Electrophilic Oxidation of 1,2,3,4-Tetramethylnaphthalene and the Photochemistry of Benzo-2,4-cyclohexadienones[1,2]

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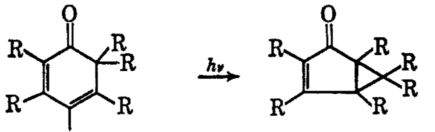
Oxidation of 1,2,3,4-tetramethylnaphthalene with peroxytrifluoroacetic acid–boron fluoride etherate in methylene chloride provided 2,2,3,4-tetramethyl-1(2H)-naphthalenone (**5**), 1,1,3,4-tetramethyl-2(1H)-naphthalenone (**6**), and 2,2,4,4-tetramethyl-1,3-dioxotetralin (**7**) in the ratio of 61:21:18 with an over-all yield of 50%. A proposed electrophilic oxidation mechanism readily accounts for these products. Irradiation of naphthalenone **5** in ether gave 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexen-2-one (**24**) as the primary photoproduct. However, no volatile products could be detected from the photolysis of naphthalenone **6** in ether or methanol.

Hexamethyl- and hexaethyl-2,4-cyclohexadienones (**1** and **2**, respectively) undergo photoisomerization to bicyclo[3.1.0]hexenones (**3** and **4**, respectively).[3,4] However, this rearrangement is sensitive to the position and number of alkyl substituents in the cyclohexadienone; in particular, if alkyl groups are lacking from position 2[1] or 2 and 5,[5] typical ring-opened products[6] derived from a *cis*-ketene[7] are obtained. In order to study further the structural requirements for these photorearrangements, it was desired to determine the influence on the isomerization when one of the two carbon–carbon double bonds of the cyclohexadienone system belonged to a fused aromatic ring.



1, R = CH_3
2, R = CH_2CH_3

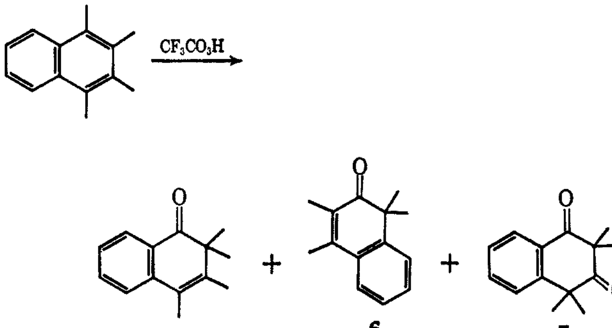
3, R = CH_3
4, R = CH_2CH_3

A reasonable synthesis for the desired benzo derivatives of **1**, namely naphthalenones **5** and **6**, appeared to be the electrophilic oxidation of 1,2,3,4-tetramethylnaphthalene. It has previously been shown that oxidation of hexaalkylbenzenes with electrophilic oxidants proceeds with Wagner–Meerwein rearrangement to give hexaalkylcyclohexadienones in good yield.[4,8] It was anticipated that electrophilic attack of peroxytrifluoroacetic acid at an α-methyl-bearing carbon of tetramethylnaphthalene would give naphthalenone **5**, whereas attack at a β-methyl-bearing carbon would provide **6**.

Results and Discussion

1,2,3,4-Tetramethylnaphthalene Oxidation.—1,2,3,4-Tetramethylnaphthalene was prepared *via* a modification of the method of Hewett,[9] although several other syntheses of the compound have been reported.[10] 2,3-Dimethylnaphthalene was chloromethylated with paraformaldehyde and hydrogen chloride in acetic acid. Hydrogenolysis of the resulting 1-chloromethyl-2,3-dimethylnaphthalene with lithium aluminum hydride in tetrahydrofuran provided 1,2,3-trimethylnaphthalene (Hewett used catalytic hydrogenolysis). Repetition of the sequence afforded a moderate yield of 1,2,3,4-tetramethylnaphthalene.

