Reactions of Singlet Oxygen. Formation of Hydroxy Ketones in the Photo-oxygenation of Fluorenylidene Derivatives[1]

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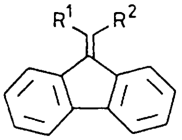
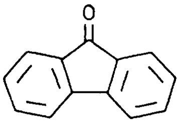
Summary Photosensitized oxygenation of fluorenylidene derivatives in methanol gives 1-hydroxyfluoren-9-one and 1-hydroxy-9-methoxy-9-(1-hydroxy-1-methylethyl)fluorene which appear to arise *via* either 1,4-cycloaddition or a peroxiran intermediate; the reaction is influenced by the nature of the substituents on the exocyclic carbon atom.

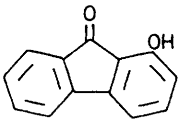
Although oxygenation of fluorenylidene derivatives has been extensively studied by Richardson[2] and Bartlett[3] no report has appeared on the oxygenation of the aromatic ring of these compounds. Photo-oxygenation of the aromatic ring has, however, been observed in the cases of some arylalkenes.[4] We now report that the photo-oxygenation of fluorenylidene derivatives gives 1-hydroxyfluoren-9-one and its derivatives either *via* 1,4-cycloaddition or *via* a peroxiran intermediate formed by reaction with singlet oxygen.



(1)

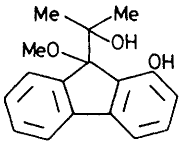


(2)



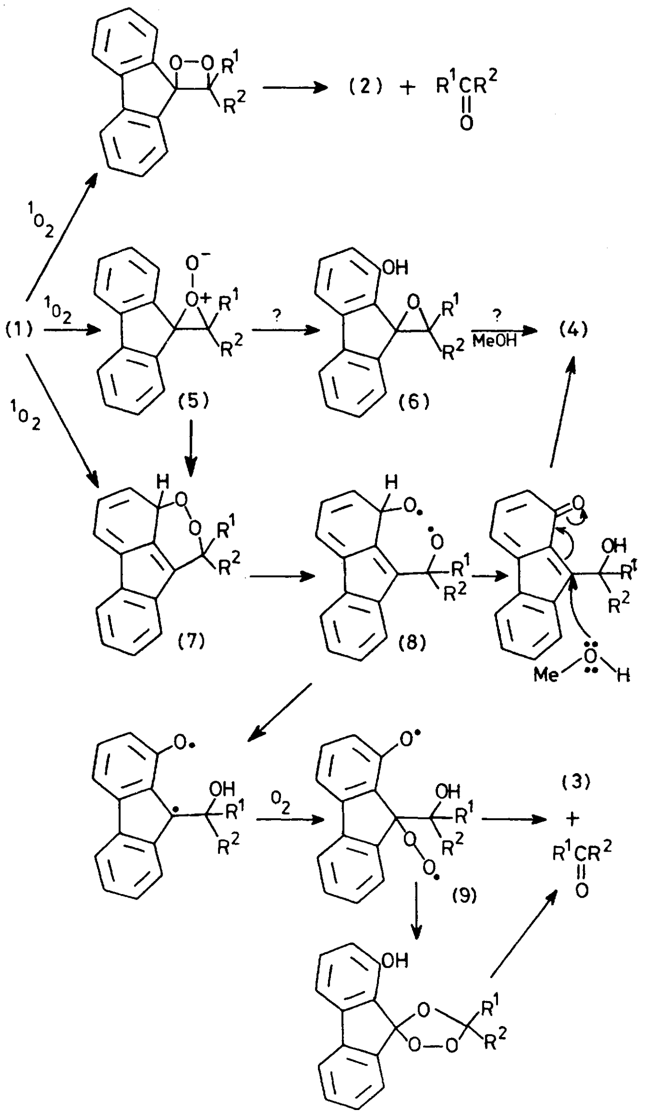
(3)

a, $R^1 = R^2 = Me$
b, $R^1 = R^2 = -[CH_2]_5-$
c, $R^1 = R^2 = H$
d, $R^1 = H, R^2 = Me$



(4)

