

Photocyclization Reaction and Triplet Lifetime of Hindered *o*-Alkyl Benzophenones¹

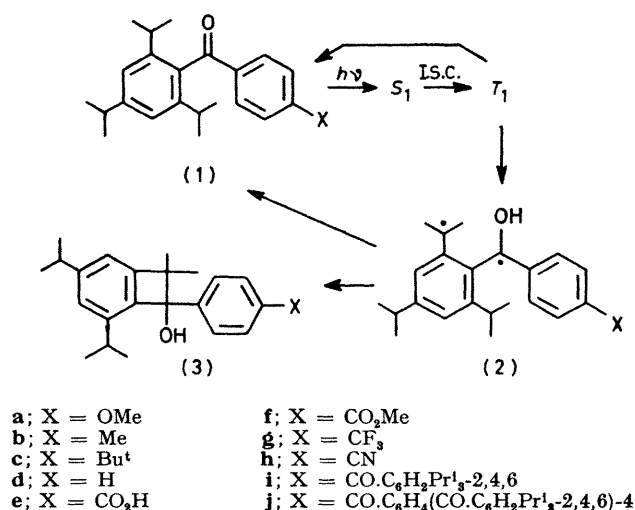
By YOSHIKATSU ITO,* YASUTOSHI UMEHARA, YUTAKA YAMADA, and TERUO MATSUURA

(Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan)

Summary The triplet lifetimes of hindered 4'-substituted-2,4,6-tri-isopropylbenzophenones decrease (increase) with the increasing electron-donating (withdrawing) ability of the ring substituents; this is the opposite effect to that expected from the rate of the intermolecular hydrogen-abstraction reaction of unhindered benzophenones.

We have recently reported a sterically promoted photocyclization reaction of 2,4,6-tri-isopropylbenzophenone (**1d**) to the corresponding benzocyclobutenol (**3d**) and its potential usefulness for the chemical storage of solar energy.² It is proposed that this reaction occurs from the triplet state T_1 , followed by formation of the biradicals (**2**) *via* intramolecular hydrogen-abstraction (Scheme).² To obtain more knowledge of the steric effect in the controversial photochemistry of 2-alkyl-substituted aromatic ketones³ and because of our interest in high energy compounds,⁴ we extended the study to a series of 2,4,6-tri-isopropylbenzophenones with various *para*-substituents, (**1a**)—(**1j**), and we observed a novel substituent effect.

As described previously,² the 2,4,6-tri-isopropylbenzophenones (**1a**)—(**1i**) produced the corresponding benzocyclobutenols (**3a**)—(**3i**) in an essentially quantitative yield by u.v. irradiation in benzene (the quantum yields are listed in the Table). The ketone (**1j**) showed no reactivity. While (**1a**)—(**1h**) reacted completely on prolonged irradiation, (**1i**) gave a photostationary mixture of 75% of (**1i**) and 25% of (**3i**) because of a photochemical back reaction (**3i**)→(**1i**)



SCHEME.

under the reaction conditions. It was found that part of the absorption spectral range of the ketones with unsaturated substituents [(**1e**), (**1f**), (**1h**), and (**1i**)] is in the visible region (ϵ_{400} 20—40) and their transformation into the corresponding cyclobutenols could be accomplished even by visible light (NaNO₂^{4a} or I₂-quinine hydrochloride⁵ filter). The

thermal reversion of (3) to (1) in each case was easily effected above 120 °C in diphenyl ether or other high-boiling solvents in good to excellent yields.

TABLE. Quantum yields for cyclobutenol formation (Φ) and triplet lifetimes (τ).^a

Ketone	Φ	τ^b /ns	τ_H/τ_X	σ^+ ^c
(1a)	0.55	54	1.7	-0.65
(1b)	0.48	62	1.5	-0.26
(1c)	0.43	64	1.4	-0.275
(1d)	0.60	90 ^d	1.0	0.00
(1e)	0.13	—	—	0.47
(1f)	0.15	127	0.71	0.49
(1g)	0.35	—	—	0.58
(1h)	0.06	152	0.59	0.67
(1i)	0.10	—	—	—
(1j)	e	—	—	—

^a Irradiated at 313 nm in benzene solution (degassed, 0.1 M).
^b $k_d \times 10^9$ l mol⁻¹s⁻¹ in benzene. ^c S. L. Murov, 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973, p. 203.
^d 225 ± 13 ns in acetonitrile from the ns laser-photolysis study (H. Hayashi, S. Nagakura, Y. Ito, Y. Umehara, and T. Matsuura, submitted to *Chem. Lett.*). ^e No reactivity.

