J. Org. Chem. **1981**, *46*, 4359–4362

Hindered Rotation in 2,4,6-Triisopropylbenzophenones[1]

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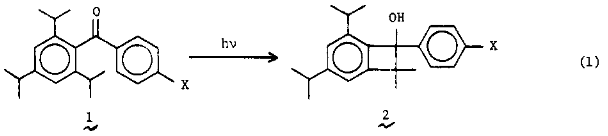
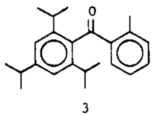
Received May 27, 1981

A variable-temperature NMR study of 4′-substituted 2,4,6-triisopropylbenzophenones was performed. With use of the prochiral ortho isopropyl groups as a probe for the dynamic process, activation parameters for the hindered rotation about the single bond linking the 2,4,6-triisopropylphenyl group and the carbonyl group (the C_1–C_7 bond) were obtained. A good linear correlation between $\Delta G^\ddagger$ of rotation and Hammett σ^+ constants of 4′-substituents was observed, giving a negative slope. The results were explained by consideration of both the conformational change of the molecule during the C_1–C_7 bond rotation, which was calculated by the molecular mechanics (MMPI) method, and the resonance interaction between the carbonyl group and the 4′-substituents. A decrease of $\Delta G^\ddagger$ with 2′-substitution was also observed and was similarly explicable by steric interaction of the 2′-substituent with the carbonyl group.

Simple carbonyl compounds have been playing a central role for the purpose of understanding and developing photochemistry of organic compounds.[2] Our interest in steric effects in the photochemistry of organic compounds has led us to study the mechanism of photochemical benzocyclobutenol formation from highly hindered 2,4,6-triisopropylbenzophenones (eq 1).[3] While elucidating the conformation of molecules in their electronically excited states is crucial for the investigation of steric effects in photochemistry, it is generally a much more difficult problem compared with that in their ground states. Therefore, at this stage the knowledge of the ground-state conformations, including their interconversions, of 2,4,6-triisopropylbenzophenones seems essential in order to understand how the behavior of the electronically excited state of a benzophenone molecule is altered by geometrical distortion. In the present paper we report an NMR study on conformational interconversions in 4′-substituted 2,4,6-triisopropylbenzophenones **1a–g** as well as **3–6**.



a, X = OMe; b, X = t-Bu; c, X = Me; d, X = H; e, X = CO_2Me; f, X = CF_3
g, X = CN



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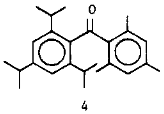

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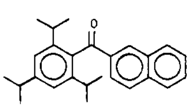

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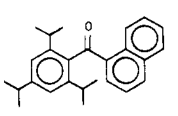

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Results and Discussion

NMR Study. Figure 1 shows the variable-temperature NMR spectra of the isopropyl methyl region of 2,4,6-triisopropylbenzophenone (**1d**). The methyl signals of the two ortho isopropyl groups vary from two doublets at 10 °C to a broad doublet at 50 °C and coalesce at 40 °C, whereas a doublet ascribable to para isopropyl methyls (Figure 1) and resonance signals in the other region (not shown) were totally unchanged at this temperature range. The NMR spectra of all the other triisopropylbenzophenones **1a–c** and **1e–g** showed an analogous temperature dependence. The observed coalescence of the ortho isopropyl methyl signals in each case is obviously arising from the steric effect of bulky ortho isopropyls, which results in a restricted rotation around the single bond (C_1–C_7) linking the 2,4,6-triisopropylphenyl ring and the carbonyl group. As the temperature is lowered, the rotation around the C_1–C_7 bond becomes slower on the NMR time scale and the geminal ortho isopropyl methyls, which are magnetically equivalent at higher temperatures, become magnetically nonequivalent because of an anisotropy influence of the carbonyl group. The use of diastereotopic isopropyl methyls in dynamic NMR spectroscopy is well-known.[4]

By use of classical line shape analysis,[4a,5] the activation parameters $\Delta G^\ddagger$, E_a, and ln A for the rotation about the C_1–C_7 bond of **1a–g** were obtained. The data are summarized in Table I. Although the barrier to rotation in terms of $\Delta G^\ddagger$ or E_a is not changed very much with 4′-substitution, there is a trend that the electron-donating substituents increase the barrier, while the electron-withdrawing substituents decrease it. In particular, a relatively good correlation (correlation coefficient $r = -0.977$) was found between $\Delta G^\ddagger{}_{31}$ and Hammett σ^+ constants of 4′-substituents (Figure 2). Poor correlation of E_a with σ^+ may be partly due to the poor precision in the determination of E_a. It is known that $\Delta G^\ddagger$ can be determined with greater precision than E_a, if the temperature range is small.[4a]

