Polar Effect in the Reaction of Photoenol-type Diradical with Molecular Oxygen

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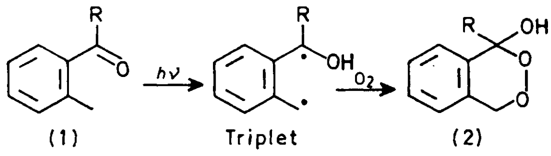
Measurement of product [(**4**) and (**5**)] quantum yields indicated that reactions of molecular oxygen with diradicals photogenerated from 2,4,6-tri-isopropylbenzophenones (**3a**—**e**) were accelerated by the presence of both electron-donating (OMe and Me) and electron-withdrawing (Cl and CF_3) substituents, this acceleration probably resulted from the zwitterionic nature of the diradicals.

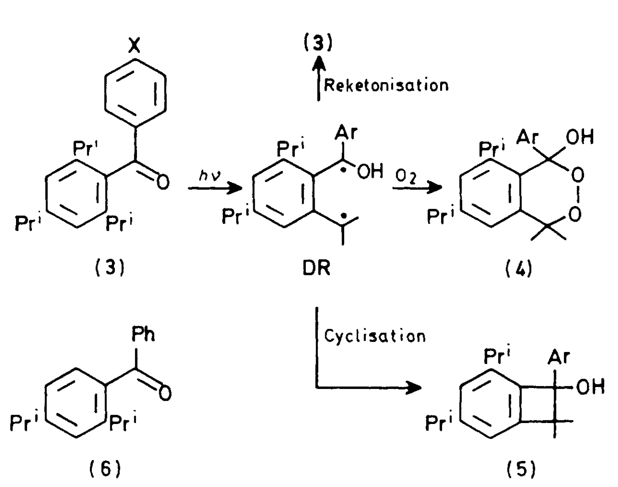
The photo-oxidation of *o*-alkylphenyl ketones (**1**) to give cyclic peroxides (**2**) has been known for many years.[1] The reaction is thought to proceed *via* trapping of triplet diradical intermediates (so-called enol triplets) with molecular oxygen (Scheme 1).[2] Because of current interest in diradical chemistry,[3] we have now examined a ring-substituent effect on this trapping reaction, using the series of 4′-substituted 2,4,6-tri-isopropylbenzophenones (**3a**—**e**) as a diradical source (Scheme 2).



(1) Triplet (2)

Scheme 1

We have previously reported that photolysis of (**3**) in degassed benzene solution affords quantitatively the corresponding benzocyclobutenols (**5**) in high quantum yields: see Φ_{CB} (degass.) in Table 1.[4] When, however, the photolyses were



Scheme 2

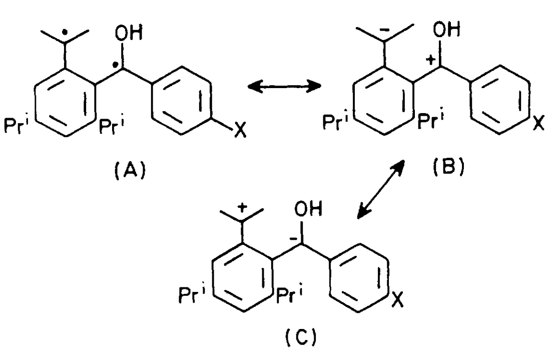
Table 1. Quantum yields for benzocyclobutenol formation (Φ_{CB}) and for cyclic peroxide formation (Φ_{PO}) from the 2,4,6-tri-isopropylbenzophenones (**3a**—**e**) and 2,4-di-isopropylbenzophenone (**6**).[a]

Subst. X in (**3**)	Hammett σ^+	Degass. Φ_{CB}	Air Φ_{CB}	Air Φ_{PO}	Air Φ_{PO}/Φ_{CB}
a OMe	−0.65	0.55[b]	0.38	0.069	0.18
b Me	−0.26	0.48[b]	0.37	0.037	0.10
c H	0.00	0.60[b]	0.45	0.022	0.049
d Cl	0.04	0.59	0.45	0.032	0.071
e CF_3	0.58	0.35[b]	0.25	0.034	0.14
(**6**)	—	0.15	0.044	0.29	6.6

[a] Irradiated at 313 nm in degassed or air-saturated benzene. [b] Ref.4.

carried out under air, the cyclic peroxides (**4**) were formed at the expense of (**5**): see Φ_{CB} (air) and Φ_{PO} in Table 1. The same reaction occurred with 2,4-di-isopropylbenzophenone (**6**), but the quantum yield for peroxide formation was considerably higher ($\Phi_{PO}=0.29$) probably owing to the much faster rate of reaction between the diradical and oxygen as compared with the rates for cyclization and reketonization processes (*cf.* Scheme 2).

