ruled out as α-diketones typically show ir carbonyl absorptions at 1730-1725 cm^{-1} (18) and ultraviolet maxima at longer wavelengths than β-diketones (19). For example, in XVII the absorption maximum is at 380 mμ (19) and in benzil, XVIII, at 370 mμ (20).

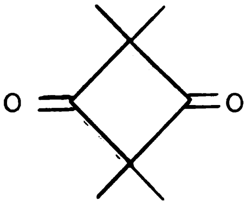


XVII

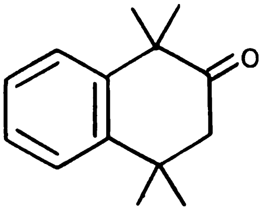


XVIII

The six-proton singlets in the nmr spectrum at τ 8.67 and 8.52 are assigned to the *gem*-dimethyl groups at C-3 and C-1 respectively. These assignments are consistent as the *gem*-dimethyl groups in 2,2,4,4-tetramethyl-1,3-dioxocyclobutane, XIX, appear at 8.69τ (21) and the *gem*-dimethyl group at C-1 in 1,1,4,4-tetramethyl-2-oxotetralin, XX, appears at 8.56τ (22).

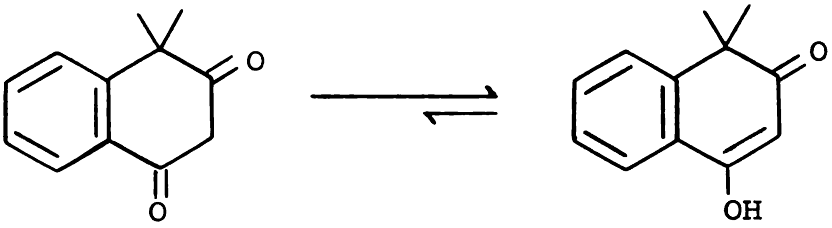


XIX



XX

Compound XIII is believed to be the first isolated 1,3-dioxotetralin. The only other 1,3-dioxotetralin reported is 4,4-dimethyl-1,3-dioxotetralin, XXI (23). How-



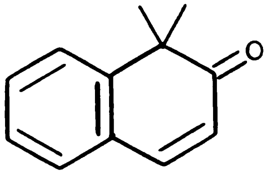
XXI XXII

ever diketone XXI seemed to be nearly completely enolic in character and is better represented by the tautomeric structure XXII.

Compound XI analyzed well for the formula $C_{14}H_{16}O$ and a parent peak at m/e 200 in the mass spectrum indicated this to be the molecular formula. Compound XI was an oil with λ_{max}^{EtOH} 308 mμ (log ε 3.91), 239 mμ (log ε 3.95) and 234 mμ (log ε 3.97). The ir spectrum of XI showed conjugated carbonyl and double bond absorptions at 1652 and 1621 cm^{-1} (liquid film), respectively. The nmr spectrum of XI had a six-proton singlet at τ 8.60 (*gem*-dimethyl group), two three-proton singlets at τ 8.00 and 7.68

(allylic methyls) and a complex multiplet for four aromatic protons centered at τ 2.76. The allylic methyls at τ 8.00 and 7.68 are tentatively assigned to the methyls at C-3 and C-4 respectively, as a methyl attached to the β carbon of a cyclic dienone exhibits a lower field signal (5,24).

This spectroscopic evidence compares favorably with similar data obtained for the known compound 1,1-dimethyl-2(1H)-naphthalenone, XXIII. Cromwell and Campbell (23) have reported ultraviolet absorption maxima for naphthalenone XXIII at 300 mμ (log ε 4.00), 294 mμ (log ε 4.00), 236 mμ (log ε 4.20) and 230 mμ (log ε 4.19), while Baddeley and Rasburn (24) have reported absorption maxima in ethanol at 310 mμ (log ε 3.75) and 230 mμ (log ε 4.38) for the same compound. The ir spectrum of XXIII showed carbonyl absorption at 1658 (nujol) or 1662 cm^{-1} (CCl_4) (25) and C=C absorption at 1624 cm^{-1} (23).



XXIII

The major product of the oxidation was 2,2,3,4-tetramethyl-2(1H)-naphthalenone, X. Compound X was a colorless oil and had a molecular formula of $C_{14}H_{16}O$, as indicated by its elemental analysis and a parent peak at m/e 200 in the mass spectrum. The ir spectrum of X had conjugated carbonyl and double bond absorptions at 1674 and 1633 cm^{-1}

(liquid film) respectively. The uv spectrum consisted of: λ_{max}^{EtOH} 340 mμ (log ε 3.14), 286 mμ (log ε 3.33), 276 mμ (log ε 3.49), 268 mμ (log ε 3.49) and 239 mμ (log ε 5.05). The nmr spectrum of X contained a six-proton singlet at τ 8.75 (gem-dimethyl group), two three-proton singlets at τ 8.05 and 7.90 (allylic methyls) and a complex multiplet equivalent to four protons at τ 2.63 (aromatic protons).

The postulated mechanism for the formation of the oxidation products is depicted in Figure 2. For simplicity 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 (27). Strong evidence has been presented by Norman and Davidson supporting the intermediacy of an electrophilic, cationic reactant in peroxytrifluoroacetic acid oxidations (28).

Naphthalenone X is presumably formed by electrophilic attack of peroxytrifluoroacetic acid at an α-methyl-bearing carbon of 1,2,3,4-tetramethylnaphthalene, leading to the intermediate carbonium ion XXIV. Wagner-Meerwein migration of a methyl group to C-2 would provide carbonium ion XXV and loss of a proton would give naphthalenone X. Similarly, the formation of naphthalenone XI is accounted for by attack of the electrophilic oxidant at a β-methyl-bearing carbon of the tetramethylnaphthalene, leading to carbonium ion XXVI. Migration of a methyl group to C-1 would afford intermediate carbonium ion XXVII and loss of a proton would give naphthalenone XI.

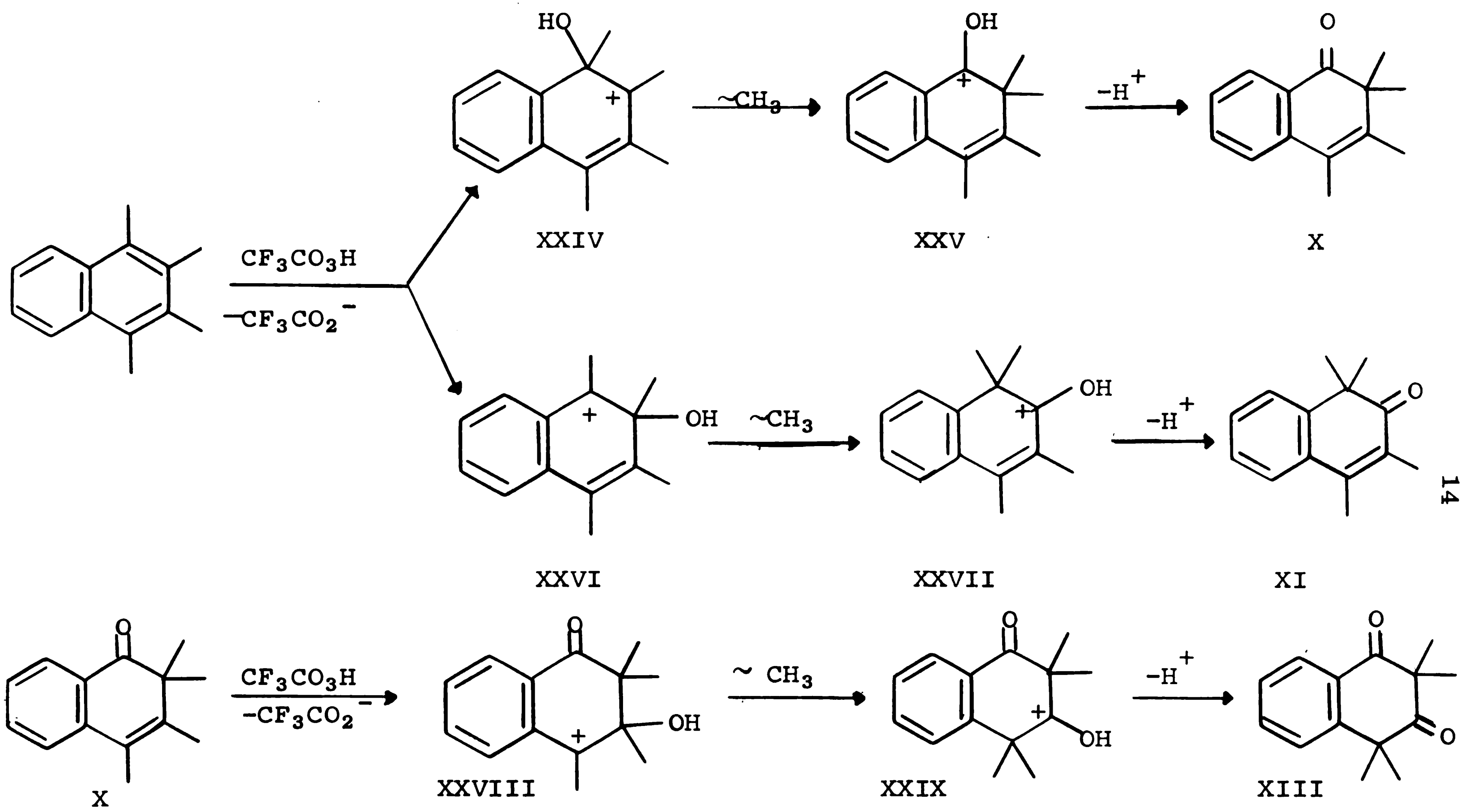
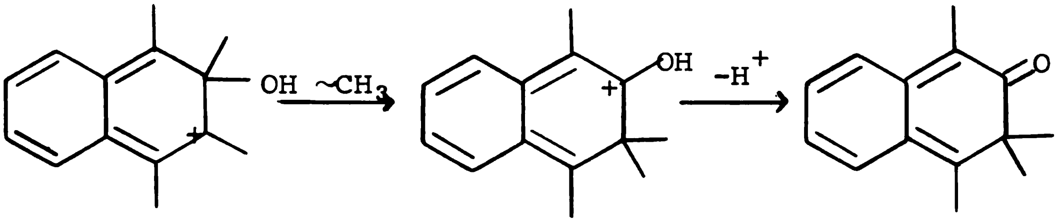


Figure 2. A mechanism for the formation of the oxidation products of 1,2,3,4-tetramethylnaphthalene.