Figure 3 depicts the lowest energy conformations of the ground state (I or I′) and the transition state (II) in the C_1–C_7 bond rotation. The X-ray analyses of **1a** and **1d** showed that in the solid state (a) the triisopropylphenyl plane is nearly completely twisted from the carbonyl plane, (b) the 4′-substituted phenyl is approximately coplanar

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Table I. Activation Parameters for Rotation around the C_1-C_7 Bond of 4′-Substituted 2,4,6-Triisopropylbenzophenones **1a–g**[a]

compd	X	$\Delta G^{\ddagger}_{31}$	E_a	ln A	σ^{+} [b]
1a	OMe	17.62 ± 0.15	18.04 ± 0.89	30.70 ± 0.89	-0.65
1b	*t*-Bu	17.10 ± 0.20	20.63 ± 1.34	35.30 ± 2.15	-0.275
1c	Me	16.78 ± 0.20	16.00 ± 1.69	28.19 ± 0.24	-0.26
1d	H	16.16 ± 0.11	17.07 ± 0.17	30.98 ± 0.28	0
1e	CO_2Me	15.43 ± 0.18	16.82 ± 0.73	31.76 ± 1.30	0.49
1f	CF_3	15.69 ± 0.18	13.69 ± 1.56	26.17 ± 2.70	0.58
1g	CN	15.28 ± 0.28	16.66 ± 0.69	31.74 ± 1.19	0.67

[a] The free energy of activation $\Delta G^{\ddagger}_{31}$ in kilocalorie/mole was calculated by the Erying equation from the value of the first-order rate constant at 31 °C, which was obtained by classical line-shape analysis. The Arrhenius activation energy E_a in kilocalorie/mole and ln A were obtained from the usual plot of ln k vs. T^{-1}. [b] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1975.

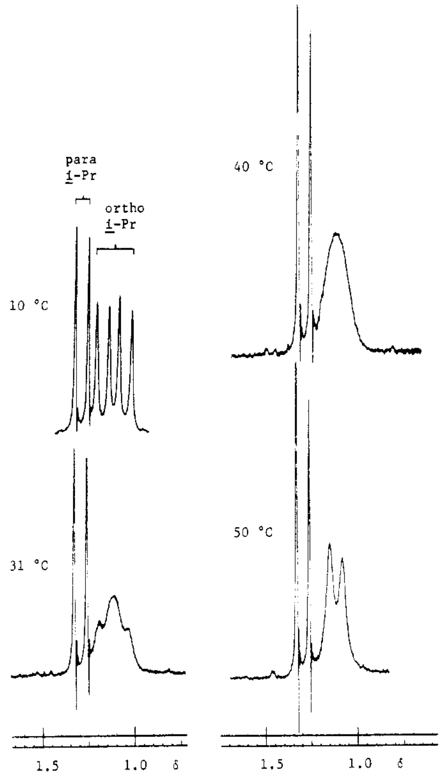

Figure 1. The NMR spectra of isopropyl methyl region of 2,4,6-triisopropylbenzophenone (**1d**) at various temperatures.

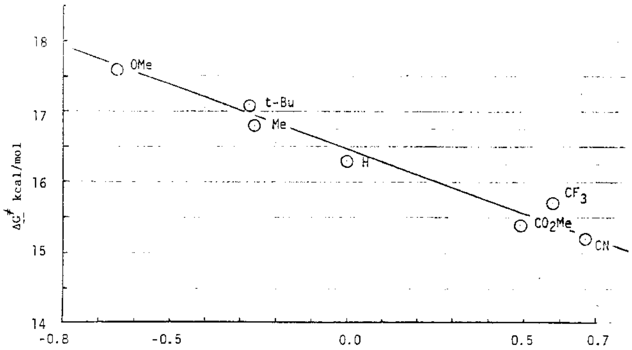

Figure 2. Hammett plot of the rotational barriers for 4′-substituted 2,4,6-triisopropylbenzophenones **1a–g**.