1,2,3,4-Tetramethylnaphthalene was oxidized at −16 to −12° 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 in 83% conversion of the tetramethylnaphthalene. The volatile products were separated by distillation and purified by vpc. The products of the oxidation were 2,2,3,4-tetramethyl-1-(2H)-naphthalenone (**5**), 61%, 1,1,3,4-tetramethyl-2-(1H)-naphthalenone (**6**), 21%, and 2,2,4,4-tetramethyl-1,3-dioxotetralin (**7**), 18%. The structures of the products follow from their analyses, spectral properties, and mode of formation. The spectroscopic and analytical data for these compounds are presented in Table I.



5 **6** **7**

Naphthalenone **5** was a colorless oil with conjugated carbonyl and double-bond absorptions in the infrared region and its nmr spectrum was consistent with the assigned structure. The preparation and identification of the isomeric tetramethylnaphthalenones **6** and **23** demanded the indicated structure for naphthalenone **5**.

Naphthalenone **6** was an oil that showed conjugated carbonyl and double-bond absorptions in the infrared region, the frequencies being somewhat lower than for

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[1] Paper VIII in a series on oxidations with peroxytrifluoroacetic acid–boron fluoride. For paper VII, see P. M. Collins and H. Hart, *J. Chem. Soc.*, in press.

[2] We are grateful to the National Science Foundation for financial support of this research.

[3] H. Hart and A. J. Waring, *Tetrahedron Letters*, 325 (1965).

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

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

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

[7] P. M. Collins and H. Hart, *ibid.*, in press.

[8] A. J. Waring and H. Hart, *J. Am. Chem. Soc.*, **86**, 1454 (1964).

[9] C. L. Hewett, *J. Chem. Soc.*, 293 (1940).

[10] (a) K. Shisido and H. Nozaki, *J. Am. Chem. Soc.*, **69**, 961 (1947); (b) M. C. Kloetzel, R. P. Dayton, and H. L. Herzog, *ibid.*, **72**, 273 (1950); (c) H. Zeiss, W. Herwig, and W. Metlesics, *ibid.*, **81**, 6203 (1959); (d) W. Hückel, R. Cramer, and S. Läufer, *Ann. Chem.*, **630**, 89 (1960).

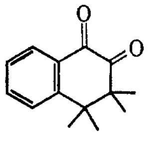
TABLE I.—PROPERTIES OF THE OXIDATION AND PHOTOPRODUCTS

Compound	Nmr spectra: Chemical shift[a]	Nmr spectra: Assignment[b]	Infrared spectra[c]: ν_{C-O}, cm^{-1}	Infrared spectra[c]: ν_{C-C} (conj), cm^{-1}	Infrared spectra[c]: ν_{C-C} (arom), cm^{-1}	Ultraviolet spectra[d]: λ, mμ	Ultraviolet spectra[d]: Log ε	Mass spectra parent peak, m/e	Empirical formula	Elemental analyses[e]: C, % Calcd	C, % Found	H, % Calcd	H, % Found
5	8.75	C-2 *gem*-dimethyls	1674	1633	1600	340	3.14	200	$C_{14}H_{16}O$	83.95	83.88	8.05	8.01
	8.05	C-4 methyl (?)				286	3.33						
	7.90	C-3 methyl (?)				276	3.49						
	2.63	Aromatic protons				268	3.49						
						239	5.05						
6	8.60	C-1 *gem*-dimethyls	1652	1621	1600	308	3.91	200	$C_{14}H_{16}O$	83.95	83.81	8.05	8.01
	8.00	C-3 methyl				239	3.95						
	7.68	C-4 methyl				234	3.97						
	2.76	Aromatic protons											
7	8.67	C-2 *gem*-dimethyls	1712		1600	289	3.12	216	$C_{14}H_{16}O_2$	77.77	77.74	7.41	7.65
	8.52	C-4 *gem*-dimethyls	1683			248	3.83						
	2.63	Aromatic protons											
24	9.28	C-6 methyl (?)	1699		1606	335	2.69	200	$C_{14}H_{16}O$	83.95	83.74	8.05	8.04
	8.84	C-6 methyl (?)				313	3.20						
	8.73	C-1 methyl (?)				301	3.29						
	8.49	C-5 methyl (?)				247	4.05						
	2.6	Aromatic protons				225	4.42						