A less likely alternative for the carbonium ion resulting from attack at a β-methyl-bearing carbon (XXX) would be methyl migration in the other direction and proton loss

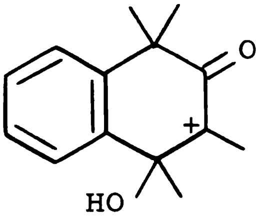


XXX XXI XXXII

to provide XXXII. However, this process would involve disruption of the aromatic ring. The loss of aromatic resonance energy required for the formation of XXXII may well explain why this product was not observed.

The over-oxidation product 2,2,4,4-tetramethyl-1,3-dioxotetralin, XIII, is accounted for by further oxidation of 2,2,3,4-tetramethyl-1(2H)-naphthalenone, X. Attack of the electrophilic oxidant at C-3 of naphthalenone X would provide the well stabilized benzylic carbonium ion XXVIII. Wagner-Meerwein migration of a methyl group to C-4 would give carbonium ion XXIX and loss of a proton would afford XIII. In order to support this mechanism, 2,2,3,4-tetramethyl-1(2H)-naphthalenone was oxidized with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride at -15°. Vpc analysis of the volatile products indicated only a trace of starting naphthalenone present and almost complete conversion to 2,2,4,4-tetramethyl-1,3-dioxotetralin.

It does not seem that the dioxotetralin XIII is formed from naphthalenone XI. The required intermediate carbonium ion XXXIII would be destabilized by a positive charge on a carbon atom α to a carbonyl. When 1,2,3,4-tetramethylnaphthalene was oxidized with a large excess of peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride at -10°, no 2,2,3,4-tetramethyl-1(2H)-naphthalenone was detected in vpc analysis of the isolated products. The two major components of the isolated volatile material were 2,2,4,4-tetramethyl-1,3-dioxotetralin (40%) and 1,1,3,4-tetramethyl-2(1H)-naphthalenone (54%).



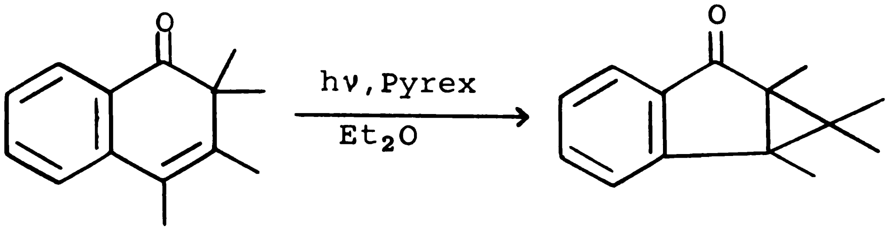
XXXIII

Vpc analysis of the products from the equimolar oxidation of 1,2,3,4-tetramethylnaphthalene indicates a preference for attack at an α-methyl-bearing carbon over attack at a β-methyl-bearing carbon of 4:1. Two factors may contribute to this preference of attack. First, the intermediate carbonium ion XXIV is better stabilized than carbonium ion XXVI. Second, an α-methyl-bearing carbon is flanked by only one methyl group, whereas a β-methyl-bearing carbon is flanked by two methyls, thus a steric approach factor may be involved.

B. The Photochemistry of 2,2,3,4-Tetramethyl-1(2H)-naphthalenone

Four types of photochemical transformations of 2,4-cyclohexadienones having blocked *ortho*-positions have been reported (see Introduction). Which photochemical process occurs seems to depend largely on the number and positions of the substituents in the cyclohexadienone molecule and on the nucleophilic character of the solvent (5,6,7,11). Most 2,4-cyclohexadienones studied undergo ring fission on photolysis in Pyrex to give a diene-ketene which is then attacked by a nucleophile present in the solvent to provide the observed product. However, highly substituted dienones, such as hexamethyl-2,4-cyclohexadienone, were recently shown to photochemically rearrange to the corresponding bicyclo[3.1.0]hexane derivatives (5,6,12). 2,2,3,4-Tetramethyl-1(2H)-naphthalenone offered a probe to study the photochemical rearrangement when one of the two C=C bonds of the cyclohexadienone system belongs to a fused aromatic ring.

Irradiation of an approximately 1.5% solution of naphthalenone X in anhydrous ether with a Hanovia L 450-w lamp was carried out in Pyrex. The reaction was monitored using vpc. Irradiation led to a decrease in the concentration of naphthalenone X and an increase in the concentration of a photoproduct which reached a maximum concentration after photolysis for two hours. The primary photoproduct was shown to be 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]-hexan-2-one, XXXIV.

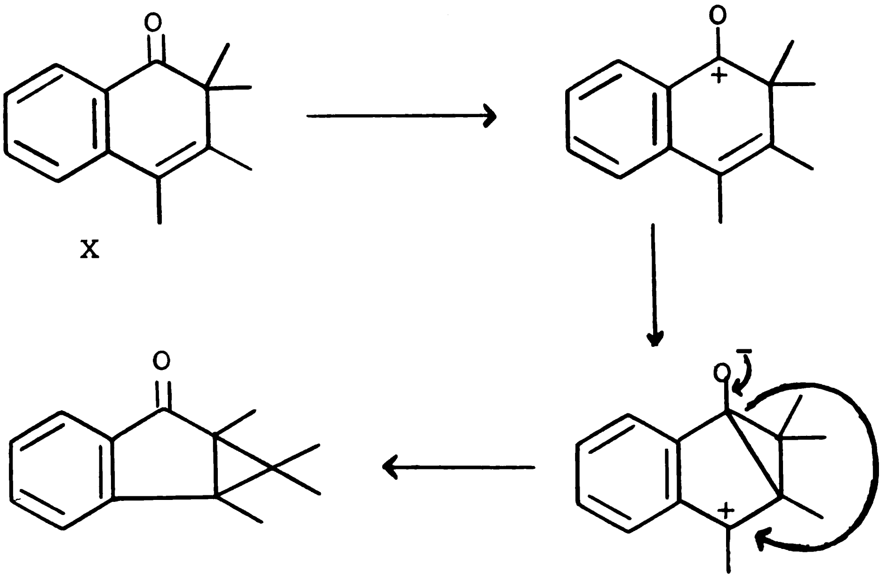


X XXXIV

The benzobicyclicketone XXXIV was shown to be isomeric with naphthalenone X by its elemental analysis and a parent peak at m/e 200 in the mass spectrum. The infrared spectrum had carbonyl absorption at 1699 cm^{-1} and only aromatic C=C stretching vibrations. The ultraviolet spectrum had maxima at: 335 mμ (log ε 2.69), 313 mμ (log ε 3.20), 301 mμ (log ε 3.29), 247 mμ (log ε 4.05) and 225 mμ (log ε 4.42). The nmr spectrum of XXXIV consisted of three-proton singlets at τ 9.28, 8.84, 8.73 and 8.49 (aliphatic methyls) and a complex multiplet equivalent to four protons at τ 2.6 (aromatic protons). The two aliphatic methyls at highest field are tentatively assigned as the gem-dimethyl group, while the methyls at τ 8.73 and 8.49 are assigned as the bridgehead methyls at C-1 and C-5 respectively.

The photo-rearrangement of naphthalenone X was found to proceed one-half as fast as the corresponding photoisomerization of hexamethyl-2,4-cyclohexadienone V under the same conditions. A 2.5 fold rate enhancement was observed when the photolysis of naphthalenone X was carried out in methanol rather than ether.

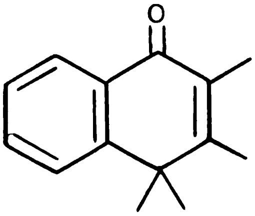
A tenable mechanism for the photochemical isomerization of 2,2,3,4-tetramethyl-1(2H)-naphthalenone to 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one is presented below. Ionic intermediates are used in the mechanism only for convenience. This "bond-crossing" mechanism is analogous to the mechanism that was established by labeling experiments for the photochemical rearrangement of hexamethyl-2,4-cyclohexadienone V to hexamethylbicyclo[3.1.0]hex-3-en-2-one, VIII (5,12).



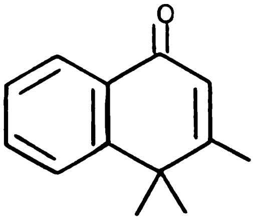
X

XXXIV

Further irradiation of the anhydrous ether solution of naphthalenone X led to a substantial decrease in the concentration of the initial photoproduct XXXIV and an increase in the concentration of a new product. This product was shown to be 2,3,4,4-tetramethyl-1(4H)-naphthalenone, XXXV. Elemental analysis of XXXV indicated an empirical formula



XXXV



XXXVI

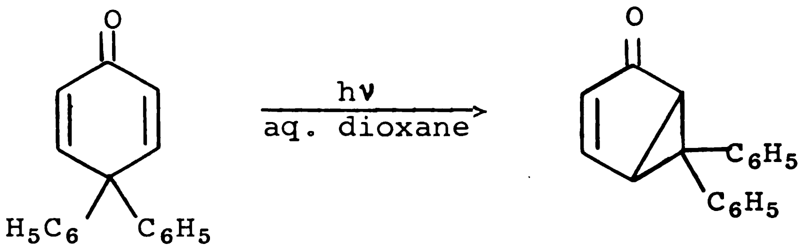
isomeric with naphthalenone X and benzobicyclicketone XXXIV. Naphthalenone XXXV had absorption maxima at 272 mμ (log ε 4.03) and 256 mμ (log ε 4.06). The ir spectrum of XXXV showed conjugated carbonyl and double bond absorptions at 1648 and 1626 cm^{-1} (CCl_4) respectively. The nmr spectrum had a six-proton singlet at τ 8.52 (gem-dimethyl group), two three-proton singlets at τ 8.02 and 7.93 (allylic methyls) and a complex multiplet for four protons at τ 2.57 (aromatic protons). The allylic methyls at τ 8.02 and 7.93 are tentatively assigned to the methyls at C-2 and C-3 respectively (5,24).

