lished by hydrolysis of **10a** with 5% aqueous HCl at 80 °C for 30 min, producing 2-cyano-1-tetralone.

Intramolecular Cycloaddition of 2-[*o*-[1-(Trimethylsilyl)hept-5-enyl]-phenyl]-3,3-dimethyl-5(*R*)-phenyloxazolidinium Iodide (2d). To a stirred suspension of 0.46 g (3 mmol) of CsF in 5 mL of acetonitrile was added 0.83 g (1.5 mmol) of the oxazolidinium iodide **2d** in 7 mL of acetonitrile at room temperature in 30 min, and the mixture was stirred overnight. The reaction mixture was evaporated in vacuo, and aqueous Na_2CO_3 was added to the residue, followed by ether extraction. The ether extract was dried over $MgSO_4$ and evaporated to give crude 8,9-*trans*-6-[2-(dimethylamino)-1(*R*)-phenylethoxy]octahydrophenanthrene (**11d**) (460 mg, 88%), which consisted of a 2:1 diastereoisomer mixture, as determined from NMR spectrum.

The diastereoisomer mixture of **11d** was separated by preparative TLC on silica gel (2:1 hexane–acetone). The major diastereoisomer, **11d-i** (53%): TLC R_f 0.52; NMR($CDCl_3$) δ 0.60–2.50 (br m, 12 H), 2.29 (s, 6 H), 2.55 (m, 2 H), 4.15–4.32 (m, 1 H), 4.68 (dd, 1 H), 6.90–7.70 (m, 9 H). The minor diastereoisomer, **11d-ii** (28%, TLC R_f 0.45), exhibited a singlet at δ 2.22, which was ascribed to methyl group on the nitrogen. **11d**: Anal. Calcd for $C_{24}H_{31}NO$: C, 82.47; H, 8.94; N, 4.01. Found: C, 82.59; H, 9.18; N, 4.13.

In an autoclave, a mixture of **11d** (460 mg), 70% aqueous $HClO_4$ (100 μL), and 10% Pd/C (250 mg) in 5 mL of acetic acid was stirred overnight under 60 kg/cm^2 of hydrogen gas. After the reaction mixture was filtered, the filtrate was diluted with 30 mL of H_2O and extracted with hexane. The hexane extract was washed with 5% aqueous HCl and brine and distilled to give *trans*-octahydrophenanthrene (**12**) (210 mg[38], 86%), $[\alpha]^{19}{}_D$ +31.6° (*c* 1.35, C_6H_{14}). Similarly, the hydrogenolysis of the major diastereoisomer **11d-i** on Pd/C afforded optically pure *trans*-octahydrophenanthrene (**12**): bp 60 °C (0.1 torr); mp 41.5–42.0 °C; $[\alpha]^{19}{}_D$ +92.9° (*c* 1.06, C_6H_{14}).

On the other hand, a mixture of **11d** (460 mg), $KHSO_4$ (150 mg), and 70% aqueous $HClO_4$ (100 μL) in 3 mL of benzene was refluxed for 3 h. The reaction mixture was added to aqueous Na_2CO_3 and extracted with ether. The ether extract was washed with 5% aqueous HCl and brine and evaporated. The residue was subjected to preparative TLC on silica gel with hexane solvent (R_f 0.63) to furnish 8,9-*trans*-hexahydrophenanthrene (**13**) (210 mg, 87%): bp 95 °C (0.1 torr). **13**: ^1H NMR ($CDCl_3$) δ 1.00–2.60 (m, 10 H), 5.68 (br d, *J* = 9.0 Hz, 1 H), 6.42 (dd, *J* = 9.0, 2.3 Hz, 1 H), 6.80–7.30(m, 4 H); ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 26.50 (2 C), 28.55, 32.78, 39.64, 42.07, 123.39, 126.01, 126.32, 127.17, 127.25, 134.72, 135.53, 139.42. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.53; H, 8.73. Intramolecular cycloadditions of **2c–i** were performed according to the procedure described above, and the cycloadducts **11c–i** thus produced were converted to *trans*-octahydrophenanthrene by hydrogenolysis on Pd/C.

8,9-*trans*-6-[2-(Dimethylamino)-1-methylethoxy]octahydrophenanthrene (11c): bp 125 °C (0.1 torr); 80%; NMR($CDCl_3$) δ 1.12 and 1.20 (two d, *J* = 6 Hz, 3 H), 0.35–2.50 (br m, 12 H), 2.14 (s, 6 H), 2.25 (m, 2 H), 3.40–3.80 (m, 1 H), 4.20–4.42 (m, 1 H), 6.70–7.35 (m, 4 H). Anal. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found C, 79.51; H, 10.30; N, 4.59.

8,9-*trans*-6-[2(*S*)-(Dimethylamino)-1(*R*)-phenylpropoxy]octahydrophenanthrene (11e) (83%): NMR ($CDCl_3$) δ 0.97 and 1.04 (two d, *J* = 6 Hz, 3 H), 2.00 and 2.09 (two s, 6 H), 0.50–2.95 (br m, 13 H), 4.03–4.25 (m, 1 H), 4.32 and 5.04 (two d, *J* = 7.5 Hz, 1 H), 6.70–7.50 (m, 9 H). Anal. Calcd for $C_{25}H_{33}NO$: C, 82.60; H, 9.15; N, 3.85. Found: C, 82.88; H, 9.19; N, 3.62.

8,9-*trans*-6-[2(*R*)-(Dimethylamino)-1(*R*)-phenylpropoxy]octahydrophenanthrene (11f) (90%): NMR ($CDCl_3$) δ 0.76 (d, *J* = 6 Hz, 3 H), 0.50–3.15 (br m, 13 H), 2.12 and 2.25 (two s, 6 H), 3.95–4.15 (m, 1 H), 4.32 (d, *J* = 8.3 Hz, 1 H), 6.65–7.40 (m, 9 H). Anal. Calcd for $C_{25}H_{33}NO$: C, 82.60; H, 9.15, N, 3.85. Found: C, 82.41; H, 9.38; N, 4.02.

8,9-*trans*-6-[3-Methoxy-2(*S*)-(dimethylamino)-1(*S*)-phenylpropoxy]octahydrophenanthrene (11g) (crude product, 85% yield): NMR ($CDCl_3$) δ 2.24 and 2.38 (two s, 6 H), 2.96 and 3.02 (two s, 3 H).

8,9-*trans*-6-[2(*R*)-(Dimethylamino)-2-phenylethoxy]octahydrophenanthrene (11h) (58%): NMR ($CDCl_3$) δ 0.70–2.60 (br m, 12 H), 2.23 (s, 6 H), 3.10–4.00 (m, 4 H), 6.90–7.50 (m, 9 H). Anal. Calcd for $C_{24}H_{31}NO$: C, 82.47; H, 8.94; N, 4.01. Found: C, 82.63; H, 9.18; N, 4.15.

8,9-*trans*-6-[2(*S*)-(Dimethylamino)-3-phenylpropoxy]octahydrophenanthrene (11i) (64%): NMR ($CDCl_3$) δ 0.70–2.70 (br m, 12 H), 2.38 (s, 6 H), 2.70–2.90 (m, 3 H), 3.48–3.65 (m, 2 H), 4.14–4.30 (m, 1 H), 6.90–7.50 (m, 9H). Anal. Calcd for $C_{22}H_{33}NO$: C, 82.60; H, 9.15; N, 3.85. Found: C, 82.84; H, 9.33; N, 4.05.

