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Formation of 1,4-Endoperoxides from the Dye-sensitized Photo-oxygenation of Alkyl-naphthalenes

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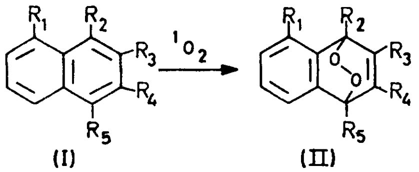
Summary 1,4-Endoperoxides are formed in the dye-sensitized photo-oxygenations of 1,4-dimethylnaphthalene (Ia), 1,8-dimethylnaphthalene (Ib), 1,4,5-trimethylnaphthalene (Ic), 1,2,4-trimethylnaphthalene (Id), and 1,2,3,4-tetramethylnaphthalene (Ie).

While the endoperoxides of anthracenes, naphthacenes, pentacenes, and other polycyclic aromatic systems resulting from the addition of singlet oxygen are well known,[1] reports of endoperoxide formation in the naphthalene series are few. Only in the case where two strongly electron-releasing (methoxy) groups are present in the 1- and 4-positions of the naphthalene nucleus have such 1,4-peroxides been isolated and characterized.[2]†



	R^1	R^2	R^3	R^4	R^5
a;	H	Me	H	H	Me
b;	Me	Me	H	H	H
c;	Me	Me	H	H	Me
d;	H	Me	Me	H	Me
e;	H	Me	Me	Me	Me

We now report that suitably substituted alkyl-naphthalenes readily form stable endoperoxides under conditions of dye-sensitized photo-oxygenation. The oxidations were conducted under close temperature control with intense external illumination and provision for rapid dissipation of the heat generated by the lamp. In a typical experiment, a solution of 1·2 g of 1,4,5-trimethylnaphthalene (Ic) in 10 ml of dry methylene chloride was irradiated using a 650 W, G.E. DWY quartz—iodine lamp in the presence of oxygen with the temperature maintained at 20 °C. Absorption of oxygen was not observed until the methylene blue sensitizer (2 mg in 1 ml of CH_2Cl_2) was added. Oxygen uptake then began immediately and continued at a steady rate until the theoretical amount had been absorbed. Standard work-up procedures‡ with provision for keeping the material at or below room temperature gave 1·2 g (85% yield) of 1,4,5-trimethylnaphthalene 1,4- endoperoxide (IIc). The peroxide, a white crystalline solid liberates I_2 from HI and decomposes slowly on heating at 40 °C. It was characterized by n.m.r. data (Table 1), its mass spectrum, ($P = 202$, weak; $P - 32 = 170$, strong), and elemental analysis.§

Similarly, the endoperoxides of 1,4-dimethylnaphthalene (IIa), 1,8-dimethylnaphthalene (IIb), 1,2,4-trimethylnaphthalene (IId), and 1,2,3,4-tetramethylnaphthalene (IIe) were prepared and identified (Table 1). Although these endoperoxides are all formed rapidly and in good yield,

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† Endoperoxides appear to be formed as intermediates in the dye-sensitized photo-oxidation of [2,2]paracyclonaphthane[3] and certain methoxy-benzenes[4] but not in the case of hexamethylbenzene.[5]

‡ Evaporation of the reaction mixture to dryness, extraction with ether, filtration through Celite, followed by removal of solvent, and recrystallization from pentane–ether.

§ Satisfactory elemental analyses were obtained for all reported endoperoxides.

TABLE 1

N.m.r. values (δ, *p.p.m.*) *for methyl singlets in naphthalenes and naphthalene endoperoxides*

	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(IIa)	(IIb)	(IIc)	(IId)	(IIe)
R^1	—	2·85	2·91	—	—	—	2·48	2·48	—	—
R^2	2·58	2·85	2·87	2·52	2·55	1·85	1·98	1·95	1·80	1·75
R^3	—	—	—	2·40	2·30	—	—	—	1·86	1·78
R^4	—	—	—	—	2·30	—	—	—	—	1·78
R^5	2·58	—	2·61	2·58	2·55	1·85	—	1·80	1·80	1·75

especially when photo-oxygenation is carried out below 0 °C, their thermal stabilities vary appreciably (Table 2). The rate of decomposition of 1,4,5-trimethylnaphthalene 1,4-endoperoxide (IIc) at 34·6 °C in solution has been determined¶ to be first order with a rate constant of $4{\cdot}9 \times 10^{-6}\,s^{-1}$ (or a half-life of 34·5 h). 1-Methylnaphthalene, 1,5-dimethylnaphthalene, acenaphthene, 5-methylacenaphthene, and 1-methoxynaphthalene do not form stable endoperoxides under the photo-oxygenation conditions described here.

TABLE 2

Half-lives (h) *for thermal decomposition of naphthalene endoperoxide*

	25 °C	51 °C
(IIa)	5	—
(IIb)	30	—
(IIc)	290	2·7
(IId)	70	—
(IIe)	—	47

Decomposition of each endoperoxide produces the original naphthalene and oxygen. That the oxygen formed is probably in the singlet state was indicated by allowing one of the peroxides (IIc) to decompose in acetone at 25 °C in the presence of 2,5-diphenyl-4-methyloxazole, an efficient singlet oxygen acceptor.[6] Examination of the reaction products by t.l.c. clearly showed the presence of *N*-acetyldibenzamide, the product known to form from dye-sensitized photo-oxidation of the oxazole.[6]

We are investigating the factors which determine the stability of alkyl-naphthalene endoperoxides as well as the use of these endoperoxides as convenient sources of singlet oxygen.[7]

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¶ Rates were determined by comparing the n.m.r. intensities of the methyl singlets associated with the naphthalenes and their endoperoxides at intervals during the thermal decomposition of the endoperoxides in $CDCl_3$ or tetrachloroethylene solutions.

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[6] H. H. Wasserman and M. B. Floyd, *Tetrahedron Supplement*, No. 7, 1966, 441.

[7] For related studies on naphthalene endoperoxides, see H. Hart and A. Oku, *Chem. Comm.*, following communication.