This spectroscopic evidence compares well with similar data obtained for the closely related compound 3,4,4-trimethyl-1(4H)-naphthalenone, XXXVI. Huffman and Bethea (29) have reported ultraviolet absorption maxima for naphthalenone XXXVI at 271 mμ (log ε 3.99) and 252 mμ (log ε 4.09) and an infrared carbonyl absorption at 6.02 μ (1661 cm^{-1}).

C. The Photochemistry of 2,3,4,4-Tetramethyl-1(4H)-naphthalenone

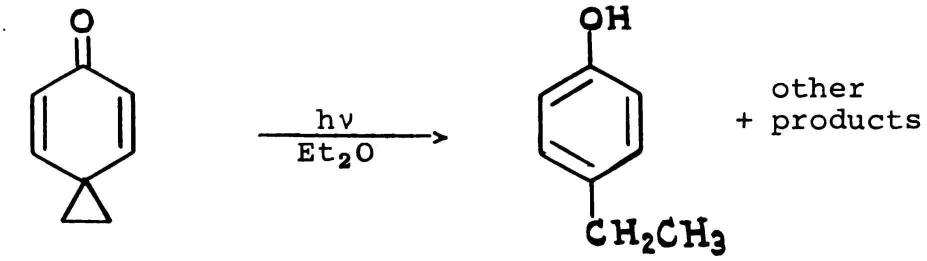
Two primary photochemical transformations of 2,5-cyclohexadienones have been described: (a) rearrangement to the corresponding bicyclo[3.1.0]hexane derivative, and (b) expulsion of a substituent from C-4, followed by aromatization to a phenol.

For example, irradiation of 4,4-diphenyl-cyclohexadienone XXXVII in aqueous dioxane with light of wavelength above 310 mμ afforded bicyclic ketone XXXVIII (30,31).



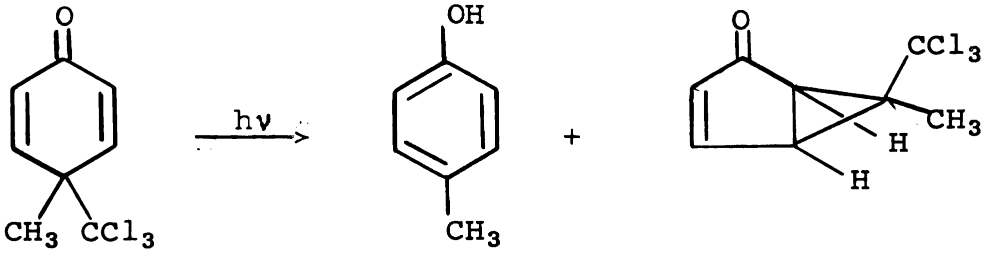
XXXVII XXXVIII

The alternative path was demonstrated recently in the photolysis of spiro[2.5]octa-4,7-dien-6-one, XXXIX, in ether which gave predominantly p-ethylphenol, XL, and three other compounds which were 1:1 adducts of starting



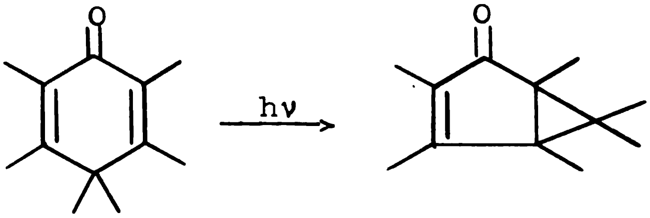
XXXIX XL

material and solvent (32). That the radical fragmentation route competes directly with the route to "lumiproduct" was shown by the irradiation of dienone XLI in a variety of solvents to give a mixture of p-cresol, XLII, and bicyclicketone XLIII (33).



XLI XLII XLIII

As expected, irradiation of hexamethyl-2,5-cyclohexadienone, XLIV, in ether or methanol gave bicyclicketone VIII (34).



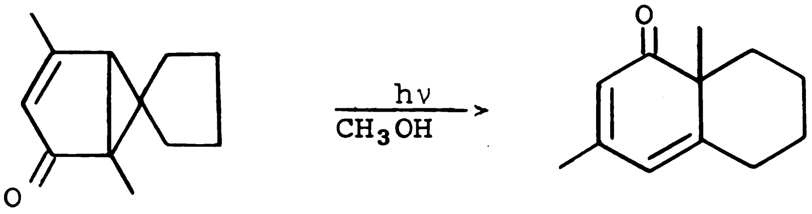
XLIV VIII

When the benzo-derivative of dienone XLIV, namely 2,3,4,4-tetramethyl-1(4H)-naphthalenone, XXXV, was irradiated in ether through a Vycor filter with a Hanovia S 200-w lamp for 4 1/2 hours, no dimunition in the concentration of naphthalenone XXXV was observed and the starting material was recovered unchanged.

Irradiation of an acid-free methanolic solution of naphthalenone XXXV through a Vycor filter with a Hanovia S 200-w lamp led to a steady decrease in the concentration of starting material. However, no volatile material could be detected by vpc analysis.

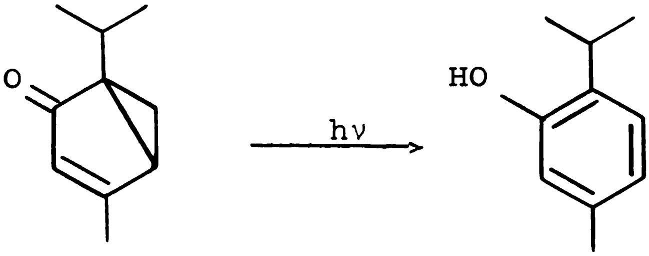
D. The Photochemistry of 3,4-Benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one

Irradiations of bicyclo[3.1.0]hexenones have been shown to lead to 2,4-cyclohexadienones or to aromatic products. For example, irradiation of bicyclicketone XLV in methanol gave dienone XLVI as the only isolated product (24). The alternative photochemical path is demonstrated



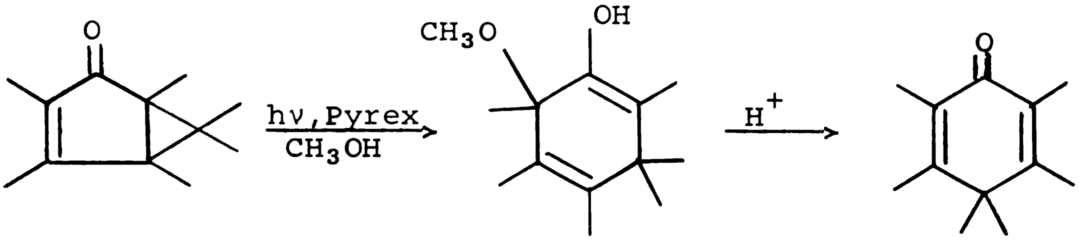
XLV XLVI

by the irradiation of umbellulone, XLVII, which quantitatively provided thymol, XLVIII (35).



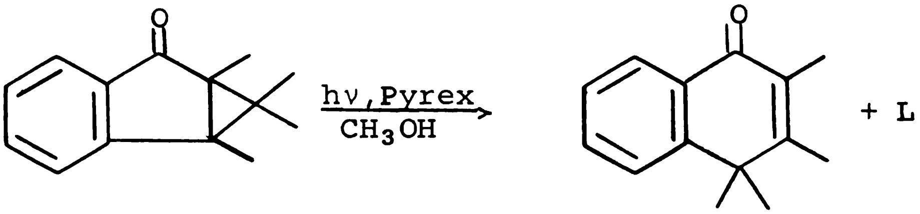
XLVII XLVIII

Very recently it has been shown that irradiation of an acid-free methanolic solution of hexamethylbicyclicketone VIII gave as the direct photoproduct compound XLIX, which rearranged to dienone XLIV on treatment with dilute HCl (34).



VIII XLIX XLIV

Irradiation of 3,4-benzo-1,5,6,6-tetramethylbicyclo-[3.1.0]hexan-2-one, XXXIV, in anhydrous ether through Pyrex with a Hanovia L 450-w lamp led to a smooth, efficient conversion to 2,3,4,4-tetramethyl-1(4H)-naphthalenone, XXXV. When the irradiation was carried out with an acid-free methanolic solution of benzobicyclicketone XXXIV, the major product isolated was again naphthalenone XXXV. However, another product from the photolysis, L, was also



XXXIV XXXV

observed. When the reaction was monitored by uv spectroscopy, a decrease in the benzobicyclicketone absorption at 301 mμ was immediately observed, and new maxima appeared at 276 and 254 mμ, typical of naphthalenone XXXV. Monitoring the photolysis by vpc showed that the relative ratio of concentrations of XXXV to L remained nearly constant during the irradiation, although the concentrations of XXXV and L each increased at the expense of the starting ketone XXXIV. It was shown that L did not rearrange under the vpc conditions to give XXXV.