[a] All spectra are in CCl_4. Shifts are reported as τ values, with TMS as an internal reference. All spectra were run at 60 Mc. [b] All areas are consistent with the assignments. A question mark indicates that the assignment is tentative. [c] All spectra are calibrated (polystyrene). All spectra are liquid film, except for **24** which is in CCl_4. [d] All spectra are in 95% ethanol. [e] Analyses were by Spang Microanalytical Laboratories, Ann Arbor, Mich.

5, as expected. The infrared and ultraviolet spectra of **6** compare favorably with data reported for the analogous 1,1-dimethyl-2(1H)-naphthalenone.[11] The nmr spectrum of **6** had a six-proton singlet at τ 8.60, which is assigned to the *gem*-dimethyl group at C-1. The two three-proton signals at τ 8.00 and 7.68 showed homoallylic coupling (quartets, $J = 0.9$ Hz) and are 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.[4,12]

The spectral data and elemental analysis for **7** suggested a tetramethyldioxotetralin. There are four possible isomers, **7–10**. The 1,4- and 2,3-dioxo isomers **9** and **10** were eliminated because rapid flipping of the nonaromatic ring would make the *gem*-dimethyl groups equivalent in each compound, leading to a single peak in the nmr spectrum. The 1,2-dioxo isomer **8** was ruled out because α-diketones typically show infrared carbonyl absorptions[13] at 1730–1725 cm^{-1} and ultraviolet maxima at longer wavelengths than β-diketones.[14] The six-proton singlets in the nmr spectrum of **7** at τ 8.67 and 8.52 are assigned to the *gem*-dimethyl groups at C-2 and C-4, respectively. These assignments are based on the following models: the *gem*-dimethyl groups in 2,2,4,4-tetramethyl-1,3-dioxocyclobutane[15] appear at τ 8.69 and the *gem*-dimethyl group at C-1 in 1,1,4,4-tetramethyl-2-oxotetralin[16] appears at τ 8.56. Compound **7** is believed to be the first isolated 1,3-dioxotetralin.[17]



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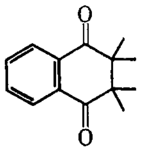

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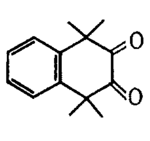

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Mechanism of the Oxidation.—The postulated oxidation mechanism is depicted in Scheme I. Strong evidence has been presented by Davidson and Norman supporting the intermediacy of an electrophilic, cationic reactant in aromatic peroxytrifluoroacetic acid oxidations.[18] Naphthalenone **5** arises by electrophilic attack of peroxytrifluoroacetic acid at an α-methyl-

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[11] (a) N. H. Cromwell and R. C. Campbell, *J. Org. Chem.*, **22**, 520 (1957); (b) G. Baddeley and J. W. Rasburn, *J. Chem. Soc.*, 3168 (1958); (c) R. C. Campbell and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 3456 (1957).

[12] P. J. Kropp, *ibid.*, **86**, 4053 (1964).

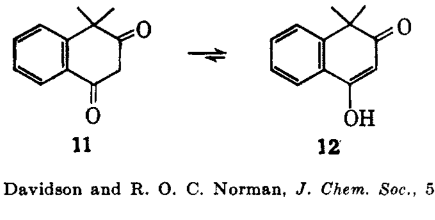
[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 132; E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, **80**, 211 (1958).

[14] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 420.

[15] N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "High Resolution NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, p 2.

[16] L. Barclay, C. Milligan, and N. Hall, *Can. J. Chem.*, **40**, 1664 (1962).