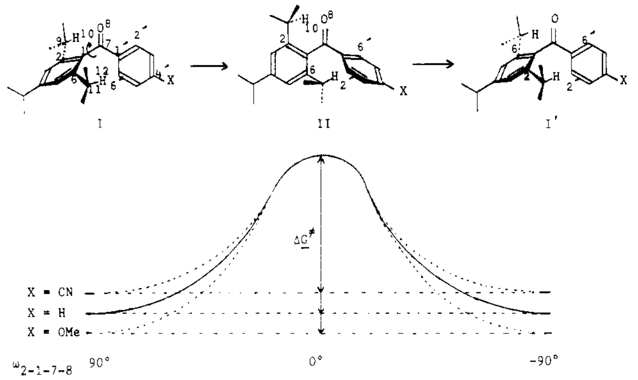

Figure 3. The simplified pictorial representation for the C_1–C_7 bond rotation of 2,4,6-triisopropylbenzophenones **1a–g**; ω denotes a dihedral angle.

with the carbonyl moiety, and (c) the methine hydrogens of the ortho isopropyls are directed toward the carbonyl side.[6] Since it has been reported recently that the conformation of benzophenone is not appreciably changed by the introduction of polar substituents into the 4-position, we assume similar ground-state conformations for the other triisopropylbenzophenones **1b**, **1c**, and **1e–g**. The calculation with the MMPI method (vide infra) reveals that the most energetically feasible rotation around the C_1–C_7 bond involves the concomitant rotation of the C_7–$C_{1'}$ bond in the same molecule, leading to the conformation that at the transition state of the C_1–C_7 rotation (Figure 3, II) where the triisopropylphenyl and the carbonyl groups are coplanar, the 4′-substituted phenyl and the carbonyl are in mutually perpendicular planes, i.e., they are deconjugated.

As a result, in the ground state (Figure 3, I or I′) the molecule is stabilized by the electron-donating 4′-substituents and is destabilized by the electron-withdrawing ones, as is readily understood by noticing the π-conjugation between the carbonyl group and the 4′-substituents. On the other hand, the energy of the transition state will be less affected by the 4′-substituents, since the 4′-substituent and the carbonyl group are deconjugated in this state. The resultant change in energy difference between the ground and the transition states is also illustrated in Figure 3, which can rationalize the observed negative slope of the plot, $\Delta G^{\ddagger}$ vs. σ^{+}, shown in Figure 2.

Based on the variable-temperature NMR study, the values of $\Delta G^{\ddagger}_{c}$ of the rotation about the C_1–C_2 bond of acetophenones and benzaldehydes (see **7**) were previously estimated to be 6–11 kcal/mol[8] and $\Delta G^{\ddagger}_{c}$ for the rotation around the C_2–C_3 bond of 2,4,6-tri-*tert*-butylbenzophenones **8** were about 18 kcal/mol.[9] Similarly in the NMR spectra of **1a** (X = OMe) the doublet of the protons at 2′- and 6′-positions was found to coalesce at low tem-

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(6) The details of the X-ray analysis will be published elsewhere.

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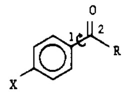

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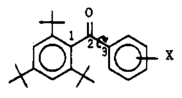
R = Me or H



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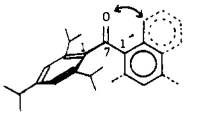
peratures (<−30 °C). However, the corresponding proton signals of **1c** (X = Me) and **1f** (X = CF_3) showed no coalescence even at −40 °C, although some broadening was observed at −40 °C in the case of **1c**. These facts indicate that (a) the C_7–$C_{1'}$ bond is much less hindered in rotation than the C_1–C_7 bond and (b) the coalescence temperature (and probably $\Delta G^{\ddagger}$ for the C_7–$C_{1'}$ bond rotation)[8] decreases in the order **1a** > **1c** > **1f**. This is the order expected from the π-conjugation between the carbonyl group and the 4′-substituents and is in alignment with the previous results.[8,9]

