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Photochemistry of Meta-Substituted and Para-Substituted Aromatic Polycarbonyl Compounds

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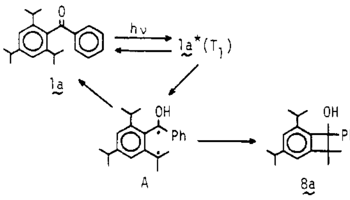
Spectroscopic (λ_{max} and E_T) and photochemical (quantum yield of benzocyclobutenol formation Φ_{CB} and Stern–Volmer quenching constant with diene K_{SV}) properties for meta-substituted polyketones **1b–f**, **2**, and **5b**, para-substituted polyketones **3a–c**, and triketone **4** having both meta and para substitution, as well as for monoketones 2,4,6-triisopropylbenzophenone (**1a**) and 2,4,6-triethylbenzophenone (**5a**), were investigated. The results have led to the proposal that the excited states of the para-substituted polyketones are better represented by assuming delocalization of the electronic excitation over all carbonyl groups in the molecule, while those of the meta-substituted ones are better represented by assuming a rapid intramolecular energy migration between the component carbonyl groups. The direction of the intramolecular energy migration in the meta-substituted polyketones was evaluated on the basis of the results of substituent effects on K_{SV} that were obtained from the study of many 2,4,6-triisopropylbenzophenones and 2,4,6-triethylbenzophenones bearing a variety of para and meta substituents (**6a–n** and **7a–f**), including the diketones **1b** (=**6i**) and **5b** (=**7e**). Irradiation of an equimolar mixture of **1a** and **5a** was also performed in order to obtain some information concerning the intermolecular energy migration between **1a** and **5a**. It is concluded that the n,π^* excitation of the carbonyl group tends to migrate in the direction benzoyl or 2,4,6-triethylbenzoyl → 2,4,6-triisopropylbenzoyl. The preferential energy migration toward the hindered triisopropylbenzoyl group is interpreted in terms of the entropy factor, i.e., relatively small decrease in internal rotational entropy upon electronic excitation of the hindered group, rather than in terms of the E_T difference between the chromophores of interest. Mechanisms for the observed stereoselective benzocyclobutenol formation from the triethyl derivatives **5** and **7** are also discussed.

Electronically excited state properties (structures, energetics, dynamics, and reactions) of basic monochromophoric compounds such as olefins, ketones, conjugated enones, and aromatic hydrocarbons have been intensively studied and many fundamental photochemical principles and reaction mechanisms have been elucidated as a result.[1] However, many photochemists appear to believe that no new principles and mechanisms are likely to be involved in the photochemistry of large polychromophoric molecules, and hence studies of these complex molecules are not essential. While we believe that this is true to some extent, we feel that full elucidation of mechanisms for energy dissipation and reactions that occur in excited polychromophoric molecules having regular structural units is an interesting problem in connection with (1) the paucity of systematic study for this type of polychromophore, (2) the hope of discovering new photochemical principles, and (3) recent interest in the photochemistry of the solid state and of organized molecular systems.[2] Since excited states of simple monocarbonyl compounds are well understood,[1,3] it seemed that polycarbonyl compounds were suitable candidates for our purpose.



(1)

We have already studied the photocyclization of 2,4,6-triisopropylbenzophenone (**1a**) into the corresponding benzocyclobutanol **8a** (eq 1) in great detail.[4-6] The reaction is thought to proceed via diradical (DR) A, which results from the ketone triplet through intramolecular hydrogen abstraction. By employing this reaction as a probe to monitor the excitation energy, we then undertook investigation of the photochemistry of meta-substituted and para-substituted aromatic polycarbonyl compounds of types **1** and **3**. Only a little photochemical study has previously been done for these types of polyketones.[7]

We now report in full detail our photochemical study of ketones **1–7**. A schematic representation for excited states of **1** and **3** and a new steric effect on electronic energy transfer are described.

Results

Preparative Photolyses. In order to prepare benzocyclobutenol (CB), a ketone solution (10^{-2} M) in benzene was irradiated for a few hours with a 400-W high-pressure mercury lamp through Pyrex under bubbling nitrogen. While the para-substituted triketone **3c** was recovered unchanged even after prolonged irradiation, all the other ketones **1–7** afforded the corresponding CB, i.e., **1a–f** → **8a–f**, **2** → **11**, **3a–b** → **12a–b**, **4** → **13**, **5a–b** → **14a–b**, **6a–n** → **15a–n**, **7a–f** → **16a–f** (Chart I). They were separated by column chromatography on silica gel. The reactions were very clean (from NMR and TLC analyses) except for **2**, where prolonged irradiation led to formation of uncharacterized byproducts in significant amounts.

The ketone **4** containing meta and para substitution has two distinct photocyclization centers. The NMR spectrum of the photoproduct **13** has a one-proton aromatic signal at a low field (δ 8.39), which is characteristic of the meta-substituted aromatic diketone such as **1b**.[5] Furthermore, a broad four-proton singlet at δ 7.88 in **4** is replaced in **13** by a four-proton AB quartet (δ 7.75 and 7.38, J = 8 Hz). These NMR patterns of **13** are consistent with the assigned structure and indicate that **4** underwent photocyclization selectively at the para-substitution site

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(1) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(2) See: "Book of Abstracts", Fifth International Conference on Photochemical Conversion and Storage of Solar Energy, Osaka, Japan, 1984.

(3) (a) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1. (b) Scaiano, J. C. *J. Photochem.* **1973–1974**, *2*, 81. (c) Dalton, J. C.; Turro, N. J. *Ann. Rev. Phys. Chem.* **1970**, *21*, 499. (d) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301. (e) Jones, G., II, *Org. Photochem.* **1981**, *5*, 1.

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

(5) Ito, Y.; Giri, B. P.; Nakasuji, M.; Hagiwara, T.; Matsuura, T. *J. Am. Chem. Soc.* **1983**, *105*, 1117.

(6) Ito, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1983**, *105*, 5237.

(7) (a) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329. (b) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *Ibid.* **1964**, *86*, 4537.

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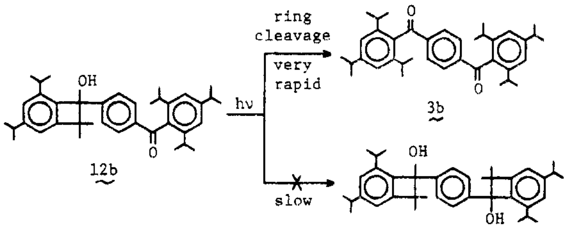
Table I. Preparative Photolyses of 2,4,6-Triisopropylbenzophenones 1–4 and 6 and 2,4,6-Triethylbenzophenones 5 and 7 in Benzene

starting ketone[a]	irradiation time,[b] h	product,[c] %		recovered ketone,[c] %
		CB	bis(CB)	
1b	3	**8b** (63)[d]		(30)[d]
	35	nd[e]		nd[e]
1c	0.5	**8c** (38)		(41)
1e	0.8	**8e** (39)	**9b** (12)	(30)
1f	0.5	**8f** (33)	**9c** (17)	(17)
2	0.5	**11** (6)		(75)
3c	38	[0]	[0]	[100]
4	1.5	**13** (16)	[0]	(80)
5a	2.2	**14a** [76]		[24]
5b	2.4	**14b** (13)		(45)
6b	3.3	**15b** [100]		[0]
6d	1.5	**15d** [100]		[0]
6f	3.0	**15f** [100]		[0]
6g	1.0	**15g** [87]		[13]
7a	2	**16a** [70]		[30]
7b	3	**16b** [77]		[23]
7d	1.5	**16d** [65]		[35]
7f	25[f]	**16f** [42]		[58]

[a] Results for the unlisted ketones were already reported.[4,5,9] [b] Internal irradiation, unless otherwise specified. [c] Isolated yields are given in parentheses. Yields estimated from NMR are in brackets. [d] Reference 5. [e] A 23% yield of anthrone **10b** was isolated. The abbreviation nd denotes "not determined". [f] External irradiation.

instead of the meta-substitution site.

In the case of the meta-substituted polyketones that possess triisopropyl substitution on both sides of the molecule **1d–f**, further photocyclization leading to the bis(benzocyclobutanols) **9a–c** also occurred.[5] However, further photocyclization was not observed for the para-substituted diketone **3b** and for the triketone **4**. We have already shown that because of the very rapid photochemical ring cleavage (>10^{10} s^{-1}) formation of bis(CB) cannot occur for **12b** (eq 2).[5] Similarly, irradiation of **13** produced only the original ketone **4**.

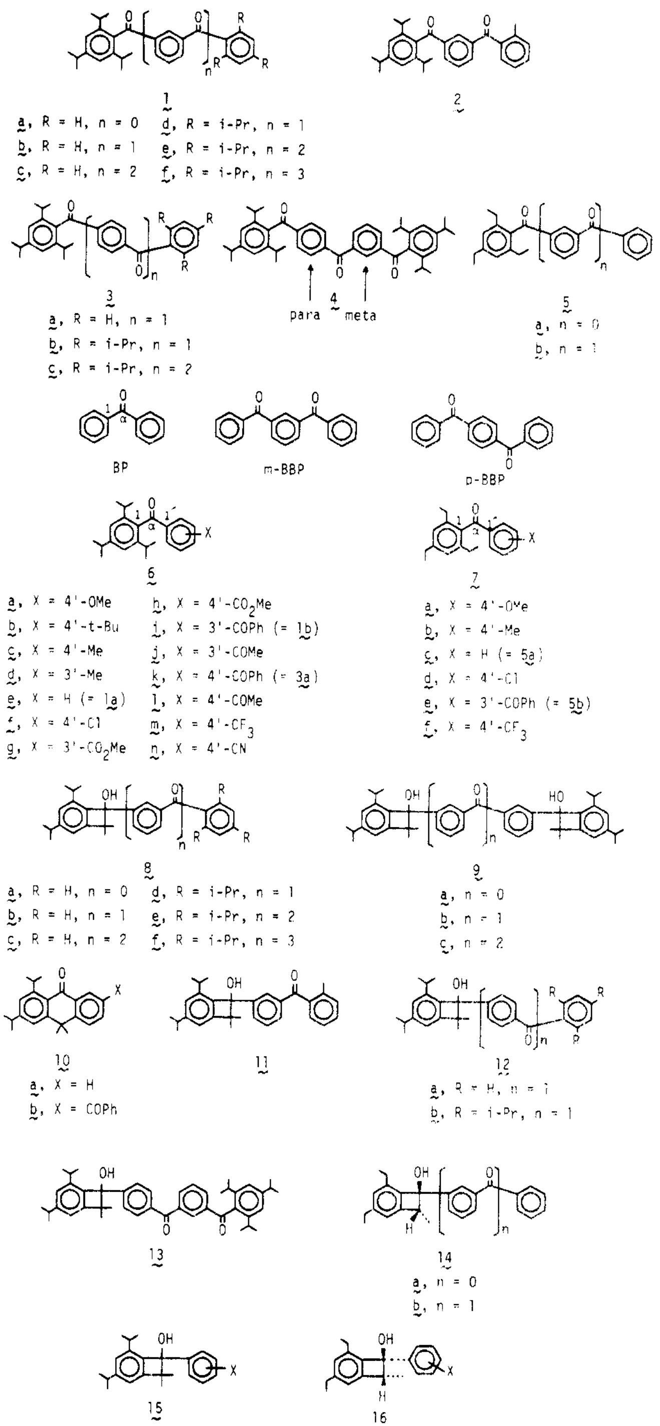


(2)

Although extended irradiation of **3a** produced essentially no byproducts, irradiation of **1b** for a long time (35 h) afforded an anthrone derivative **10b** (23% yield) in addition to **8b**. As was already reported, very close examination of a photolysate from **1a** also disclosed formation of a trace amount of anthrone **10a**.[6] An analogous inefficient anthrone formation might have occurred in other cases, but it was not studied. The results of the preparative photolyses are summarized in Table I.

