Photoinduced Oxygenation of an Epoxynaphthoquinone

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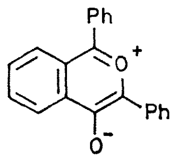
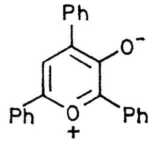
Summary Photoinduced oxygenation of epoxynaphthoquinone (**3**) in benzene gave 3-acetyl-3-acetoxyphthalide (**4**) and 3-acetoxy-3-methylisochroman-1,4-dione (**5**) in good yields *via* the reaction of singlet oxygen with a transient carbonyl ylide.

IN recent years, the thermal or photochemical oxygenation of ylides,[1] carbenes,[2] and nitrones[3] has attracted considerable interest from both the mechanistic and synthetic points of view. However, the oxygenation of carbonyl ylides has been limited to stable pyrylium oxides such as the diphenylbenzopyrylium oxide (**1**)[1a] and the 2,4,6-triphenylpyrylium oxide (**2**).[1b] We have already reported the photoinduced cycloaddition of epoxynaphthoquinones to olefins and carbonyl compounds[4] and we now report the photoinduced oxygenation of 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**3**).

A dilute benzene solution of (**3**) (4 mM) was saturated with oxygen and irradiated through a Pyrex filter for 0 5 h with a 300 W high-pressure Hg lamp under bubbling oxygen Separation of the products on a Florisil column gave 3-acetyl-3-acetoxyphthalide (**4**) (m p 97—99 °C, 43%) and 3-acetoxy-3-methylisochroman-1,4-dione (**5**) (m p 101—102 °C, 13%).



(1)



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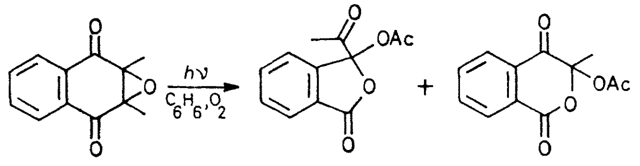

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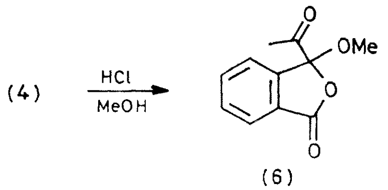
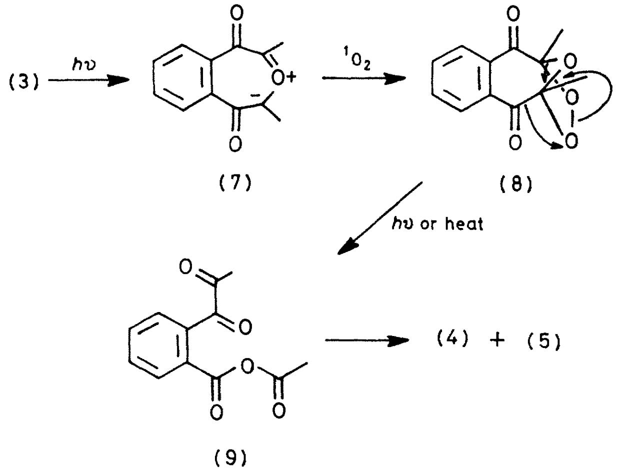


(6)

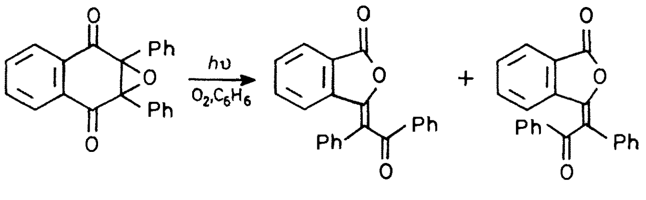
The oxygenated products (**4**) and (**5**) have the empirical formula $C_{12}H_{10}O_5$ and were characterised by the following spectral data, (**4**) i r (KBr) 1785 (phthalide C=O), 1765 (αα-dialkoxy ketone), and 1735 cm^{-1} (ester), ^{1}H n m r (CDCl$_3$) δ 2·16 (Ac) and 2 33 (OAc), ^{13}C n m r (CDCl$_3$) δ 199·2 (ketone), 168·6 and 166·9 (ester), and 101·0 (acetal) p p m (**5**), i r (KBr) 1740 (ester) and 1700 cm^{-1} (conjugated ketone), ^{1}H n m r (CDCl$_3$) δ 1 80 (Me) and 2·10 (OAc), ^{13}C n m r (CDCl$_3$) δ 187·5 (ketone), 169·1 and 159·4 (ester), and 100 4 (acetal) p p m On treatment with hydrochloric acid in methanol, (**4**) was converted into 3-acetyl-3-methoxyphthalide (**6**)

Similar photolysis of a degassed benzene solution of (**3**) gave only dimers and isomerised products[5] Compounds (**4**) and (**5**) were not observed in the photolysate When (**3**) was irradiated in benzene–methanol (40:1) containing Rose Bengal, the photo-oxygenation proceeded more quickly and (**4**) and (**5**) were obtained in 68 and 16% yields, respectively In the presence of β-carotene the rate of photo-oxygenation was greatly retarded The effect of Rose Bengal and the quenching experiment suggested the involvement of singlet oxygen in the photo-oxygenation of (**3**), and the most probable mechanism for the reaction is shown in the Scheme Singlet oxygen adds to the carbonyl



SCHEME

ylide (**7**) in a manner analogous to the cycloadditions of reactive dipolarophiles The ozonide (**8**) thus formed undergoes a Baeyer–Villiger-type rearrangement to give the diketoanhydride (**9**), which finally isomerises to (**4**) and (**5**) The transformation of (**8**) into (**4**) and (**5**) through (**9**) has some precedent in the oxygenation of closely related ylides[1a,c] However, irradiation of 2,3-diphenyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**10**) under similar conditions led only to a slow photoisomerisation to the alkylidene phthalides (**11a**) and (**11b**)[6] and no oxygenated products were obtained



(10) (11a) (11b)

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[1] (a) E F Ullman and W A Henderson Jr , *J Am Chem Soc* , 1967, **86**, 4390, (b) H H Wasserman and D L Pavia, *Chem Commun* , 1970, 1459, (c) A Padwa and E Vega, *J Org Chem* , 1975, **40**, 175.

[2] D P Highley and R W Murray, *J Am Chem Soc* , 1975 **96**, 3330

[3] C S Foote and T Y Ching, *Tetrahedron Lett* , 1975, 2771

K Maruyama and A Osuka, *Chem Lett* , 1979, 77, see also S Arakawa *J Org Chem* , 1977, **42**, 3800

[5] K Maruyama and A Osuka, *J Org Chem* , 1980, **45**, in the press

[6] H Kato H Tezuka, K Yamaguchi, K Nowada, and Y Nakamura, *J Chem Soc , Perkin Trans* 1 1978, 1029