Intramolecular Hydrogen Abstraction from Triplet States of 2,4,6-Triisopropylbenzophenones: Importance of Hindered Rotation in Excited States[1]

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Abstract: Photochemically initiated benzocyclobutenol formation from a variety of 4′-substituted (4′-X) 2,4,6-triisopropylbenzophenones **1a–f** (**a**, X = OMe; **b**, X = Me; **c**, X = H; **d**, X = CO_2Me; **e**, X = CF_3; **f**, X = CN) as well as from 2,4,6-trimethylbenzophenone (**3a**) and 2,4,6-triethylbenzophenone (**3b**) was studied. The quantum yields of the benzocyclobutenols **2a–f** ranged from 0.60 for **2c** to 0.06 for **2f** in benzene. By usual Stern–Volmer quenching and sensitization methods using diene as quencher or sensitizer, various photokinetic data for these ketones, i.e., triplet lifetime (τ_T) and its temperature dependence (E_a and log A), rate constant for intramolecular hydrogen abstraction from *o*-isopropyl methine hydrogens (k_r) and its isotope effect (k_H/k_D), rate constant for bimolecular triplet quenching (k_2) with hydrogen donors (Bu_3SnH, mesitylene, and cyclooctane), and intersystem crossing yield (Φ_T), were estimated. The effect of 4′-substituents (4′-X) on k_r (or τ_T) was unusual for a series of compounds **1a–c** and **1e** in that k_r decreased in going from **1a** (X = OMe) to **1e** (X = CF_3). This novel substituent effect was interpreted on the basis of hindered rotation in the excited state around the bond linking the 2,4,6-triisopropylphenyl and carbonyl groups. This interpretation was nicely supported by the results obtained for E_a (unusually large, e.g., E_a = 9.0 kcal/mol for **1c**), k_H/k_D (1.5 for **1c**), and k_2 (increased in going from **1a** to **1e**). It is deduced that an increased $n\pi^*$ character of aromatic ketone triplets results in an increased barrier to rotation (viz., an increased double-bond character) about the C_{Ar}—C(=O) single bond in the triplet excited state.

Introduction

o-Alkyl phenyl ketones belong to a typical class of photochromic compounds. Upon absorption of light they can reversibly generate a synthetically very useful intermediate called *o*-xylylene (a typical diradicaloid hydrocarbon).[2] Some of them, however, are known to photocyclize to give highly strained benzocyclobutenols, usually

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(1) Photoinduced Reactions. 142.

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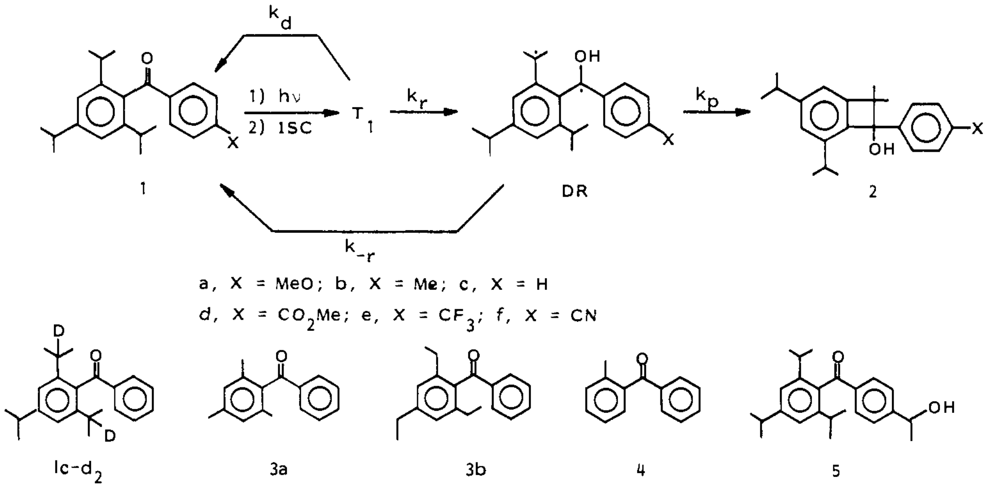
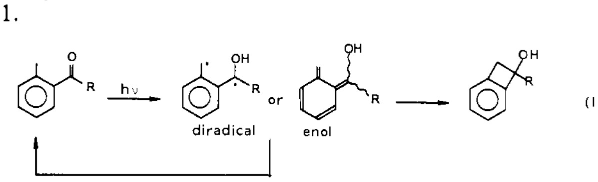
Scheme I



in low quantum yields (<0.1).[3] These reactions are outlined in eq 1.



It is generally agreed that the primary step of reaction 1 is an intramolecular hydrogen abstraction initiated by the nπ* triplet or singlet carbonyl group, leading to diradical and diradicaloid intermediates, i.e., triplet diradical (=enol triplet) and cis and trans enols.[3-5] By the use of laser spectroscopy many workers succeeded in the direct detection of these transient species including ketone triplet, although there is a significant controversy in their assignment.[4b-d]

Another problem presented by Wagner is the existence of two kinetically distinct triplets for 2,6-disubstituted-phenyl ketones,[3d,4b] while the same situation for the 2-substituted case was readily understandable from consideration of two possible conformations (syn and anti).[3d,d] As was noted by Wagner[3d] and Scaiano,[4b] the

photokinetics of 2,6-disubstituted aromatic ketones are still uninterpretable. Furthermore, it is noteworthy that the transients observed in the laser photolysis of 2,6-disubstituted benzophenones are completely different from those detected in 2-substituted benzophenones.[4e]

With these problems in mind we undertook a quantitative study on the photochemistry of 2,4,6-triisopropylbenzophenone (**1c**).[6]

Table I. Lowest Singlet and Triplet Energies (E_S and E_T), Their Separations ($E_S - E_T$), Absorption Maxima in the ππ* Region ($\lambda_{\pi\pi^*}$ (log ε)), and Intersystem Crossing Yields (Φ_T) for 2,4,6-Trialkylbenzophenones Ia-f, **3a**, and **3b**

compd	X	E_S[a]	E_T[b]	$E_S - E_T$[c]	$\lambda_{\pi\pi^*}$ nm (log ε)[d]	Φ_T[e]
1a	OMe	76.4	70.2	6.2	270 (4.3)	1.0
1b	Me	75.4	70.4	5.0	253 (4.3)	0.87
1c	H	74.7	68.8	5.9	242 (4.2)	1.0
1d	CO_2Me	71.3	68.1	3.2	252 (4.4)	0.95
1e	CF_3	72.2	67.6	4.6	242 (4.2)	1.0[f]
1f	CN	71.1	66.0	5.1	251 (4.4), 260 (4.4)	1.0
3a		74.7	67.8	6.9	243 (4.2)	1.0
3b		74.7	68.1	6.6	243 (4.2)	1.0[f]
benzophenone		75.4[g]	68.8	6.6	248 (4.3)[g]	1.0[g]

[a] In kcal/mol. Estimated from absorption spectra (ππ*) measured in cyclohexane. Error ±0.4 kcal/mol. [b] In kcal/mol. Estimated from phosphorescence spectra measured at 77 K in ethanol. Error ±0.5 kcal/mol. [c] In kcal/mol. [d] In cyclohexane. [e] From sensitized cis-trans isomerization of cis-1,3-pentadiene at 25 °C. Error ±0.1. [f] Assumed. [g] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1975.

In contrast to other *o*-alkyl aromatic ketones hitherto studied,[3] **1c** underwent photocyclization to the corresponding benzocyclobutenol (**2c**) quantitatively with remarkably high efficiency, e.g., $\Phi_{CB} = 0.77$ in acetonitrile.[6a] This allowed us to perform the quenching of product (**2c**) formation by the Stern-Volmer method. The merit of this method was recently discussed.[8]

Studying the mechanism of an endothermic photoreaction such as **1c** → **2c**, which as a result of the thermal back-reaction **2c** → **1c** releases significant amounts of energy ($\Delta H = -21$ kcal/mol[9]), can serve as a guide for searching useful solar energy conversion systems.[10]

In this paper we describe the photoreactions of several hindered *o*-alkyl benzophenones **1a–f** as well as the less hindered ones **3a** and **3b**. The importance of steric effects which control the triplet lifetimes of some of these ketones will be demonstrated. Steric factors on the behavior of a diradical intermediate generated from **1c** will be discussed elsewhere.[11]

Results

Spectroscopic Study. All of the 4′-substituted 2,4,6-triisopropylbenzophenones **1a–f** as well as 2,4,6-trimethylbenzophenone

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Table II. Quantum Yields of Cyclobutenol Formation (Φ_{CB}), Triplet Lifetimes (τ_T), and Arrhenius Parameters (E_a and log A) for 2,4,6-Triisopropylbenzophenones 1a–f and 1c-d_2

			τ_T, ns			
compd	X	Φ_{CB}[a, b]	quen[a, c]	direct[d]	E_a, kcal/mol[e]	log A[e]
1a	OMe	0.55	42	53 ± 5	9.59 ± 0.45	14.42 ± 0.33
1b	Me	0.48	51	110 ± 10	8.76 ± 0.51	13.71 ± 0.37
1c	H	0.60	90	191 ± 20	9.09 ± 0.40	13.73 ± 0.29
1d	CO_2Me	0.15	127	*f*	4.18 ± 0.20	9.94 ± 0.15
1e	CF_3	0.35	179	355 ± 15	*f*	*f*
1f	CN	0.06	152	*f*	5.60 ± 0.26	10.93 ± 0.19
1c-d_2[g]	H	0.51	103	*f*	*f*	*f*

[a] The values obtained in a degassed benzene (0.05 M in ketone) with 313-nm irradiation at 25 °C. [b] Maximum error, 10%. [c] Calculated from diene-quenching constants ($k_q\tau_T$) based on an assumption of diffusion-controlled quenching ($k_q = 5 \times 10^9$ M^{-1} s^{-1} in benzene at 25 °C[13]). Maximum error, 10%. [d] Directly determined by laser photolysis technique.[6c,16] Hexane was used as the solvent except for 1c, where heptane was used. [e] From a least-squares fit of the plot log $\tau_T(\text{quen})^{-1}$ vs. T^{-1} The errors quoted represent standard deviations. [f] Not determined. [g] Deuterium content, 75% (from NMR).