Finally it should be mentioned that only a single stereoisomer of CB was obtained from 2,4,6-triethylbenzophenones **5** and **7** in each case.[8] The stereochemistry of this isomer was assigned on the basis of the unusually high-field NMR signal of the methyl hydrogen on the cyclobutene ring (δ 0.78–0.84; see Experimental Section), which probably resulted from anisotropic shielding by the adjacent cis phenyl ring.[9]

Chart I



General Remarks on Quantitative Photolyses. In order to obtain the quantum yield for benzocyclobutenol formation Φ_{CB} and the Stern–Volmer quenching constant K_{SV} ($=k_q\tau$) with 2,5-dimethyl-2,4-hexadiene as quencher, degassed benzene solutions containing ketone (0.05 M) and diene (0–0.05 M) were irradiated with potassium chromate filtered light (313 nm) on a merry-go-round apparatus at 25 °C. The quantity of CB produced was determined with high-pressure liquid chromatography (HPLC). The reactions were stopped at a very low conversion (<1%) in order to suppress the effect of back photoreaction and further photocyclization.[5] The results are summarized in Tables II–IV.

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(8) In contrast, Kitaura and Matsuura[9] claimed the formation of both cis and trans isomers (molar ratio, 1:1) from **5a** in benzene. The reason for this discrepancy is unclear.

(9) Kitaura, Y.; Matsuura, T. *Tetrahedron* **1971**, *27*, 1597.

Table II. Spectroscopic and Photochemical Properties of Aromatic Polycarbonyl Compounds 1–5

compd	λ_{max},[a] nm (ϵ)	phosphorescence[b] 0–0 band, kcal/mol	phosphorescence[b] rel intensity	Φ_{CB}[c]	K_{SV}[c] M^{-1}
1a	242 (15 700) 349 (63)	ca. 69 (68.5), 69.1*	0.022 (0.039)	0.60[d,e]	450
1b	233 (38 000) 351 (152)	68.6 (67.6)	0.015	0.64[f,g]	570
1c	234 (41 500) 348 (290)	68.4 (67.6)	0.033	0.56	490
1d	232 (37 500) 347 (185)	68.9 (67.9)	0.011 (0.043)	0.79[f]	640
1e	233 (46 000) 350 (260)	68.5 (67.9)	0.0077 (0.024)	0.76	480
1f	235 (63 500) 350 (385)	68.5 (67.5)	0.0048	0.70	465
2	230 (35 000) 350 (191)	68.7	*h*	0.11	65
3a	260 (30 000) 349 (170)	65.6	0.0064	0.16[f]	455
3b	262 (32 000) 350 (300)	*h*	*h*	0.10[f]	255
3c	265 (68 000) 346 (448)	64.5	*h*	0	*h*
4	238 (16 100) 260 (29 100) 352 (337)	65.2	*h*	0.13	500
5a	243 (16 000) 349 (80)	69.1	*h*	0.14	800
5b	233 (43 000) 348 (175)	68.6 68.5*	*h*	0.09	1960
BP[j]	248 (19 400) 346 (120)	68.9 (68.4), 68.6*	1.00 (1.00)		32500[i]
m-BBP[k]	247 (36 800) 345 (230)	68.7 (67.8)	1.27 (0.70)		12500[i]
p-BBP[l]	260 (35 000) 348 (359)	66.3 (65.4)	0.69		6000[i]

[a] In cyclohexane. [b] In ethanol at 77 K; maximum error, 0.2 kcal/mol. The values marked with * are in ether–pentane–ethanol (5:5:2) glass. [c] In degassed benzene at 25 °C; maximum error, 10%. [d] Reference 4. [e] Φ for **10a** ~0.0001; ref 6. [f] Reference 5. [g] Φ for **10b** = 0.0027. [h] Not measured. [i] Determined from phosphorescence quenching in degassed benzene at room temperature, using 2,5-dimethyl-2,4-hexadiene as quencher. [j] Benzophenone. [k] *m*-Benzoyl benzophenone. [l] *p*-Benzoylbenzophenone.

Meta-Substituted Polyketones of Type 1. As summarized in Table II, the compounds **1a–f** exhibit absorption maxima at virtually the same regions, ca. 350 (n,π^*) and 235 nm (π,π^*), and the E_T values estimated from their weak (relative to benzophenone (BP)) phosphorescence spectra are nearly the same ($E_T \sim 69$ kcal/mol in ethanol glass). The fact that the spectral data for **1b–f** are similar to those of the parent ketone **1a** implies that each carbonyl group in the molecule is relatively independent because of the lack of conjugation. The values for Φ_{CB} and for K_{SV} obtained from observed linear diene-quenching plot of the CB formation are also approximately similar in this series (Φ_{CB} = 0.56–0.79 and K_{SV} = 450–640 M^{-1}). The small variations in Φ_{CB} in going from the parent ketone **1a** to the polyketones **1b–f** indicate that the excitation decay from the nonreactive carbonyl groups (unstrained carbonyl groups) is not important. The low Φ_{CB} value observed for the compound **2** (0.11) is most likely due to the efficient energy wastage via rapid photoenolization[10] of the 2-methylbenzophenone (2-MBP) moiety.

Para-Substituted Polyketones of Type 3. As compared with the meta-substituted polyketones, the para-substituted ones **3a–c** exhibit a large red shift of the π,π^* absorption maximum (260–265 nm) with a similar n,π^* absorption maximum at ca. 350 nm (Table II). Furthermore, their E_T and Φ_{CB} are much lower than those of **1** and depend considerably on the number of the carbonyl groups in the molecule. The lowering of Φ_{CB} in the order **1a** > **3a** ~ **3b** ≫ **3c** may be due to increasing π,π^* character of the T_1 state in going from **1a** to **3a** and **3b** to **3c**, since their π,π^* absorption maxima move to longer wavelengths in the same order (Table II). Comparison of K_{SV} for the pair **3a** (455 M^{-1}) and **3b** (255 M^{-1}) with K_{SV} for the pairs **1b** (570 M^{-1}) and **1d** (640 M^{-1}) and **1c** (490 M^{-1}) and **1e** (480 M^{-1}) discloses that K_{SV} for the para-substituted polyketones **3** depends on the number of the 2,4,6-triisopropyl substitution (i.e., the number of reactive carbonyl groups) in contrast to the meta-substituted ones **1**, where their K_{SV} is nearly independent of the number of reactive carbonyl groups.

Other Polyketones. Table II also shows results for the other polyketones. The three absorption maxima observed for the triketone **4** are consistent with the presence of both para-substituted and meta-substituted diketone moieties. The respective values of E_T, Φ_{CB}, and K_{SV} were similar to those of **3a**. As noted above, **4** photocyclized only at the para-substitution site. The selective cyclization is understandable in terms of the usual "energy sink" concept, since the para-substituted carbonyl group has a lower E_T value than the meta-substituted one, as readily seen from comparison of the E_T values of **3** and *p*-BBP with those of **1** and *m*-BBP (Table II).

The compounds **5a** and **5b** were studied to compare with the triisopropyl counterparts **1a** and **1b**. The spectroscopic properties of **5a** and **5b** are quite similar to those of **1a** and **1b**, respectively. The quantum yield Φ_{CB} for **5a** and **5b** is lower than that for **1a** and **1b**. (In general Φ_{CB} for 2,4,6-triisopropylbenzophenones is higher than that for 2,4,6-triethylbenzophenones, as shown in Table III. We have already suggested that one of the reasons for this trend is that the efficiency for cyclization of DR to CB is enhanced by steric congestion.[11]) It is noticeable that K_{SV} for **5a** (800 M^{-1}) is considerably different from **5b** (1960 M^{-1}) in contrast to the comparable K_{SV} values of **1a** and **1b**.

4′- or 3′-X-Substituted 2,4,6-Triisopropylbenzophenones and 2,4,6-Triethylbenzophenones. Table III lists spectroscopic and photochemical data for many 2,4,6-triisopropylbenzophenones and 2,4,6-triethylbenzophenones (**6–7**) bearing a variety of para and meta substituents. Substituent effects on spectroscopic properties (λ_{max} and E_T) for several 4′-X-2,4,6-triisopropylbenzophenones (**6**, X = MeO, Me, H, CO_2Me, CF_3, and CN) have already reported and discussed.[4] Parallel results were obtained for the triethyl series and thus they will not be discussed in this paper.

Figure 1 shows a Hammett plot of the relative Stern–Volmer quenching constant, $\log(K_{SVH}/K_{SVX})$ vs. σ^+ (or σ), for two series of compounds **6a–n** and **7a–f**. The relevant data for K_{SV} and σ^+ (or σ) of each compound are listed in Table III. One can see that the triisopropyl series **6**, *including* the diketones **1b** (=**6i**) and **3a** (=**6k**), obeys roughly a single straight line with a negative ρ value, while the triethyl series **7**, *excluding* the diketone **5b** (=**7e**), obeys a straight line with a positive ρ value. One should remember that the n,π^* excitation in the diketones **1b**, **3a**, and **5b** may potentially reside on both of the carbonyl groups in the molecule, considering the almost equal E_T values of the following monocarbonyl compounds: **1a**, ca.

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[10] (a) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405. (b) Wagner, P. J. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1981; Vol. 3, p 381.

[11] Ito, Y.; Nishimura, H.; Matsuura, T.; Hayashi, H. *J. Chem. Soc., Chem. Commun.* 1981, 1187.

Table III. Spectroscopic and Photochemical Properties of 4′- or 3′-X-2,4,6-Triisopropylbenzophenones 6 and 4′- or 3′-X-2,4,6-Triethylbenzophenones 7

compd	substituent X	λ_{max},[a] nm (ϵ)	phosphorescence 0–0 band,[b] kcal/mol	Φ_{CB}[c]	K_{SV},[c] M^{-1}	σ^{+}[d]
6a	4′-OMe	270 (20 500) 343 (97)	70.2[e]	0.55[e]	210	−0.65
6b	4′-*t*-Bu	254 (19 800) 348 (73)	*f*	0.43	320	−0.275
6c	4′-Me	253 (20 600) 348 (74)	70.4[e]	0.48[e]	255	−0.26
6d	3′-Me	246 (13 800) 350 (68)	69.5	0.68	365	−0.065
6e (=**1a**)	H	242 (15 700) 349 (63)	ca. 69	0.60[e]	450	0.00
6f	4′-Cl	257 (20 300) 352 (81)	*f*	0.59	445	0.04
6g	3′-CO_2Me	242 (16 400) sh 352 (84)	*f*	0.45	525	0.37
6h	4′-CO_2Me	252 (27 400) 361 (81)	68.1[e]	0.15[e]	635	0.49
6i (=**1b**)	3′-COPh	233 (38 000) 351 (152)	68.6	0.64[g]	570	0.34[h]
6j	3′-COMe	223 (43 700) 240 (20 100) sh 351 (300) sh	*f*	0.25[g]	635	0.38[h]
6k (=**3a**)	4′-COPh	260 (30 000) 349 (170)	65.6	0.16[g]	455	0.43[h]
6l	4′-COMe	258 (28 600) 363 (175) sh	*f*	0.06[g]	570	0.50[h]
6m	4′-CF_3	242 (14 200) 358 (61)	67.6[e]	0.35[e]	895	0.58
6n	4′-CN	251 (24 500) 260 (21 400) 362 (86)	66.0[e]	0.06[e]	760	0.67
7a	4′-OMe	270 (35 100) 342 (139)	69.9	0.17	1850	−0.65
7b	4′-Me	253 (20 100) 347 (88)	69.9	0.20	1135	−0.26
7c (=**5a**)	H	243 (16 000) 350 (78)	69.1	0.14[e]	800	0.00
7d	4′-Cl	254 (23 900) 352 (182)	69.0	0.24	1000	0.04
7e (=**5b**)	3′-COPh	233 (43 000) 348 (175)	68.6	0.09	1960	0.34[h]
7f	4′-CF_3	238 (18 500) 357 (154)	67.8	0.10	425	0.58

[a] In cyclohexane. [b] In ethanol at 77 K. [c] In degassed benzene at 25 °C. [d] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1975; p 203. [e] Reference 4. [f] Not measured. [g] Reference 5. [h] σ value.

