Octamethylnaphthalene 1,4-Endoperoxide

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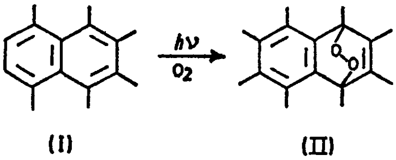
Summary Octamethylnaphthalene, on direct irradiation through Pyrex in the presence of oxygen, rapidly forms a stable 1,4-endoperoxide.

The recent report[1] that hexamethylbenzene does not form an endoperoxide when subjected to dye-sensitized oxidation prompts us to report our results on the photo-oxidation of octamethylnaphthalene (I)[2] and other highly substituted naphthalenes.[3] In contrast with hexamethylbenzene, (I) readily forms a stable, crystalline 1,4-endoperoxide.

In a typical experiment, a solution of 1·2 g of (I) in 400 ml of hexane was irradiated for 2·5 h (450 W Hanovia Type L lamp, Pyrex, 20°), during which time a steady stream of dry air was passed through the solution. A small amount of hexane-insoluble material† which formed during the photolysis was removed by filtration. The soluble products (3 spots on t.l.c.) were column chromatographed (silica gel, chloroform eluant). The first fraction was unchanged (I) (0·1 g). The second fraction (0·94 g, 69%) is considered to be the endoperoxide (II) (m.p. 139—140° from cyclo-



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† The structure of this material has not yet been established.

hexane). A minor third fraction, yellow oil, ν(C=O) 1700 cm^{-1}, was also isolated.†

Control experiments showed that (I) was not oxidized by air at room temperature in the absence of light. To test the involvement of singlet oxygen, a solution of (I) (20 mg) and methylene blue (1 mg) in methylene chloride (10 ml) was irradiated in the presence of oxygen (GE 500 W flood lamp, room temperature, 15 min). Photo-oxidation to (II) occurred rapidly, whereas no (II) formed under these conditions without the dye sensitizer.‡ Prolonged irradiation of (I) in the absence of oxygen in several solvents through Pyrex or Vycor gave only unchanged starting material.

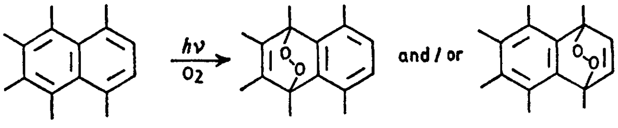
The structure of (II) rests on a correct elemental analysis, the absence of carbonyl bands in the i.r. spectrum, and an n.m.r. spectrum (CCl_4) which consisted of four singlets with equal areas, at τ 7·67 (methyls at C-5 and C-8), 7·84 (methyls at C-6 and C-7), 8·21 and 8·23 (bridgehead and allylic methyls, exact assignment not known). Consistent with the presence of a peroxide function, (II) instantaneously liberated iodine from hydriodic acid (in acetic acid). (II) was inert, however, to prolonged treatment at room temperature with $NaBH_4$ or $LiAlH_4$ in a variety of solvents. When heated under reflux for extended periods in di-n-butyl ether, (II) was slowly converted into (I) (and presumably singlet oxygen).

Octamethylnaphthalene has a λ_{max} in ethanol at 308 nm (log ϵ 3·76) as well as a more intense band at 251 nm. We suggest that either (I) or a dye can absorb the light energy and sensitize the formation of singlet oxygen, which then adds to ground state (I) (see steps a—c). Step (c) is probably easy, since (I) is highly strained and reacts readily with many common dienophiles (maleic anhydride, dimethyl acetylenedicarboxylate, arynes).[4]

$$\text{(I)} \xrightarrow{h\nu} \text{(I)}^* \qquad \text{(a)}$$

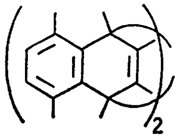
$$\text{(I)}^* + {}^3O_2 \longrightarrow \text{(I)} + {}^1O_2 \qquad \text{(b)}$$

$${}^1O_2 + \text{(I)} \longrightarrow \text{(II)} \qquad \text{(c)}$$



(III) (IV) (V)

1,2,3,4,5,8-Hexamethylnaphthalene (III)[2] was also photolysed in the presence of oxygen to determine whether endoperoxide (IV) or (V) would predominate. The principal oxygen-containing product had an n.m.r. spectrum with four aliphatic methyls (τ 8·30) and two aromatic methyls (τ 7·67), consistent with (IV) but not (V).§



(A)

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‡ Compare with ref. 1, and with the preceding communication.

§ Another product of this reaction is a hydrocarbon dimer, thought to have a structure of the type (A). The n.m.r. spectrum consisted of singlets at τ 8·53, 8·37, 7·62 and 3·28, relative areas 3:3:3:1; additional work is needed to establish unequivocally the structure.

[1] H. H. Wasserman, P. S. Mariano, and P. M. Keehn, *J. Org. Chem.*, 1971, **36**, 1765.
[2] A. Oku, T. Kakihana, and H. Hart, *J. Amer. Chem. Soc.*, 1967, **89**, 4554.
[3] H. H. Wasserman and D. L. Larsen, preceding communication.
[4] H. Hart and A. Oku, unpublished results.