(**3a**) and 2,4,6-triethylbenzophenone (**3b**) possess well-separated $n\pi^*$ absorptions in cyclohexane. A characteristic vibrational progression of the carbonyl group was observed in each case. As usual, these $n\pi^*$ bands were blue-shifted in ethanol with loss of fine structure. The phosphorescence spectra of these compounds were weak in intensity and exhibited much less structure, when compared with the phosphorescence of benzophenone. The $n\pi^*$ absorption and phosphorescence of all these compounds including benzophenone itself occurred at a similar region of wavelength. The energies of the lowest singlet and triplet states (E_S and E_T) and their separations ($E_S - E_T$), estimated from 0–0 bands of the $n\pi^*$ absorption and phosphorescence spectra, are listed in Table I. Table I also lists the wavelength ($\lambda_{\pi\pi^*}$) and the intensity (log ϵ) at the maximum $\pi\pi^*$ absorption, together with the intersystem crossing yield (Φ_T) which was determined from the photosensitized cis–trans isomerization of *cis*-1,3-pentadiene.[12] The values of Φ_T were close to unity for all the compounds measured.

Preparative Photolyses. Preparative photolyses of the 2,4,6-triisopropylbenzophenones **1a** – **f** were performed in a benzene solution through a Pyrex filter under bubbling nitrogen. In all cases the corresponding benzocyclobutenols **2a–f** were produced in excellent yields. The preparations of **2c** and of the benzocyclobutenols from **3a** and **3b** have been reported.[3f]

Quantum Yields of Cyclobutenol Formation and Triplet Lifetimes for 2,4,6-Triisopropylbenzophenones. The quantum yields of the cyclobutenols **2a–f** (Φ_{CB}) were determined in a degassed benzene solution (0.05 M) at 25 °C by irradiation with potassium chromate filtered light (313 nm). The results are shown in Table II. The formation of these cyclobutenols was quenched by additions of 2,5-dimethyl-2,4-hexadiene (0.004–0.05 M), giving a good linear Stern–Volmer plot in each case. From the slope of this line ($=k_q\tau_T$) the triplet lifetime (τ_T) of the reactant ketone was calculated, assuming that the quenching occurred nearly with a diffusion rate, i.e., $k_q = 5 \times 10^9$ M^{-1} s^{-1} in benzene at 25 °C.[13] According to the mechanism described in Scheme **I**, τ_T and Φ_{CB} can be represented by

$$\tau_T = 1/(k_r + k_d) \tag{2}$$

$$\Phi_{CB} = \Phi_T k_r \tau_T k_p/(k_p + k_{-r}) = \Phi_T k_r \tau_T P_p \tag{3}$$

$$P_p = k_p/(k_p + k_{-r}) \tag{3}$$

where k_d denotes the sum of rate constants for other triplet decay processes which are competing with the intramolecular hydrogen abstraction (the rate constant k_r) and P_p is a probability of product formation from a diradical intermediate DR.

In the cases of **1a–d** and **1f** a temperature dependence of the Stern–Volmer slope was also studied, and the Arrhenius parameters E_a and log A were estimated from the plot log τ_T^{-1} vs. T^{-1}. In making this plot, we used the k_q values estimated from the equation presented by Scaiano;[14] log $k_q = 11.95 - (1326/RT)$. The values of τ_T at 25 °C, E_a, and log A are also summarized in Table II.

Table III. Kinetic Data (P_p, k_r, and k_d) Derived from Maximum Quantum Yields for Cyclobutenol Formation (Φ_{CB}^{max})[a]

compd	X	Φ_{CB}^{max}[b]	P_p[c]	k_r, s^{-1}[d]	k_d, s^{-1}[e]
1a	OMe	0.74	0.74	1.8×10^7	5.8×10^6
1b	Me	0.63	0.76	1.4×10^7	5.6×10^6
1c	H	0.77	0.78	8.6×10^6	2.5×10^6
1d	CO_2Me	0.21	0.71	1.8×10^6	6.1×10^6
1e	CF_3	0.51	0.69	2.8×10^6	2.8×10^6
1f	CN	0.08	0.75	0.53×10^6	6.1×10^6
1c-d_2[f]	H	0.65	0.79	6.3×10^6	3.4×10^6

[a] In a degassed benzene (0.05 M in ketone) at 25 °C irradiated at 313 nm. [b] Maximized with the addition of 0.2–0.5 M pyridine. Maximum error, 10%. [c] Calculated from eq 4. [d] Calculated from eq 3. [e] Calculated from eq 2. [f] Deuterium content, 75% (from NMR).

It should be noted that the E_a values for **1a–c** are unusually large.[15] The τ_T values for **1a–f** predict from the relationship of eq 2 that the hydrogen abstraction rate k_r may be increased by para substitution with the electron-donating groups (Me and OMe) and may be decreased by para substitution with the electron-withdrawing ones (CO_2Me, CF_3, and CN).

The triplet lifetimes of **1a–c** and **1e** were also determined by directly monitoring transient absorptions due to the ketone triplets (Table II).[16] Although τ_T determined by either method (quenching or direct) somewhat disagreed except in the case of **1a**, we adopted for later calculations and discussion the values deterimined by the quenching method simply because of consistency of the data.

Effect of Pyridine on the Cyclobutenol Formation. Enhancement of quantum yields by the addition of Lewis bases such as alcohol, pyridine, and phosphate is frequently used in the study of Norrish type II reactions of phenyl alkyl ketones to obtain kinetic parameters concerning both ketone triplets and diradical intermediates of interest.[17] This technique was repeated in our case. Thus the quantum yields of **2a–f** increased with additions of pyridine and then leveled off at 0.2–0.5 M pyridine. These maximum quantum yields (Φ_{CB}^{max}) are listed in Table III, from which P_P values were calculated according to the Wagner's expression (eq 4).[18]

$$P_P = \Phi_{CB}/\Phi_{CB}^{max} \tag{4}$$

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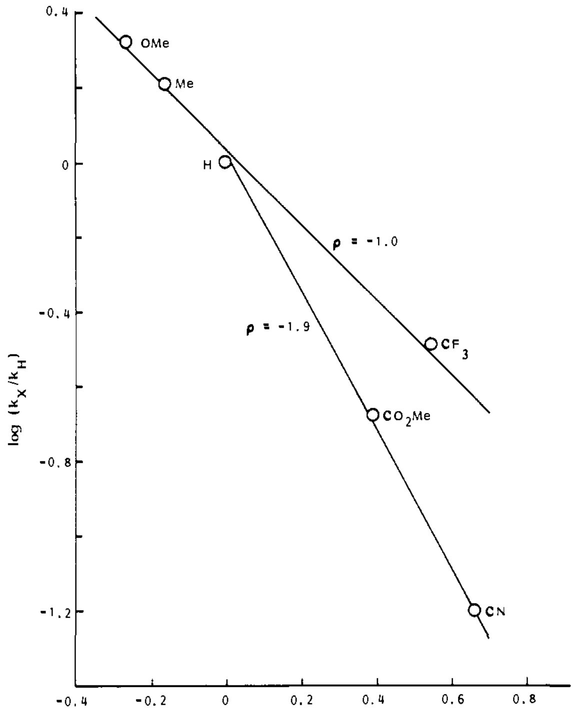

Figure 1. Hammett plot of the hydrogen-abstraction rate k_r for the 2,4,6-triisopropylbenzophenones **1a–f**.

Then the values of k_r and k_d were available from eq 2 and 3 on the basis of the known values of Φ_{CB}, τ_T, and P_P. The values of P_P, k_r, and k_d thus obtained are summarized in Table III.

