# Photochemistry of 2-Isopropenylbenzophenone

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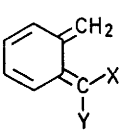
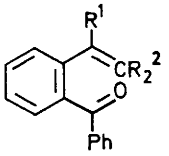
*Summary* Irradiation of 2-isopropenylbenzophenone gives an *o*-quinodimethane intermediate, which can be trapped or monitored kinetically.

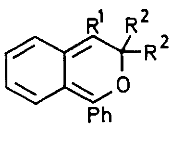
Irradiation of 2-methylbenzophenone has been reported to give two isomeric enols, (**1**) and (**2**).[1,2] The stereochemistry of these hydroxy-*o*-quinodimethanes (*o*-xylylenes) was partially assigned on the basis of their electronic absorption spectra.[2] Formation of a similar type of intermediate (**3**) in irradiation of the ketone (**4**) has been suggested.[3] We now report the results of steady state and flash photolysis experiments on the less substituted compound, 2-isopropenylbenzophenone (**5**), the photochemistry of which involves the intermediate (**6**).

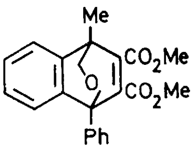
Irradiation† of (**5**)[4] in benzene containing an excess of dimethyl butynedioate afforded a 40% yield of (**7**), m.p. 120—122°.‡ Similarly, irradiation† in *trans*-1,2-dichloroethylene solution gave a product (20% yield; m.p. 106°) formulated as (**8**). The stereochemistry of the latter has not been determined but the n.m.r. data suggest that the *trans*-stereochemistry of the olefin has been retained ($J_{AB}$ 6·5 Hz) (the *cis*-olefin gives an oil showing $J_{AB}$ 10 Hz). Irradiation† in hexane in the presence of oxygen gave a cyclic peroxide (**8**) (m.p. 83—84°) in about 15% yield.

Flash photolysis§ of (**5**) ($3 \times 10^{-3}$M) in either cyclohexane or ethanol results in the appearance of transient absorption in the region 380—530 nm ($\lambda_{max.}$ *ca.* 445 nm). The lifetime in degassed cyclohexane solution was 18 ± 1 ms and in degassed ethanol was 27 ± 2 ms. In the presence of oxygen (1 atm) these lifetimes were reduced to 17 ± 1 and 22 ± 1 ms, respectively. The rate constant for reaction of the intermediate with the acetylenic ester, measured by means of a 'quenching' plot,[2] was found to be $21 \pm 1\text{M}^{-1}\,\text{s}^{-1}$.


(1) X = OH, Y = Ph
(2) X = Ph, Y = OH


(4) R$^1$ = Ph, R$^2$ = Me
(5) R$^1$ = Me, R$^2$ = H


(3) R$^1$ = Ph, R$^2$ = Me
(6) R$^1$ = Me, R$^2$ = H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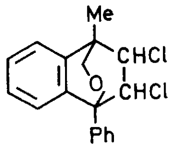
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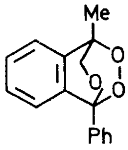
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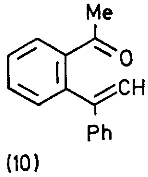
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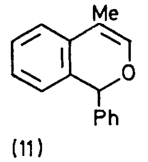
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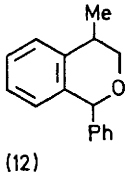
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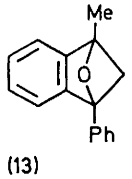
(13)

The results provide strong evidence for the formation of (**6**) in the photoreaction of (**5**). The products (**7**) and (**8**) arise from simple Diels–Alder reaction of (**6**) with the dienophiles; the peroxide (**9**) is a known product of trapping of photo-enols.[2,5] As with the alkylbenzophenones,[2] the flash photolysis results suggest that the peroxide formation is a result of reaction between the *o*-quinodimethane and molecular oxygen, each in the ground state.[2] We expected

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† Rayonnet Reactor, '3500' lamps, 30°. Solutions were flushed with nitrogen except where noted otherwise.

‡ The crystalline compounds described gave satisfactory elemental analyses and n.m.r., i.r., and mass spectral data consistent with the assigned structures.

§ Flash energy 200 J; temperature of sample 25°. Details of the apparatus will be published later.

that the enol (**1**) and the vinyl ether (**6**) would have similar electronic spectra;[2] this was found to be the case. Furthermore, the rate of reaction of (**6**) with the acetylenic ester is of similar magnitude to the rates of reactions of (**1**) and (**2**),[2] and other similar enols.[6] The high degree of reactivity of (**6**) is further illustrated by the fact that a poor dienophile such as the dichloroethylene also gives an adduct, albeit in poor yield.

Irradiation of (**5**) in ether in the absence of trapping agents results in the slow disappearance of the ketone, but the nature of the product isolated depends on the light source used. Irradiation at 350 nm† gives a low yield of (**10**) (m.p. 54—55°), whereas use of an 85 W mercury lamp and a Pyrex filter gave (**11**) (37% yield) as an unstable oil. The structure (**11**) was assigned on the basis of i.r. and n.m.r. data, including information from spin decoupling and Overhauser effect experiments. Catalytic hydrogenation of (**11**) gave (**12**), m.p. 35—37°. Formation of (**11**) might involve photoreaction of (**6**) with visible light; (**10**) could arise from an alternative mode of cyclization of (**5**) to give (**13**). However, there is no evidence for either of these proposals. A rearranged product such as that found by Huffman and Ullman[3] in the photoreaction of (**4**) was not found in the present study.

The financial support of the National Research Council of Canada is acknowledged.

(*Received*, 21*st May* 1973; *Com.* 735.)

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[1] G. Porter and M. F. Tchir, *Chem. Comm.*, 1970, 1372.
[2] G. Porter and M. F. Tchir, *J. Chem. Soc.* (*A*), 1971, 3772.
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[4] E. D. B. Barnett, J. W. Cook, and I. G. Nixon, *J. Chem. Soc.*, 1927, 504.
[5] (*a*) P. Yates, A. C. Mackay and F. X. Garneau, *Tetrahedron Letters*, 1968, 5389; (*b*) T. Matsuura and Y. Kitaura, *Tetrahedron*, 1969, **25**, 4487.
[6] M. F. Tchir, unpublished results.