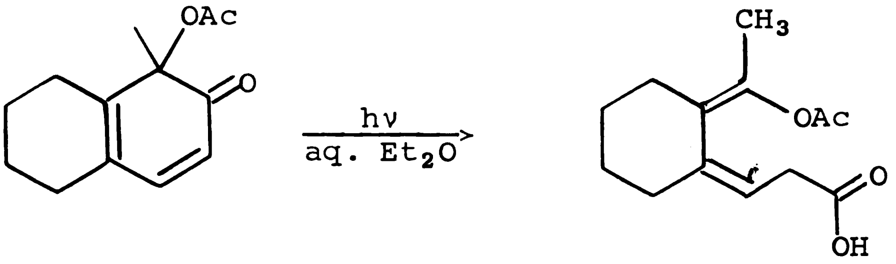
From these observations it can not be asserted whether naphthalenone XXXV is or is not a direct photoproduct of XXXIV. The identity and photochemistry of L is obviously of critical importance in establishing whether L is an intermediate in the photochemical rearrangement.

E. The Photochemistry of 1,1,3,4-Tetramethyl-2(1H)-naphthalenone

There are two benzo-derivatives of hexamethyl-2,4-cyclohexadienone V, namely naphthalenones X and XI. The photochemistry of 2,2,3,4-tetramethyl-1(2H)-naphthalenone, X, has already been discussed.

Irradiation of a solution of 1,1,3,4-tetramethyl-2(1H)-naphthalenone, XI, in anhydrous ether with a Hanovia L 450-w lamp was carried out in Pyrex. After irradiation for 3 1/2 hours a slight decrease in the concentration of starting material was observed, but no volatile material could be detected by vpc analysis. Similar results were observed when a methanolic solution of naphthalenone XI was irradiated for 2 hours through quartz with a Hanovia L 450-w lamp.

These results parallel those described by Quinkert in a preliminary report (10). Even in the presence of cyclohexylamine, no amide could be isolated from the photolysis of 1,1-dimethyl-2(1H)-naphthalenone, XXIII. Irradiation of 1-acetoxy-1-methyl-2(1H)-naphthalenone in ether saturated with water led to a mixture of dimers, the substrate simply behaving like an α,β-unsaturated ketone. That the fused ring must be aromatic in order to produce such results was demonstrated by the photolysis of LI.



LI LII

Irradiation of LI in aqueous ether gave LII as the main product accompanied by a mixture of phenols. The stereochemistry of LII has not been determined.

EXPERIMENTAL

A. General Procedures

All ultraviolet spectra were measured with a Unicam Model SP-800 or a Beckman Model DB spectrophotometer. The infrared spectra were obtained on a Unicam Model SP-200 infrared spectrometer and all ir spectra were calibrated (polystyrene). All nmr spectra were measured with a Varian A-60 spectrometer using tetramethylsilane as an internal reference. The mass spectra were carried out by Mr. H. Harris of this laboratory with a Consolidated Electrodynamic Corp. 21-103C instrument operating at an ionizing potential of 70 v. Elemental analyses are by Spang Microanalytical Laboratories, Ann Arbor, Michigan. Melting points are uncorrected.

B. Preparation of 1,2,3,4-Tetramethylnaphthalene (13)

1. 1-Chloromethyl-2,3-dimethylnaphthalene (13)

2,3-Dimethylnaphthalene (40.0 g, 0.256 mole) was added to a solution of paraformaldehyde (20.4 g) in 250 ml of acetic acid through which hydrogen chloride gas had been passed to give a clear solution. The suspension was stirred vigorously at room temperature for 21 hours and then left at room temperature for an additional 18 hrs. The resulting solution was diluted with water (200 ml) and extracted with benzene (3 x 100 ml). The benzene extract was washed with dilute sodium carbonate solution and then dried over anhydrous magnesium sulfate. After removal of the solvent on a rotary evaporator, the residue was distilled, bp 121-123^0 (0.1 mm), providing 34.6 g (0.17 mole) of 1-chloromethyl-2,3-dimethylnaphthalene, mp 84-87^0 (lit. val. (13) 86-87^0). The yield was 66.3%.

2. 1,2,3-Trimethylnaphthalene (13)

A solution of 34.6 g (0.17 mole) of 1-chloromethyl-2,3-dimethylnaphthalene in 200 ml of dry tetrahydrofuran was added over 2.5 hours to a suspension of 3.8 g (0.1 mole) of lithium aluminum hydride in 170 ml of dry, vigorously stirred, refluxing tetrahydrofuran. The mixture was stirred at reflux for an additional 3 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 75 ml of 10% HCl and 75 ml of water. The resulting mixture was extracted with ether (3 x 150 ml) and the separated ether layer was dried over anhydrous magnesium sulfate. The ether solution was evaporated to an oil which was distilled, bp 119-122^0 (2 mm) and provided 23.6 g (0.139 mole) of 1,2,3-trimethylnaphthalene, mp 25-27^0 (lit. val. (13) 27-28^0). The yield was 81.8%.

3. 1-Chloromethyl-2,3,4-trimethylnaphthalene (13)

To 11.2 g of paraformaldehyde in 140 ml of acetic acid through which hydrogen chloride gas had been passed to give a clear solution was added 23.6 g (0.139 mole) of 1,2,3-trimethylnaphthalene. After 22 hrs of vigorous stirring, during which the solid chloromethyl compound separated, the solution was diluted with water and extracted with benzene. The benzene extract was washed with dilute sodium carbonate solution and then dried over anhydrous magnesium sulfate. After removing the solvent the residue was 19.2 g (0.088 mole) of 1-chloromethyl-2,3,4-trimethylnaphthalene, mp 92-96° (lit. val. (13) 94-95°). The yield was 63.5%.

4. 1,2,3,4-Tetramethylnaphthalene (13)

1-Chloromethyl-2,3,4-trimethylnaphthalene (19.2 g, 0.088 mole) in dry tetrahydrofuran (150 ml) was added over 1.5 hrs to a suspension of lithium aluminum hydride (4 g, 0.121 mole) in 150 ml of dry, vigorously stirred, refluxing tetrahydrofuran. The mixture was stirred at reflux for an additional 3 hrs. After cooling, water was added and the mixture extracted with ether (3 x 100 ml). The organic extract was dried over anhydrous magnesium sulfate and the solvent evaporated. The residue was recrystallized twice from 95% ethanol and provided 13.5 g (0.073 mole) of 1,2,3,4-tetramethylnaphthalene, mp 104-106° (lit. val. (13) 106.5-107.5°). The yield from 2,3-dimethylnaphthalene is 28.6%. The uv and nmr values of 1,2,3,4-tetramethylnaphthalene correspond exactly to those of the literature: $\lambda_{max}^{95\%EtOH}$ (322), 293, and (282) mμ (Ref. 36). The nmr spectrum (CCl_4 soln) contained singlets at τ 7.62 (6H; β methyls), τ 7.43 (6H; α methyls) and two multiplets centered at τ 2.72 (2H) and τ 2.10 (2H) (Ref. 37).

C. The Oxidation of 1,2,3,4-Tetramethylnaphthalene

1. The Reaction with 10% Excess Oxidant at -16 to -12°.

A solution of peroxytrifluoroacetic acid (38) prepared from 0.725 ml of 90% hydrogen peroxide (0.0268 mole) and 6.2 g (0.0295 mole) of trifluoroacetic anhydride in 10 ml of freshly distilled methylene chloride, was cooled to -18° and added with stirring over 80 min to a solution of 4.5 g (0.0244 mole) of 1,2,3,4-tetramethylnaphthalene in 50 ml of methylene chloride which had previously been cooled via a carbon tetrachloride-dry ice bath to -18°. Boron trifluoride etherate (8.1 ml of 47% $BF_3 \cdot Et_2O$, 0.0268 mole) was added concurrently with the addition of the peracid. The temperature of the solution was maintained between -16° and -12° throughout the addition. After further stirring for 90 min at -18°, 50 ml of water was added and the organic layer was separated. The organic layer was washed with water (3 x 75 ml), saturated sodium bicarbonate (3 x 100 ml), extracted with 10% aqueous sodium hydroxide (4 x 100 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 again extracted with methylene chloride (3 x 50 ml), which yielded on evaporation 0.06 g of a dark viscous oil. Vapor phase chromatography (20' x 1/4" SE-30 column, 220^0, flow rate 90 ml/min of helium) indicated seven components. This material was not further investigated.

The methylene chloride fraction was dried over anhydrous magnesium sulfate and evaporated to afford a deep red viscous oil. This material was vacuum distilled at 0.05 mm to afford 3.19 g of a yellow liquid, bp $88-90^0$. The pot residue was 0.97 g of deep red very viscous material. Vapor phase chromatography (20' x 1/4" SE-30 column, 230^0, flow rate 60 ml/min of helium) showed that the crude oil had components with the following retention times: 18.0 min (13.6%), 23.1 min (15.7%), 24.5 min (47.2%), 33.6 min (23.4%). The compound of longest retention time was identified by its mp ($105-106^0$), uv spectrum, and retention time as 1,2,3,4-tetramethylnaphthalene. Conversion of tetramethylnaphthalene was 83.3%. Final purification of all compounds was achieved by vpc. The purity of the compounds was checked by vpc on two different stationary phases and always found to be at least 98% homogeneous. None of the compounds were found to be thermally interconvertible under the vpc column conditions.

a. Product Identification

(1) 2,2,4,4-Tetramethyl-1,3-dioxotetralin. This was the compound with a retention time of 18.0 min. It was a yellow oil with $\lambda_{max}^{95\%EtOH}$ 289 mμ (log ε 3.12) and 248 mμ (log ε 3.83). Its ir spectrum (liquid film) showed principal bands at 1712 and 1683 ($\nu_{C=O}$) and 1600 cm^{-1} ($\nu_{C=C}$, aromatic). The mass spectrum indicated a parent peak at m/e 216. The nmr spectrum (CCl_4 soln) consisted of sharp singlets at τ 8.67 (6H) and τ 8.52 (6H) due to the gem-dimethyl groups at C-3 and C-1 respectively, and a complex multiplet centered at τ 2.63 (4H; aromatic protons).

Anal.	Calcd for $C_{14}H_{16}O_2$:	C, 77.77; H, 7.41.
	Found:	C, 77.74; H, 7.65.