From the observation of the isopropyl methyl signals, we also estimated the rotational barriers around the C_1–C_7 bond of **3**–**6**. It was found that the barrier decreased with 2′-substitution, i.e., $\Delta G^{\ddagger}_{31}$ for **3** (<13.8 kcal/mol) and **4**[10] were smaller than that of **1d** (16.16 kcal/mol) and $\Delta G^{\ddagger}_{31}$ of **6** (14.20 ± 0.08 kcal/mol) was smaller than that of **5**.[11] The similar decrease of a rotational barrier in spite of the increased steric congestion about the bond under consideration has been frequently noted.[9,12] The explanation used previously[9,12a] will be applicable to our compounds. Thus in the ground states of **3**, **4**, and **6** there is a steric interaction between the 2′-substituent and the carbonyl group in each case (refer to **9**). The ground-state conformations of **3** and **6** were unequivocally determined by X-ray analysis.[6] In the transition states for the C_1–C_7 rotation, however, there is less interaction of the 2′-substituent with the carbonyl group, because they occupy mutally perpendicular planes just as shown with **1a**–**g** (Figure 3). Consequently 2′-substitution will decrease $\Delta G^{\ddagger}$ for the C_1–C_7 bond rotation by elevating the energy of the ground state.



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Molecular Mechanical Calculation. The lowest energy conformation of 2,6-diisopropylbenzophenone rotating around its C_1–C_7 bond was calculated by the MMPI method.[13] With the Wiberg–Boyd bond drive technique,[14] the calculated changes in the steric energy E_s and the dihedral angles $\omega_{2'\text{-}1'\text{-}7\text{-}8}$, $\omega_{1\text{-}6\text{-}11\text{-}12}$, and $\omega_{1\text{-}2\text{-}9\text{-}10}$ are described as a function of the angle $\omega_{2\text{-}1\text{-}7\text{-}8}$ (90–−90°) in Figure 4. In the calculation the atoms C_1, $C_{1'}$, C_7 and O_8 were assumed to stay on the same plane during the rotation. The transition-state conformation visualized in Figure 3 (II) was drawn based on the result of this calculation. It can readily be seen from Figure 4 that as the dihedral angle $\omega_{2\text{-}1\text{-}7\text{-}8}$ approaches zero from 90°, the unsubstituted phenyl ring rotates synchonously. Thus $\omega_{2'\text{-}7\text{-}8}$ increases from 0° and at the transition state ($\omega_{2\text{-}1\text{-}7\text{-}8}$ = −5°) $\omega_{2'\text{-}1'\text{-}7\text{-}8}$ becomes 90°, i.e., the carbonyl and the unsubstituted phenyl groups are twisted at a right angle. After the transition state ($\omega_{2\text{-}1\text{-}7\text{-}8}$ = −5–−90°), $\omega_{2'\text{-}1'\text{-}7\text{-}8}$ further increased to 180°, where the configuration of the molecule is exactly the same as the initial configuration. Figure 4 also shows that as the C_1–C_7 bond starts to rotate, the angle $\omega_{1\text{-}2\text{-}9\text{-}10}$ gradually increases due to the steric repulsion evidently between the atoms O_8 and H_{10}. The angle $\omega_{1\text{-}2\text{-}9\text{-}10}$ reaches 42° at the transition state and suddenly decreases[15] far after the transition state ($\omega_{2\text{-}1\text{-}7\text{-}8}$ = −50°). The angle $\omega_{1\text{-}6\text{-}11\text{-}12}$ was almost invariable during the C_1–C_7 bond rotation. The energy difference between the transition state (E_s = 59.24 kcal/mol) and the ground state (E_s = 43.88 kcal/mol) was 15.36 kcal/mol, which is in good agreement with the $\Delta G^{\ddagger}$ value for **1d** determined by NMR (Table I).