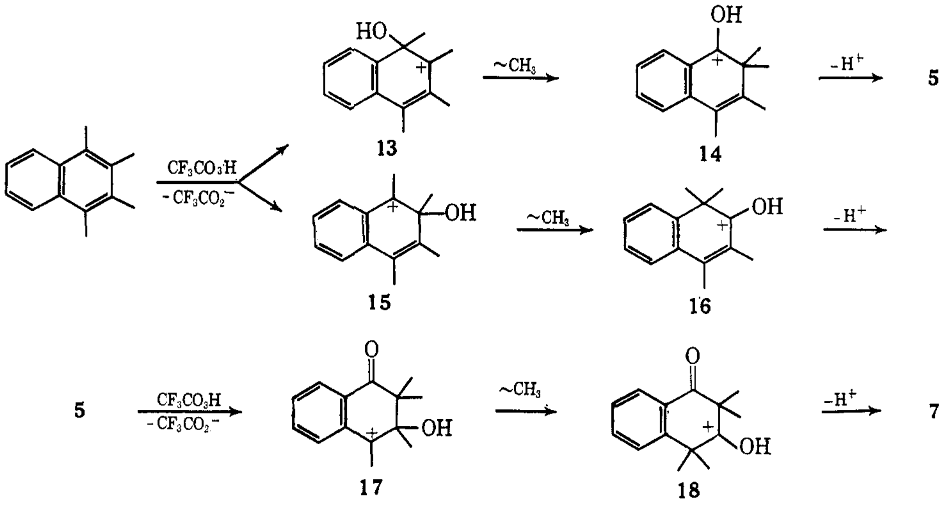
[17] The only other 1,3-dioxotetralin reported is 4,4-dimethyl-1,3-dioxotetralin (**11**).[11c] However, diketone **11** seemed to be nearly completely enolic and is better represented by the tautomeric structure **12**.



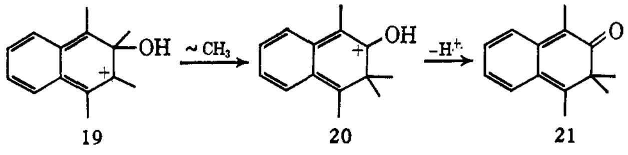
11 **12**

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

SCHEME I

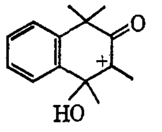


bearing carbon of 1,2,3,4-tetramethylnaphthalene, leading to the intermediate carbonium ion **13**. Wagner–Meerwein migration of a methyl group to C-2 provides carbonium ion **14** which loses a proton to give naphthalenone **5**. Similarly, the formation of naphthalenone **6** is accounted for by attack of the electrophilic oxidant at a β-methyl-bearing carbon of the tetramethylnaphthalene, leading to carbonium ion **15**. Migration of a methyl group to C-1 affords intermediate carbonium ion **16** which, on proton loss, gives naphthalenone **6**. A less likely alternative for **15** would be methyl migration in the other direction and proton loss to provide **21**. This process, however, would involve disruption of the aromatic ring and is not observed.



19 **20** **21**

The overoxidation product 2,2,4,4-tetramethyl-1,3-dioxotetralin (**7**) is accounted for by further oxidation of naphthalenone **5**. Attack of the electrophilic oxidant at C-3 of **5** gives the benzylic carbonium ion **17**. Wagner–Meerwein migration of a methyl group to C-4 gives carbonium ion **18** which, on proton loss, affords **7**. In order to support this mechanism, naphthalenone **5** 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 material and almost complete conversion to 2,2,4,4-tetramethyl-1,3-dioxotetralin (**7**). It does not seem that **7** is formed from naphthalenone **6**, because the required intermediate carbonium ion **22** would be destabilized by a positive charge on a carbon atom α to a carbonyl. In support of this contention, oxidation of 1,2,3,4-tetramethylnaphthalene with a large excess of peroxytrifluoroacetic acid–boron fluoride etherate in methylene chloride at −10° gave no naphthalenone **5**. The two major components of the isolated volatile material were the dioxotetralin **7** (40%) and naphthalenone **6** (54%).



