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AN EFFECT OF TRIFLUOROMETHYL GROUP ON PHOTOSENSITIZING BEHAVIOR OF BENZOPHENONE DERIVATIVES

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2,2'-Bis(trifluoromethyl)benzophenone acted as an efficient and stable photosensitizer in energy transfer and hydrogen transfer reactions.

It has been known that the perfluoroalkyl substitution on to a dyestuff molecule increases its durability against light.1) Effect of perfluoroalkyl substitution onto a photosensitizer, however, has been still remained to be clarified. Recently Asai and Neckers reported that benzophenone (BP), one of the typical triplet photosensitizers, implanted on a fluorocarbon polymer support was relatively stable upon photosensitizing the dimerization of indene in comparison with a free one, though the sensitizing efficiency decreased to some extent.2) It seemed that the sensitizer degraded mainly via hydrogen abstraction and/or oxetane formation with indene.

In this communication, we describe noteworthy photosensitizing behaviors of trifluoromethylated benzophenones, **3** - **5**, which have triplet energy (E_T) values nearly equal to that of the parent BP, as shown in Table 1, namely the trifluoromethyl substitution slightly perturbs the triplet energy level.

Upon the photoreductions of BP derivatives in ethanol or 2-propanol, both **4** and **5** abstracted hydrogen from the solvent more efficiently than **1** to give the corresponding reduction products of benzpinacol or benzhydrol structure, as shown in Table 1. On the other hand, the reducibility of **3** was lower than that of **1** by a factor of 5.6 in 2-propanol and 2.5 in ethanol. The compound **2** was deactivated by intramolecular hydrogen abstraction5) to be inactive for the reaction. The trifluoromethyl substitution on the aromatic ketone was regarded to enhance an $n \rightarrow \pi^*$ character of the lowest excited state and consequently to strengthen the hydrogen-abstracting power.3,4) Increased steric hindrance in **3** caused by the

1 ; R = H
2 ; o-CH_3
3 ; o-CF_3
4 ; m-CF_3
5 ; p-CF_3

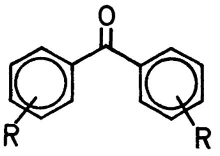

Table 1. Photoreduction of benzophenone derivatives in ethanol

Benzophenone	E_T-value[a)] kcal mol^{-1}	Relative quantum yield for photoreduction of benzophenone[b)]	Reduction product
1	68	1.0	Benzpinacol
2	72	0.00_3	--
3	66	0.4	o-CF_3-BH[c)]
4	67	1.1	m-CF_3-BP[d)]
5	66	1.2	p-CF_3-BP[e)]

a) Each E_T-value was obtained from phosphorescence spectra in Freon-113 solution at room temperature (1 cal = 4.184 J).

b) Each sample solution containing benzophenone derivative (11 mmol dm^{-3}) in ethanol was irradiated at 366 nm from a 500-W high-pressure mercury lamp under a nitrogen atmosphere, and the reaction was followed by HPLC. Each relative quantum yield in reference to that of BP (**1**) was determined in separate runs.

c) o-CF_3-BH; bis(2-trifluoromethylphenyl)methanol (o-trifluoromethylbenzhydrol).

d) m-CF_3-BP; 1,1,2,2-tetrakis(3-trifluoromethylphenyl)ethane-1,2-diol (m-trifluoromethyl-benzpinacol).

e) p-CF_3-BP; 1,1,2,2-tetrakis(4-trifluoromethylphenyl)ethane-1,2-diol (p-trifluoromethyl-benzpinacol).

trifluoromethyl substitution on the both o-positions of BP, however, seemed to suppress effectively the hydrogen-abstracting power. From a viewpoint of the molecular-designing of photosensitizer, it is noteworthy that **3** resists to the photoreduction even in such hydrogen-donating solvents. Consequently, if there is no particular paths through which the triplet state deactivates, **3** would effectively photosensitize an energy-transfer reaction.

In order to verify the presumption, the energy transfer sensitization in the dimerization of indene (**6**) was investigated by use of the above ketones in a benzene solution. The results are summarized in Table 2. o-Trifluoromethyl derivative (**3**) sensitized the reaction as efficiently as **1**, and yet hardly degraded during the reaction. While the m- and p-trifluoromethyl derivatives, **4** and **5** respectively, both degraded to give the corresponding reduction products and oxetanes with higher yields in comparison with that from **1**. The compound **2** hardly sensitized the dimerization, but mostly degraded into a complex mixture. The results suggested that the o-trifluoromethyl groups suppressed the degradation of the ketone moiety. The substituent at the position ortho to the carbonyl group would prevent sterically the approach of a substrate molecule to the carbonyl moiety of the sensitizer, but not affect the energy transfer process.