The Table shows that Φ and Hammett σ^+ values are unrelated. This is as expected, since benzocyclobutenol formation should depend on the efficiencies of intersystem crossing (I.S.C.) ($S_1 \rightarrow T_1$) and cyclization from (2) to (3) as well as on the efficiency of intramolecular hydrogen-abstraction [$T_1 \rightarrow$ (2) (Scheme)].

Quenching of the cyclobutenol formation using 2,5-dimethylhexa-2,4-diene as quencher in benzene solution at 25 °C yielded a linear Stern-Volmer plot. The triplet lifetime (τ) of the respective 2,4,6-tri-isopropylbenzophenones was calculated from the slope of this plot (Table). It can readily be seen that electron-donating substituents (X = OMe, Me, and Bu^t) decrease the τ value, whereas electron-withdrawing substituents (X = CO₂Me and CN) increase it. A Hammett plot of the ratio of the τ values τ_H/τ_X vs. σ^+ gave a reasonably good correlation with $\rho = -0.35$ (Figure).[†] Since this negative ρ value is in sharp contrast with the positive ρ value (0.6) of a similar Hammett plot for the intermolecular hydrogen-abstraction reaction of unhindered benzophen-

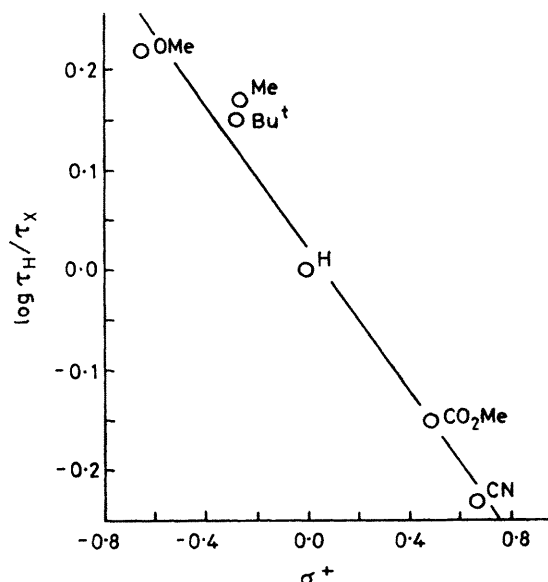


FIGURE. Hammett plot of the triplet lifetime.

ones,⁶ there is obviously a strong effect of the bulky isopropyl groups at the *ortho*-positions in the 2,4,6-tri-isopropylbenzophenones (1).

The effects of ring substituents on the hydrogen abstraction reaction by the excited triplet states of aromatic ketones is dependent on many factors, including steric effects. As one of the steric effects, we have shown that a sterically hindered rotation of the C-C single bond between the carbonyl group and the tri-isopropylphenyl group in compounds (1) in their excited triplet states may be important in determining their triplet lifetimes.²

We thank the Ministry of Education of Japan for financial support through Special Project Research.

(Received, 22nd August 1980; Com. 927.)

[†] A plot against σ substituent parameters gave an upward curve.

¹ For Part 126 of the series Photoinduced Reactions, see J. Saito, T. Matsuura, and C. Hélène, *Photochem. Photobiol.*, in the press.

² Y. Ito, Y. Umehara, T. Hijiya, Y. Yamada, and T. Matsuura, *J. Am. Chem. Soc.*, in the press.

³ P. K. Das, M. V. Encinas, R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, 1979, **101**, 6965.

⁴ (a) Y. Ito, T. Matsuura, and H. Yokoya, *J. Am. Chem. Soc.*, 1979, **101**, 4010; (b) Y. Ito, T. Matsuura, and H. Kondo, *ibid.*, 1979, **101**, 7105.

⁵ J. G. Calvert and J. N. Pitts, Jr., 'Photochemistry,' Wiley, New York, 1966, p. 736.

⁶ (a) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, 1969, **1**, 159; see also (b) P. J. Wagner, M. J. Thomas, and E. Harris, *J. Am. Chem. Soc.*, 1976, **98**, 7675; (c) P. J. Wagner and H. M. H. Lam, *ibid.*, 1980, **102**, 4167.