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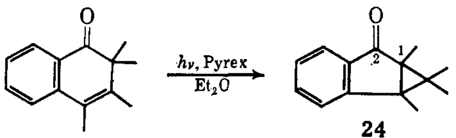
Vpc analysis of the products from the oxidation of 1,2,3,4-tetramethylnaphthalene with an equimolar amount of oxidant indicates a preference for attack at an α-methyl-bearing carbon over attack at a β-methyl-bearing carbon by 4:1, because the intermediate carbonium ion **13** is better stabilized than carbonium ion **15**.

Photochemistry of Naphthalenone 5.—Irradiation of an approximately 1.5% solution of naphthalenone **5** 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 **5** and an increase in the concentration of a photoproduct which reached a maximum concentration after 2 hr. The primary photoproduct[19] is 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexen-2-one (**24**). Ketone **24** was shown to be isomeric with naphthalenone **5** 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 aromatic C=C stretching vibrations (1606 cm^{-1}). It is noteworthy that no band appeared for $\nu_{\mathrm{C=C(nonarom)}}$. The nmr spectrum of **24** consisted of four sharp three-proton singlets (aliphatic methyls) and a complex multiplet equivalent to four aromatic protons. The two aliphatic methyls at highest field are tentatively assigned as the *gem*-dimethyl group, the signal at τ 9.28 being



5 **24**

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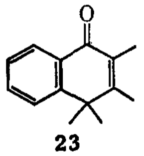
(19) Further irradiation of naphthalenone **5** in ether provided 2,3,4,4-tetramethyl-1(4H)-naphthalenone (**23**). The investigation of this photoisomerization will be the subject of a separate paper.

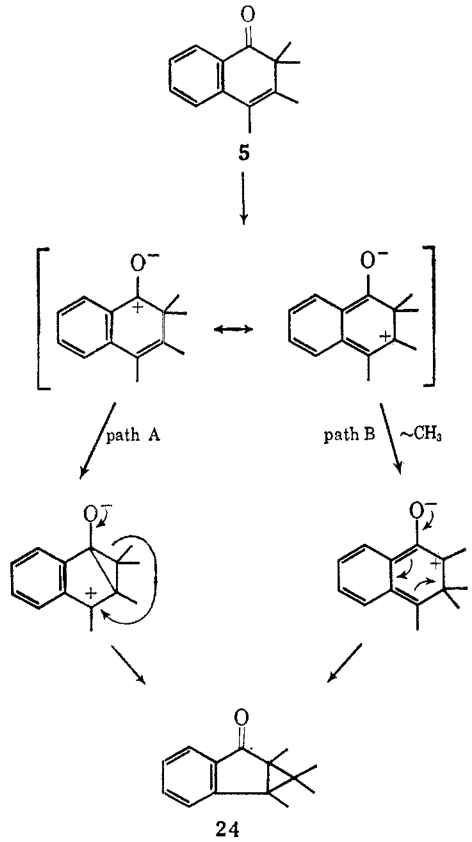


23

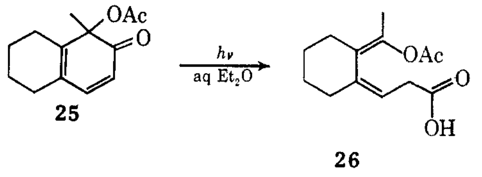
due to the methyl *syn* to and shielded by the aromatic ring. The methyls at τ 8.73 and 8.49 are assigned as the bridgehead methyls at C-1 and C-5, respectively. The photorearrangement of naphthalenone **5** was found to proceed one-half as fast as the corresponding photoisomerization of hexamethyl-2,4-cyclohexadienone (**1**) under the same conditions. A 2.5-fold rate enhancement was observed when the photolysis of naphthalenone **5** was carried out in methanol rather than ether.