9-Isopropylidene fluorene (**1a**) was photo-oxygenated in methanol containing 10% benzene with Rose Bengal as sensitizer. After irradiation for 5 h in a water cooled bath with a 500 W tungsten lamp, the mixture was chromatographed on silica gel to give three main products: fluoren-9-one (**2**) (5%), 1-hydroxyfluoren-9-one (**3**) (33%), m.p. 117—118 °C, *m/e* 196,† and 1-hydroxy-9-methoxy-9-(1-hydroxy-1-methylethyl)fluorene (**4**) (17%), m.p. 98—99 °C, *m/e* 270 and 238; ν (KBr) 3420 (OH) cm^{-1}; δ (CCl_4) 9·22 (s, 1H), 7·65 (m, 7H), 3·43 (s, 1H), 2·85 (s, 3H), 1·72 (s, 3H), and 0·80 (s, 3H). Similarly photo-oxygenation of 9-cyclohexylidenefluorene (**1b**) in dichloromethane, followed by silica gel chromatography, led to the isolation of (**2**) (11%), (**3**) (46%), and cyclohexanone (53%), consuming 1·6 equiv. of oxygen. To confirm whether these products arise from the reaction of singlet oxygen, (**1b**) in dichloromethane was irradiated for 26 h in the absence of a sensitizer with oxygen bubbling through the reaction mixture; only a trace of (**2**) was obtained and (**3**) was not formed. It therefore appears that (**3**) arises from the reaction with singlet oxygen and the formation of (**2**) presumably involves a radical process[3] to some extent in addition to the formation of a 1,2-dioxetan (Scheme 1).



Scheme 1

When 9-methylenefluorene (**1c**) was photo-oxygenated in dichloromethane with Methylene Blue for 8 h, no appreciable reaction was observed. For 9-ethylidenefluorene (**1d**), the reaction was quite slow, and after 17 h irradiation, (**2**) was obtained in 49% yield accompanied

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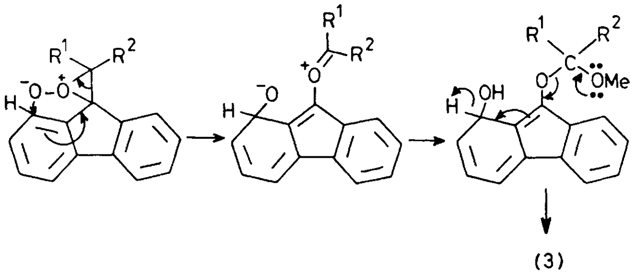
† I.r. and n.m.r. spectra of (**3**) are identical with those reported in The Aldrich Library, 1970.

with 7% of the starting material. Compound (**1d**) was also photo-oxygenated, under similar conditions, in the absence of a sensitizer with oxygen bubbling through the reaction mixture to give (**2**) (29%) and unchanged (**1d**) (53%).



Scheme 2

Compound (**1d**) did not give (**3**). These results suggest that a very delicate electron density requirement exists for the formation of (**3**). We tentatively suggest that (**3**) forms *via* 1,4-cycloaddition to give (**7**) which undergoes O–O bond cleavage to give (**8**) and addition of oxygen to give (**9**). A possible mechanism for the formation of (**3**) and (**4**) is shown in Scheme 1. Scheme 2 shows the mechanism for the formation of (**3**) as suggested by a referee. The introduction of an hydroxy group in these reactions may also involve reduction of an intermediate peroxiran by nearest internal aromatic olefin to give the 1-hydroxy-9-fluorenylidene oxide (**6**), which would react with methanol to produce (**4**).

Attempts to trap (**6**) were unsuccessful because of methylation of the hydroxy group. A dichloromethane solution of (**1a**) was photo-oxygenated at −78 °C, and an excess of diazomethane was added. The temperature was gradually raised to room temperature and silica gel chromatographic analysis showed the formation of 1-methoxy-9-fluorenone (41%) and (**2**) (5%).

The effect of acid on the photo-oxygenation was also studied. A solution of (**6a**) in methanol containing 10% benzene was irradiated with catalytic amounts of acetic acid resulting in the formation of (**2**) (1%), (**3**) (40%), and (**4**) (43%). A significant amount of solvent incorporation product was obtained from (**1a**) under these conditions.

(*Received*, 19*th October* 1977; *Com.* 1089.)

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[1] Presented at the 36th Annual Meeting of the Chemical Society of Japan, Osaka, April 1977; for previous paper in this series, see W. Ando and K. Watanabe, *Chem. Letters*, 1977, 947.

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[3] P. D. Bartlett and M. E. Ladis, *J. Amer. Chem. Soc.*, 1977, **99**, 3033.

[4] J. Rigaudy, M. Maumy, P. Capdevielle, and L. Breton, *Tetrahedron*, 1977, **33**, 53; C. W. Jefford and C. G. Rimbault, *Tetrahedron Letters*, 1976, 2479; C. W. Jefford, A. F. Boschung, and C. G. Rimbault, *Helv. Chim. Acta*, 1976, **59**, 2542.