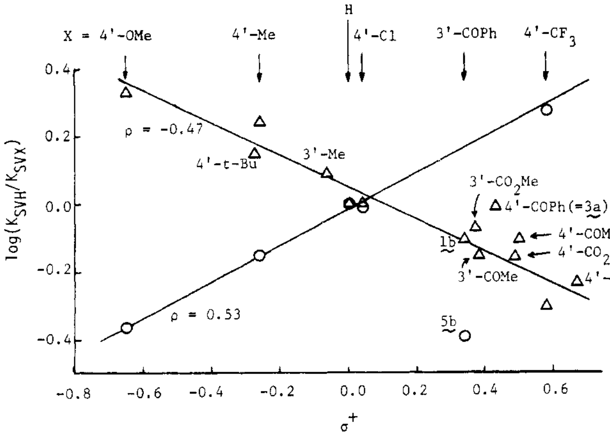


Figure 1. Hammett plot of log (K_{SVH}/K_{SVX}) vs. σ^{+} (or σ for COPh and COMe) for substituted 2,4,6-triisopropylbenzophenones **6a–n** (△) and substituted 2,4,6-triethylbenzophenones **7a–f** (○).

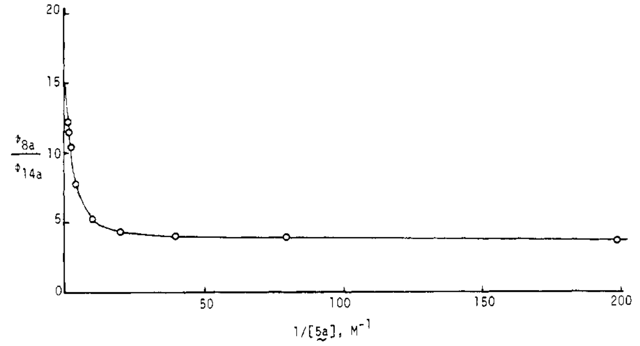


Figure 2. Relative yield (Φ_{8a}/Φ_{14a}) of two CB's produced from photolyses of equimolar mixtures of 2,4,6-triisopropylbenzophenone (**1a**) and 2,4,6-triethylbenzophenone (**5a**) as a function of the ketone concentration.

69 kcal/mol; **5a**, 69.1 kcal/mol; BP, 68.9 kcal/mol (Table II). These results will be discussed later.

Photolyses of Equimolar Mixtures of 1a and 5a. Photolyses of equimolar mixtures of **1a** and **5a** in degassed benzene were carried out at varied ketone concentrations ([**1a**] = [**5a**] = 0.005–1.0 M). The corresponding cyclobutenols **8a** and **14a** were produced and the molar ratio of **8a** to **14a** Φ_{8a}/Φ_{14a} was determined by HPLC analyses. Figure 2 shows a plot of Φ_{8a}/Φ_{14a} against the reciprocal concentration of the ketone 1/[**5a**].

Effects of *tert*-Butyl Alcohol on Φ_{CB}. Table IV shows the effects of added *tert*-butyl alcohol (2 M) on Φ_{CB} for several 2,4,6-triisopropylbenzophenones. For **1a** and **1b**, Φ_{CB} was found to slightly increase upon addition of the

Table IV. Effects of Solvent on Φ_{CB} for Several 2,4,6-Triisopropylbenzophenones

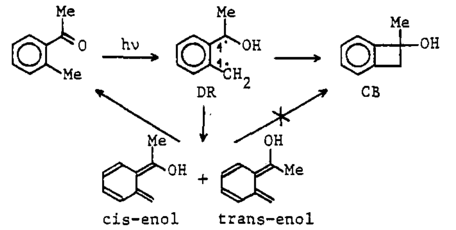
	solvent	
compd	benzene	*t*-BuOH (2 M)-benzene
1a	0.60[a]	0.68
1b	0.64[b]	0.68
3a	0.16[b]	0.097
3b	0.10[b]	0.03
6h	0.15[a]	0.13
6n	0.06[a]	0.05

[a] Reference 4. [b] Reference 5.

alcohol, probably as a result of interaction of the diradical intermediates such as A with the added alcohol through hydrogen bonding, which retards reketonization.[4,12] In the cases of **3a**, **3b**, **6h**, and **6n**, Φ_{CB} was decreased by the addition of the alcohol. Possibly the higher π,π^* character in their T_1 states compared with **1a** and **1b** (vide supra) is responsible for this decrease.

Discussion

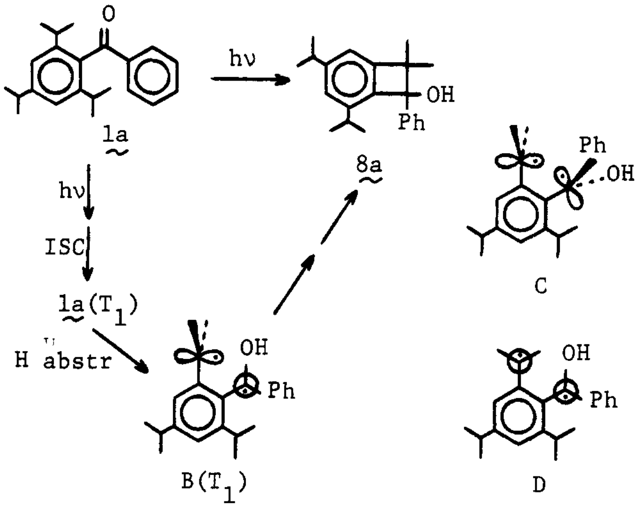
Some Reflections on the Mechanism for CB Formation. Several mechanisms appear plausible in order to understand the stereoselective CB formation of 2,4,6-triethylbenzophenones **7** → **16**. First, there is an opinion in the so-called photoenolization of *o*-alkylphenyl ketones that benzocyclobutanol (CB) is only formed from diradical (DR) and that cis or trans ground signlet state enol leads only to the starting ketone (eq 3).[13] DR and excited triplet state enol are believed to be the same species.[14] Ground singlet state enols were detected by transient spectroscopy, trapped by dienophiles such as maleic anhydride and dimethyl acetylenedicarboxylate, and even isolated in particular cases,[10] yet there exists no experimental evidences that they cyclize to the CB form.



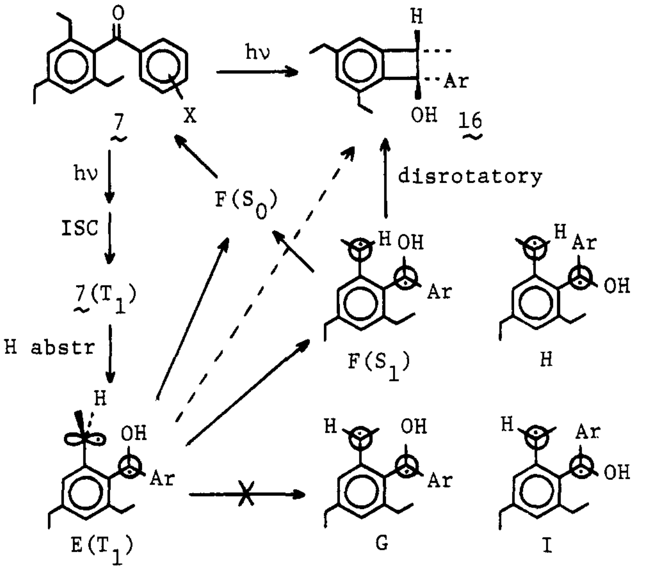
(3)

Equation 3 suggests that the excited singlet state enol may intervene in the course of transformation from DR to CB in some cases, because spin-inversion must occur before cyclization.[13b] Previously we used only diradical-like structures for the intermediates (or the transition states) B–D shown in Scheme I,[4,6] since the ground singlet state enol is a typical diradicaloid hydrocarbon.[15] We proposed that the CB formation **1a** → **8a** proceeded in the sequence **1a**(S_0) → **1a**(T_1) → B(T_1) → C(S) → **8a**(S_0) and assumed that the parallel odd-orbital structure D having large steric repulsions from the adjacent ring substituents was not involved in this transformation.[4,6]

Scheme I

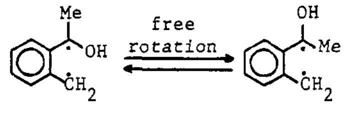


Scheme II



The stereoselective CB formation from 2,4,6-triethylbenzophenones **7** → **16** may be understood by an analogous scheme (Scheme II). In this case, however, the parallel structure F seems energetically accessible, owing to the smaller steric hindrance. Note that F is approached from the initial DR conformation E by only a partial rotation (i.e., a twisting) around the single bond to the ĊHMe group. A rotation to the reverse direction giving G is sterically less favorable. According to the Woodward–Hoffmann rule the structure F(S_1) (the excited singlet state enol) should undergo a disrotatory ring closure, leading to **16**. As aforementioned, F(S_0) (the ground singlet state enol) will exclusively generate the original ketone **7**.

Previously it was proposed for simple *o*-alkylacetophenone diradicals that their syn–anti rotation is free to occur within their lifetimes (eq 4).[14a,16] In the case of the



(4)

diradical E(T_1), however, the free syn–anti rotation seems unlikely, since the CB formation is stereoselective. We have recently pointed out that the odd-orbital rotation in B(T_1) is not free.[6] This conclusion was drawn mainly from

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(12) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

(13) (a) Carré, M. C.; Viriot-Villaume, M. L.; Caubère, P. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2542. (b) Sevin, A.; Bigot, B.; Pfau, M. *Helv. Chim. Acta* **1979**, *62*, 699. (c) Wagner, P. J. *Pure. Appl. Chem.* **1977**, *49*, 259.

(14) (a) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965. (b) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *Ibid.* **1983**, *105*, 5143.

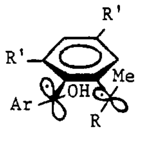
(15) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270.

(16) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.

the fact that cyclization of **1a** into **8a** is photochemically reversible but DR A photogenerated from **1a** and the one photogenerated from **8a** are not equivalent species (i.e., DR A is not thermally equilibrated between its different conformations and spin multiplicities). We have also disclosed from the dynamic NMR study of **1a** that the rotational rate around the bond linking C=O and the triisopropylphenyl group (bond 1–α) is slow: 14.5 s^{-1} at 31 °C.[17]

The second mechanism starts from an assumption conflicting with the previous[13] opinion; i.e., one assumes that CB is formed through intervention of the ground singlet state enol. Since the stereochemical constraints in the syn–anti rotation of DR E(T_1) are smaller than B(T_1), E(T_1) may generate four possible enol structures F–I, among which F and H are more likely to be produced because of less crowding than G and I. The observed stereoselectivity can arise from the allowed conrotatory closure of H(S_0) into **16**, if F(S_0) exclusively reketonizes to **7** without ring-closure to CB. It is known that, while *trans*-enols are trappable with dienophiles, *cis*-enols such as the structure F are very short-lived because of their facile reketonization and cannot be trapped by dienophiles.[10] However, as far as one believes the validity[13a] of the mechanism described in eq 3, the first mechanism (Scheme II) is preferable to the second one.