The rate constant k_d is a composite of many factors such as radiative and nonradiative decays, self-quenching,[21] solvent quenching, and impurity quenching, which are competing with the intramolecular hydrogen abstraction (k_r). While the 2,4,6-triisopropylbenzophenones **1a–f** seem to have larger k_d values than other simple aromatic ketones,[19,20] we will not discuss these points further.

From Table III we can readily see that k_r decreases in parallel with the electron-withdrawing ability of the 4′-substituents. A Hammett plot of this result is shown in Figure 1 ($\rho = -1.0$ and -1.9). It was quite unexpected[19,20] that the values of k_r decreased in the order **1a** (X = OMe) > **1b** (X = Me) > **1c** (X = H) > **1e** (X = CF_3). In sharp contrast, triplet quenching of these four ketones by some hydrogen donors exhibited a perfectly expected substituent dependence (see the next section).

Table IV. Triplet Lifetimes (τ_T) of 2,4,6-Triisopropylbenzophenones 1a–**c** and 1e in the Presence of Hydrogen Donors[a]

		hydrogen donors			
		Bu_3SnH[b]		mesitylene[d]	cyclooctane[e]
compd	X	τ_T, ns	k_2, M^{-1} s^{-1} [c]	τ_T, ns	τ_T, ns
1a	OMe	39	9.2×10^6 [f]	38	*g*
1b	Me	17	2.0×10^8	37	*g*
1c	H	10	4.5×10^8	44	26
1e	CF_3	3.9	1.3×10^9	70	15

[a] A degassed solution of 0.05 M ketone irradiated at 313 nm at 25 °C. τ_T was determined from the diene-quenching constant ($k_q\tau_T$) obtained in the presence of hydrogen donors. Maximum error in τ_T, 10%. [b] 0.2 M in benzene ($k_q = 5 \times 10^9$ M^{-1} s^{-1}).[13] [c] The rate constant for triplet quenching by Bu_3SnH. Calculated from eq 6. [d] Used as a solvent. The same k_q value as in benzene was assumed, i.e., $k_q = 5 \times 10^9$ M^{-1} s^{-1}. [e] Used as a solvent ($k_q = 4.2 \times 10^9$ M^{-1} s^{-1}).[13] [f] Subject to a large error due to a small difference between τ_T and $\tau_T{}^0$ in eq 6. [g] Not determined.

Table V. Quantum Yields of Cyclobutenol Formation (Φ_{CB}) and Triplet Lifetimes (τ_T) for Less Hindered *o*-Alkyl Benzophenones **3a**, 3b, and **4**[a]

		τ_T, ns		
compd	Φ_{CB}	quen	sens[b]	direct
3a	0.0076	580, 20	7 ± 4	580 ± 10[c]
3b	0.14	160	*d*	*d*
1c	0.60	90	*d*	191 ± 20[d]
4	0	3.5[e]	0.17, >10[f]	2.8[g]

[a] General remarks mentioned in Table II (footnotes *a-d*) are valid, unless otherwise specified. [b] From sensitized cis–trans isomerization of *cis*-1,3-pentadiene in benzene. [c] In heptane. [d] Not determined. [e] In EtOH (ref 4d). [f] Reference 3d. [g] In EtOH (Hamanoue, K., private communication).

Triplet Quenching with Hydrogen Donors. Triplet lifetimes of **1a–c** and **1e** in the presence of hydrogen donors (RH) are summarized in Table IV. These were determined by the aforementioned quenching experiment with 2,5-dimethyl-2,4-hexadiene. Three hydrogen donors were employed: (a) 0.2 M tri-*n*-butylstannane in benzene, (b) mesitylene, and (c) cyclooctane. The second and third ones were used as a neat solvent.

The rate constant for triplet quenching (k_2) by the tin hydride can be estimated according to eq 6, where $\tau_T{}^0$ and τ_T denote the

$$\mathbf{1}(T_1) + RH \xrightarrow{k_2} \text{quenching} \tag{5}$$

$$k_2 = (1/\tau_T - 1/\tau_T{}^0)/[RH] \tag{6}$$

triplet lifetime of each ketone in the absence and presence of the hydrogen donor (Bu_3SnH), respectively. Values of $\tau_T{}^0$ can be found in Table II and [RH] = 0.2 M. The estimated k_2 values are also listed in Table IV. The value of **1c** (4.5×10^8 M^{-1} s^{-1}) was similar to that observed for benzophenone itself (2.9×10^8 M^{-1} s^{-1}).[22]

Table IV demonstrates that an additional decay path due to bimolecular interaction with the hydrogen donors (reaction 5) reduces the triplet lifetime of each ketone. While Table IV lists the k_2 values only for the Bu_3SnH case, the same values for the other two cases (mesitylene and cyclooctane) can also be calculated by eq 6, provided that appropriate k_q and $\tau_T{}^0$ values are available. Based on the assumptions that the diffusion rate k_q in mesitylene is the same as in benzene ($k_q = 5 \times 10^9$ M^{-1} s^{-1}) and k_q in cyclooctane is 4.2×10^9 M^{-1} s^{-1} [13] and that $\tau_T{}^0$ can be approximated by τ_T in Table II, the estimated k_2 values are as follows: in mesitylene 3.5×10^5 (**1a**), 1.0×10^6 (**1b**), 1.5×10^6 (**1c**), and 1.2×10^6 M^{-1} s^{-1} (**1e**); in cyclooctane 3.7×10^6 (**1c**) and 8.2×10^6 M^{-1} s^{-1} (**1e**).

It is obvious that k_2 tends to increase with the increasing electron-withdrawing ability of the 4′-substituents, as expected.[19,20]

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(18) This expression is based on an assumption that the reketonization pathway from a DR-pyridine complex can be neglected.[17c] While this is often the case with the Norrish type II reaction of phenyl alkyl ketones, exceptional cases (cyano- and carbomethoxy-substituted valerophenones) were recently reported.[19] However, as is mentioned in the text, the magnitude of E_a for **1a–d** and **1f** (Table II) is completely consistent with the k_r and k_d values (Table III). This indicates that the relationship of eq 4 is approximately realized in our cases.

(19) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329.

(20) (a) Wagner, P. J.; Thomas, M. J.; Harris, E. *J. Am. Chem. Soc.* **1976**, *98*, 7675. (b) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *Ibid.* **1973**, *95*, 5604. (c) Yang, N. C.; Dusenbery, R. L. *Mol. Photochem.* **1969**, *1*, 159. (d) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466.

(21) (a) Wolf, M. W.; Legg, K. D.; Brown, R. E.; Singer, L. A. *J. Am. Chem. Soc.* **1975**, *97*, 4490. (b) Wolf, M. W.; Brown, R. E.; Singer, L. A. *Ibid.* **1977**, *99*, 526. The quantum yields for **2c** and **2d** in benzene appear to slightly increase with the ketone concentration: **2c**, Φ_{CB} = 0.57, 0.61, 0.60, 0.61, 0.67, 0.63, 0.66, and 0.69 respectively at 0.052, 0.075, 0.105, 0.129, 0.153, 0.176, 0.222, and 0.254 M of **1c**; **2d**, Φ_{CB} = 0.12, 0.13, 0.14, 0.15, 0.16, 0.17, and 0.15 respectively at 0.020, 0.040, 0.050, 0.060, 0.075, 0.090, and 0.100 M of **1d**. These results suggest that the self-quenching effect for **1c** and **1d** is not very important under our reaction conditions. The observed slight increase in Φ_{CB} can be ascribed to a weak Lewis base property of the ketone molecule.[17d]

(22) Scaiano, J. C. *J. Am.* Chem. *Soc.* **1980**, *102*, 5400.

This is in sharp contrast with the unusual substituent effect observed in k_r (Table III).

Effect of Deuteration. Incorporation of deuterium into two *o*-isopropyl methines of **1c** was achieved through 254-nm irradiation of **1c** in a mixture of D_2O and acetonitrile. Under these conditions a reversible photoreaction **1c** $\rightleftarrows$ **2c** occurs,[11] resulting in the deuterium incorporation to give **1c**–d_2. Values of Φ_{CB}, τ_T, P_P, k_r, and k_d for **1c**–d_2 in benzene were obtained according to the same procedures as outlined above and are summarized in Tables II and III. The isotope effect on k_r (k_H/k_D) was found to be 1.5 after correction for the deuterium content.

Data for Less Hindered 2,4,6-Trialkylbenzophenones. The values of Φ_{CB} and τ_T for **3a** and **3b** in benzene were similarly estimated and are summarized in Table V, together with those of **1c** and 2-methylbenzophenone (**4**) for comparison.