(2) 1,1,3,4-Tetramethyl-2(1H)-naphthalenone. This had a R_t of 23.1 min and showed $\lambda_{max}^{95\%EtOH}$ 308 mμ (log ε 3.91), 239 mμ (log ε 3.95) and 234 mμ (log ε 3.97). Its ir spectrum (liquid film) had principal bands at 1652, 1621 ($\nu_{C=O}$ and $\nu_{C=C}$, conjugated) and 1600 cm^{-1} (shoulder, $\nu_{C=C}$, aromatic). The mass spectrum indicated a parent peak at m/e 200. The nmr spectrum (CCl_4 soln) showed a singlet at τ 8.60 (6H; gem-dimethyl), two singlets at τ 8.0 and 7.68 (each 3H; allylic methyls) and a complex multiplet centered at τ 2.76 (4H; aromatic protons). The nmr spectrum, when examined at a sweep width of 100 cycles,

showed the peaks due to the allylic methyls to be poorly resolved quartets, J = 0.9 cps.

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

Found: C, 83.81; H, 8.01.

(3). <u>2,2,3,4-Tetramethyl-1(2H)-naphthalenone</u>. This colorless oil had a R_t of 24.5 min and had the following uv characteristics: $\lambda_{max}^{95\%EtOH}$ 340 mμ (log ε 3.14), 286 mμ (shoulder, log ε 3.33), 276 mμ (log ε 3.49), 268 mμ (log ε 3.49) and 239 mμ (log ε 5.05). The principal ir bands (liquid film) occurred at 1674, 1633 ($\nu_{C=O}$ and $\nu_{C=C}$, conjugated) and 1600 cm^{-1} ($\nu_{C=C}$, aromatic). The mass spectrum indicated a parent peak at m/e 200. The nmr spectrum (CCl_4 soln) contained singlets at τ 8.75 (6H; <u>gem</u>-dimethyl), τ 8.05 and 7.90 (each 3H; allylic methyls) and a complex multiplet centered at τ 2.63 (4H; aromatic protons).

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

Found: C, 83.88; H, 8.01.

2. <u>The Reaction with a Large Excess of Oxidant</u>

Three grams (0.016 mole) of 1,2,3,4-tetramethylnaphthalene was dissolved in 50 ml of methylene chloride and oxidized in the presence of 54 ml of 47% boron trifluoride etherate (0.18 mole) with a solution of peroxytrifluoroacetic acid prepared from 41.3 g (0.20 mole) of trifluoroacetic anhydride and 4.8 ml of 90% hydrogen peroxide (0.18 mole). The peroxytrifluoroacetic acid solution and boron trifluoride etherate were added concurrently over 80 min, the reaction mixture being kept below -10°. After further stirring for 1 hr at -16°, the mixture was washed with water (3 x 200 ml), saturated sodium bicarbonate (3 x 300 ml) and again with water (3 x 100 ml). The sodium bicarbonate extract was acidified and extracted with methylene chloride, which provided on evaporation 0.14 g of a dark viscous oil. This material was not further investigated.

The methylene chloride fraction was evaporated and gave 2.6 g of a deep red viscous oil. Vacuum distillation (125°, 0.45 mm) of this oil afforded 0.74 g of an orange liquid. Vapor phase chromatography (20' x 1/4" SE-30 column, 220°, 90 ml/min of helium) showed that the distillate had components with retention times of 4.3 min (5.4%), 12.4 min (40.4%) and 17.8 min (54.3%). The compounds with the longest retention times were shown by their ir spectra to be 2,2,4,4-tetramethyl-1,3-dioxotetralin and 1,1,3,4-tetramethyl-2(1H)-naphthalenone respectively. The compound with R_t 4.3 min was not identified, but was found to be an oil with $\lambda_{max}^{95\%EtOH}$ 315, 276 (sharp), 241 (shoulder) and 212 mμ, and principal ir bands (CCl_4 soln) at 1800 (vs), 1110, and 1045 (s) cm^{-1}.

D. The Oxidation of 2,2,3,4-Tetramethyl-1(2H)-naphthalenone

A solution of 56 mg (2.8×10^{-4} mole) of 2,2,3,4-tetramethyl-1(2H)-naphthalenone in 4 ml of methylene chloride was oxidized in the presence of 0.1 ml of 47% boron trifluoride etherate (3.5×10^{-4} mole) with the usual oxidant prepared from 84 mg (4.0×10^{-4} mole) of trifluoroacetic anhydride and 10 μl (3.5×10^{-4} mole) of 90% hydrogen peroxide in 1.5 ml of methylene chloride. The addition took place over 10 min and the mixture was allowed to stir at -16^0 for 30 min. Work-up resulted in the isolation of 51 mg of material. Vpc analysis (10' x 1/4" FFAP column, 235^0, 45 ml/min of helium) of the volatile portion indicated only a trace amount of starting material (R_t 16.0 min) and almost complete conversion to 2,2,4,4-tetramethyl-1,3-dioxotetralin (R_t 11.2 min), the latter being identified by its ir spectrum.

E. General Photolysis Procedure

Unless stated to the contrary, all photolyses were conducted with a 450-watt Hanovia Type L mercury lamp and the light was filtered through a Pyrex glass sleeve. The solution to be irradiated was placed in a Pyrex test tube, sealed with a serum cap and attached to the outside of a Hanovia Pyrex immersion well, 2-3 cm from the center of the mercury arc. This apparatus was then placed in an ice bath, which maintained the temperature of the solution during irradiation between 2 and 6^0.

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

A solution of 115 mg of 2,2,3,4-tetramethyl-1(2H)-naphthalenone in 7 ml of ether was irradiated through Pyrex using a 450-watt Hanovia Type L mercury lamp. The photolysis was monitored by vpc, aliquots being removed at intervals of 20-30 min during a total irradiation time of 150 min. Examination of the samples on a 10' x 1/4" carbowax column at 225^0 with a gas flow of 50 ml/min of helium showed a progressive decrease in the concentration of the naphthalenone (R_t 16.6 min) and an increase in the concentration of a photoproduct with R_t 9.5 min. The concentrations of the starting naphthalenone and photoproduct were equal after 88 ± 2 min. The concentration of the photoproduct reached a maximum after 120 ± 5 min and further irradiation led to a significant increase in the concentration of another compound with R_t 23.6 min at the expense of the initial photoproduct (see Section H). The initial photoproduct was purified by vpc (above conditions) and shown to be <u>3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one</u>. The colorless oil had major bands in its ir spectrum (CCl_4 soln) at 1699 (vs, $\nu_{C=O}$) and 1606 cm^{-1} ($\nu_{C=C}$, aromatic). It is noteworthy that no band appeared for $\nu_{C=C}$, nonaromatic. The uv spectrum consisted of $\lambda_{max}^{95\%EtOH}$ 335 mμ (log ε 2.69), 301 mμ (log ε 3.29), 247 mμ (shoulder, log ε 4.05) and 225 mμ (log ε 4.42). The mass spectrum indicated a parent peak at m/e 200. The nmr spectrum (CCl_4 soln) showed singlets at τ 9.28, 8.84, 8.73, 8.49 (each 3H; aliphatic methyls) and a complex multiplet centered at τ 2.6 (4H; aromatic protons). The two aliphatic methyls at highest field are tentatively assigned as the *gem*-dimethyl group while the methyls at τ 8.73 and τ 8.49 are assigned as the bridgehead methyls at C-1 and C-5 respectively.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05.
Found: C, 83.74; H, 8.04.

G. The Dark Reaction of 2,2,3,4-Tetramethyl-1(2H)-naphthalenone in Ether

A solution of 9 mg of 2,2,3,4-tetramethyl-1(2H)-naphthalenone in 0.9 ml of ether was placed in a pyrex test tube, sealed with a serum cap, and stored in the dark. The reaction was monitored by vpc (10' x 1/4" Carbowax column, 208°, 60 ml/min of helium). Aliquots were removed after 2 hrs and 168 hrs. No reaction could be detected after this time and only starting material was recovered.

H. Further Irradiation of 2,2,3,4-Tetramethyl-1(2H)-naphthalenone in Ether

A 1.5% solution of 2,2,3,4-tetramethyl-1(2H)-naphthalenone in ether was irradiated through Pyrex with a 450-watt Hanovia Type L mercury lamp. The photolysis was monitored by vpc (10' x 1/4" Carbowax column, 225°, 50 ml/min of helium). Aliquots examined during the first

120 min of photolysis indicated a progressive decrease in the concentration of the naphthalenone (R_t 16.6 min) and an increase in the concentration of the photoproduct, 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one with R_t 9.5 min (see Section F). However, after 40 min of irradiation the appearance of another compound (R_t 23.6 min) had been observed. After 120 min of irradiation the concentration of benzobicyclicketone decreased and the concentration of the overphotoproduct sharply increased. The concentrations of the benzobicyclicketone and the overphotoproduct were equal after 140±4 min and after 200 min the concentration of benzobicyclicketone was negligible.

The overphotoproduct was purified by vpc (above conditions) and shown to be <u>2,3,4,4-tetramethyl-1(4H)-naphthalenone</u>. This compound was a white solid, mp 76-78^0, and had $\lambda_{max}^{95\%EtOH}$ 272 mμ (log ε 4.03) and 256 mμ (log ε 4.06). The ir spectrum (CCl_4 soln) had principal bands at 1648 ($\nu_{C=O}$, conjugated), 1626 (shoulder, $\nu_{C=C}$, conjugated) and 1605 cm^{-1} ($\nu_{C=C}$, aromatic). The nmr spectrum (CCl_4 soln) showed singlets at τ 8.52 (6H; <u>gem</u>-dimethyl), τ 8.02 and 7.93 (each 3H; allylic methyls) and a complex multiplet centered at τ 2.57 (4H; aromatic protons). The allylic methyls at τ 8.02 and τ 7.93 are tentatively assigned to the methyls at C-2 and C-3 respectively.

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

Found: C, 84.04; H, 8.18.