Finally, we note that the completely perpendicular pictorial representation for the diradicals B and E (Schemes I and II) is only an approximation. Their exact conformation (immediately after the intramolecular hydrogen abstraction) is probably more similar to the structure J, which is not very different from the enol structure. Since stereospecific and apparently concerted triplet-state photoreactions are known,[18] it can be viewed as highly likely that the stereospecific cyclization of E(T_1) to **16** also proceeds directly without going through F(S_1) (the dotted line in Scheme II). This route, of course, corresponds to the sequence B(T_1) → C → **8a**, the reaction mechanism proposed previously for 2,4,6-triisopropylbenzophenone (**1a**).[4,6]

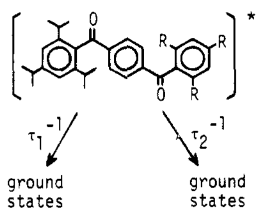


J

R = Me or H

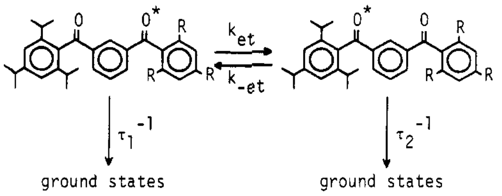
Contrasting Excited-State Structure between Meta-Substituted and Para-Substituted Polyketones.[19] Wagner has reported that K_{SV} of *p*-acetylvalerophenone, which has one "reactive" carbonyl group, is two times that of *p*-divalerylbenzene, which has two "reactive" carbonyl groups ("reactive" means capable of undergoing type II elimination).[7a] Similarly, K_{SV} of the para-substituted diketone **3a** (455 M^{-1}), which has only one reactive carbonyl group, was about two times that of **3b** (255 M^{-1}), which has two reactive carbonyl groups. By contrast, K_{SV} observed for the pairs **1b** (570 M^{-1}) and **1d** (640 M^{-1}) and **1c** (490 M^{-1}) and **1e** (480 M^{-1}) indicates that their K_{SV} is nearly independent of the number of the reactive carbonyl group. This difference, coupled with the fact that E_T for the para-substituted polyketones **3a–c** is lower than that for the meta-substituted ones **1b–f** which in turn is almost equal to E_T of the parent ketone **1a**, led us to propose that the electronic excitation in the para-substituted compounds is delocalized over all of the carbonyl groups in the molecule, while the excited states of the meta-substituted ones are better represented by a rapid intramolecular energy migration between the component carbonyl groups rather than by delocalization of the excitation energy (Schemes III and IV).

Scheme III



3a, R = H; 3b, R = i-Pr

Scheme IV



1b, R = H; 1d, R = i-Pr

In the former situation (Scheme III), the observed triplet decay triplet τ^{-1} may be taken as the simple sum of the decay rates from the component carbonyl groups, i.e.,

$$\tau^{-1} = \tau_1^{-1} + \tau_2^{-1} \tag{5a}$$

As a result, K_{SV} ($=k_q\tau$) of the para polyketone with two reactive carbonyl groups may be reduced to about $^1/_2$ that of the para polyketone having only one reactive carbonyl group.

The latter situation is illustrated in Scheme IV. If the pseudoequilibrium conditions are satisfied (k_{et}, $k_{-et} \gg \tau_1^{-1}$, τ_2^{-1}), one can readily derive eq 5b.[21,22d] Thus, the ex-

$$\tau = \frac{K + 1}{\tau_1^{-1} + K(\tau_2)^{-1}} \tag{5b}$$

perimentally measured triplet lifetime τ (and hence K_{SV}) depends on the ratio of the rates for the forward and backward intramolecular energy migration ($k_{et}/k_{-et} = K$) as well as on the lifetimes of the localized excited states (τ_1 and τ_2). This point will be touched upon later.

Interpretation of the Hammett Plot. As seen from Figure 1, substituent effects on log (K_{SVH}/K_{SVX}) were

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[17] Ito, Y.; Umehara, Y.; Yamada, Y.; Matsuura, T.; Imashiro, F. *J. Org. Chem.* **1981**, *46*, 4359.

[18] (a) Schuster, D. I.; Brown, R. H.; Resnick, B. M. *J. Am. Chem. Soc.* **1978**, *100*, 4504. (b) Shaik, S. S.; Epiotis, N. D. *Ibid.* **1980**, *102*, 122 and references therein.

[19] In our previous papers[4,6,20] we have consistently assumed that $k_q = k_{dif}$ ($=5 \times 10^9$ M^{-1} s^{-1} in benzene at 25 °C) in order to estimate τ from K_{SV} ($=k_q\tau$). Herein we do not use such indirectly determined τ values as a discussion tool, since it has recently been shown that, in the case of triisopropylbenzophenone derivatives, k_q is definitely slower than the diffusion rate ($k_q \sim 1.2 \times 10^9$ M^{-1} s^{-1}).[20b] The incorrect assignment of the k_q value, however, does not change any previous conclusions except the absolute value.

[20] (a) Ito, Y.; Kawatsuki, N.; Matsuura, T. *Tetrahedron Lett.* **1984**, *25*, 2801. (b) Ito, Y.; Kawatsuki, N.; Matsuura, T. *Ibid.* **1984**, *25*, 4525.

[21] Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461.

[22] (a) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474. (b) Bays, J. P.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1980**, *102*, 727. (c) Encinas, M. V.; Funabashi, K.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 1167. (d) Maharaj, U.; Winnik, M. A. *Chem. Phys. Lett.* **1981**, *82*, 29. (e) Encinas, M. V.; Scaiano, J. C. *Ibid.* **1979**, *63*, 305. (f) Fang, F.; Fukuda, R.; Brown, R. E.; Singer, L. A. *J. Phys. Chem.* **1978**, *82*, 246.

opposite in direction between the two series of compounds **6a–n** and **7a–f**. A negative correlation obtained for some of the triisopropylbenzophenones **6** (X = 4′-OMe, 4′-Me, H, and 4′-CF_3) was already rationalized on the basis of restricted rotations (twistings) around bonds 1–α and 1′–α.[4,23] These two rotations were regarded as synchronous and as the rate-determining step for intramolecular hydrogen abstraction from the benzylic position of an ortho isopropyl group.[4] The positive correlation observed for the less hindered 2,4,6-triethylbenzophenones **7a–f** except **5b** (=**7e**), by contrast, indicates[4] that rotations (twistings) around bonds 1–α and 1′–α of these molecules are sufficiently free that these rotations are incapable of controlling the rate of intramolecular hydrogen abstraction and hence incapable of controlling the triplet lifetime.

The observation that the Stern–Volmer quenching constants obey a single straight line either for **6** or for **7** for a variety of substituents is probably fortuitous, since the triplet lifetime τ is influenced by many factors such as intramolecular hydrogen abstraction and various other decay processes that are competing with it. The hydrogen abstraction rate will depend on the nature (n,π^* or π,π^*) of the T_1 state.[3a–c] Furthermore, for the triisopropyl series **6** the restricted rotation around bonds 1–α and 1′–α is an important factor for the determination of τ.[4] Substituent effects on the triplet quenching rate by diene k_q may also present a problem, although, as was reported previously,[4,20b] variation in k_q was not pronounced for several triisopropylbenzophenone derivatives.

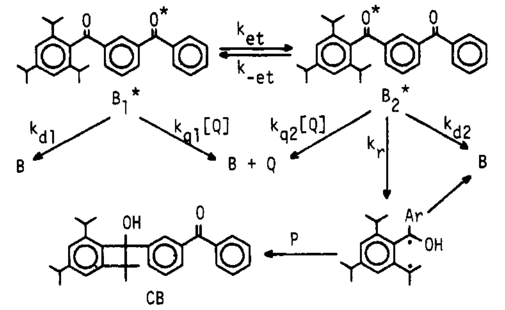
Despite the existence of the above-mentioned complexities when interpreting the Hammett plot, we wish to comment on the findings about the three diketones **1b** (=**6i**), **3a** (=**6k**), and **5b** (=**7e**). In these cases, X = COPh and the electronic excitation is expected to be distributed over the two carbonyl groups within a molecule in two distinct ways, i.e., Scheme III for **3a** and Scheme IV for **1b** and **5b**. We consider the following two points to be noteworthy.

(1) Of the triisopropylbenzophenones studied here, the compound **3a** deviates most significantly from the straight line (Figure 1); i.e., K_{SV} of **3a** is a little too small to be correlated to its σ value. This results may be ascribed to the additional triplet decay term originating from delocalization of the electronic excitation, i.e., the τ_2^{-1} term in eq 5a.

(2) While the hindered diketone **1b** obeys a Hammett correlation, the less hindered diketone **5b** does not (Figure 1). The K_{SV} value of **5b** is too large to be correlated to σ. Normally one might suppose that both for **1b** and for **5b** the rapid intramolecular energy migration should lead to a larger K_{SV} value than would have been expected from the Hammett plot, since BP and m-BBP possess a very large K_{SV} (32500 and 12500 M^{-1}, respectively; Table II). As is verified from an examination of eq 11 (vide infra), the observed different Hammett correlation between **1b** and **5b** can qualitatively be understood by assuming that the electronic excitation in **1b** is present mainly at the strained carbonyl group ($k_{et} \gg k_{-et}$ in Scheme IV), whereas the excitation in **5b** is partitioned comparably between both carbonyl groups ($k_{et} \sim k_{-et}$ in Scheme IV).

Estimation of the Ratio k_{et}/k_{-et}. Of course, eq 5b can be utilized in an attempt to estimate K (=k_{et}/k_{-et}). Unfortunately, since the directly determined τ for many of **1–7** are not available to us,[24] we must resort to the K_{SV} data in order to estimate K. Scheme V illustrates various decay processes and energy migration processes associated with the meta-substituted diketone **1b**, where B_1^* and B_2^* are localized excited triplet states and Q is diene quencher. Intramolecular energy migration between aromatic carbonyl groups that is nearly thermoneutral can be very rapid (>10^9 s^{-1})[22a–c] and appears to be faster than analogous intermolecular energy migration (~10^8 M^{-1} s^{-1}).[22d–f] In scheme V, therefore, an intermolecular contribution to the energy migration was neglected ([B] = 0.05 M). Under the steady-state assumption for both B_1^* and B_2^* the expressions 6–8 were obtained, where $\Phi_{CB}°$ and Φ_{CB} are the quantum yields for CB formation in the absence or presence of Q, respectively, and α and β are the fractions of competitive absorption of light producing B_1^* and B_2^* respectively ($\alpha + \beta = 1$).

