Registry No. **1a**, 117860-73-8; **1b**, 117860-74-9; **1c**, 117860-75-0; **1d**, 117860-76-1; **1e**, 117860-77-2; **1f**, 117860-78-3; **1g**, 117860-79-4; **1h**, 117860-80-7; **1i**, 117860-81-8; **2a**, 117860-82-9; **2b**, 117860-83-0; **2c**, 117860-84-1; **2d**, 117860-85-2; **2e**, 117860-86-3; **2f**, 117860-87-4; **2g**, 117860-88-5; **2h**, 117860-89-6; **2i**, 117860-90-9; Me_3SnH, 1631-73-8.

Photochemistry of Bichromophoric Aromatic Diketones: The Effect of Methylene Chain

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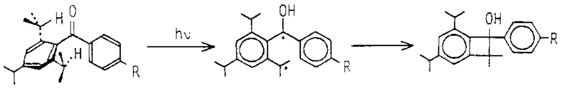
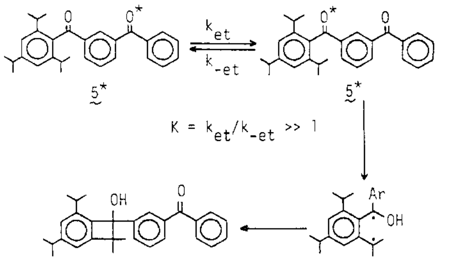
Reaction mechanism for photocyclization of 2,4,6-triisopropylbenzophenone (TIBP, **3**) into its benzocyclobutenol has been studied in great detail (eq 1).[1-3] Subsequent studies on bichromophoric *m*-acyl-substituted TIBP such as **5** have revealed[4] that two constituent carbonyl groups in the molecule are relatively independent because of their cross-conjugation, e.g., the absorption spectrum of **5** is approximately equal to the sum of the absorption spectra of benzophenone BP (**1**) and TIBP. Furthermore, it has been deduced from quenching experiments of the reaction that the triplet excitation is rapidly equilibrated between the two carbonyl groups in the molecule, with the equilibrium highly shifted toward the hindered carbonyl group ($k_{\text{et}} \gg k_{-\text{et}}$ in eq 2). The preferential energy transfer toward the hindered carbonyl group was explained on the basis of entropy considerations.[4]

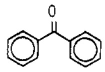


(1)



(2)

It has recently been reported that, for conjugated polyenes or polyynes bearing a suitable chromophore at each end, very efficient energy transfer or charge transfer is possible through the conjugated linker.[5] Considering the potential utility of these conjugated molecules as novel molecular electronic devices for memory and switching, we are interested in the mechanism of the totally efficient intramolecular energy migration in diketone **5**. In this connection, we now studied the photochemistry of bichromophoric aromatic diketones **6a–c**, where the two chromophores are separated by one to three methylene groups. Phosphorescence and photocyclization quantum yield studies suggest that the efficiency for intramolecular energy transfer is **6c** > **6b** ≳ **6a**.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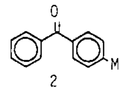
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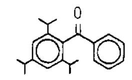
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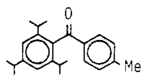
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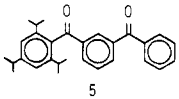
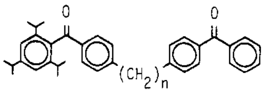
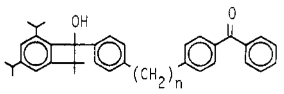

5


6a - c


7a - c

a, n = 1; b, n = 2; c, n = 3

Results

Spectroscopic Study. Phosphorescence spectra of diketones **6a–c** were measured in rigid glasses at 77 K ([**6**] ~ 10^{-3} M). Their shapes and positions of emission maxima were very similar to those of BP. Triplet energies (E_T) estimated from the phosphorescence 0–0 band, the relative phosphorescence intensities, and the absorption maxima of π,π^* and n,π^* bands for **6a–c** are summarized in Table I. The data for reference compounds **1–5** are also listed in the same table for comparison.