It should be noted that the diene quenching experiment for **3a** appears to give an upward curve (Figure 3) from which involvement of both a long-lived triplet ($\tau_T \sim 580$ ns) and a short-lived one ($\tau_T \sim 20$ ns) was indicated according to a quadratic Stern–Volmer equation. The triplet lifetime of **3a** determined by two other methods, i.e., by photosensitized cis–trans isomerization of *cis*-1,3-pentadiene using **3a** as sensitizer[6a] and by monitoring the decay of the triplet absorption induced by laser excitation,[16] were 7 and 580 ns, respectively. Failure to detect a longer lived component of two observable triplets by the sensitized *cis*-1,3-pentadiene isomerization is common.[23] Thus these data seem to indicate that **3a** has two kinetically distinct triplets, as previously reported with **4** and some 2-alkyl-substituted acetophenones.[3d,4b,5]

Discussion

Nature of Excited States. From inspection of Table I it can be seen that all the excited-state properties (E_T, E_S, $E_S - E_T$, $\lambda_{\pi\pi^*}$, and Φ_T) of **1c**, **3a**, and **3b** are very similar to those of benzophenone itself, indicating that their T_1 states are predominantly nπ^* in nature.

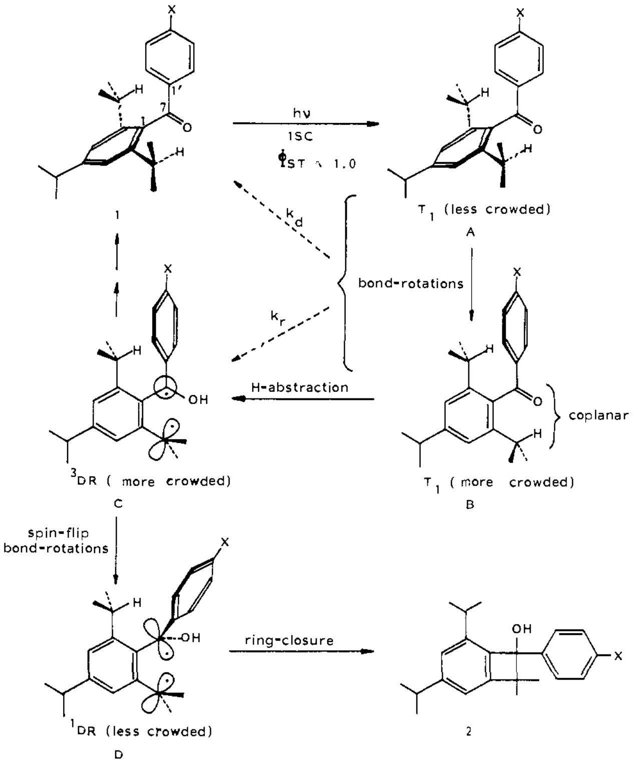
Table I also shows that throughout the series **1a–f** the T_1 levels are lowered (or raised) by ring substitution with electron-withdrawing (or -donating) groups, as expected for triplet states of nπ^* character.[19,20,24] The $\pi\pi^*$ absorption maxima ($\lambda_{\pi\pi^*}$), however, suggest that the $\pi\pi^*$ triplet states are lowered by ring substitution with any group except CF_3. As a result, we are unable to assign the T_1 states of **1a** (X = OMe), **1b** (X = Me), **1d** (X = CO_2Me), and **1f** (X = CN), i.e., whether they are still of nπ^* character or not, while it is evident that the quantity of $\pi\pi^*$ character in the T_1 states systematically increases in the order **1e** (X = CF_3) < **1c** (X = H) < **1b** (X = Me) < **1a** (X = OMe). A similar trend was found with phenyl alkyl ketone triplets.[19,20]

In any event, all the 2,4,6-triisopropylbenzophenones **1a–f** seem to have a significant amount of nπ^* character in their lowest triplet states, since they produced the corresponding benzocyclobutenols in medium to good efficiencies (Table II).

Primary Processes of Triplet 2,4,6-Triisopropylbenzophenones. Transformation of the hindered benzophenones **1a–f** into the corresponding benzocyclobutenols **2a–f** apparently involves the nπ^* triplet-induced intramolecular abstraction of a benzylic hydrogen from ortho isopropyls (Scheme I), since α- or β-naphthyl 2,4,6-triisopropylphenyl ketone having pure $T_1(\pi\pi^*)$ character showed no photochemical reactivity.[6a] The irrelevance of Φ_{CB} and the amount of nπ^* character in the T_1 states of these benzophenones (Table II; also see Table II in ref 6a) were interpreted, by analogy to the Norrish type II reaction, in terms of intervention of the diradical intermediate DR (Scheme I).[6a]

The remarkable findings we have acquired concerning the primary processes of the triplet 2,4,6-triisopropylbenzophenones are (1) the unusually large E_a ($\sim$9 kcal/mol) obtained for **1a–c** from the Arrhenius plot of τ_T^{-1} (Table III), (2) the relatively small effect of deuteration on k_r obtained for **1c** ($k_H/k_D = 1.5$, Table III), (3) the unexpected dependence in τ_T or k_r on 4′-substitution (Tables II and III), and (4) the ordinary substituent dependence of the values for k_2 (Table IV). These novel properties of the hindered triplet benzophenones cannot be understood without consideration of the stereochemistry of the molecules.

Scheme II



Scheme II illustrates a plausible mechanism involving the simplified (idealized) geometries of nπ^* triplet states (A and B) and diradical intermediates (C and D). A crucial feature of this scheme is that the two aromatic planes in a molecule are always held at a nearly perpendicular angle, as the reaction proceeds, i.e., as the carbonyl or the hydroxymethyl moiety rotates. In other words, a hindered rotation around the C_1–C_7 bond involves a concomitant rotation about the C_7–$C_{1'}$ bond. A molecular model reveals that this feature arises from a steric effect of the bulky *o*-isopropyl groups. The conformations of various transition states and intermediates (A–D) were deduced from various facts we have discovered (vide infra). The ground-state conformations of **1a** and **1c** were proved by X-ray crystallography.[7] The conformational interconversion in the hindered benzophenones **1a–f** in the ground states was recently studied by us with dynamic NMR (DNMR) spectroscopy and molecular mechanics (MM) calculation.[7] In fact, the conformation for B (highly crowded) is described according to the results of these studies, based on an assumption that gross geometries of big molecules such as **1a–f** in their excited states are nearly the same as those in their ground states.[25]

Thus at the Franck–Condon state the 2,4,6-triisopropylphenyl plane of the hindered benzophenones **1a–f** is nearly completely twisted from the pseudoplane of the 4′-substituted benzoyl group in the most strain-free conformation (A).[7] This conformation is unfavorable for the intramolecular hydrogen abstraction to occur in view of either, so called, the stereoelectronic requirement for hydrogen abstraction[26] or simply the long distance between the carbonyl oxygen and the ortho benzylic hydrogen.[27] Therefore,

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(23) Wagner, P. J. *J. Photochem.* **1979**, *10*, 387.

(24) Leigh, W. J.; Arnold, D. R.; Humphreys, R. W. R.; Wong, P. C. *Can. J. Chem.* **1980**, *58*, 2537.

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

(26) Reference 15, p 386.

(27) The X-ray crystal structure of **1a**[7] has revealed that the distances between the carbonyl oxygen and each of the two ortho isopropyl methine hydrogens are 2.88 and 2.97 Å. These distances are too long for the intramolecular hydrogen abstraction to occur.[28]

(28) (a) Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163. (b) Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283.

prior to the hydrogen abstraction the rotation of the C–C single bond linking the 2,4,6-triisopropylphenyl group and the carbonyl group (C_1–C_7) must occur against a strong steric repulsion to give a suitable conformation (B), where the triisopropylphenyl is nearly coplanar with the carbonyl moiety and hydrogen abstraction is geometrically possible. Note that conformation B is much more crowded than A because of steric repulsion between 2,6-diisopropyl and 4′-substituted benzoyl groups and hence the process A → B will be slow.