Scheme V



$$\Phi_{CB}° = Pk_r \frac{\beta(k_{et} + k_{d1}) + \alpha k_{et}}{(k_{-et} + k_{d2} + k_r)(k_{et} + k_{d1}) - k_{-et}k_{et}} \quad (6)$$

$$\Phi_{CB} = Pk_r\,[(\beta(k_{et} + k_{d1} + k_{q1}[Q]) + \alpha k_{et})/((k_{-et} + k_{d2} + k_r + k_{q2}[Q])(k_{et} + k_{d1} + k_{q1}[Q]) - k_{-et}k_{et})] \quad (7)$$

$$\frac{\Phi_{CB}°}{\Phi_{CB}} = \frac{\beta k_{d1} + k_{et}}{\beta(k_{d1} + k_{q1}[Q]) + k_{et}}[(k_{d2} + k_r + k_{q2}[Q]) \times (k_{et} + k_{d1} + k_{q1}[Q]) + k_{-et}(k_{d1} + k_{q1}[Q])]/[(k_{d2} + k_r)(k_{et} + k_{d1}) + k_{-et}k_{d1}] \quad (8)$$

Provided that $k_{et} \gg k_{d1}$ and $k_{et} \gg k_{q1}[Q]$ ([Q] < 0.05 M), eq 8 can be simplified to eq 9, which gives the Stern–Volmer constant for triplet quenching by diene as in eq 10. In these equations, $K = k_{et}/k_{-et}$ and τ_1 and τ_2 are the lifetimes of the localized excited states B_1^* and B_2^*, respectively; i.e., $\tau_1 = 1/k_{d1}$ and $\tau_2 = 1/(k_{d2} + k_r)$. The observed linear quenching plot by diene and the weak phosphorescence (Table II), as well as the picosecond laser spectroscopic observation demonstrating that only one ketone triplet was detectable upon photolysis of **1b**,[24] support that the above conditions for k_{et} are satisfied. Equation 10 can be rearranged to eq 11, where K_{SV1} (= $k_{q1}\tau_1$) and K_{SV2} (=$k_{q2}\tau_2$) are putative Stern–Volmer constants for quenching of B_1^* and B_2^*, respectively.

$$\frac{\Phi_{CB}°}{\Phi_{CB}} = 1 + \frac{k_{q1} + Kk_{q2}}{\tau_1^{-1} + K(\tau_2)^{-1}}[Q] \quad (9)$$

$$K_{SV} = \frac{k_{q1} + Kk_{q2}}{\tau_1^{-1} + K(\tau_2)^{-1}} \quad (10)$$

$$\left(\frac{K_{SV}}{K_{SV1}} - 1\right)k_{q1} = \left(1 - \frac{K_{SV}}{K_{SV2}}\right)Kk_{q2} \quad (11)$$

It is obvious from eq 10 (or eq 11) that $K_{SV} \simeq k_{q2}\tau_2 = K_{SV2}$ if K is very large, that $K_{SV} \simeq k_{q1}\tau_1 = K_{SV1}$ if K is near zero, and that K_{SV} is between K_{SV1} and K_{SV2} if K is not

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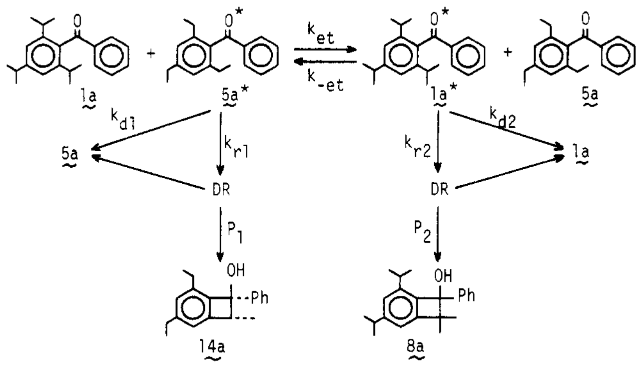
(23) Ito, Y.; Umehara, Y.; Yamada, Y.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1160.

(24) Nakayama, T.; Hidaka, T.; Kuramoto, T.; Hamanoue, K.; Teranishi, H.; Ito, Y.; Matsuura, T. *Chem. Lett.* **1984**, 1953.

Scheme VI



a limiting value. Evaluation of a precise K value from eq 10 (or eq 11) is a difficult problem on account of the difficulty in determining precise τ_1 (or K_{SV1}) and τ_2 (or K_{SV2}). The finding that K_{SV} of **1b** (570 M^{-1}) is close to that of **6j** (635 M^{-1}) but is very different from that of *m*-BBP (12 500 M^{-1}) indicates that K is very large for **1b**. Of the compounds studied here (Tables II and III) *m*-BBP and **6j** are the best model compounds for B_1* and B_2*, respectively. Calculation of K from eq 11 on the basis of the assumption that K_{SV2} equals K_{SV} of **6j** and that K_{SV1} equals K_{SV} of *m*-BBP, however, is impossible because, owing to either the unsuitability of the model compound or the experimental error in K_{SV} (±10%), the former assumption leads to an improbable situation: K_{SV} of **1b** $< K_{SV2}$.[25]

Intermolecular Case. As seen from Figure 2, the ratio Φ_{8a}/Φ_{14a} is almost constant (ca. 3.6) in the lower concentration region of the ketones ([**1a**] = [**5a**] < 0.025 M) and increases conspicuously with increasing concentrations of the ketones ([**1a**] = [**5a**] > 0.025 M), reaching the intercept 15 at 1/[**5a**] = 0. The increase in Φ_{8a}/Φ_{14a} with increasing concentrations of the ketones can be ascribed to occurrence of the intermolecular energy migration from **5a** to **1a** in preference to the energy migration from **1a** to **5a**. The intermolecular energy transfer should be unimportant in the region where Φ_{8a}/Φ_{14a} is nearly constant.

On the basis of the mechanism described in Scheme VI the following equations (eq 12–14) can be derived under the steady-state assumption for **5a*** and **1a***. In these equations Φ_{CB}^{5a} and Φ_{CB}^{1a} are the quantum yields of CB formation from independent irradiation of **5a** and **1a**, respectively (eq 15 and 16), τ_1 and τ_2 are the triplet lifetimes

$$\Phi_{14a} = P_1 k_{r1}[(\alpha(k_{d2} + k_{r2}) + k_{-et}[\mathbf{5a}])/((k_{d2} + k_{r2}) \times (k_{d1} + k_{r1} + k_{et}[\mathbf{1a}]) + k_{-et}[\mathbf{5a}](k_{d1} + k_{r1}))] \quad (12)$$

$$\Phi_{8a} = P_2 k_{r2}[(\beta(k_{d1} + k_{r1}) + k_{et}[\mathbf{1a}])/((k_{d2} + k_{r2}) \times (k_{d1} + k_{r1} + k_{et}[\mathbf{1a}]) + k_{-et}[\mathbf{5a}](k_{d1} + k_{r1}))] \quad (13)$$

$$\frac{\Phi_{8a}}{\Phi_{14a}} = \frac{P_2 k_{r2}[\beta(k_{d1} + k_{r1}) + k_{et}[\mathbf{1a}]]}{P_1 k_{r1}[\alpha(k_{d2} + k_{r2}) + k_{-et}[\mathbf{5a}]]} = \frac{\beta\Phi_{CB}^{1a}}{\alpha\Phi_{CB}^{5a}} + \frac{\Phi_{CB}^{1a}\tau_1[k_{et}[\mathbf{1a}]/[\mathbf{5a}] - k_{-et}\beta\tau_2/\alpha\tau_1]}{\Phi_{CB}^{5a}\tau_2[\alpha/\tau_2[\mathbf{5a}] + k_{-et}]} \quad (14)$$

$$\Phi_{CB}^{5a} = P_1 k_{r1}/(k_{d1} + k_{r1}) = P_1 k_{r1}\tau_1 \quad (15)$$

$$\Phi_{CB}^{1a} = P_2 k_{r2}/(k_{d2} + k_{r2}) = P_2 k_{r2}\tau_2 \quad (16)$$

of **5a** and **1a**, respectively (eq 15 and 16), and α and β are the fractions of incident light absorbed competitively by **5a** and **1a**, respectively ($\alpha + \beta = 1$). The values of α and β under the experimental conditions (313-nm irradiation, [**1a**] = [**5a**]) were calculated as 0.55 and 0.45, respectively, from the absorption coefficients of **5a** and **1a** at 313 nm (44 and 36 M^{-1} cm^{-1}, respectively).

Since eq 14 has the shape of a hyperbola with respect to Φ_{8a}/Φ_{14a} vs. 1/[**5a**], the relationships in eq 17 and 18 can be obtained from the intercept (15) and the asymptotic value (3.6) of Figure 2. From eq 18 one calculates $\Phi_{CB}^{1a}/\Phi_{CB}^{5a}$

$$(\Phi_{CB}^{1a}\tau_1 k_{et})/(\Phi_{CB}^{5a}\tau_2 k_{-et}) = (\Phi_{CB}^{1a}K_{SV1}k_{q2}k_{et})/(\Phi_{CB}^{5a}K_{SV2}k_{q1}k_{-et}) = 15 \quad (17)$$

$$(\beta\Phi_{CB}^{1a})/(\alpha\Phi_{CB}^{5a}) = 3.6 \quad (18)$$

= 4.4, which is in good agreement with the value evaluated by using Φ_{CB} listed in Table II, i.e., 0.60/0.14 = 4.3. This agreement implies that the kinetic parameters in Scheme VI (k_{d1}, k_{d2}, k_{r1}, k_{r2}, P_1, and P_2) do not significantly change with the variation in ketone concentration ([**1a**] = [**5a**] = 0.005–1.0 M). We have already reported that Φ_{CB} of **1a** is only slightly dependent on [**1a**] (0.05–0.25 M).[4]

Substitution of the appropriate data listed in Table II (Φ_{CB}^{5a} = 0.14, K_{SV1} = 800 M^{-1}, Φ_{CB}^{1a} = 0.60, and K_{SV2} = 450 M^{-1}) into eq 17 affords that $k_{et}/k_{-et} = 2.0(k_{q1}/k_{q2})$. Since the triplet quenching rate for **5a** may be somewhat larger than that for **1a** in view of the (presumably) smaller steric hindrance to triplet–triplet energy transfer[19,26] ($k_{q1} > k_{q2}$), we conclude that $k_{et}/k_{-et} > 2$.

Steric Control in Electronic Energy Transfer. The ratios of rate constants for the forward and reverse energy migration processes k_{et}/k_{-et} that were deduced from the earlier discussion are summarized as follows: for **1b**, $k_{et} \gg k_{-et}$; for **5b**, $k_{et} \sim k_{-et}$; for the intermolecular system (**1a** + **5a**), $k_{et}/k_{-et} > 2$. It is evident from inspection of this result that the triplet excitation of the carbonyl group tends to flow from the benzoyl or 2,4,6-triethylbenzoyl groups to the 2,4,6-triisopropylbenzoyl group. The small variations in Φ_{CB} and K_{SV} in the series of compounds **1a–c,e,f** (Table II) may be at least partly due to this preferential energy migration to the triisopropylbenzoyl group.

Consideration of only triplet energy differences between the carbonyl groups of interest appears insufficient to account for the above noted tendency in the energy migration. Although the phosphorescence measurements for the monoketones **1a**, **5a**, and BP (Table II) could not unambiguously demonstrate the existence of slight E_T gaps between these ketones because of the experimental error (±0.2 kcal/mol), cyclic voltammograms of **1a**, **5a**, and BP in acetonitrile containing 0.1 M Et_4NClO_4 have revealed that their reduction potentials ($-(E_{pa} + E_{pc})/2$ vs. Ag/AgCl; working electrode, Pt) are different: 1.925, 1.906, and 1.781 V, respectively (error, ±0.005 V). (We are indebted to Professor Z. Yoshida's laboratory for the CV measurements.) This result suggests, according to the previous report claiming the good parallel correlation between the n,π* triplet energy and the polarographic $E_{1/2}$ of aromatic ketones,[7a,27] that the E_T values of these ketones are slightly different and are in the order **1a** $\gtrsim$ **5a** > BP within a small range (~0.5 kcal/mol). Eventually we must infer that the 2,4,6-triisopropylbenzoyl group tends to collect the n,π* excitation in spite of the unfavorable energetic situation in terms of E_T, i.e., in terms of an enthalpy scale.[28] It seems likely that an entropy factor is important in the case of the triisopropylbenzoyl group.

