Effect of Ring Substituents on the Lifetime of Biradicals photogenerated from 2,4,6-Tri-isopropylbenzophenones

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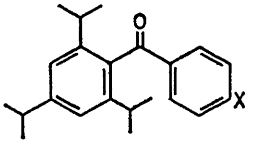
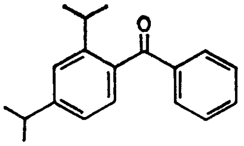
Summary The lifetime of biradicals photogenerated from 2,4,6-tri-isopropylbenzophenones was found to be relatively insensitive to the 4′-substituent.

Well established methods for the production of biradicals include the Norrish type II photoreaction of γ-hydrogen-containing aromatic ketones and the photoenolization of *ortho*-alkyl-phenyl ketones.[1] Of fundamental interest in the chemistry of biradicals are the factors which determine the biradical lifetimes. Recent ns-laser photolysis studies showed that the lifetimes of several type II biradicals were rather insensitive to changes in temperature and γ-substitution, but somewhat sensitive to solvent effects.[2]

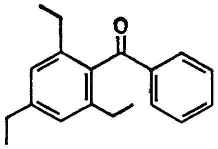


(1)

a; X = OMe b; X = Me
c; X = H d; X = CO$_2$Me
e; X = CN f; X = CF$_3$



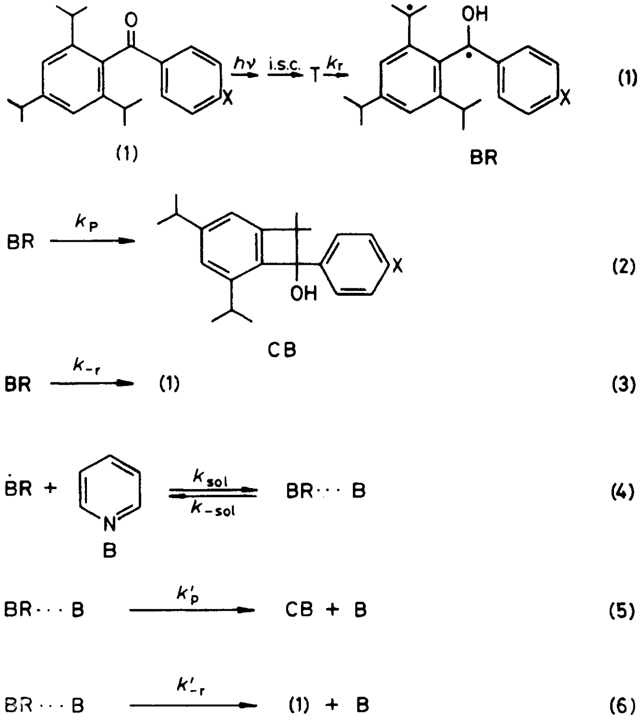
(2)



(3)

We have recently reported that the triplet state of 2,4,6-tri-isopropylbenzophenone (**1c**) is transformed to a transient biradical (BR, X = H), followed by collapse to the corresponding benzocyclobutenol (CB, X = H), as shown in equations (1) and (2).[3a] Intermediacy of the biradical in this photoreaction was then demonstrated using a laser photolysis technique.[4] We have now examined the effect of *para*-ring substituents on the lifetime of the biradicals derived by photolysis of the 2,4,6-tri-isopropylbenzophenones (**1a**—**f**).

It is known that irradiation of (**1a**—**f**) in benzene solution gives the corresponding benzocyclobutenols in excellent yields.[3] Addition of pyridine (< 0·5 M) to the benzene solution was found to increase the quantum yield of benzocyclobutenol formation (Φ_{CB}) in each case. An analogous enhancement of quantum yields by additives such as alcohol and pyridine is commonly observed with the Norrish type II reaction of phenyl alkyl ketones.[5] From this analogy, the observed increase in Φ_{CB} on addition of pyridine (B) was thought to result from the formation of a complex BR . . . B between BR and B (equation 4).[5]



Applying the expression derived first by Scaiano (equation 7)[5c] to our system, the product $k\tau_{BR}$ was estimated as the intercept/slope ratio of the plot $\Phi^0_{CB}/(\Phi_{CB} - \Phi^0_{CB})$ *vs.* $1/[B]$. In equation (7) Φ^0_{CB} and Φ_{CB} represent the quantum

$$\frac{\Phi^0_{CB}}{\Phi_{CB} - \Phi^0_{CB}} = \frac{P_p}{P'_p - P_p}\,(1 + 1/k\tau_{BR}[B]) \qquad (7)$$

$$P_p = k_p/(k_p + k_{-r}) : \quad P'_p = k'_p/(k'_p + k_{-r});$$
$$\tau_{BR} = 1/(k_p + k_{-r}); \quad k = k_{sol}(k'_p + k'_{-r})/(k_{-sol} + k'_p + k_{-r})$$

yields of benzocyclobutenol formation in the absence and presence of pyridine, respectively, P_p and P'_p are the probability of product formation from uncomplexed and complexed biradicals, respectively, and τ_{BR} is the biradical lifetime. The P_p value was also obtainable from the intercept of the same plot, provided that the reketonization pathway from BR . . . B can be neglected, *i.e.* $k'_{-r} \ll k'_p$. This is often the case with the Norrish type II reaction of phenyl alkyl ketones.[5] The values of $k\tau_{BR}$ and P_p thus determined with benzene as solvent are summarized in the Table, which also includes the data for less hindered ketones (**2**) and (**3**), for comparison.