The Φ_{PO}/Φ_{CB} ratios are listed in the last column of Table 1. The ratios for the series (**3a**—**e**) increased with the increase in either electron-donating (X = Me, OMe) or electron-withdrawing (X = Cl, CF_3) ability of the 4′-substituents with respect to (**3c**) (X = H). Since, as we have already reported,[5] the lifetime of the diradical intermediate DR is insensitive to *para*-substitution, this trend suggests that the reaction between DR and O_2 is promoted both by electron-donating and by electron-withdrawing substituents.†



Scheme 3

According to Russell and Bemis the triphenylmethanide anion reacts with oxygen more readily than the triphenylmethyl radical.[7] On the basis of this finding, the observed novel substituent dependency of the Φ_{PO}/Φ_{CB} ratio (Table 1) can be rationalized in the following way.

Although the diradical DR reacting with oxygen is probably in its triplet state,[2] it can possess some singlet character *via* spin–orbit coupling, thus acquiring some ionic nature due to contributions from the zwitterionic resonance structures (B) and (C) in Scheme 3.‡ Polar substituents (both electron-donating and withdrawing) may increase the contribution of the ionic structures (B and C, respectively) and result in increased reactivity towards oxygen, as was in fact observed (Table 1).† Our present result is reminiscent of Firestone's criteria[9] which state that a V-shaped Hammett plot will result from stepwise [4 + 2] cycloaddition reactions.

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References

1 P. Yates, A. C. Mackay, and F. X. Garneau, *Tetrahedron Lett.*, 1968, 5389; Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1597; T. Matsuura and Y. Kitaura, *ibid.*, 1969, **25**, 4487; D. M. Findlay and M. F. Tchir, *J. Chem. Soc., Chem. Commun.*, 1974, 514; M. Carré, M. Viriot-Villaume, and P. Caubère, *J. Chem. Soc., Perkin Trans.* 1, 1979, 2542; M. Viriot-Villauem, M. Carré, and P. Caubère, *ibid.*, 1979, 1395.

2 R. Haag, J. Wirz, and P. J. Wagner, *Helv. Chim. Acta*, 1977, **60**, 2595; R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, 1977, **99**, 7713; D. M. Findlay and M. F. Tchir, *J. Chem. Soc., Faraday Trans.* 1, 1976, **72**, 1096; H. Lutz, E. Breheret, and L. Lindqvist, *ibid.*, 1973, **69**, 2096.

3 For a review, see 'Diradicals,' ed. W. T. Borden, Wiley, New York, 1982.

4 Y. Ito, H. Nishimura, Y. Umehara, Y. Yamada, M. Tone, and T. Matsuura, *J. Am. Chem. Soc.*, 1983, **105**, 1590.

5 Y. Ito, H. Nishimura, T. Matsuura, and H. Hayashi, *J. Chem. Soc., Chem. Commun.*, 1981, 1187.

6 Y. Ito and T. Matsuura, *J. Am. Chem. Soc.*, in the press.

7 G. A. Russell and A. G. Bemis, *J. Am. Chem. Soc.*, 1966, **88**, 5491.

8 L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 92.

9 R. A. Firestone, *Tetrahedron*, 1977, **33**, 3009.

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† Calculation of k_O and k_O' from the quantum yield data (Table 1) is possible by the procedure described previously[6] [k_O, rate constant for quenching of triplet (**3**) with oxygen; k_O', rate constant for reaction between DR and oxygen]. The calculated results are, for k_O: 6.0×10^9 (OMe), 4.8×10^9 (Me), 1.9×10^9 (H), 1.8×10^9 (Cl), and 1.2×10^9 (CF_3) $dm^3\ mol^{-1}\ s^{-1}$; for k_O': 2.9×10^8 (OMe), 9.7×10^7 (Me), 3.0×10^7 (H), 3.9×10^7 (Cl), and 7.3×10^7 (CF_3) $dm^3\ mol^{-1}\ s^{-1}$. In the calculation for the Cl derivative (**3d**) a diradical lifetime of 3.5 μs was assumed.[5]

‡ According to Salem and Rowland a diradical singlet can be regarded as a resonance mixture of a pure diradical state and zwitterionic states (Scheme 3).[8]