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[25] Equation 11 can also be applied to the calculation of K for the diketones **2** and **5b**. However, we must postpone this attempt for want of the data for suitable model compounds.

[26] Herkstroeter, W. G.; Jones, L. B.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4777.

[27] Loutfy, R. O.; Loutfy, R. O. *J. Phys. Chem.* **1972**, *76*, 1650.

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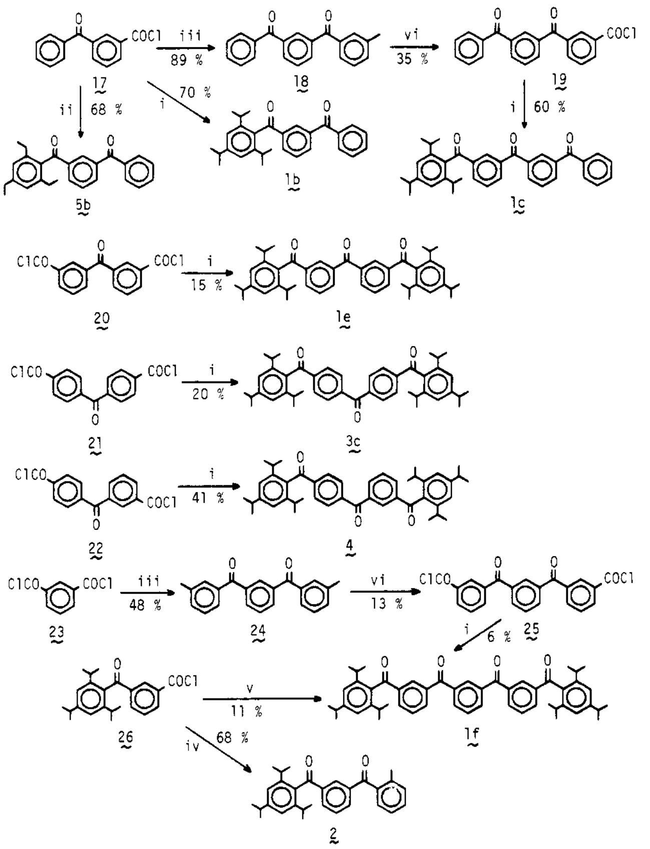
Scheme VII[a]



[a] (i) 1,3,5-(i-Pr)$_3$C$_6$H$_3$/AlCl$_3$/CS$_2$; (ii) 1,3,5-Et$_3$C$_6$H$_3$/AlCl$_3$/CS$_2$; (iii) 1,3-(MgBr)(Me)C$_6$H$_4$/THF/−78 °C; (iv) 1,2-(MgBr)(Me)C$_6$H$_4$/THF/−78 °C; (v) 1,3-(MgBr)$_2$C$_6$H$_4$/THF/−78 °C; (vi) (1) CrO$_3$/H$_2$SO$_4$/AcOH, (2) SOCl$_2$

Table V. Summary of Melting Points (Boiling Points) and IR Spectra

compd[a]	mp, °C (recrystn solv), or bp, °C [mmHg]	IR,[b] cm^{-1} (C=O and/or OH)
1c	122–123 (hexane)	1680,1660
1e	92–94 (EtOH–pentane)	1670
1f	139–140 (hexane)	1665
2	96–97 (EtOH)	1675
3c	233–236 (hexane)	1670
4	149–150 (hexane)	1680,1665*
5b	88–89 (hexane)	1665
6d	80–81 (hexane)	1663
6f	92–94 (hexane)	1660
6g	118–120 (hexane)	1725,1665*
7a	152–157 [0.85]	1665*
7b	134–136 [0.3]	1665*
7d	43–44 (hexane)	1670*
7f	117–119 [0.19]	1675*
8c	144–145 (CHCl–hexane)	3400,1660
8e	165–167 (EtOH–pentane)	3680,1670
8f	114–115 (EtOH–pentane)	3550,1670
10b	163–165 (EtOH)	1680,1665
11	96–97 (EtOH–pentane)	3580,1660
13	129–130 (pentane)	3640,1680,1660
14b	oil	3500,1665
15b	161–162 (hexane)	3580
15d	73–74 (MeOH)	3610
15f	135–136 (hexane)	3620
15g	107–109 (MeOH)	3540,1725
16a	oil	3480*
16b	oil	3470*
16d	89–90 (hexane)	3400
16f	oil	3440*

[a] Satisfactory C, H analytical data were obtained for all compounds except **5b**, **8c**, **11**, **14b**, and **16f**; in these cases high-resolution mass spectra were obtained. In the cases of **6f**, **7d**, **7f**, **15f**, and **16d**, satisfactory halogen analyses were also obtained. [b] Nujol except where marked by * (neat).

The MO calculation of BP shows that the barrier to rotation around bond 1–α is much higher in the excited state than in the ground state.[29] Thus loss of rotational degrees of freedom, i.e., the entropy loss, is expected to occur upon electronic excitation of BP. However, when we consider the highly hindered molecule **1a**, the corresponding entropy loss induced by the electronic excitation of **1a** may be much less than the BP case, because the rotation around bonds 1–α and 1′–α of **1a** is already restricted in the ground state.[17]

The same line of entropy consideration for the excited state of diketone **1b** (cf. Scheme V) predicts that the total entropy of B$_2$* is considerably larger than that of B$_1$*.[30] Accordingly, even if the E_T difference between the component carbonyl groups predicts that $k_{et} < k_{-et}$, k_{et} may well far exceed k_{-et} for such polyketones as **1b**. In principle, k_{et}/k_{-et} should be controlled by the free energy difference rather than by the E_T (enthalpy) difference.

In the case of **5b**, the rotation about bonds 1–α and 1′–α should be less restricted compared with **1b** because of the less bulky ortho substituents, and hence, the entropy factor may be less important. In fact the Hammett plot (Figure 1) suggested that $k_{et} \sim k_{-et}$ for **5b**. An analogous entropy consideration for the **1a** + **5a** system (cf. Scheme VI) predicts a larger total entropy for the **1a*** + **5a** state than for the **1a** + **5a*** state. Thus k_{et} can exceed k_{-et} as actually observed (Figure 2), although a reverse situation ($k_{et} \lesssim k_{-et}$) would be anticipated from consideration of the relative E_T levels of **1a** and **5a**.

In the consideration of overall energetics for inter- and intramolecular electronic energy transfer processes, one usually worries about only the singlet or triplet energy separations between the donors and the acceptors (ΔE_S or ΔE_T), i.e., only the enthalpy factor.[31] Our present results raise the possibility that an entropy factor may also be important in certain cases where ΔE_S or ΔE_T is small. In other words, steric effects such as hindered rotation can potentially play a crucial role in controlling reversible energy-transfer processes involving a sterically hindered donor or acceptor. According to the Boltzmann distribution expression or the relationship between free energy and equilibrium constant, the distribution is exponentially proportional to the energy differences. Thus, even a small energy difference such as caused by the rotational entropy difference can profoundly affect energy partition in the excited states (k_{et}/k_{-et}). We suspect that a pseudoequilibrium may be attainable even when k_{et}/k_{-et} is quite large

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(29) Hoffmann, R.; Swenson, J. R. *J. Phys. Chem.* **1970**, *74*, 415.

(30) Loss of rotational freedom about one single bond corresponds to a ca. 4.0-eu decrease in internal rotational entropy: Bunnett, J. F. In "Investigations of Rates and Mechanisms of Reactions"; Lewis, E. S., Ed.; Wiley: New York, 1974; Chapter 8. According to Hopkins and his co-workers, steric hindrance to several internal rotations is primarily responsible for the unusually low basicity of 2,6-di-*tert*-butylpyridine (DTBP) in aqueous solutions; e.g., the barrier to the internal rotation of the methyl groups on DTBP increases nearly 1 kcal/mol upon protonation: Hopkins, H. P., Jr.; Jahagirdar, D. V.; Moulik, P. S.; Aue, D. H.; Webb, H. M.; Davidson, W. R.; Pedly, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 4341.

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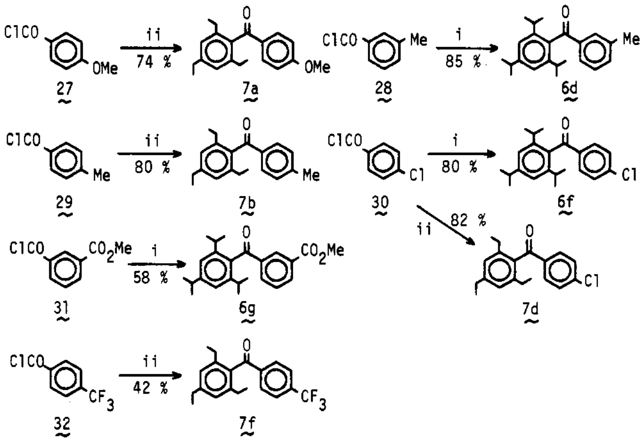
Table VI. Summary of NMR Data