Interestingly, despite of its lower reactivity in hydrogen abstraction, **3** sensitized the reduction of 4-(dimethylamino)azobenzene (MAB, **7**) to a hydrazo form ($\mathrm{MABH_2}$), as shown in Table 2. The reduction sensitized by BP was proved to proceed via hydrogen transfer, as shown in the following Schemes 1 and 2, and the

Table 2. Photosensitized dimerization of indene (**6**) and reduction of azobenzene (**7**) by benzophenone derivatives

Sensitizer	Relative quantum yields[a)]		
	Dimerization of **6**[b)]	Degradation of sensitizer[b)]	Reduction of **7**[c)]
1	1.0	1.0	1.0
2	0.0_5	2.3	0.0_3
3	0.8	0.0_4	1.6
4	0.8	2.1	1.4
5	0.6	3.2	1.0

a) Each relative quantum yield was determined in separate runs in reference to that of BP (**1**).

b) Each sample solution containing **6** (100 mmol $\mathrm{dm^{-3}}$) and a sensitizer (3 mmol $\mathrm{dm^{-3}}$) in benzene was irradiated at 366 nm from a 400-W high-pressure mercury lamp under a nitrogen atmosphere, and the reaction was followed by GLC and HPLC. The degradation products of the sensitizer were oxetane and benzpinacol derivatives, which were isolated and assigned by NMR, IR, and satisfactory elemental analyses.

c) Each sample solution containing **7** (2.5 mol $\mathrm{dm^{-3}}$) and a sensitizer (5.5 mmol $\mathrm{dm^{-3}}$) in ethanol was irradiated in a same manner as (b) and the reduction was followed by spectrophotometric method.

$$\mathrm{BP} \underset{k_d}{\overset{h\nu}{\rightleftarrows}} {}^{3}\mathrm{BP}^{*} \xrightarrow[k_1]{\mathrm{RH}} \mathrm{BPH}^{\bullet} \xrightarrow[k_2]{\mathrm{MAB}} \mathrm{BP} + \mathrm{MABH}^{\bullet} \qquad \text{Scheme 1.}$$

$$\mathrm{BPH}^{\bullet} + \mathrm{MABH}^{\bullet} \begin{array}{l} \xrightarrow{k_3} \mathrm{MABH_2} + \mathrm{BP} \\ \xrightarrow[k_4]{} \mathrm{BPH_2} + \mathrm{MAB} \end{array} \qquad \text{Scheme 2.}$$

$$\Phi = \frac{k_1[\mathrm{RH}]}{k_1[\mathrm{RH}] + k_d} \times \frac{k_3}{k_3 + k_4} = \phi_1 \times \phi_2 \qquad (1)$$

quantum yield, Φ, of the reaction was given by Eq. 1,⁶⁾ where ϕ_1 and ϕ_2 meant the probability of the foreward reaction of ^{3}BP* in Scheme 1 (hydrogen abstraction from ethanol) and that of the upward reaction of the ketyl radical (BPH$^\bullet$) with MABH$^\bullet$ in Scheme 2 (hydrogen transfer from BPH$^\bullet$ to NABH$^\bullet$), respectively. No coupling of BPH$^\bullet$ occurred in the presence of MAB to give benzpinacol ((BPH)$_2$).6) Also no positive evidence was obtained regarding the disproportionation of MABH$^\bullet$. The photosensitized reduction by **3**, therefore, might be regarded to proceed in the same scheme as in **1**. The reactivity ratio, k_3:k_4, of **1** was 1:4.4, indicating that its ketyl radical (BPH$^\bullet$) had a lower reducing power.6) The k_3:k_4 ratio of **3** in the present work was found to be about 3:1. An increased reducing power of the ketyl radical from **3** would be caused by the steric hindrance due to the o-trifluoromethyl groups to prevent the formation of a stable coplaner structure and the hydrogen-abstraction from neighboring hydrogen donors. Even if the disproportionation process of MABH$^\bullet$ was taken into account, one would be readily noticed that the ketyl radical should be more reactive than estimated in the above consideration.

In summary, the trifluoromethyl substitution on to o- and o'-positions of BP not only suppressed the reaction with indene and/or solvent molecule, but afforded to retain a powerful energy-transfer efficiency comparabale to that of the parent BP, and yet the o,o'-bis(trifluoromethyl) compound (**3**) promoted a hydrogen-transfer sensitization. These results provided a useful guiding principle for molecular designing of stable and efficient photosensitizers.

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