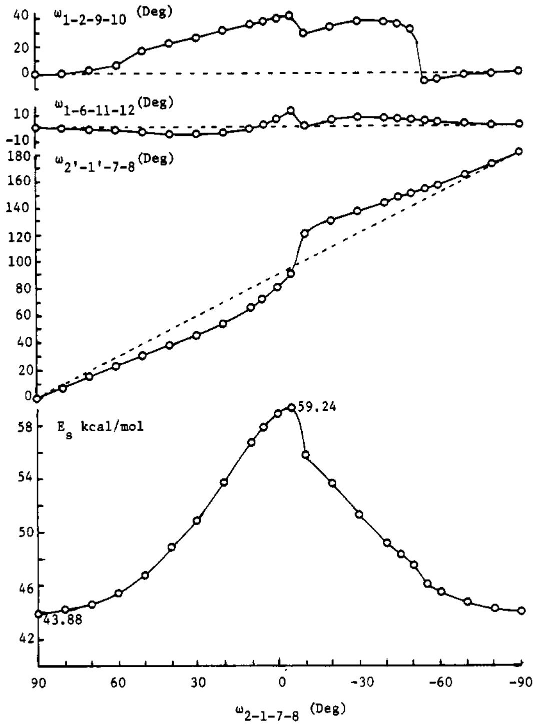

Figure 4. The changes of the steric energy E_s and the dihedral angles $\omega_{2'\text{-}1'\text{-}7\text{-}8}$, $\omega_{1\text{-}6\text{-}11\text{-}12}$, and $\omega_{1\text{-}2\text{-}9\text{-}10}$ in the C_1–C_7 rotation of 2,6-diisopropylbenzophenone were calculated by the MMPI method. The dihedral angle $\omega_{2\text{-}1\text{-}7\text{-}8}$ was varied from 90 to −90°. See Figure 3 for the position numbers of atoms.

Experimental Section

All melting points were uncorrected. The routine NMR and IR spectra were recorded on Varian T-60 and JASCO IRA-1 spectrometers, respectively. Variable-temperature NMR spectra were taken in $CDCl_3$ with a Varian HA-100 spectrometer, using Me_4Si as the internal standard. Temperatures were measured with methanol on ethylene glycol shift (±0.5 °C). Line-shape analysis was performed with a NEC PC-8001 personal computer, employing a program which was designed based on the assumption that the exchanging isopropyl group can be approximated to two separate pairs of an uncoupled AB spin system.[4a,5] The temperature dependence of the chemical shifts and coupling constants was neglected. The values of T_2 were obtained based on the observed width at half-height of para isopropyl methyl signals at each temperature. The experimental and calculated spectra were compared visually.

Materials. 2,4,6-Triisopropyl-4′-methoxybenzophenone (**1a**)[16] and 2,4,6-triisopropylbenzophenone (**1d**)[17] were previously prepared by the Friedel–Crafts reaction.

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[10] The NMR spectrum of **4** showed no coalescence up to −40 °C.

[11] The methyl signals for the two ortho isopropyls were a broad doublet at 31 °C in the case of **6**, whereas they were almost at coalescence at the same temperature in the case of **5**.

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Table II. Steric Energy of the Transition (TS) and the Ground States (GS) in the C_1-C_7 Bond Rotation of 2,6-Diisopropylbenzophenone Calculated by the MMPI Method

steric energy [a]	GS	TS	Δ
bond stretching	1.34	3.00	1.66
angle bending	2.65	9.44	6.79
torsion	30.98	32.04	1.06
van der Waals	9.35	15.59	6.24
others [b]	−0.44	−0.83	−0.39
total steric energy	43.88	59.24	15.36

[a] Kilocalorie/mole. [b] Sum of stretch-bend, torsion-bend, and dipole energies.

2,4,6-Triisopropyl-4′-*tert*-butylbenzophenone (1b). Into a solution containing 44.1 g (216 mmol) of 1,3,5-triisopropylbenzene and 28 g (210 mmol) of aluminum chloride in 63 mL of carbon disulfide was added dropwise a solution containing 30 g (153 mmol) of 4-*tert*-butylbenzoyl chloride and 14.7 g (72 mmol) of 1,3,5-triisopropylbenzene in 40 mL of carbon disulfide. After having been refluxed for 12 h, the mixture was poured into an ice–hydrochloric acid mixture and extracted with benzene. the organic layer was washed successively with water, 5% sodium hydroxide solution, and water and was dried with sodium sulfate. After evaporation of the solvent and crystallization from methanol, 21 g (38% yield) of **1b** was obtained as colorless crystals: mp 120–121 °C; NMR ($CDCl_3$) δ 7.77 and 7.43 (4 H, AB, *J* = 8 Hz, arom), 7.07 (2 H, s, arom), 3.18–2.36 (3 H, m, $\mathbf{CH}(CH_3)_2$), 1.33 (9 H, s, $C(\mathbf{CH_3})_3$), 1.4–1.0 (18 H, m, $CH(\mathbf{CH_3})_2$); IR (Nujol) 1660 cm^{-1} (C═O).

Anal. Calcd for $C_{26}H_{36}O$: C, 85.66; H, 9.95. Found: C, 85.74; H, 10.13.