Preparative Photolyses. Irradiations of diketones **6a–c** in benzene solutions (0.01–0.05 M) with the Pyrex-filtered light for 10 h produced the corresponding benzocyclobutenols **7a–c**. The products were isolated by column chromatography on silica gel. Product balance was excellent in each case (isolation yield: 90% for **7a**, 84% for **7b**, 80% for **7c**).

Quantum Yields. Degassed benzene solutions of **6a–c** (0.001–0.05 M) were irradiated on a merry-go-round apparatus with the potassium chromate filtered light (mainly 313 nm) at 25 °C. The products **7a–c** were analyzed by HPLC, and their quantum yields Φ_{CB} were calculated with reference to the photocyclization of **3** (Φ_{CB} = 0.60 at 0.1 M[1]). The results are summarized in Table II.

Discussion

The n,π^* and π,π^* absorption spectra of diketones **6a–c** (Table I) are approximately equal in both wavelength and absorption coefficient to the combined spectrum of 4-methylbenzophenone (**2**) and 4-methyl-2′,4′,6′-triisopropylbenzophenone (**4**). Thus, any ground-state intramolecular electronic interactions between the two benzophenone chromophores are not detectable from the absorption spectra of **6a–c**.

The phosphorescence intensities for **6a** and **6b** in ethanol glass or methylcyclohexane (MC) glass at 77 K are moderate: their relative intensities are 0.2–0.4 as compared with that of BP (1.0) (Table I). The phosphorescence intensity for **6c** is also moderate in ethanol glass (the relative intensity, 0.32). In MC glass, in contrast, **6c** is weakly phosphorescent, and its intensity (0.053) is as low as that of TIBP (0.039). The low quantum yield of emission for TIBP is ascribable to intramolecular hydrogen abstraction.[1-3] The moderate but reduced phosphorescence efficiency for **6a** and **6b** (and **6c** in ethanol) as compared with BP is not surprising, because some of the light is absorbed directly by the isopropyl-substituted benzophenone chromophore.

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(1) Ito, Y.; Umehara, Y.; Hijiya, T.; Yamada, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1980**, *102*, 5917.

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

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

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(5) (a) Effenberger, F.; Schlosser, H.; Bauerle, P.; Maier, S.; Port, H.; Wolf, H. C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 281. (b) Stiegman, A. E.; Miskowski, V. M.; Perry, J. W.; Coulter, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 5884.

0022-3263/89/1954-0506$01.50/0

Table I. Triplet Energies, Phosphorescence Intensities, and Absorption Maxima of π,π^* and n,π^* Bands

	E_T, kcal/mol[a] (relative intensity)[b]		
compd	ethanol	MC	λ_{max}, nm (ϵ)[c]
6a	68.7 (0.33)	68.3 (0.20)	258 (40 000), 345 (289)
6b	68.9 (0.42)	68.4 (0.20)	255 (32 300), 345 (245)
6c	68.8 (0.32)	68.3 (0.053)	255 (34 100), 345 (248)
1[d]	68.9 (1.00)	68.4 (1.00)	248 (19 400), 346 (120)
2	69.2[e]	68.7[e]	252 (18 800), 345 (160)
3[d]	~69 (0.022)	68.5 (0.039)	242 (15 700), 349 (63)
4[d]	70.4	not measured	253 (20 600), 348 (74)
5[d]	68.6 (0.015)	68.0	233 (38 000), 351 (152)

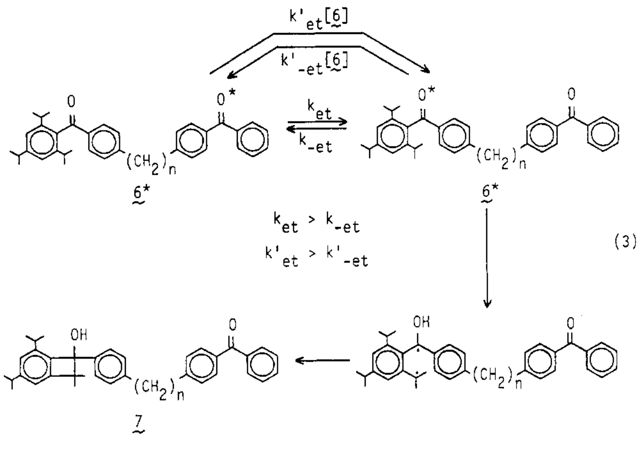
[a] Estimated from phosphorescence *O–O* band in ethanol or methylcyclohexane (MC) glass at 77 K. [b] Relative phosphorescence intensity at 77 K (1.00 for benzophenone (1)). [c] In MC at room temperature. [d] Reference 4. [e] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1975.