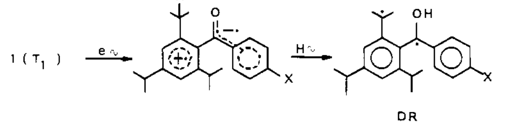
Once the conformation B is achieved, the hydrogen abstraction may well happen readily (B → C in Scheme II). It has been reported that the rate for an intramolecular benzylic hydrogen abstraction is very fast for less hindered *o*-alkyl aromatic ketones ($\sim 10^9$ s^{-1}).[3d,5] As a result, the intramolecular hydrogen-abstraction rate k_r may be controlled in some cases by the restricted rotation around C_1–C_7 (A → B) rather than by the direct abstraction step (B → C), as will become evident later.

On the other hand, geometrically the bimolecular triplet quenching with hydrogen donors (Bu_3SnH, mesitylene, and cyclooctane) does not require precedence by such a hindered rotation. They require only diffusional encounters of two reactant molecules. Therefore, the overall change in the bimolecular reaction rate k_2 with 4′-substitution through a series of compounds **1a–c** and **1e** should be that expected from the known ring-substituent effect on reactivity for excited phenyl ketones.[19,20] In fact, this was confirmed by the increase in the k_2 value from **1a** (X = OMe) to **1e** (X = CF_3) (Table IV).

Likewise, other decay processes (the rate constant k_d), which are competing with the intramolecular hydrogen abstraction, will not require C_1–C_7 bond rotation. Thus **1d** and **1f**, where τ_T is mainly controlled by k_d (Table III), have no reason to exhibit a large activation energy E_a. On the other hand, **1a–c**, where τ_T is controlled by k_r (Table III), can possess an unusually large E_a, as was actually observed ($E_a \sim 9$ kcal/mol, Table II), on account of the hindered rotation about the C_1–C_7 bond which determines the rate k_r. The E_a values for hydrogen abstraction by ketone triplets usually range from 2 to 7 kcal/mol.[29]

As suggested previously,[6a] the solution of **1c** in ethanol underwent upon photolysis both intramolecular and intermolecular hydrogen abstractions to give **2c** and **5**, respectively. It was found that while at room temperature **2c** was formed as a major product, **5** became an almost exclusive product at low temperatures (<–40 °C).[30] This drastic change in product distribution also reflects the much larger activation barrier to intramolecular hydrogen abstraction than to intermolecular hydrogen abstraction.

An isotope effect (k_H/k_D) for hydrogen abstraction from C–H bonds by ketone triplets is usually larger than 2.5.[29b,31,32] The observed isotope effect for **1c** ($k_H/k_D = 1.5$) is too small for the type of hydrogen abstraction process with a large activation barrier ($E_a \sim 9$ kcal/mol). This again strongly supports the fact that k_r is dominated by the rate of the process A → B, not by the direct hydrogen-abstraction step (B → C). An alternative explanation for the small isotope effect is the occurrence of a rate-determining electron-transfer process prior to proton transfer (eq 7). This



(7)

process, however, could be eliminated from the effect of the 4′-substituents on k_r (Table III). This point will be mentioned again below.

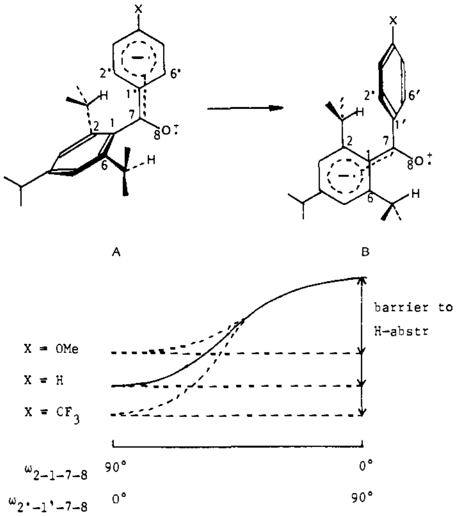


Figure 2. A simplified energy diagram for the process A → B (synchronous rotation around C_1–C_7 and C_7–$C_{1'}$ bonds): ω denotes a dihedral angle.

Discussions on the values of E_a and k_2 and on the isotope effect now make it clear that the hindered rotation about the C_1–C_7 bond (A → B) can be a crucial factor for the determination of k_r. This conclusion was further substantiated by the novel substituent effect on τ_T or k_r (Tables II and III). It is very striking that for a series of the compounds **1a–c** and **1e** the substituent dependence in k_r is just opposite to what is found in k_2. Obviously, differing amounts of nπ* and ππ* character in the lowest triplets are not responsible for the observed change in k_r with 4′-substitution.[19,20,34] An explanation in terms of the variation of E_T with 4′-substitution is less attractive, since the overall change in E_T for compounds **1a–f** is small (Table I). The participation of an intramolecular charge transfer in the hydrogen abstraction (eq 7) is unlikely, since the k_r values decreased with the increasing electron-withdrawing ability of the 4′-substituents (Table III).

As mentioned above, the most plausible explanation for k_r (and τ_T) is given by taking the conformational change A → B in Scheme II as the rate-determining step.[34] At this point, however, we have to explicitly consider the conformation of the 4′-substituted phenyl group as well as that of the 2,4,6-triisopropylphenyl group. Figure 2 illustrates a simplified energy diagram for the process A → B and a delocalized description[35] of the nπ* excited state corresponding to the conformations A and B. A similar energy diagram for the electronic ground state nicely explained the effect of 4′-substitution on the hindered rotation which was observed for **1a–f** by DNMR technique.[7,36]

Thus as readily seen from Figure 2, the less crowded conformation A can be stabilized by an electron-withdrawing 4′-substituent, e.g., X = CF_3, and destabilized by an electron-donating one, e.g., X = OMe, whereas the energy level of conformation B will be less affected by the 4′-substituent (X) because of deconjugation between the carbonyl group and X. Therefore, the energy difference between A and B, which can be regarded as

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(29) (a) Reference 15, p 237. (b) Scaiano, J. C.; Encinas, M. V. *J. Am. Chem. Soc.* **1981**, *103*, 6393. (c) Maharaj, U.; Winnik, M. A. *Ibid.* **1981**, *103*, 2328.

(30) Ito, Y., unpublished result.

(31) (a) Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 2789. (b) Yip, R. W.; Siebrand, W. *Chem. Phys. Lett.* **1972**, *13*, 209. (c) Coulson, D. R.; Yang, N. C. *J. Am. Chem. Soc.* **1966**, *88*, 4511.

(32) A smaller isotope effect ($k_H/k_D < 1.5$) seems common for interaction with electron donors, e.g., phenols[33] and Bu_3SnH.[29b]

(33) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154.

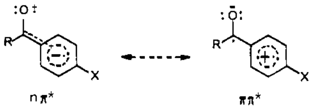
(34) In the cases of **1d** and **1f**, however, their (presumable) higher ππ* character in the T_1 states may also be contributing to their small reactivities (i.e., small k_r or large τ_T). A deviation from the less steep Hammett line ($\rho = -1.0$) for both cases (Figure 1) is a support for this.

(35) Wagner, P. J.; Lam, H. M. H. *J. Am. Chem. Soc.* **1980**, *102*, 4167.

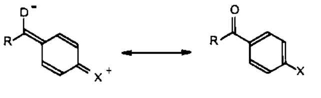
(36) From the DNMR study the rotational rate around the hindered C_1–C_7 bond in the ground state (k_{rot}) was found to increase by a factor of 50 in going from **1a** (X = OMe) to **1f** (X = CN); i.e., the k_{rot} values at 31 °C were 1.4 (**1a**), 5.8 (**1b**), 14.5 (**1c**), 59 (**1d**), 34 (**1e**), and 68 (**1f**) s^{-1}, respectively.[7] The overall increase in k_r was ca. 30 times from **1f** to **1a** (Table III). Note that both substituent effects are in opposite directions to each other. Also note that k_{rot} corresponds to the rate of a full rotation around the bond, whereas the hydrogen-abstraction rate k_r may correspond to the rate of only a partial rotation or a twisting around the bond. In fact k_r was much larger than k_{rot}.

an energy barrier to the hydrogen abstraction, should be increased (or decreased) by 4′-substitution with the electron-withdrawing (or -donating) groups. The experimentally determined k_r values (Table III) precisely reflect these resonance effects caused by the 4′-substituents.