By similar Friedel–Crafts reactions, 4′-methyl- (**1c**), 4′-carbomethoxy- (**1e**), 4′-trifluoromethyl- (**1f**), 4′-cyano- (**1g**), and 2′-methyl- (**3**) substituted 2,4,6-triisopropylbenzophenones, 2-(2,4,6-triisopropylbenzoyl)naphthalene (**5**), and 1-(2,4,6-triisopropylbenzoyl)naphthalene (**6**) were prepared from the corresponding acid chlorides and 1,3,5-triisopropylbenzene on similar scales.

1c. Colorless crystals were obtained from methanol in a 36% yield: mp 87–87.5 °C; NMR ($CDCl_3$) δ 7.70 and 7.19 (4 H, AB, *J* = 8 Hz, arom), 7.00 (2 H, s, arom), 3.2–2.3 (3 H, m, $\mathbf{CH}(CH_3)_2$), 2.40 (3 H, s, *p*-CH_3), 1.4–0.9 (18 H, m, $CH(\mathbf{CH_3})_2$); IR (Nujol) 1660 cm^{-1} (C═O).

Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.56; H, 9.19.

1e. Pale yellow crystals were obtained from *n*-hexane in a 46% yield: mp 142–143 °C; NMR ($CDCl_3$) δ 8.05 and 7.80 (4 H, AB, *J* = 8 Hz, arom), 7.01 (2 H, s, arom), 3.91 (3 H, s, OCH_3), 3.12–2.34 (3 H, m, $\mathbf{CH}(CH_3)_2$), 1.29 (6 H, d, *J* = 7 Hz, *p*-$CH(\mathbf{CH_3})_2$), 1.01 (12 H, d, *J* = 7 Hz, *o*-$CH(\mathbf{CH_3})_2$); IR (Nujol) 1670 (ketone); 1730 cm^{-1} (ester).

Anal. Calcd for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25. Found: C, 79.03; H, 8.40.

1f. Colorless crystals were obtained from hexane in a 32% yeild; mp 89–91 °C; NMR ($CDCl_3$) δ 7.92 and 7.62 (4 H, AB, *J* = 8 Hz, arom), 7.00 (2 H, s, arom), 3.20–2.34 (3 H, m, $\mathbf{CH}(CH_3)_2$), 1.30 (6 H, d, *J* = 7 Hz, *p*-$CH(\mathbf{CH_3})_2$), 1.14 (12 H, d, *J* = 7 Hz, *o*-$CH(\mathbf{CH_3})_2$); IR ($CDCl_3$) 1680 cm^{-1} (C═O).

Anal. Calcd for $C_{23}H_{27}F_3O$: C, 73.38; H, 7.23; F, 15.14. Found: C, 73.12; H, 7.31; F, 14.84.

1g. Pale yellow crystals were obtained from ethanol in a 24% yield: mp 149–150 °C; NMR ($CDCl_3$) δ 7.96 and 7.74 (4 H, AB, *J* = 8 Hz, arom), 7.09 (2 H, s, arom), 3.14–2.06 (3 H, m, $\mathbf{CH}(CH_3)_2$), 1.29 (6 H, d, *J* = 7 Hz, *p*-$CH(\mathbf{CH_3})_2$), 1.11 (12 H, d, *J* = 7 Hz, *o*-$CH(\mathbf{CH_3})_2$); IR (Nujol) 2235 (C≡N), 1670 cm^{-1} (C═O).

Anal. Calcd for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.59; H, 8.14; N, 4.14.

3. Colorless crystals were obtained from ethanol in a 30% yield: mp 103–104 °C; NMR ($CDCl_3$) δ 7.05–7.40 (4 H, m, arom), 7.00 (2 H, s, arom), 2.35–3.17 (3 H, m, $\mathbf{CH}(CH_3)_2$), 2.72 (3 H, s, *o*-CH_3), 1.30 (6 H, d, *J* = 7 Hz, *p*-$CH(\mathbf{CH_3})_2$), 1.15 (12 H, d, *J* = 7 Hz, *o*-$CH(\mathbf{CH_3})_2$); IR (Nujol) 1650 cm^{-1} (C═O).

Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.93; H, 9.27.

5. Pale yellow crystals were obtained from ethanol in a 60% yield: mp 155–157 °C; NMR ($CDCl_3$) δ 8.4–7.3 (7 H, m, naph), 7.10 (2 H, s, arom), 3.4–2.3 (3 H, m, $\mathbf{CH}(CH_3)_2$), 1.33 (6 H , d, *p*-$CH(\mathbf{CH_3})_2$), 1.3–0.9 (12 H, br, *o*-$CH(\mathbf{CH_3})_2$); IR (Nujol) 1655 cm^{-1} (C═O).