compd	δ in $CDCl_3$			
	arom	methine[a] or methylene	methyl	OH
1c	8.27 (1 H, s),[b] 8.15–7.3 (12 H, m), 6.99 (2 H, s)	2.80 (1 H, sep, *J* = 7 Hz), 2.58 (2 H, sep, *J* = 7 Hz)	1.29 (6 H, d, *J* = 7 Hz), 1.13 (12 H, br d, *J* = 7 Hz)	
1e	8.22 (2 H, s),[b] 7.90 (4 H, d, *J* = 8 Hz),[b] 7.49 (2 H, t, *J* = 8 Hz), 7.00 (4 H, s)	2.91 (2 H, sep, = 7 Hz), 2.60 (4 H, sep, *J* = 7 Hz)	1.27 (12 H, d, *J* = 7 Hz), 1.14 (24 H, br d, *J* = 7 Hz)	
1f	8.27 (2 H, s),[b] 8.08 (1 H, s),[b] 7.93 (6 H, d, *J* = 8 Hz),[b] 7.48 (3 H, t, *J* = 8 Hz),[b] 6.98 (4 H, s)	2.90 (2 H, sep, *J* = 7 Hz), 2.57 (4 H, sep, *J* = 7 Hz)	1.27 (12 H, d, *J* = 7 Hz), 1.11 (24 H, br d, *J* = 7 Hz)	
2	8.08 (1 H, s),[b] 7.98 (2 H, d, *J* = 8 Hz),[b] 7.44 (1 H, t, *J* = 8 Hz),[b] 7.20 (4 H, br s), 6.95 (2 H, s)	2.91 (1 H, sep, *J* = 7 Hz), 2.58 (2 H, sep, *J* = 7 Hz)	2.28 (3 H, s), 1.27 (6 H, d, *J* = 7 Hz), 1.09 (12 H, br d, *J* = 7 Hz)	
3c	7.92 (8 H, s), 7.08 (4 H, s)	2.84 (2 H, sep, *J* = 7 Hz), 2.61 (4 H, sep, *J* = 7 Hz)	1.29 (12 H, d, *J* = 7 Hz), 1.13 (24 H, br d, *J* = 7 Hz)	
4	8.32 (1 H, s),[b] 7.98 (2 H, d, *J* = 8 Hz),[b] 7.88 (4 H, br s), 7.54 (1 H, t, *J* = 8 Hz),[b] 7.06 (4 H, br s)	2.82 (2 H, sep, *J* = 7 Hz), 2.60 (4 H, sep, *J* = 7 Hz)	1.27 (12 H, d, *J* = 7 Hz), 1.11 (24 H, br d, *J* = 7 Hz)	
5b	8.12 (1 H, s),[b] 8.0–7.2 (8 H, m), 6.87 (2 H, s)	2.62 (2 H, q, *J* = 7 Hz), 2.38 (4 H, q, *J* = 7 Hz)	1.26 (3 H, t, *J* = 7 Hz), 1.07 (6 H, t, *J* = 7 Hz)	
6d	7.7–7.1 (4 H, m), 6.97 (2 H, s)	2.91 (1 H, sep, *J* = 7 Hz), 2.61 (2 H, sep, *J* = 7 Hz)	2.34 (3 H, s), 1.27 (6 H, d, *J* = 7 Hz) 1.30–0.9 (12 H, br)	
6f	7.72 and 7.37 (4 H, AB, *J* = 8.5 Hz), 7.03 (2 H, s)	2.94 (1 H, sep, J = 7 Hz), 2.58 (2 H, sep, *J* = 7 Hz)	1.28 (6 H, d, *J* = 7 Hz), 1.26–0.9 (12 H, br)	
6g	8.52 (1 H, s)[b] 8.22 (1 H, d, *J* = 8 Hz),[b] 7.95 (1 H, d, *J* = 8 Hz),[b] 7.46 (1 H, t, *J* = 8 Hz), 7.07 (2 H, s)	2.96 (1 H, sep, *J* = 7 Hz), 2.60 (2 H, sep, *J* = 7 Hz)	3.90 (3 H, s), 1.31 (6 H, d, *J* = 7 Hz), 1.11 (12 H, br d, *J* = 7 Hz)	
7a	7.73 and 6.84 (4 H, AB, *J* = 9 Hz), 6.93 (2 H, s)	2.61 (2 H, q, *J* = 7 Hz), 2.40 (4 H, q, *J* = 7 Hz)	3.80 (3 H, s), 1.22 (3 H, t, *J* = 7 Hz), 1.03 (6 H, t, *J* = 7 Hz)	
7b	7.62 and 7.14 (4 H, AB, *J* = 8 Hz), 6.88 (2 H, s)	2.66 (2 H, q, *J* = 7 Hz), 2.37 (4 H, q, *J* = 7 Hz)	2.36 (3 H, s), 1.26 (3 H, t, *J* = 7 Hz), 1.06 (6 H, t, *J* = 7 Hz)	
7d	7.68 and 7.29 (4 H, AB, *J* = 9 Hz), 6.89 (2 H, s)	2.63 (2 H, q, *J* = 7 Hz), 2.34 (4 H, q, *J* = 7 Hz)	1.24 (3 H, t, *J* = 7 Hz), 1.05 (6 H, t, *J* = 7 Hz)	
7f	7.91 and 768 (4 H, AB, *J* = 8 Hz), 6.98 (2 H, s)	2.69 (2 H, q, *J* = 7 Hz), 2.36 (4 H, q, *J* = 7 Hz)	1.25 (3 H, t, *J* = 7 Hz), 1.06 (6 H, t, *J* = 7 Hz)	
8c	8.11–7.10 (13 H, m), 6.95 (1 H, s), 6.77 (1 H, s)	2.86 (2 H, br sep, *J* = 7 Hz)	1.42 (3 H, s), 1.25 (6 H, d, *J* = 7 Hz), 1.17 (6 H, d, *J* = 7 Hz), 0.80 (3 H, s)	2.85 (1 H, br s)
8e	8.20 (1 H, s),[b] 8.00–7.20 (7 H, m), 6.98 (3 H, s), 6.80 (1 H, s)	3.10–2.16 (5 H, br m)	1.45 (3 H, s), 1.24 (12 H, d, *J* = 7 Hz), 1.3–0.9 (18 H, br m), 0.85 (3 H, s)	2.60 (1 H, s)
8f	8.35–7.3 (12 H, m), 7.05 (3 H, s), 6.87 (1 H, s)	3.1–2.3 (5 H, br m)	1.47 (3 H, s), 1.40–0.9 (30 H, br m), 0.83 (3 H, s)	2.70 (1 H, s)
9b	7.8–7.2 (8 H, m), 7.00 (2 H, s),[b] 6.82 (2 H, s)[b]	3.2–2.3 (4 H, m)	1.45 (6 H, s), 1.25 (12 H, d, *J* = 7 Hz), 1.16 (6 H, d, *J* = 7 Hz), 1.13 (6 H, d, *J* = 7 Hz), 0.82 (6 H, s)	2.50 (2 H, s)
9c	8.2–7.2 (12 H, m), 7.05 (2 H, s), 6.88 (2 H, s)	3.2–2.3 (4 H, br m)	1.45 (6 H, s), 1.4–1.0 (24 H, m), 0.81 (6 H, s)	2.75 (2 H, s)
10b	8.49 (1 H, d, *J* = 2.5 Hz), 8.17–7.2 (9 H, m)	4.32 (1 H, sep, *J* = 7 Hz), 2.98 (1 H, sep, *J* = 7 Hz)	1.77 (6 H, s), 1.32 (12 H, d, *J* = 7 Hz)	
11	7.75–7.37 (4 H, m), 7.24 (4 H, br s), 7.02 (1 H, s),[b] 6.86 (1 H, s)[b]	2.80 (2 H, br sep, *J* = 7 Hz)	2.26 (3 H, s), 1.42 (3 H, s), 1.27 (6 H, d, *J* = 7 Hz), 1.13 (6 H, d, *J* = 7 Hz), 0.80 (3 H, s)	2.68 (1 H, s)
13	8.39 (1 H, s),[b] 7.98 (2 H, d, *J* = 8 Hz),[b] 7.55 (1 H, t, *J* = 8 Hz),[b] 7.75 and 7.38 (4 H, AB, *J* = 8 Hz), 7.08 and 7.06 (3 H, 2 s), 6.92 (1 H, s)	3.07–2.45 (5 H, m)	1.47 (3 H, s), 1.29 (12 H, d, *J* = 7 Hz), 1.17 (18 H, br d, *J* = 7 Hz), 0.85 (3 H, s)	2.63 (1 H, s)
14b	7.8–6.9 (9 H, m), 6.90 (1 H, br s), 6.74 (1 H, br s)	3.58 (1 H, q, *J* = 7 Hz), 2.63 (2 H, q, *J* = 7 Hz), 2.44 (2 H, q, *J* = 7 Hz)	1.22 (3 H, t, *J* = 7 Hz), 1.13 (3 H, t, *J* = 7 Hz), 0.84 (3 H, d, *J* = 7 Hz)	2.12 (1 H, br s)
15b	7.29 and 7.16 (4 H, AB, *J* = 8 Hz), 7.06 (1 H, s),[b] 6.87 (1 H, s)[b]	2.93 (2 H, br sep, *J* = 7 Hz)	1.46 (3 H, s), 1.30 (9 H, s), 1.38–1.1 (12 H, m), 0.81 (3 H, s)	2.47 (1 H, s)
15d	6.99 (5 H, br s),[b] 6.79 (1 H, s)[b]	2.88 (2 H, sep, *J* = 7 Hz)	2.23 (3 H, s), 1.40 (3 H, s), 1.22 (6 H, d, *J*	2.42 (1 H, s)

			= 7 Hz), 1.19 (3 H, d, *J* = 7 Hz), 1.15 (3 H, d, *J* = 7 Hz), 0.81 (3 H, s)	
15f	7.19 (4 H, s), 7.02 (1 H, s),[b] 6.85 (1 H, s)[b]	3.2–2.6 (2 H, br m)	1.42 (3 H, s), 1.26 (6 H, d, *J* = 7 Hz), 1.18 (3 H, d, *J* = 7 Hz), 1.14 (3 H, d, *J* = 7 Hz), 0.81 (3 H, s)	2.47 (1 H, s)
15g	8.0–7.8 (2 H, m), 7.45–7.3 (2 H, m), 7.05 (1 H, s),[b] 6.86 (1 H, s)[b]	2.92 (1 H, sep, *J* = 7 Hz), 2.87 (1 H, sep, *J* = 7 Hz)	3.86 (3 H, s), 1.46 (3 H, s), 1.29 (6H, d, *J* = 7 Hz), 1.22 (3 H, d, *J* = 7 Hz), 1.14 (3 H, d, *J* = 7 Hz), 0.81 (3 H, s)	2.62 (1 H, br s)
16a	7.09 and 6.74 (4 H, AB, *J* = 9 Hz), 6.89 (1 H, s), 6.77 (1 H, s)	3.55 (1 H, q, *J* = 7 Hz), 2.62 (2 H, q, *J* = 7 Hz), 2.46 (2 H, q, *J* = 7 Hz)	3.72 (3 H, s), 1.23 (3 H, t, *J* = 7 Hz), 1.11 (3 H, t, *J* = 7 Hz), 0.81 (3 H, d, *J* = 7 Hz)	2.60 (1 H, s)
16b	7.01 (4 H, s), 6.90 (1 H, s), 6.78 (1 H, s)	3.50 (1 H, q, *J* = 7 Hz), 2.61 (2 H, q, *J* = 7 Hz), 2.43 (2 H, q, *J* = 7 Hz)	2.21 (3 H, s), 1.21 (3 H, t, *J* = 7 Hz), 1.08 (3 H, t, *J* = 7 Hz), 0.81 (3 H, d, *J* = 7 Hz)	2.86 (1 H, s)
16d	7.18 (4 H, s), 6.93 (1 H, s), 6.82 (1 H, s)	3.58 (1 H, q, *J* = 7 Hz), 2.61 (2 H, q, *J* = 7 Hz), 2.47 (2 H, q, *J* = 7 Hz)	1.26 (3 H, t, *J* = 7 Hz), 1.12 (3 H, t, *J* = 7 Hz), 0.82 (3 H, d, *J* = 7 Hz)	2.56 (1 H, s)
16f	7.37 and 7.19 (4 H, AB, *J* = 8 Hz), 6.88 (1 H, s), 6.77 (1 H, s)	3.53 (1 H, q, *J* = 7 Hz), 2.62 (2 H, q, *J* = 7 Hz), 2.41 (2 H, q, *J* = 7 Hz)	1.23 (3 H, t, *J* = 7 Hz), 1.10 (3 H, t, *J* = 7 Hz), 0.78 (3 H, d, *J* = 7 Hz)	2.95 (1 H, s)

[a] The two small peaks on either side of the septet could not be seen under normal conditions. [b] Finely split (*J* = 1.5–2.5 Hz).

Scheme VIII[a]



[a] (i) 1,3,5-(i-Pr)$_3$C$_6$H$_3$/AlCl$_3$/CS$_2$; (ii) 1,3,5-Et$_3$C$_6$H$_3$/AlCl$_3$/CS$_2$

(say 100), since the intramolecular energy transfer events are very rapid (even ~10^{12} s^{-1} [22a–c]).

Experimental Section

The NMR, IR, UV, and mass spectra were measured with Varian T-60, JASCO IRA-1, Shimadzu UV-200, and JEOL-JMS-DX 300 spectrometers, respectively. Emission spectra were recorded on a Shimadzu RF-500 spectrometer, equipped with accessories for phosphorescence measurements (PHA-1).