The very weak phosphorescence of **6c** in MC glass is probably ascribable to the efficient intramolecular energy transfer from the BP moiety to the TIBP moiety, i.e., the electronic excitation is efficiently localized at the TIBP moiety rather than at the BP moiety. This result further confirms the previous[4] conclusion that energy migration among several aromatic carbonyl groups tends to occur toward a more hindered carbonyl group. Since diketone **6c** has a three-methylene spacer, a rapid intramolecular triplet energy transfer by the exchange mechanism is possible via a sandwich-type conformation (the $n = 3$ rule).[6] (However, it should be mentioned that the $n = 3$ rule is not always true for intramolecular triplet energy transfer.[7]) In ethanol glass, where **6c** is moderately phosphorescent, the existence of its sandwich conformer appears to be unimportant. This is understandable by assuming that ethanol is a good solvent for **6c** and that MC is a poor solvent for **6c**. A good solvent will disrupt the sandwich conformation by solvation.[6a,8]

In the case of **6a** and **6b** having a short methylene chain ($n = 1$ or 2), an optimum sandwich conformation is geometrically prevented. As a result, the intramolecular energy migration will be slow, and the excited BP moiety will have time to emit phosphorescence.

Inspection of Table II reveals that Φ_{CB} for **6a** decreases (from 0.58 to 0.39) with decreasing concentration of **6a** (from 0.05 to 0.0025 M). A similar trend is observable for **6b** to some extent. By contrast, Φ_{CB} for **6c** (0.39–0.36) is essentially independent of the concentration (0.05–0.001 M). These differences can be explained by the mechanism in eq 3.

In this mechanism, $k_{et} > k_{-et}$ and $k'_{et} > k'_{-et}$.[4] The rates for the intramolecular energy migration processes (k_{et} and k_{-et}) should be independent of the concentration of **6**, while those for the intermolecular ones (k'_{et}[**6**] and k'_{-et}[**6**]) are of course concentration-dependent. However, as aforementioned, the intramolecular energy migration is very rapid only for **6c**, owing to the substantial population of its sandwich conformation. Therefore, in the case of **6c**, contribution of the intermolecular processes is presumably negligible, resulting in the concentration-independent Φ_{CB} as observed (Table II). In the case of **6a**, the intermolecular processes are probably competitive with the intramolecular ones, resulting in the concentration-dependent Φ_{CB}. An intermediate situation is expected for **6b**.



(3)

The phosphorescence results refer to a frozen system where conformations accessible in fluid solution may not be present. Thus, while intramolecular energy transfer may not be possible at 77 K, it may be occurring in fluid solution. Consequently conclusions concerning energy transfer efficiency at low temperature may not be applicable at room temperature. In the above explanation of Φ_{CB}, however, we did not consider this possibility. Further study is required to elucidate this problem.

It is known that nearly thermoneutral intramolecular energy migration between two aromatic carbonyl groups can be very rapid ($>10^9$ s^{-1})[9] and is faster than analogous intermolecular energy migration ($\sim10^8$ M^{-1} s^{-1}).[10] These energy transfers are thought to occur by the usual exchange mechanism.

The mechanism for the intramolecular energy transfer in the cross-conjugated bichromophoric molecule **5** is unknown. The experimental results only suggest that the rate is extremely rapid and the excitation is virtually equilibrated between the two chromophores prior to relaxation to the ground state.[4,11] For bichromophoric molecules with a conjugated polyene spacer, the electronic excitation is efficiently transferred via the polyene chain, irrespective of the chain length.[5a] In these cases, it is concluded that the transfer is not of the exchange type.

For present phosphorescence and quantum yield studies on **6a–c** suggest that the intramolecular energy migration is less (compared with **6c**) efficient for **6a** and **6b**, which bear a one-methylene or a two-methylene spacer, respectively. On the other hand, for **6c**, which carries a three-methylene spacer, the intramolecular energy migration is efficiently occurring via a sandwich conformation, probably through the exchange mechanism.