Anal. Calcd for $C_{26}H_{30}O$: C, 87.10; H, 8.44. Found: C, 86.99; H, 8.54.

6. Pale yellow crystals were obtained from ethanol in a 27% yield: mp 149–149.5 °C; NMR ($CDCl_3$) δ 9.20–9.10 and 8.00–7.05 (7 H, m, naph), 7.00 (2 H, s, arom), 3.05–2.20 (3 H, m, $\mathbf{CH}(CH_3)_2$), 1.15 (6 H, d, *J* = 7 Hz, *p*-$CH(\mathbf{CH_3})_2$), 1.05 (12 H, d, *J* = 7 Hz, *o*-$CH(\mathbf{CH_3})_2$); IR (Nujol) 1650 cm^{-1} (C═O).

Anal. Calcd for $C_{26}H_{30}O$: C, 87.10; H, 8.44. Found: C, 86.84; H, 8.73.

2,4,6-Triisopropyl-2′,4′,6′-trimethylbenzophenone (4). This compound was prepared by the Grignard reaction. Thus the Grignard reagent prepared[18] from 12 g (43 mmol) of 2,4,6-triisopropylbromobenzene and 1.1 g (46 mmol) of magnesium turnings in 80 mL of ether was added over 1 h at room temperature to a solution of 7.8 g (43 mmol) of 2,4,6-trimethylbenzoyl chloride[19] in 40 mL of ether. After being kept for 4 h at room temperature and for an additional 30 min at refluxing temperature, the reaction mixture was treated with 50 mL of ethanol to decompose the residual Grignard reagent and the whole was poured into 200 mL of 5% aqueous solution of hydrochloric acid. The organic layer was separated, dried with sodium sulfate, and evaporated. The residue was separated by preparative thin-layer chromatography (silica gel, 50% benzene/hexane, R_f 0.6) and after recrystallization from methanol 1.2 g (8% yield) of **4** was obtained as colorless crystals: mp 77–80 °C; NMR ($CDCl_3$) δ 7.00 (2 H, s, arom), 6.80 (2 H, s, arom), 3.20–2.50 (3 H, m, $\mathbf{CH}(CH_3)_2$), 2.27 (3 H, s, *p*-CH_3), 2.20 (6 H, s, *o*-CH_3), 1.24 (6 H, d, *J* = 7 Hz, *p*-$CH(\mathbf{CH_3})_2$), 1.13 (12 H, d, *J* = 7 Hz, *o*-$CH(\mathbf{CH_3})_2$); IR ($CDCl_3$) 1640 cm^{-1} (C═O).

Anal. Calcd for $C_{25}H_{34}O$: C, 85.66; H, 9.78. Found: C, 85.90; H, 9.98.

MMPI Calculation. The MMPI calculation was carried out on the FACOM M-200 computer at the Data Processing Center of Kyoto University. A MMPI program (QCPE PROGRAM No 318) that Professor Ōsawa of Hokkaido University kindly provided us was used.[13] The obtained steric energies for the ground and the transition states are summarized in Table II.

Registry No. 1a, 76893-80-6; **1b**, 76893-81-7; **1c**, 74766-25-9; **1d**, 33574-11-7; **1e**, 76893-83-9; **1f**, 74766-27-1; **1g**, 76893-84-0; **3**, 78823-28-6; **4**, 78823-29-7; **5**, 78823-30-0; **6**, 78823-31-1; 1,3,5-triisopropylbenzene, 717-74-8; 4-*tert*-butylbenzoyl chloride, 1710-98-1; 4-methylbenzoyl chloride, 874-60-2; 4-(carbomethoxy)benzoyl chloride, 7377-26-6; 4-(trifluoromethyl)benzoyl chloride, 329-15-7; 4-cyanobenzoyl chloride, 6068-72-0; 2-methylbenzoyl chloride, 933-88-0; 2-naphthalenecarbonyl chloride, 2243-83-6; 1-naphthalenecarbonyl chloride, 879-18-5; 2,4,6-triisopropylbromobenzene, 21524-34-5; 2,4,6-trimethylbenzoyl chloride, 938-18-1.

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