I. A Comparison of the Rate of Photolysis of 2,3,4,5,6,6-Hexamethylcyclohexa-2,4-dienone in Ether and 2,2,3,4-Tetramethyl-1(2H)-naphthalenone in Ether and Methanol

Eleven milligrams of 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone in 1.1 ml of ether, 11 mg of 2,2,3,4-tetramethyl-1(2H)-naphthalenone in 1.1 ml of ether, and 11 mg of the tetramethylnaphthalenone in 1.1 ml of methanol were irradiated at the same time through Pyrex using a 450-watt Hanovia Type L mercury lamp. Each reaction was monitored by vpc (10' x 1/4" FFAP column, 233^0, 45 ml/min of helium). Analysis of the data indicated that 50% of the hexamethylcyclohexadienone in ether had disappeared after 28±3 min. It required 55±4 min for 50% of the tetramethylnaphthalenone in ether to disappear, and 50% of the tetramethylnaphthalenone in methanol was photolysed in 23±2 min.

J. Irradiation of 3,4-Benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one in Ether

A solution of 5 mg of 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one in 1.0 ml of ether was irradiated in a Pyrex test tube using a 450-watt Hanovia Type L mercury lamp. Aliquots were removed after 30 min and 60 min and examined on a 10' x 1/4" FFAP column at 235^0 with a gas flow of 45 ml/min. The benzobicyclicketone (R_t 9 min) was converted smoothly and efficiently to 2,3,4,4-tetramethyl-1(4H)-naphthalenone (R_t 20.8 min). After 30 min irradiation 30% of the benzobicyclicketone remained, accompanied by 70% of the cross-conjugated naphthalenone and after 60 min, 97% of the latter product was present. The cross-conjugated naphthalenone was identified by its retention time and characteristic uv spectrum.

K. The Dark Reaction of 3,4-Benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one in Ether

A solution of 2 mg of 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one in 0.6 ml of ether was placed in a pyrex test tube, sealed with a serum cap, and stored in the dark. The reaction was monitored by vpc (10' x 1/4" FFAP column, 235°, 45 ml/min of helium). No reaction could be detected after 234 hours.

L. Irradiation of 3,4-Benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one in Methanol

A solution of 4 mg of 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one in 0.8 ml of methanol (distilled from sodium methoxide) was irradiated through Pyrex with a 450-watt Hanovia Type L mercury lamp. All glassware to come in contact with the benzobicyclicketone was washed with ammonium hydroxide, distilled water, and methanol distilled from sodium methoxide. The photolysis was monitored by uv and vpc (10' x 1/4" FFAP column, 235°, 45 ml/min of helium).

Following the photolysis by uv led to an immediate decrease of the uv band at 301 mμ. The photoproduct had a much greater extinction coefficient and exhibited bands at 254 and 276 mμ in methanol. Aliquots examined by vpc indicated a progressive decrease in the concentration of starting material (R_t 8.4 min) and an increase in the concentration of two new compounds with R_t's of 16.6 and 20.8 min.

After 6 min irradiation 70% of the benzobicyclicketone remained, accompanied by 7% of the material with R_t 16.6 min and 23% of the material with R_t 20.8 min. After 13 min irradiation 23% of the benzobicyclicketone was present, 19% of the compound with R_t 16.6 min and 58% of the compound with R_t 20.8 min. By its uv and ir spectra the compound with longest R_t was shown to be 2,3,4,4-tetramethyl-1(4H)-naphthalenone. The compound with R_t 16.6 min was not identified. However, enough of a sample of this compound was obtained to show that with repeated passage through the vpc (above conditions) no thermal rearrangement of the compound occurs on the vpc column.

M. Irradiation of 2,3,4,4-Tetramethyl-1(4H)-naphthalenone in Ether

A solution of 5 mg of 2,3,4,4-tetramethyl-1(4H)-naphthalenone in 1.0 ml of ether in a quartz test tube was irradiated through a Vycor filter with a 200-watt Hanovia Type S mercuty lamp. Aliquots removed after 30 min, 90 min, and 270 min and examined by vpc (10' x 1/4" FFAP column, 235°, 40 ml/min of helium) indicated there was no decrease in the concentration of the original naphthalenone (R_t 21.8 min). Only starting material was recovered, as shown by the ir spectrum.

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

A solution of 5 mg of 2,3,4,4-tetramethyl-1(4H)-naphthalenone in 1.0 ml of methanol in a quartz test tube was irradiated through a Vycor filter with a 200-watt Hanovia Type S mercury lamp. The reaction was monitored by vpc (above conditions). A steady decrease in the concentration of the starting material (R_t 21.8 min) was observed. Thus 30% of the naphthalenone was photolyzed after 30 min, 60% after 2 hr, and after 14 hrs no trace of starting material could be detected. However, no volatile material with $R_t < 33.6$ min was present.

O. Irradiation of 1,1,3,4-Tetramethyl-2(1H)-naphthalenone in Ether Through Pyrex

A solution of 7 mg of 1,1,3,4-tetramethyl-2(1H)-naphthalenone in 0.7 ml of ether was irradiated through Pyrex using a 450-watt Hanovia Type L mercury lamp. The photolysis was monitored by vpc. After irradiation for 220 min a slight decrease in the concentration of starting naphthalenone (R_t 11.1 min) was observed, but no compound with $R_t <$ 32.5 min could be detected.

P. Irradiation of 1,1,3,4-Tetramethyl-2(1H)-naphthalenone in Methanol Through Quartz

A solution of 6 mg of 1,1,3,4-tetramethyl-2(1H)-naphthalenone in 1.8 ml of methanol was placed in a quartz test tube, sealed with a serum cap, attached to the outside of the Hanovia quartz immersion well, and irradiated with a 450-watt Hanovia Type L mercury lamp. The photolysis was monitored by vpc. After irradiation for 130 min a substantial decrease in the concentration of starting naphthalenone was observed, but no compound with $R_t < 36.8$ min could be detected.

Q. Reaction of 1,1,3,4-Tetramethyl-2(1H)-naphthalenone with Methylmagnesium Iodide

1,1,3,4-Tetramethyl-2(1H)-naphthalenone (65 mg, 3.3×10^{-4} mole) in 1.5 ml ether was added dropwise to a stirred methyl Grignard solution at 25^0. This Grignard solution was prepared from 60 mg (4.2×10^{-4} mole) of methyl iodide and 11 mg (4.5×10^{-4} mole) of magnesium in 2 ml of dry ether. The solution was then heated under reflux for 30 min. The mixture was hydrolyzed with saturated ammonium chloride. The organic layer was separated and combined with the ether extract (2 x 5 ml) of the aqueous layer and dried over anhydrous magnesium sulfate. Removal of the solvent left an oil. Vpc analysis (10' x 1/4" Carbowax column, 220^0, 40 ml/min of helium) indicated a single product with R_t 9.9 min. The colorless oil isolated had $\lambda_{max}^{95\%EtOH}$ 295, 233, and

220 mμ. The nmr spectrum (CCl_4 soln) consisted of a singlet at τ 8.62 (6H; <u>gem</u>-dimethyl), a broad singlet (h_w = 8 cps) at τ 7.95 (6H; allylic methyls), two singlets at τ 5.00 and 4.88 (each 1H; terminal methylenes) and a complex multiplet centered at τ 2.97 (4H; aromatic protons). On the basis of the uv spectrum (39) and the expected reaction paths, the product is tentatively assigned the structure of 1,1,3,4-tetramethyl-2-methylene-1,2-dihydronaphthalene.

SUMMARY

1. The oxidation products of 1,2,3,4-tetramethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride at -12^0 were: 2,2,3,4-tetramethyl-1(2H)-naphthalenone (61%), 1,1,3,4-tetramethyl-2(1H)-naphthalenone (21%), and 2,2,4,4-tetramethyl-1,3-dioxotetralin (18%). The overall yield was 50%, based on 83% conversion of 1,2,3,4-tetramethylnaphthalene.

2. When 1,2,3,4-tetramethylnaphthalene was oxidized with a large excess of peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride at -10^0, no 2,2,3,4-tetramethyl-1(2H)-naphthalenone was detected. The isolated products were: 1,1,3,4-tetramethyl-2(1H)-naphthalenone (54%), 2,2,4,4-tetramethyl-1,3-dioxotetralin (40%), and an unidentified compound (6%).

3. 2,2,3,4-Tetramethyl-1(2H)-naphthalenone was oxidized with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride to 2,2,4,4-tetramethyl-1,3-dioxotetralin.

4. Irradiation of 2,2,3,4-tetramethyl-1(2H)-naphthalenone in ether through Pyrex gave 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one as the primary photoproduct. The naphthalenone was found to photolyze one-half as fast as hexamethyl-2,4-cyclohexadienone.

5. Further irradiation of 2,2,3,4-tetramethyl-1(2H)-naphthalenone in ether through Pyrex provided 2,3,4,4-tetramethyl-1(4H)-naphthalenone.

6. Irradiation of 3,4-benzo-1,5,6,6-tetramethylbicyclo-[3.1.0]hexan-2-one in ether through Pyrex proceeded smoothly to give 2,3,4,4-tetramethyl-1(4H)-naphthalenone. When the photolysis was carried out in acid-free methanol, 2,3,4,4-tetramethyl-1(4H)-naphthalenone was again the major photoproduct (75%), but an unidentified product (25%) was also detected. The photochemical relationship of the unidentified product to 2,3,4,4-tetramethyl-1(4H)-naphthalenone was not established.

7. 2,3,4,4-Tetramethyl-1(4H)-naphthalenone was recovered unchanged from irradiation in ether through a Vycor filter. Irradiation of the naphthalenone in methanol led to a steady decrease in its concentration, but no volatile products could be detected by vpc.

8. Irradiation of 1,1,3,4-tetramethyl-2(1H)-naphthalenone in ether through Pyrex or in methanol through quartz resulted in a decrease in the concentration of starting material, but no volatile products were detected by vpc.