Experimental Section

^{1}H NMR spectra were obtained on a Varian T-60 or a JEOL GX-400 spectrometer employing CDCl$_3$ as the solvent. IR, UV,

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(8) However, solvent effects on the $n = 3$ rule are as yet to be elucidated: cf. Siemiarczuk, A.; McIntosh, A. R.; Ho, T.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224 and references cited therein.

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(10) (a) Maharaj, U.; Winnik, M. A. *Chem. Phys. Lett.* **1981**, *82*, 29. (b) Encinas, M. V.; Scaiano, J. C. *Ibid.* **1979**, *63*, 305. (c) Fang, F.; Fukuda, R.; Brown, R. E.; Singer, L. A. *J. Phys. Chem.* **1978**, *82*, 246.

(11) The triplet lifetimes of BP,[12] TIBP,[13] and **5**[13] in benzene at room temperature are 6900, 332, and 480 ns, respectively.

(12) Wolf, M. W.; Brown, R. E.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 526.

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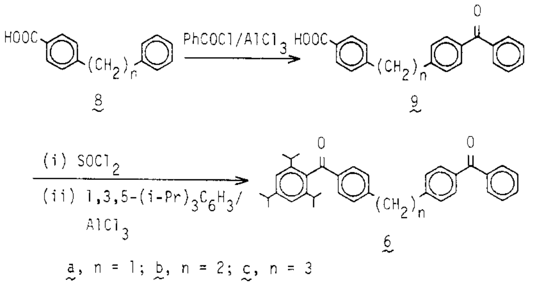
Table II. Quantum Yields for Cyclobutenol Formation Φ_{CB} at Several Concentrations in Benzene[a]

	concentration, M					
compd	0.1	0.05	0.01	0.005	0.0025	0.001
6a		0.58	0.47	0.44	0.39	
6b		0.57	0.57	0.53		0.47
6c		0.39	0.36	0.38		0.37
3[b]	0.60	0.57	0.61	0.59		

[a] Estimated maximum error of relative values, ±0.02. [b] Reference 2.

mass, and emission spectra were obtained on JASCO IRA-1, Shimadzu UV-240, JEOL JMS-DX 300, and Shimadzu RF-500 spectrometers, respectively. Thin-layer chromatography was done on a Merck TLC plastic sheet precoated with silica gel 60 F_{254} (for analytical purposes) or on a Merck Kieselgel 60 PF_{254} (for preparative purposes). Column chromatography was carried out on silica gel (Wakogel C-200). HPLC analyses were performed with a JASCO Twinkle chromatograph, with a silica gel column (SS-05) and with hexane–ethyl acetate eluent.

The diketones **6a–c** were prepared as outlined in eq 4.



(4)

4-(4-Benzoylbenzyl)benzoic Acid (9a). This compound was prepared according to the reported procedure.[14] **9a**: colorless crystals; mp 185.5–188.5 °C (lit.[14] mp 181.5–182.5 °C); NMR (60 MHz) δ 8.1–7.15 (13 H, m, arom), 4.10 (2 H, s, CH_2); IR (Nujol) 1695 and 1660 cm^{-1} (C=O).

4-[2-(4-Benzoylphenyl)ethyl]benzoic Acid (9b) and 4-[3-(4-benzoylphenyl)propyl]benzoic acid (9c) were prepared by a similar procedure to that for the preparation of **9a**.[14] Thus, to a well-stirred solution containing 8.5 g (35 mmol) of 4-(3-phenylpropyl)benzoic acid (**8c**)[15] and 25 g (190 mmol) of aluminum chloride in carbon disulfide (70 mL) was added dropwise 8.4 g (60 mmol) of benzoyl chloride in carbon disulfide (30 mL) over a period of 1 h at room temperature. The mixture was heated under reflux for 2 h, and after being cooled it was poured over ice–water containing 100 mL of concentrated hydrochloric acid (30%). After extraction with ether, the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ and then with water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was fractionally crystallized from acetone to afford 5.8 g (47%) of **9c**: mp 110–115 °C; NMR (60 MHz) δ 8.1–7.0 (13 H, m), 2.8–2.5 (4 H, m), 2.3–1.7 (2 H, m); MS, *m/e* (relative intensity) 344 (M^+, 16), 300 (29), 209 (55), 196 (100), 105 (56).