Preparation of Starting Ketones. The polyketones **1c,e,f**, **2**, **3c**, **4**, and **5b** and the monoketones **6d,f,g** and **7a,b,d,f** were synthesized as outlined in Schemes VII and VIII. The yields are not optimized. The preparation of other starting ketones, i.e., **1a,b,d**, **3a,b**, **5a**, and **6a–c,h,j,l–n** has already been described.[4,5,17] UV and phosphorescence data of these ketones are listed in Tables II and III. NMR, IR, and other data of the new ketones are given in Tables V and VI.

3-Benzoylbenzoyl Chloride (17). A solution consisting of 75 g (750 mmol) of chromium trioxide, 40 mL of concentrated sulfuric acid, 120 mL of water, and 190 mL of acetic acid was added dropwise to a refluxing solution of 30 g (153 mmol) of 3-methylbenzophenone in 370 mL of acetic acid. After the reaction mixture was stirred overnight under gentle reflux, it was cooled to room temperature and poured into ice–water. The precipitate was filtered and washed completely with water. The residue was dissolved in a dilute sodium hydroxide solution, and the solution was filtered. The filtrate was acidified with dilute sulfuric acid, and the new precipitate was collected, then washed with water, and dried to give 30 g (87% yield) of 3-benzoylbenzoic acid: mp 161.2–162.6 °C (lit.[32] mp 161–162 °C).

The acid was dissolved in 300 mL of thionyl chloride and was allowed to reflux overnight. The reaction mixture was evaporated under reduced pressure to remove the excess thionyl chloride, and the residue was recrystallized from *n*-hexane to afford 14 g (43% yield) of **17**: colorless crystals, mp 49–51 °C; NMR (CDCl$_3$) δ 8.50–7.47 (9 H, m, arom); IR (Nujol) 1770, 1750, and 1650 cm^{-1} (C=O).

(3-Benzoylphenyl)(3-methylphenyl)methanone (18). A solution of (3-methylphenyl)magnesium bromide, prepared from 5.0 g (29 mmol) of *m*-bromotoluene and 0.71 g (29 mmol) of magnesium turnings in 20 mL of dry THF, was added over 1 h at −78 °C to a solution of 6.0 g (24.5 mmol) of the chloride **17** in 30 mL of dry THF. After the reaction mixture was stirred for an additional 1 h at this temperature, it was allowed to warm to room temperature, and 50 mL of water was added. The mixture was extracted with ether (3 × 20 mL), and the organic layer was washed with 1 N NaOH solution and then with water and dried over MgSO$_4$. After rotary evaporation of the solvent, the residue was recrystallized from ethanol to give 6.6 g (89% yield) of **18**: mp 40–44 °C; NMR (CDCl$_3$) δ 7.60–7.30 (13 H, m, arom), 2.40

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(32) Parham, W. E.; Sayed, Y. A. *J. Org. Chem.* **1974**, *39*, 2051.

(3 H, s, CH_3); IR (Nujol) 1660 cm^{-1} (C═O).

[3-(3-Benzoylbenzoyl)phenyl][2,4,6-tris(1-methylethyl)-phenyl]methanone (1c). With a procedure similar to that for the preparation of **17**, the diketone **18** was converted via the carboxylic acid into 3-(3-benzoylbenzoyl)benzoyl chloride (**19**) in overall 35% yield. The carboxylic acid: 83% yield; mp 173–176 °C; IR (Nujol) 1700 and 1660 cm^{-1} (C═O). The acid chloride **19**: 42% yield; mp 106–110 °C; IR (Nujol) 1770, 1740, and 1660 cm^{-1} (C═O). A solution of 1.2 g (5.7 mmol) of 1,3,5-triisopropylbenzene (TIPB) in 5 mL of carbon disulfide was added at room temperature to a solution of 1.5 g (4.3 mmol) of **19** and 1 g (7.5 mmol) of aluminum chloride in 20 mL of carbon disulfide, and the mixture was stirred for 12 h at room temperature. After usual workup (pouring into ice–water containing hydrochloric acid, extraction with ether, and washing and drying the ethereal layer),[5,17] the residue of rotary evaporation was recrystallized from *n*-hexane to afford 1.3 g (60% yield) of **1c** as colorless crystals.

[3-(3-(3-(2,4,6-Tris(1-methylethyl)benzoyl)benzoyl)-benzoyl)phenyl][2,4,6-tris(1-methylethyl)phenyl]methanone (1f). The Grignard reaction between isophthaloyl chloride (20 g, 100 mmol) and (3-methylphenyl)magnesium bromide (ca. 205 mmol) was carried out as described above (cf. preparation of **18**). The residue of rotary evaporation was recrystallized from methanol to give 15 g (48% yield) of [3-(3-methylbenzoyl)-phenyl](3-methylphenyl)methanone (**24**) as colorless crystals; mp 94–97 °C; NMR ($CDCl_3$) δ 8.12–7.90 (3 H, m, arom), 7.68–7.22 (9 H, m, arom), 2.40 (6 H, s, CH_3); IR (Nujol) 1660 cm^{-1} (C═O).

The diketone **24** was converted to 3-[3-(3-(chlorocarbonyl)-benzoyl)benzoyl]benzoyl chloride (**25**) by a similar procedure described above (cf. preparation of **17**). The carboxylic acid: 20% yield; mp >250 °C; IR (Nujol) 1690 and 1660 cm^{-1} (C═O). The acid chloride **25**: 62% yield; NMR ($CDCl_3$) δ 8.58–7.35 (12 H, m, arom). The Friedel–Crafts reaction between **25** (6.7 g, 16.2 mmol) and TIPB (10 g, 49 mmol) was performed as usual (cf. preparation of **1c**). The residue of rotary evaporation was separated by column chromatography on silica gel (150 g) with benzene as eluent, followed by recrystallization from hexane, to furnish 730 mg (6% yield) of **1f**.

The tetraketone **1f** was also prepared by the Grignard reaction between the acid chloride **26**[5] (9 g, 24.5 mmol) and the Grignard reagent[33] prepared from 4.7 g (20 mmol) of *m*-dibromobenzene and 1 g (40 mmol) of magnesium turnings in 20 mL of dry THF, in a similar manner to that for the preparation of **18**. The residue of rotary evaporation was separated by column chromatography on silica gel with benzene–hexane (2:1 v/v) as eluent, to afford 950 mg (11% yield) of **1f**.

[3-(2-Methylbenzoyl)phenyl][2,4,6-tris(1-methylethyl)-phenyl]methanone (2). The Grignard reaction between the acid chloride **26** (10 g, 27 mmol) and the Grignard reagent prepared from 4 g (41 mmol) of *o*-bromotoluene and 1 g (41 mmol) of magnesium turnings in 60 mL of dry THF was carried out in a manner similar to that used for the preparation of **18**. The residue of rotary evaporation was recrystallized from hexane to provide 7.8 g (68% yield) of **2**.

Bis[3-(2,4,6-tris(1-methylethyl)benzoyl)phenyl]methanone (1e), Bis[4-(2,4,6-tris(1-methylethyl)benzoyl)phenyl]-methanone (3c), and [3-(2,4,6-Tris(1-methylethyl)benzoyl)-phenyl][4-(2,4,6-tris(1-methylethyl)benzoyl)phenyl]-methanone (4) were synthesized by the Friedel–Crafts reaction between the corresponding acid chlorides (**20**, **21**, and **22**) and TIPB according to the usual procedure (cf. preparation of **1c**). In each case the residue of rotary evaporation was separated by columm chromatography on silica gel using benzene as eluent, followed by recrystallization from hexane, to furnish either colorless crystals of **1e** and **4** or pale yellow crystals of **3c**. 3,3′- (**20**),[34] 4,4′- (**21**),[35] and 3,4′-carbonylbis(benzoyl chloride) (**22**)[36] were obtained from chromium trioxide oxidation of 3,3′-, 4,4′-, and 3,4′-dimethylbenzophenone, respectively, followed by reaction with thionyl chloride (cf. preparation of **17**).

(3-Benzoylphenyl)(2,4,6-triethylphenyl)methanone (5b). The Friedel–Crafts reaction between **17** (6.5 g, 26 mmol) and 1,3,5-triethylbenzene (TEB) (4.3 g, 26 mmol) was carried out in the usual way (cf. preparation of **1c**; reaction temperature, 35 °C). The residue of rotary evaporation was recrystallized from hexane to provide 6.7 g (68% yield) of **5b**.

Preparation of the Monoketones. The monoketones **6d,f,g** and **7a,b,d**, and **f** were prepared by the usual Friedel–Crafts reaction (cf. preparation of **1c**; reaction temperature, room temperature except the preparation of **7f**, where it was 46 °C). The acid chlorides **27–30** are commercially available. The acid chlorides **31**[37] and **32**[38] and 4-carbomethoxybenzoyl chloride[39] (for preparation of **6h**) were synthesized by the literature method.

Preparative Photolyses. These were carried out as described previously.[4,5] The results are summarized in Table I. NMR and IR spectra, melting (or boiling) points, and analytical data for the photoproducts are summarized in Tables V and VI. The data for unlisted products were already reported.[4,5,9]

Two stereoisomers (dl and meso) can exist for each bis(CB) **9a–c**. In the case of **9a**, the corresponding two stereoisomers were isolated as already reported.[5] In the case of **9b** and **9c**, only one stereoisomer was isolated in each case, but their structures were evident from their NMR spectra (Table VI). Isolation of another stereoisomer was not attempted for these substrates.

Quantitative Photolyses. These were carried out as described previously.[4,5] The results are summarized in Tables II–IV and in Figure 2.

Registry No. **1a**, 33574-11-7; **1b**, 84369-67-5; **1c**, 94474-44-9; **1d**, 84369-68-6; **1e**, 94474-45-0; **1f**, 94474-46-1; **2**, 96825-43-3; **3a**, 84369-66-4; **3b**, 76893-85-1; **3c**, 94474-47-2; **4**, 94474-48-3; **5a**, 33574-10-6; **5b**, 96825-44-4; **6a**, 76893-80-6; **6b**, 76893-81-7; **6c**, 74766-25-9; **6d**, 96825-45-5; **6f**, 88655-96-3; **6g**, 96825-46-6; **6h**, 76893-83-9; **6j**, 84369-70-0; **6l**, 84369-69-7; **6m**, 74766-27-1; **6n**, 76893-84-0; **7a**, 96825-47-7; **7b**, 96825-48-8; **7d**, 96825-49-9; **7f**, 96825-50-2; **8b**, 84369-72-2; **8c**, 96825-51-3; **8e**, 96825-52-4; **8f**, 96825-53-5; **9b**, 96825-54-6; **9c**, 96825-55-7; **10b**, 96825-69-3; **11**, 96825-56-8; **13**, 96825-52-4; **14a**, 96825-57-9; **14b**, 96844-91-6; **15b**, 96825-58-0; **15d**, 96825-59-1; **15f**, 88656-02-4; **15g**, 96825-60-4; **16a**, 96825-61-5; **16b**, 96825-62-6; **16d**, 96825-63-7; **16f**, 96825-64-8; **17**, 77301-47-4; **18**, 96825-65-9; **19** (carboxylic acid), 96825-67-1; **19**, 96825-66-0; **20**, 6472-69-1; **21**, 6423-31-0; **22**, 96825-68-2; **24**, 85566-05-8; **25** (carboxylic acid), 85566-07-0; **25**, 85566-08-1; **27**, 100-07-2; **28**, 1711-06-4; **29**, 874-60-2; **30**, 122-01-0; **31**, 3441-03-0; **32**, 329-15-7; 3-methylbenzophenone, 643-65-2; 3-benzoylbenzoic acid, 579-18-0; isophthaloyl chloride, 99-63-8; 2,5-dimethyl-2,4-hexadiene, 764-13-6.

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