In general, an nπ^* state of an aromatic ketone triplet has some $\pi\pi^*$ character obtained from a vibronic mixing and/or a thermal equilibrium (eq 8a).[19,20,37] We can now view the substituent effect on k_r from another aspect. The observed decrease in k_{rot} (the rotational rate around the C_1–C_7 bond determined by DNMR[36]) with the decrease in the electron-donating nature of the 4′-substituent was explained based on an energy diagram similar to Figure 2.[7] However, it can also be rationalized readily in terms of a different contribution of two resonance structures **8** and **9** (eq 8b). Since the most energetically feasible rotation about the C_1–C_7 bond requires occurrence of a synchronous rotation around the C_7–$C_{1'}$ bond,[7] a higher contribution of **8**, which means more double-bond character in the C_7–C_1' bond, necessarily results in the decrease in k_{rot}, as observed.[36] Likewise the decrease in k_r in going from the electron-donating to -withdrawing substituents (Table III) should stem from an increase of double-bond character in the C_7–$C_{1'}$ bond, excepting the ambiguous cases of **1d** and **1f**.[34] This means that the greater nπ^* nature in the triplet 2,4,6-triisopropylbenzophenones (**1a** < **1b** < **1c** < **1e**) results in the higher bond order at the C_7–$C_{1'}$ bond. It is probable that the same situation occurs for all aromatic ketone triplets. It is interesting to note that Wagner's representations for nπ^* and $\pi\pi^*$ triplets (**6** and **7**, respectively) imply that the bond order of C_{Ar}—C(=O) bond may be higher in the nπ^* triplet state than in the $\pi\pi^*$ triplet state.



nπ^* 6 $\pi\pi^*$ 7 (8a)



8 9 (8b)

ground state

R = 2,4,6-triisopropylphenyl

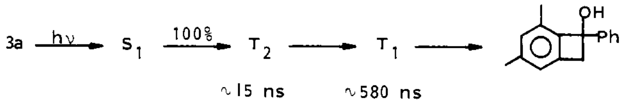
In conclusion, we have interpreted all novel properties (τ_T, k_r, E_a, k_H/k_D, and k_2) of the triplet 2,4,6-triisopropylbenzophenones by the slow conformational change A → B, followed by the fast hydrogen-abstraction process (B → C).[34] It is deduced that an increase in nπ^* character for the aromatic ketone triplets results in a higher rotational barrier (bond order) around the C_{Ar}—C(=O) bond in the triplet state.

Fate of Diradicals. The resultant diradical formed through the intramolecular hydrogen abstraction (B → C in Scheme II) is a triplet diradical (^{3}DR) with two odd orbitals oriented at approximately right angles to each other. Therefore, the probability of product (**2**) formation from ^{3}DR (P_P) may depend on two crucial factors: (1) the efficiency of triplet to singlet intersystem crossing and (2) the ease of C_1–C_7 bond rotation which leads to the two odd orbitals facing each other. As will be discussed elsewhere,[11] the spin-flip and the odd-orbital rotation are expected to occur concomitantly (C → D in Scheme II).

The triplet diradical C will partly return to the parent ketone **1** through intersystem crossing. The intervention of the corresponding enol for this reketonization process, however, still remains to be answered (see footnote 20 in ref 6a).

Less Hindered 2,4,6-Trialkylbenzophenone Triplets. Although our quenching and sensitization data with diene gave no evidence that two kinetically distinct triplets are involved in the photochemistry of **1a–f** and **3b**, 2,4,6-trimethylbenzophenone (**3a**) was suspected to have two observable triplets (a long-lived and a short-lived ones; Table V).[38] A possible reaction mechanism for **3a** is described in Scheme III. The symbols T_2 and T_1 represent the short-lived ($\tau_T \sim$ 15 ns) and long-lived ($\tau_T \sim$ 580 ns) triplet, respectively. The intersystem crossing from S_1 to T_2 should be stoichiometric since the measured Φ_T equals unity (Table I). We suspect, as does Wagner for the two triplets of γ-2,4,6-tetramethylvalerophenone,[3d] that T_2 and T_1 have, to each other, different twist angles between the 2,4,6-trimethylphenyl and the carbonyl planes. Presumably the two distinct twist angles in the triplet state are not allowed for the 2,4,6-triisopropylbenzophenones **1a–f** and 2,4,6-triethylbenzophenone (**3b**), because the bulky ortho substituents have severely limiting space available for the carbonyl group.

Scheme III



It was previously recognized that photokinetics of 2,6-dialkyl-substituted acetophenones were difficult to interpret.[3d,4b] We have found that the same is true with the benzophenone derivatives. As summarized in Table V, the lifetimes of the triplets which are directly responsible for the cyclobutenol formation (the intramolecular hydrogen abstraction) are 90, 160, 580, and 0.17 ns respectively for **1c**, **3b**, **3a**, and **4**. The steric hindrance due to ortho substituents decreases in the order **1c** > **3b** > **3a** > **4**. In order to understand these data, thorough consideration of various steric and electronic factors, e.g., (1) change in n$\pi^*/\pi\pi^*$ mixing resulting from 2,4,6-trialkyl substitution[20a] or orbital rotation,[39] (2) steric hindrance against the approach of two reaction centers, (3) strength of C–H bonds which are to be cleaved (Me > Et > *i*-Pr), (4) higher triplet reactivity of acetophenone than benzophenone toward hydrogen abstraction,[40] and (5) conformational equilibrium,[3a] will probably be required.

Experimental Section

All melting points were uncorrected. The NMR, IR, UV, and emission spectra were recorded on Varian T-60, JASCO IRA-1, Shimadzu UV-200, and Shimadzu RF-500 spectrometers, respectively.

Materials. Preparations of 2,4,6-triisopropylbenzophenones **1a–f**, 2,4,6-trimethylbenzophenone (**3a**), and 2,4,6-triethylbenzophenone (**3b**) have been described.[3f,7] Benzene solvent used for quantitative experiments was of spectral grade and *cis*-1,3-pentadiene was Tokyo Kasei's ultrapure material (<0.2% trans). They were used without further purification. 2,5-Dimethyl-2,4-hexadiene, mesitylene, and cyclooctane were distilled prior to use. Tri-*n*-butylstannane was prepared according to the literature method[41] and stored under nitrogen.

Preparative Photolyses. Preparative photolyses of 2,4,6-triisopropylbenzophenone (**1c**), **3a**, and **3b** to give the corresponding benzocyclobutenols (IUPAC name, 1,2-dihydrobenzocyclobuten-1-ols) have been reported.[3f] Under similar conditions (a 400 mL solution of 10^{-2} M of ketone in benzene irradiated with a 400-W high-pressure Hg lamp (Pyrex) under N_2 for 4 h), 4,6-diisopropyl-2,2-dimethyl-1-(4′-substituted phenyl)-1,2-dihydrobenzocyclobuten-1-ols **2a**, **b** and **2d–f** were prepared. The NMR and TLC analyses of the reaction mixture showed that the photoreaction proceeded nearly quantitatively in each case. The products were purified by column chromatography on silica gel (benzene–hexane eluent), followed by recrystallization to afford colorless crystals. Isolation yield, melting point (recrystallization solvent), and spectral and analytical data are summarized below.

2a: 64%; 102–103 °C (hexane); NMR ($CDCl_3$) δ 7.16 and 6.78 (4 H, AB, J = 8.5 Hz, arom), 7.02 (1 H, s, arom), 6.84 (1 H, s, arom), 3.77 (3 H, s, OCH_3), 2.91 (2 H, sep, J = 7 Hz, $CH(CH_3)_2$), 2.46 (1 H, s, OH), 1.44 (3 H, s, 2-CH_3), 1.28 (6 H, d, J = 7 Hz, 4-$CH(CH_3)_2$), 1.23 (3 H, d, J = 7 Hz, 6-$CH(CH_3)_2$), 1.17 (3 H, d, J = 7 Hz, 6-$CH(CH_3)_2$), 0.81 (3 H, s, 2-CH_3); IR (Nujol) 3610 cm^{-1} (OH).

Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.75; H, 9.09.

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(38) Because of this finding, the previous[6a] conclusion that τ_T of **3a** is controlled by the rotational rate around the C_1–C_7 bond is groundless.