Similarly, **9b** was obtained from 4-(2-phenylethyl)benzoic acid (**8b**)[16] in 50% yield. **9b**: NMR (60 MHz) δ 8.1–7.0 (13 H, m), 2.98 (4 H, s); IR (Nujol) 1695 and 1650 cm^{-1} (C=O); MS, *m/e* (relative intensity) 330 (M^+, 19), 195 (100).

4′-(4-Benzoylbenzyl)-2,4,6-triisopropylbenzophenone (6a). The acid **9a** (4.8 g, 15 mmol) was dissolved in 50 mL of thionyl chloride and was allowed to reflux for 7 h. The reaction mixture was evaporated under reduced pressure to remove the excess thionyl chloride. The resulting residue exhibited a characteristic IR absorption of acid chloride: IR (neat) 1780, 1750, 1660 cm^{-1}.

To a well-stirred solution containing the above residue and 2.7 g (20 mmol) of aluminum chloride in carbon disulfide (30 mL) was added dropwise 6 g (28 mmol) of 1,3,5-triisopropylbenzene in carbon disulfide (20 mL) over a period of 30 min at room temperature. The mixture was stirred for additional 4 h at room temperature. After usual workup (pouring into ice–water containing hydrochloric acid, extraction with ether, washing, drying and evaporation), the residue was recrystallized from hexane to furnish 3.8 g (48%) of diketone **6a**. Further purification was carried out by preparative TLC, followed by recrystallization from hexane. **6a**: colorless crystals, mp 79–80 °C (hexane); NMR (60 MHz) δ 7.84–7.06 (13 H, m) and 7.00 (2 H, s) for aromatic protons, 4.09 (2 H, s, CH_2), 2.91 (1 H, sep, J = 7 Hz, CH), 2.52 (2 H, sep, J = 7 Hz, CH), 1.30 (6 H, d, J = 7 Hz, *p-i*-Pr methyl), 1.13 (12 H, br t, *o-i*-Pr methyl[17]); IR (Nujol) 1665 cm^{-1} (C=O); MS, *m/e* (relative intensity) 502 (M^+, 33), 307 (100); HRMS calcd for $C_{36}H_{38}O_2$ 502.2871, found 502.2843. Anal. Calcd for $C_{36}H_{38}O_2$: C, 86.02; H, 7.62. Found: C, 85.94; H, 7.58.

4′-[2-(4-Benzoylphenyl)ethyl]-2,4,6-triisopropylbenzophenone (6b) and 4′-[3-(4-benzoylphenyl)propyl]-2,4,6-triisopropylbenzophenone (6c) were prepared in a similar manner as described above for **6a**. Yields were 44 and 50%, respectively.

6b: colorless crystals, mp 128–129 °C (hexane); NMR (400 MHz) δ 7.78–7.21 (13 H, m) and 7.07 (2 H, s) for aromatic protons, 3.02 (4 H, s, CH_2), 2.94 (1 H, sep, J = 6.8 Hz, CH), 2.63 (2 H, sep, J = 6.8 Hz, CH), 1.29 (6 H, d, J = 6.9 Hz, *p-i*-Pr methyl), 1.17 (6 H, d, J = 6.8 Hz, *o-i*-Pr methyl[17]), 1.05 (6 H, d, J = 6.8 Hz, *o-i*-Pr methyl[17]); IR (Nujol) 1660 cm^{-1} (C=O); MS, *m/e* (relative intensity) 516 (M^+, 70), 473 (36), 320 (56), 307 (100); HRMS calcd for $C_{37}H_{40}O_2$ 516.3029, found 516.3063. Anal. Calcd for $C_{37}H_{40}O_2$: C, 86.00; H, 7.80. Found: C, 85.89; H, 7.83.