Tenable mechanisms for the photochemical isomerization of naphthalenone **5** to benzobicyclic ketone **24** are presented in Scheme II. Ionic intermediates are used in the mechanisms for convenience. We favor the "bond-crossing" mechanism (path A) because it is analogous to the mechanism that was established[4] by labeling experiments for the photochemical rearrangement of hexamethyl-2,4-cyclohexadienone (**1**) to bicyclo[3.1.0]hexenone (**3**).[20]

Scheme II



Photochemistry of Naphthalenone 6.—Irradiation of a solution of naphthalenone **6** in anhydrous ether with a Hanovia L 450-w lamp was carried out in Pyrex. After irradiation for 3.5 hr, 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 **6** was irradiated for 2 hr through quartz with a Hanovia L 450-w lamp. These results parallel those described by Quinkert in a preliminary report.[21] Even in the presence of cyclohexylamine, Quinkert observed that no amide could be isolated from the photolysis of 1,1-dimethyl-2(1H)-naphthalenone. Irradiation of 1-acetoxy-1-methyl-2(1H)-naphthalenone in ether saturated with water led to a mixture of dimers, the substance 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 **25** in aqueous ether which gave **26** as the main product (stereochemistry undetermined), accompanied by a mixture of phenols.



Experimental Section

1,2,3,4-Tetramethylnaphthalene.—A solution of 34.6 g (0.17 mole) of 1-chloromethyl-2,3-dimethylnaphthalene[9] in 200 ml of dry tetrahydrofuran was added over 2.5 hr 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 hr, 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 three 150-ml portions of ether 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° (2 mm), and provided 23.6 g (81.8%) of 1,2,3-trimethylnaphthalene, mp 25–27° (lit.[9] mp 27–28°).

Repetition of the chloromethylation[9] and lithium aluminum hydride reduction provided 1,2,3,4-tetramethylnaphthalene in an over-all yield from 2,3-dimethylnaphthalene of 28.6%. The melting point[9] and ultraviolet[22] and nmr[23] spectra corresponded to those in the literature.

Oxidation of 1,2,3,4-Tetramethylnaphthalene.—A solution of peroxytrifluoroacetic acid[24] 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 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 three 75-ml portions of water, three 100-ml portions of saturated sodium bicarbonate, extracted with four 100-ml portions of 10% aqueous sodium hydroxide, and washed with three 100-ml portions of water. The sodium hydroxide and methylene chloride fractions were investigated separately. The basic fraction was acidified with dilute hydrochloric acid and extracted with three 50-ml portions of methylene chloride, which yielded on evaporation 0.06 g of a dark viscous oil. Vapor phase chromatography (20 ft × 0.25 in. SE-30 column; 220°; 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°. The pot residue was 0.97 g of a deep red, very viscous material. Vapor phase chromatography (20 ft × 0.25 in. SE-30 column; 230°; flow rate 60 ml/min of helium) showed that the distilled oil had components with the following retention times: 18.0 min (13.6%), 23.1 min (15.7%), 24.5 min (47.2%), and 33.6 min (23.4%). The compound of longest retention time was identified by its melting point, ultraviolet spectrum, and retention time as recovered 1,2,3,4-tetramethylnaphthalene. Conversion of tetramethylnaphtha-

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[20] Work is continuing to establish firmly the mechanism of this isomerization.

[21] G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965).

[22] W. L. Mosby, *J. Am. Chem. Soc.*, **75**, 3349 (1953).

[23] F. Yew, R. Kurland, and B. Mair, *Anal. Chem.*, **36**, 843 (1964).

[24] W. D. Emmons, *J. Am. Chem. Soc.*, **76**, 3468 (1954).

lene 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. Each compound was thermally stable under the vpc conditions. In order of increasing retention times, the products were identified as **2,2,4,4-tetramethyl-1,3-dioxotetralin** (**7**), **1,1,3,4-tetramethyl-2(1H)-naphthalenone** (**6**), and **2,2,3,4-tetramethyl-1(2H)-naphthalenone** (**5**). Spectroscopic and analytical properties of each compound are presented in Table I and discussed in the text.