The Table clearly shows that the magnitude of overall change in $k\tau_{BR}$ is small in the series (**1a**—**e**), although the large error limits do not allow trends in $k\tau_{BR}$ to be detected. Since the steric environment around the hydroxy-group of BR, which will exert a major influence on the through-hydrogen-bond complexation between BR and B,[5] is the same for the 2,4,6-tri-isopropylbenzophenones (**1a**—**e**), these ketones seem to have roughly equal k values. As a result, the respective values of τ_{BR} for (**1a**—**e**) will be of approximately the same magnitude. This conclusion was supported by a laser experiment (*vide infra*). The P_p values of (**1a**—**e**) were larger than those of (**2**) and (**3**) (Table), indicating that the cyclization of BR to CB is promoted by steric congestion as was suggested before.[3a]

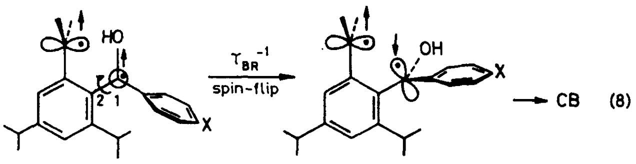
TABLE. Properties of biradicals photogenerated from the 2,4,6-tri-isopropylbenzophenones (**1a**—**f**) and the related compounds (**2**) and (**3**).

	X	$k\tau_{BR}$/l mol$^{-1\,a}$	P_p^{b}	$\tau_{BR}/\mu s^{c}$
(**1a**)	OMe	16	0·71	2·1
(**1b**)	Me	11	0·71	2·4
(**1c**)	H	16	0·78	3·1^{d}
(**1d**)	CO_2Me	17	0·66	^{e}
(**1e**)	CN	21	0·66	^{e}
(**1f**)	CF_3	^{e}	^{e}	4·5
(**2**)	—	3·8	0·46	^{e}
(**3**)	—	3·4	0·34	^{e}

[a] Maximum error is 100%. [b] Error limit ±0·05. [c] From ns-laser experiments. Error limit ±0·5 μs. n-Hexane was used as the solvent except in the case of (**1c**), where n-heptane was used.[4] [d] From ref. 4. [e] Not determined.

Direct measurement of τ_{BR} was carried out with the ns-laser photolysis technique previously reported.[4] The results are listed in the Table. While the electron-withdrawing groups appear to increase the τ_{BR} values slightly ($\times 2$ in going from OMe to CF_3), their overall change is small as just mentioned. Note that the lifetimes of biradicals photogenerated from various types of *ortho*-alkyl-phenyl ketones varied by nearly two orders of magnitude depending on the molecular structure.[6]

In view of the stereoelectronic requirement for hydrogen abstraction by n,π^* excited carbonyl compounds, the triplet states of (**1a**—**f**) should initially produce a triplet BR (**4**), in which the orbitals at two radical centres are perpendicular.[3a] Also, from consideration of the ground-state conformations of (**1a**—**f**) studied by a variable-temperature n.m.r. technique and a molecular mechanics calculation,[7] in the triplet BR (**4**) the ketyl radical centre and the *para*-substituents X are presumably deconjugated owing to steric repulsion between the two substituted phenyl rings. It seems probable that the observed small dependence of τ_{BR} on *para*-substitution with the group X is ascribable to this deconjugation and τ_{BR} is controlled by the rate of spin-flip which will occur synchronously[3a] with the C(1)–C(2) bond rotation. This rotation can occur readily, because it involves conformational conversion from the highly sterically crowded BR (**4**) into the less crowded BR (**5**) (equation 8). Scaiano has suggested that the lifetime of type II biradicals is controlled by the rate of triplet to singlet intersystem crossing.[2a,5b]



(4)
highly crowded

(5)
less crowded

Finally, the k value for the 2,4,6-tri-isopropylbenzophenones (**1**) estimated from the $k\tau_{BR}$ and τ_{BR} values (Table) is *ca.* 5×10^6 l mol^{-1} s^{-1} for each compound, much smaller than rates for diffusion-controlled processes in solution. Assuming that k_{sol} is equal to the diffusion-controlled rate constant, then this suggests that the kinetically controlled interaction between BR and pyridine, $k_{sol} \ll k'_p + k'_{-r}$, is not established, or that k_{sol} is less than the diffusion-controlled rate constant.

(*Received*, 6*th August* 1981; *Com.* 949.)

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