6c: oil; bp 195 °C (0.01 mmHg); NMR (400 MHz) δ 7.80–7.25 (13 H, m) and 7.06 (2 H, s) for aromatic protons, 2.93 (1 H, sep, J = 6.8 Hz, CH), 2.77–2.71 (4 H, m, CH_2), 2.63 (2 H, sep, J = 6.9 Hz, CH), 2.03 (2 H, quin, J = 7.7 Hz, CH_2), 1.29 (6 H, d, J = 6.8 Hz, *p-i*-Pr methyl), 1.17 (6 H, d, J = 6.9 Hz, *o-i*-Pr methyl[17]), 1.06 (6 H, d, J = 6.9 Hz, *o-i*-Pr-methyl[17]); IR (neat) 1660 cm^{-1} (C=O); MS, *m/e* (relative intensity) 530 (M^+, 22), 487 (100), 307 (66), 105 (67); HRMS calcd for $C_{38}H_{42}O_2$ 530.3183, found 530.3159. Anal. Calcd for $C_{38}H_{42}O_2$: C, 85.99; H, 7.98. Found: C, 85.77; H, 7.99.

Preparative Photolyses. Irradiations were carried out with a 400-W high-pressure mercury lamp through a Pyrex filter under bubbling nitrogen. A typical procedure for **6b** is as follows. A solution of **6b** (604 mg, 1.17 mmol) in benzene (100 mL) was irradiated for 15 min. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel. Elution with benzene afforded 507 mg (84%) of benzocyclobutenol **7b**, which was recrystallized from hexane to give colorless crystals. Similar irradiations of **6a** and **6c** afforded **7a** (90%) and **7c** (80%), respectively.

7a: colorless crystals; mp 117–119 °C (hexane); NMR (60 MHz) δ 7.9–6.9 (13 H, m), 6.99 (1 H, s) and 6.80 (1 H, s) for aromatic protons, 4.01 (2 H, s, CH_2), 2.87 (2 H, sep, J = 7 Hz, CH), 2.53 (1 H, s, OH), 1.44 (3 H, s, CH_3), 1.26 (6 H, d, J = 7 Hz, CH_3), 1.22 (3 H, d, J = 7 Hz, CH_3), 1.15 (3 H, d, J = 7 Hz, CH_3), 0.82 (3 H, s, CH_3); IR (Nujol) 3520 (OH), 1660 cm^{-1} (C=O); UV (cyclohexane) λ 256 (ε 17100), 345 (189) nm; MS, *m/e* (relative intensity) 502 (M^+, 22), 307 (100); HRMS calcd for $C_{36}H_{38}O_2$ 502.2871, found 502.2882. Anal. Calcd for $C_{36}H_{38}O_2$: C, 86.02; H, 7.62. Found: C, 86.30; H, 7.60.

7b: colorless crystals; mp 126–127.5 °C (hexane); NMR (400 MHz) δ 7.78–7.07 (13 H, m), 7.06 (1 H, s) and 6.88 (1 H, s) for aromatic protons, 3.02–2.92 (4 H, A_2B_2 m, CH_2), 2.92 (2 H, sep, J = 7.0 Hz, CH), 2.53 (1 H, broad s, OH), 1.45 (3 H, s, CH_3), 1.28 (6 H, d, J = 7.0 Hz, CH_3), 1.22 (3 H, d, J = 6.9 Hz, CH_3), 1.17 (3 H, d, J = 7.0 Hz, CH_3), 0.81 (3 H, s, CH_3); UV (cyclohexane) λ 345 (ε 161) nm; MS, *m/e* (relative intensity) 516 (M^+, 35), 473

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(30), 320 (64), 307 (100); HRMS calcd for $C_{37}H_{40}O_2$ 516.3028, found 516.3046.