Oxidation of 1,2,3,4-Tetramethylnaphthalene with a Large Excess of Oxidant.—1,2,3,4-Tetramethylnaphthalene (3 g, 0.016 mole) 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 (0.18 mole) of 90% hydrogen peroxide. 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 three 200-ml portions of water, three 300-ml portions of saturated sodium bicarbonate, and again with three 100-ml portions of water. 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 ft × 0.25 in. 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 infrared spectra to be 2,2,4,4-tetramethyl-1,3-dioxotetralin (7) and 1,1,3,4-tetramethyl-2(1H)-naphthalenenone (6), respectively. The compound with a retention time of 4.3 min was not identified but was found to be an oil with $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 315, 276 (sharp), 241 (shoulder), and 212 mμ and principal infrared bands (CCl_4 solution) at 1800 (vs), 1110, and 1045 (s) cm^{-1}.

Oxidation of Naphthalenone 5.—A solution of 56 mg (2.8×10^{-4} mole) of naphthalenone **5** 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° for 30 min. Work-up resulted in the isolation of 51 mg of material. The vpc analysis (10 ft × 0.25 in. FFAP column; 235°; 45 ml/min of helium) of the volatile portion indicated only a trace amount of starting material (retention time 16.0 min) and almost complete conversion to 2,2,4,4-tetramethyl-1,3-dioxotetralin (retention time 11.2 min), the latter being identified by its infrared spectrum.

General Photolysis Procedure.—All photolyses were conducted with a 450-w Hanovia Type L mercury lamp. 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 between 2 and 6° during irradiation.

Irradiation of Naphthalenone 5 in Ether.—A solution of 115 mg of naphthalenone **5** in 7 ml of ether was irradiated through Pyrex. 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 ft × 0.25 in. Carbowax column at 225° with a gas flow of 50 ml/min of helium showed a progressive decrease in the concentration of the naphthalenone (retention time 16.6 min) and an increase in the concentration of a photoproduct with a retention time of 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 a retention time of 23.6 min at the expense of the initial photoproduct.[19] The initial photoproduct was purified by vpc (above conditions) and shown to be **3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexen-2-one** (**24**), with spectral and analytical properties as presented in Table I.

Dark Reaction of Naphthalenone 5 in Ether.—A solution of 9 mg of 2,2,3,4-tetramethyl-1(2H)-naphthalenone (**5**) 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 ft × 0.25 in. Carbowax column; 208°; 60 ml/min of helium). Aliquots were removed after 2 and 168 hr. No reaction could be detected after this time and only starting material was recovered.

Comparison of the Photolysis Rates of Hexamethylcyclohexa-2,4-dienone (1) and Naphthalenone 5.—Hexamethylcyclohexa-2,4-dienone (**1**, 11 mg) in 1.1 ml of ether, 11 mg of naphthalenone **5** in 1.1 ml of ether, and 11 mg of **5** in 1.1 ml of methanol were irradiated at the same time through Pyrex. Each reaction was monitored by vpc (10 ft × 0.25 in. FFAP column; 233°; 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 naphthalenone **5** in ether to disappear, whereas 50% of **5** in methanol was photolyzed in 23 ± 2 min.

Irradiation of Naphthalenone 6 in Ether.—A solution of 40 mg of naphthalenone **6** in 6 ml of ether was irradiated through Pyrex. The photolysis was monitored by vpc. After irradiation for 220 min, a slight decrease in the concentration of starting naphthalenone (retention time 11.1 min) was observed, but no compound with a retention time <32.5 min could be detected.

Irradiation of Naphthalenone 6 in Methanol.—A solution of 50 mg of naphthalenone **6** in 10 ml of methanol was placed in a quartz test tube, sealed with a serum cap, attached to the outside of a Hanovia quartz immersion well, and irradiated. 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 a retention time <36.8 min could be detected.

Registry No.—**5**, 13145-36-3; **6**, 13145-37-4; **7**, 13145-38-5; **24**, 13145-39-6; 1,2,3,4-tetramethylnaphthalene, 3031-15-0.