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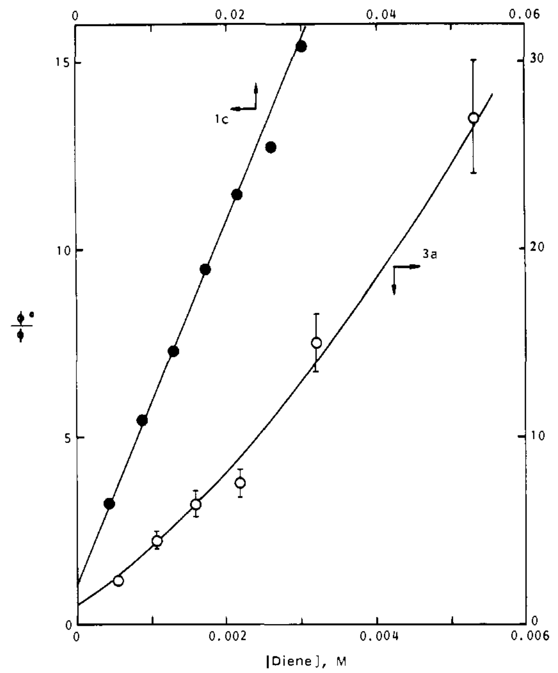

Figure 3. Quenching of benzocyclobutenol formation from 2,4,6-triisopropylbenzophenone (**1c**) or 2,4,6-trimethylbenzophenone (**3a**) by 2,5-dimethyl-2,4-hexadiene in benzene: **1c**, at 19.3 ± 0.4 °C (left and up scales); **3a**, at 25.0 ± 0.4 °C (right and down scales).

2b: 63%; 124–125 °C (hexane); NMR (CDCl$_3$) δ 7.13 (4 H, s, arom), 7.07 (1 H, s, arom), 6.89 (1 H, s, arom), 2.93 (2 H, sep, J = 7 Hz, C*H*(CH$_3$)$_2$), 2.45 (1 H, s, OH), 2.31 (3 H, s, 4′-CH$_3$), 1.45 (3 H, s, 2-CH$_3$), 1.27 (6 H, d, J = 7 Hz, 4-CH(C*H*$_3$)$_2$), 1.22 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 1.17 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 0.82 (3 H, s, 2-CH$_3$); IR (Nujol) 3620 cm^{-1} (OH).

Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.38; H, 9.49.

2d: 85%; 161–162 °C (hexane); NMR (CDCl$_3$) δ 7.87 and 7.24 (4 H, AB, J = 8 Hz, arom), 6.99 (1 H, s, arom), 6.82 (1 H, s, arom), 3.87 (3 H, s, OCH$_3$), 3.17–2.43 (2 H, m, C*H*(CH$_3$)$_2$), 2.63 (1 H, s, OH), 1.43 (3 H, s, 2-CH$_3$), 1.24 (6 H, d, J = 7 Hz, 4-CH(C*H*$_3$)$_2$), 1.18 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 1.13 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 0.79 (3 H, s, 2-CH$_3$); IR (Nujol) 3590 (OH), 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25. Found: C, 78.33; H, 8.08.

2e: 65%; 133–135 °C (ethanol); NMR (CDCl$_3$) δ 7.55 and 7.33 (4 H, AB, J = 9 Hz, arom), 7.03 (1 H, s, arom), 6.86 (1 H, s, arom), 3.2–2.5 (2 H, m, C*H*(CH$_3$)$_2$), 2.15 (1 H, s, OH), 1.47 (3 H, s, 2-CH$_3$), 1.28 (6 H, d, J = 7 Hz, 4-CH(C*H*$_3$)$_2$), 1.21 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 1.17 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 0.81 (3 H, s, 2-CH$_3$); IR (Nujol) 3600 cm^{-1} (OH).

Anal. Calcd for $C_{23}H_{27}F_3O$: C, 73.38; H, 7.23. Found: C, 73.09; H, 7.33.

2f: 85%; 130–131 °C (hexane); NMR (CDCl$_3$) δ 7.64 and 7.39 (4 H, AB, J = 8 Hz, arom), 7.11 (1 H, s, arom), 6.94 (1 H, s, arom), 2.83 (2 H, sep, J = 7 Hz, C*H*(CH$_3$)$_2$), 2.49 (1 H, s, OH), 1.44 (3 H, s, 2-CH$_3$), 1.26 (6 H, d, J = 7 Hz, 4-CH(C*H*$_3$)$_2$), 1.19 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 1.14 (3 H, d, J = 7 Hz, 6-CH(C*H*$_3$)$_2$), 0.80 (3 H, s, 2-CH$_3$); IR (Nujol) 3480 (OH), 2225 cm^{-1} (C≡N).

Anal. Calcd for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.70; H, 8.38; N, 4.19.

Quantitative Photolyses. All irradiations were done, after degassing the solution in 17 × 120 mm Pyrex tubes by four freeze–thaw cycles below 10^{-2} mmHg, on a merry-go-round apparatus by 313-nm light which was isolated from a 400-W high-pressure mercury lamp with a K_2CO_3 (1.3%)–K_2CrO_4 (0.13%) filter solution. In all cases the reaction was stopped at a small conversion (<4%).

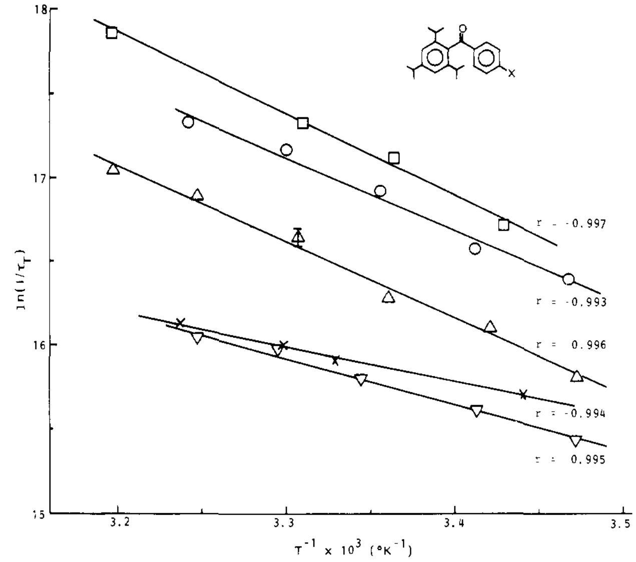

Figure 4. Arrhenius plot for the triplet lifetimes of 2,4,6-triisopropylbenzophenones determined by Stern–Volmer quenching with 2,5-dimethyl-2,4-hexadiene in benzene: □, X = OMe; ○, X = Me; △, X = H; ×, X = CO$_2$Me; ▽, X = CN. A typical error for the ln (1/τ_T) value is depicted with a bar. Correlation coefficients for each line are also shown.

The benzocyclobutenols were analyzed by high-pressure liquid chromatography (Jascosil SS-05 silica gel column, hexane–ethyl acetate eluent) using methyl 2-naphthyl ketone as an internal standard. 1,3-Pentadiene was analyzed on a 6-m GC column containing 20% 1,2,3-tris(2-cyanoethoxy)propane using hexane as an internal standard.

For quantum yield measurements the benzocyclobutenol formation from **1c** in benzene solution (0.1 M) was used as a standard (Φ_{CB} = 0.60).[6a]

A typical straight diene quenching plot for **1c** and an upward quenching curve obtained for **3a** are shown in Figure 3. Arrhenius plots are illustrated in Figure 4.

Preparation of 1c-*d*$_2$. A solution containing 3.0 g (9.7 mmol) of **1c** and 15 g of D$_2$O (750 mmol) in dry acetonitrile (210 mL) was irradiated with a 10-W low-pressure mercury lamp (254 nm) under bubbling nitrogen for 28 h. After evaporation the solid residue consisting of deuterated **2c** (main component) and **1c** was heated in an oil bath at 170 °C for 4 h to decompose[3f] **2c** into **1c**. The resultant mixture was purified, successively, by recrystallization (ethanol), column chromatography (silica gel), and recrystallization (ethanol) to afford 1.4 g (47% yield) of **1c**-*d*$_2$: mp 101–102.4 °C (lit.[42] 97–99 °C). The NMR analysis demonstrated that 75% of the *o*-isopropyl methine hydrogens were replaced by deuterium.

Acknowledgment. We are indebted to the Ministry of Education of Japan for financial aid under a special project research.

Registry No. **1a**, 76893-80-6; **1b**, 74766-25-9; **1c**, 33574-11-7; **1c**-*d*$_2$, 84559-59-1; **1d**, 76893-83-9; **1e**, 74766-27-1; **1f**, 76893-84-0; **2a**, 84559-60-4; **2b**, 84559-61-5; **2c**, 33574-16-2; **2d**, 84559-62-6; **2e**, 84559-63-7; **2f**, 84559-64-8; **3a**, 954-16-5; **3b**, 33574-10-6; H, 1333-74-0; D, 7782-39-0; Bu$_3$SnH, 688-73-3; *cis*-1,3-pentadiene, 1574-41-0; pyridine, 110-86-1; mesitylene, 108-67-8; cyclooctane, 292-64-8.

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