9. Control experiments demonstrated that none of the photochemically interesting compounds studied were reactive in the dark with the solvents used in the irradiation studies.

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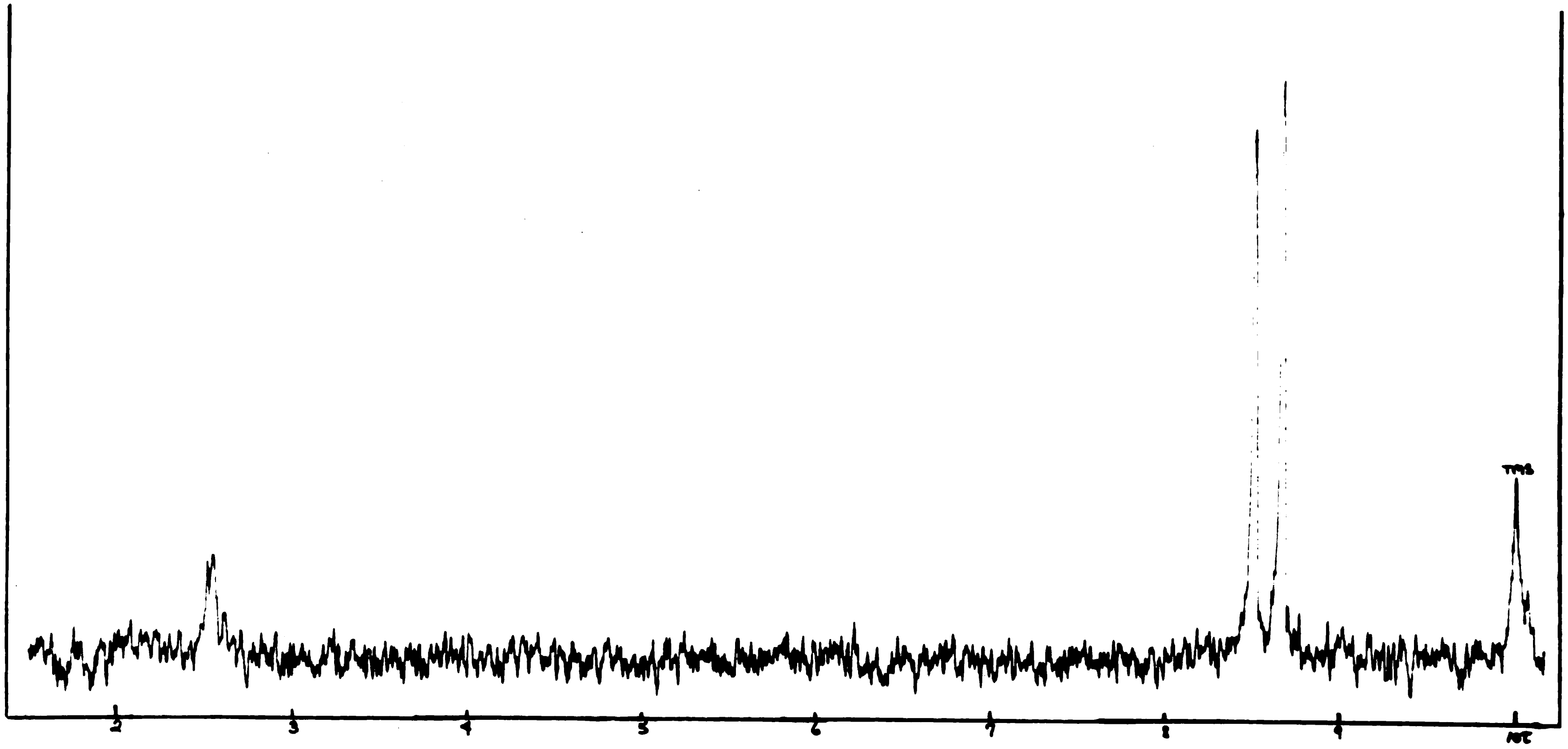
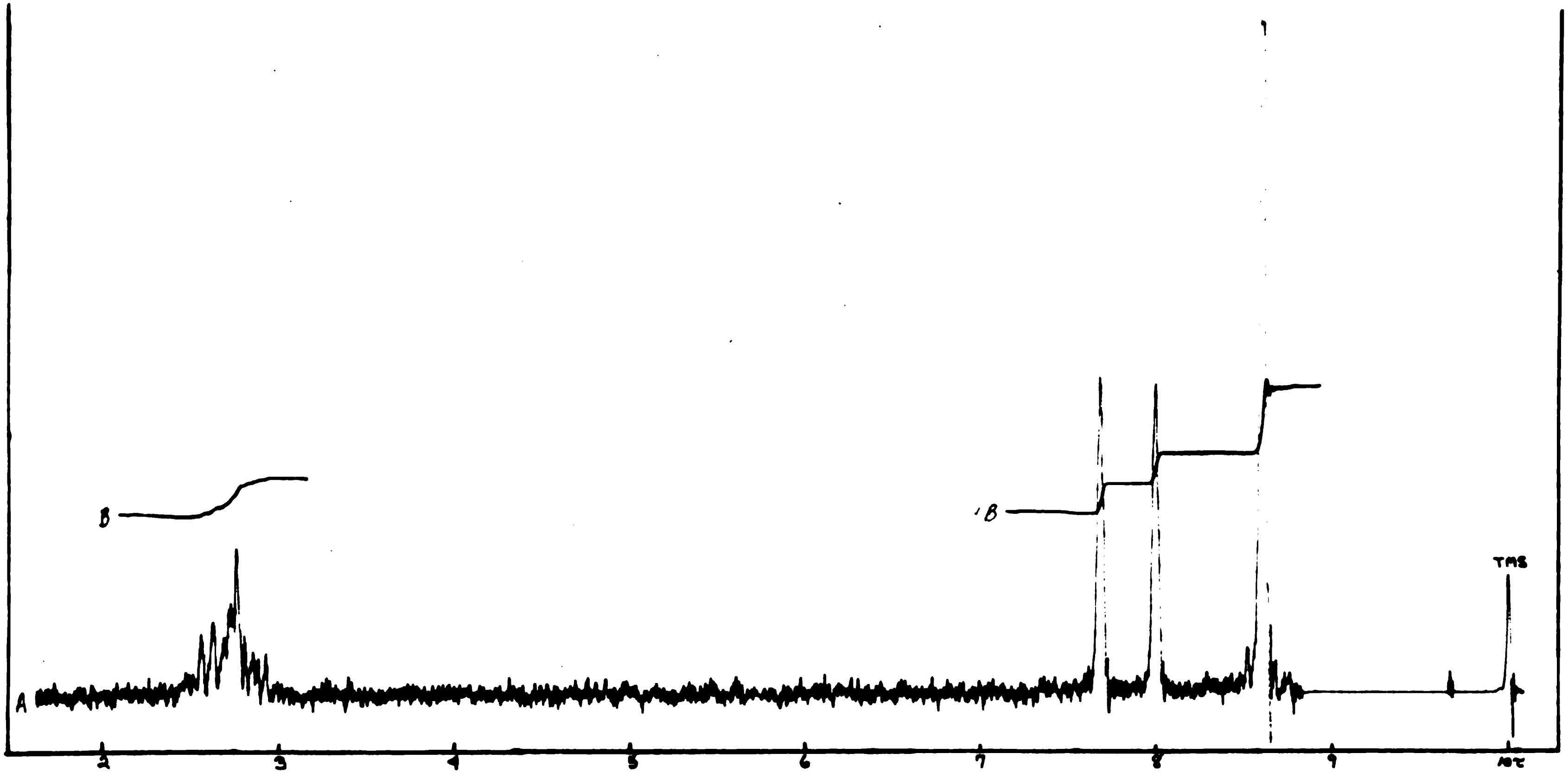
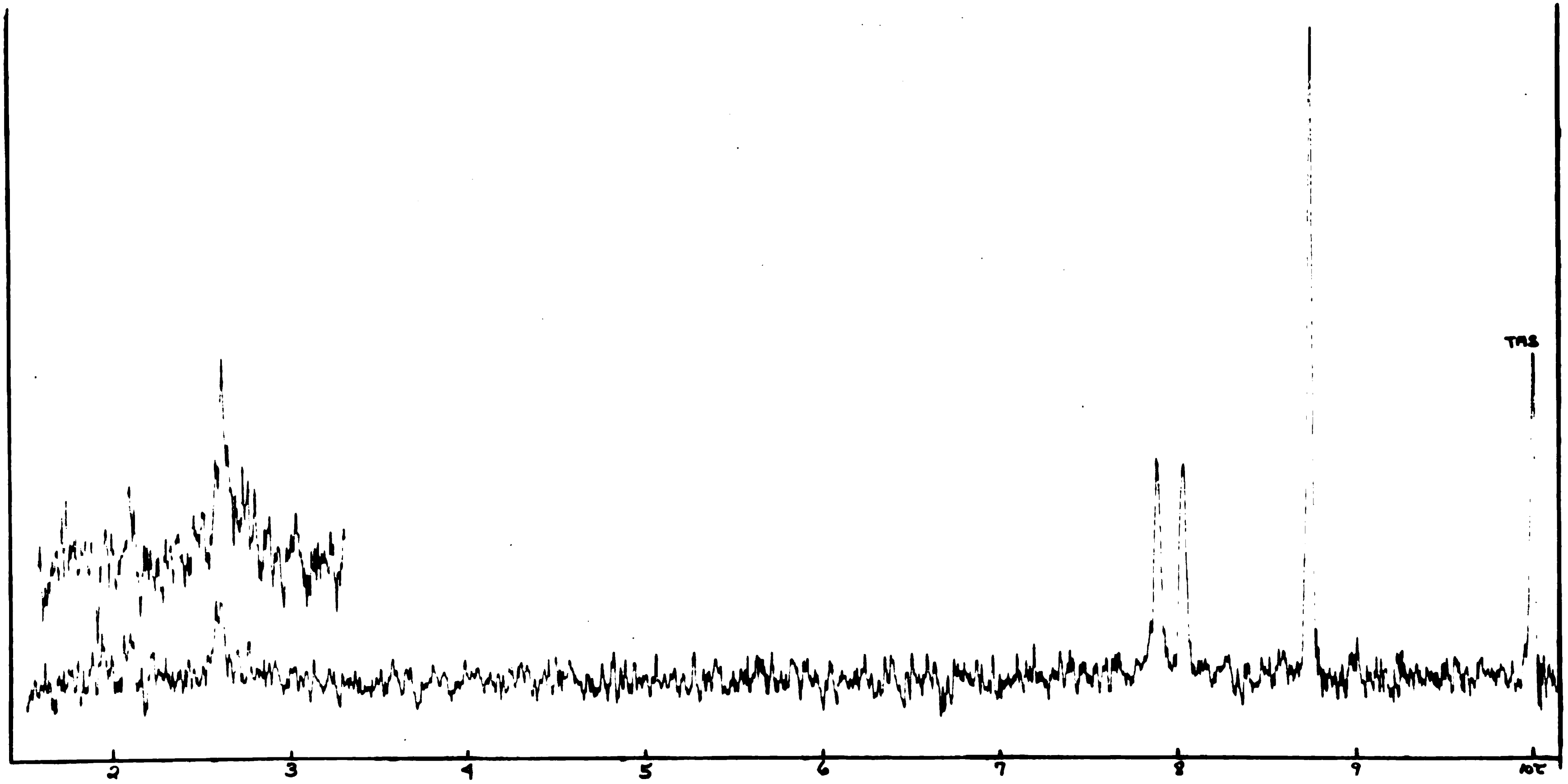
APPENDIX



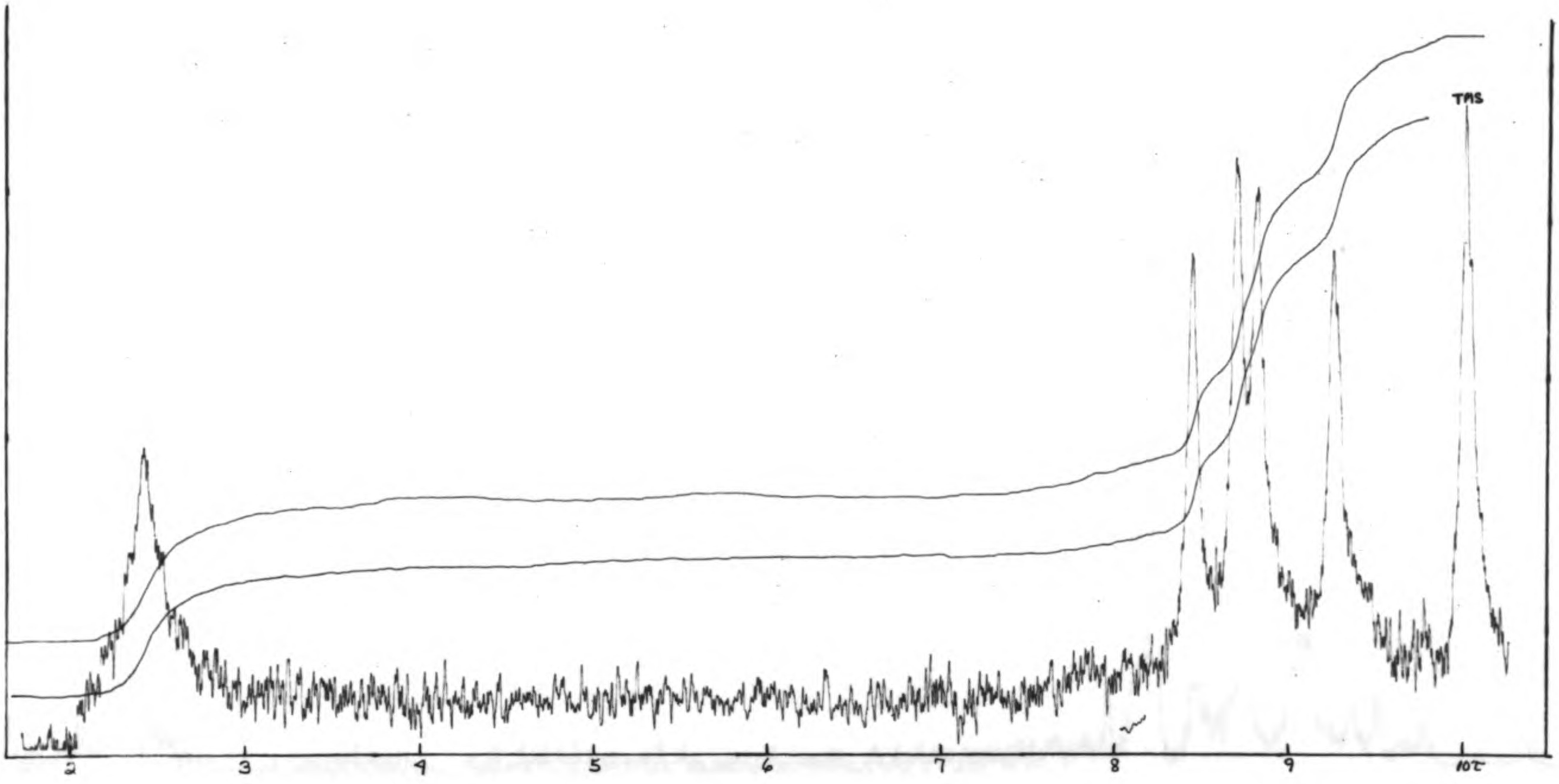
1. NMR Spectrum of 2,2,4,4-Tetramethyl-1,3-dioxotetralin.



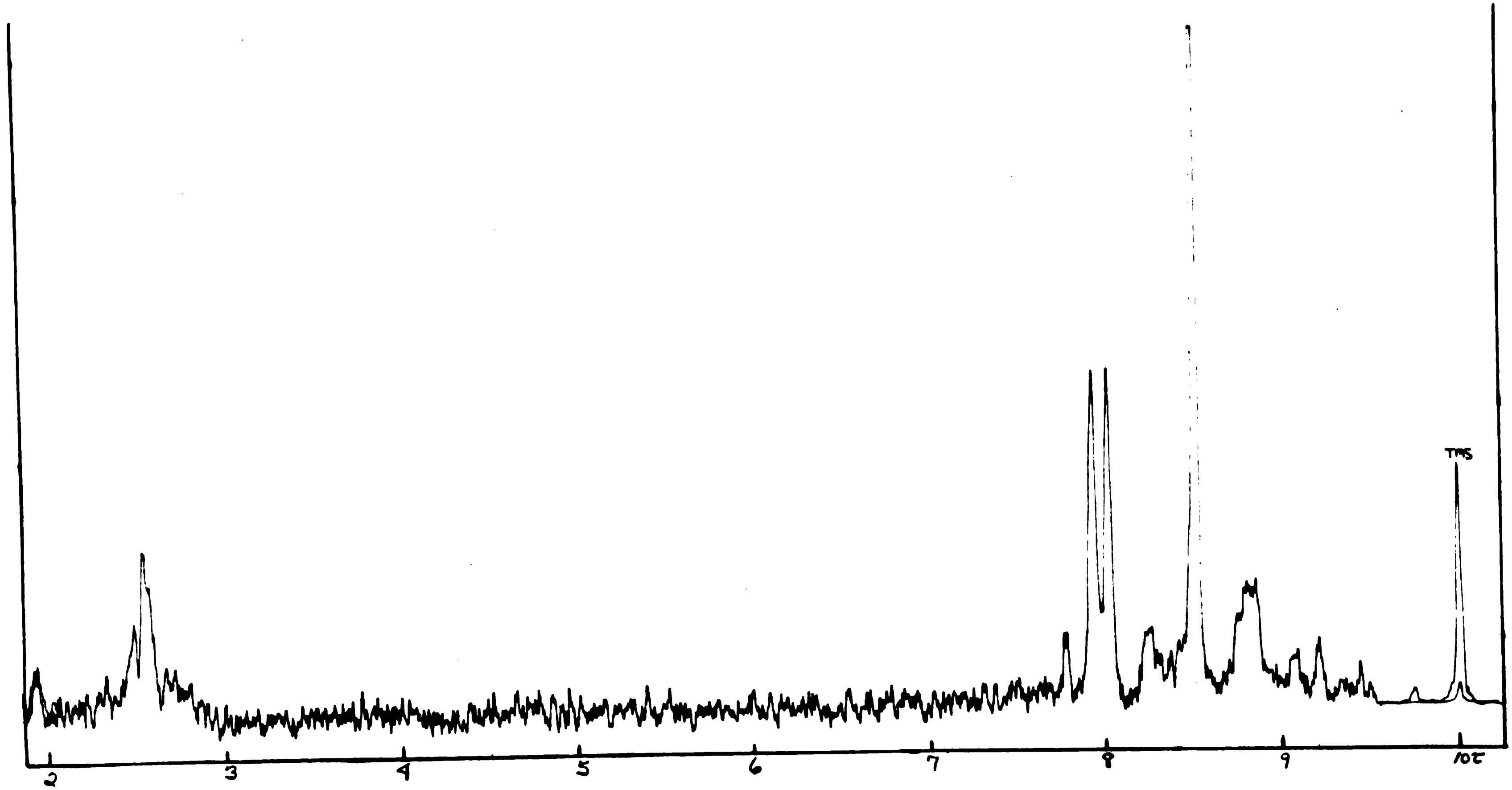
2. NMR Spectrum of 1,1,3,4-Tetramethyl-2(1H)-naphthalenone.



3. NMR Spectrum of 2,2,3,4-Tetramethyl-1(2H)-naphthalenone.



4. NMR Spectrum of 3,4-Benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexan-2-one.



5. NMR Spectrum of 2,3,4,4-Tetramethyl-1(4H)-naphthalenone.