7c: oil; NMR (400 MHz) δ 7.80–7.11 (13 H, m), 7.06 (1 H, s) and 6.88 (1 H, s) for aromatic protons, 2.91 (2 H, sep, $J = 7.1$ Hz, CH), 2.72 (2 H, t, $J = 7.7$ Hz, CH_2), 2.67 (2 H, t, $J = 7.6$ Hz, CH_2), 2.52 (1 H, broad s, OH), 1.99 (2 H, quin, $J = 7.7$ Hz, CH_2), 1.45 (3 H, s, CH_3), 1.27 (6 H, d, $J = 7.1$ Hz, CH_3), 1.23 (3 H, d, $J = 7.1$ Hz, CH_3), 1.17 (3 H, d, $J = 7.1$ Hz, CH_3), 0.81 (3 H, s, CH_3); UV (cyclohexane) λ 344 (ε 151) nm; MS, *m/e* (relative intensity) 530 (M^+, 12), 487 (100), 307 (64), 105 (51); HRMS calcd for $C_{38}H_{42}O_2$ 530.3184, found 530.3092.

Quantum Yields. Solutions containing diketones **6a–c** in benzene (0.001–0.05 M) were placed in 17 × 120 mm Pyrex tubes and degassed by four freeze–thaw cycles below 10^{-2} mmHg. These samples were irradiated on a merry-go-round apparatus at 25 °C. The light that was isolated from a 400-W high-pressure mercury lamp with a K_2CO_3 (1.3%)–K_2CrO_4 (0.13%) filter solution (mainly 313 nm) was employed. The benzocyclobutenols **7a–c** produced (conversion <5%) were analyzed by HPLC by using diphenylsulfone as an internal standard. The benzocyclobutenol formation from **3** in benzene solution (0.1 M) was used as actinometry ($\Phi_{CB} = 0.60$). The light absorbed by each sample was corrected by a factor $(1 - 10^{-A})$, where A is the absorbance of the solution ($A = \epsilon cl$: $\epsilon = \epsilon$ at 313 nm, c = the initial concentration of **6a–c** or **3**, $l = 1$ cm).

Simple Direct Titration of Organolithium Reagents Using *N*-Pivaloyl-*o*-toluidine and/or *N*-pivaloyl-*o*-benzylaniline

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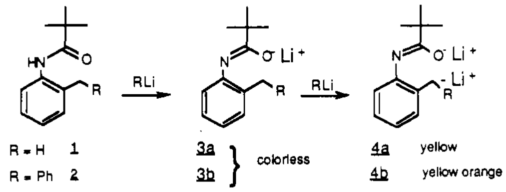
During the last decade, the use of alkyl- and aryllithium reagents in organic synthesis has increased as the result of important developments of the chemistry of many organometallic species. Accurate determination of the concentration of the reagents is generally necessary to generate reactive intermediates. Several methods[2-10] of titration have been described; some of them use the formation of a colored dianion species at the end point. The Gilman and Cartlege[2] and the diphenylacetic[7] methods are the most widely used. Recently, Juaristi et al.[10] reported a method for the determination of alkyllithium concentration based on the use of 4-biphenylmethanol as reagent indicator.

We report here a new and efficient method for the accurate determination of organolithium species by direct titration. We noticed that when **1**[1] or **2**[1] in THF is treated with organolithium reagents, the initial reaction produces a colorless solution of the enamide **3a** or **3b**, but when the formation of the enamide is complete, a drop of the organolithium species immediately gives an intense yellow or yellow-orange color due to the formation of the dianion **4a** or **4b** (Scheme I). We emphasize that the solution containing the reagent indicator **1** or **2** is completely colorless, even after addition of 0.992 equiv of the alkyllithium species. This is not the case for the simple methods described in the literature. *N*-pivaloyl-*o*-toluidine and *N*-pivaloyl-*o*-benzylaniline are easily accessible from commercially available compounds in one step in gram quantities. They are crystalline compounds, nonhygroscopic, stable, and may be stored without any special precautions.

Scheme I



The visible spectra of the colored solutions obtained when **1** and **2** were treated with 1.05 equiv of BuLi (THF, room temperature) show an absorption with $\lambda_{max} = 435$ and 440 nm, respectively. By comparison, the dianion of 4-biphenylmethanol shows an absorption at $\lambda_{max} = 483$ nm in THF at 20 °C.[10]

The titration results are summarized in Table I. In the case of tBuLi, addition of 1 equiv of tBuOLi did not change the result, indicating that there is no interaction between the reagent and a strong lithium alkoxide. The titration of MeLi with **1** does not display an as intensely colored end point as that of BuLi or tBuLi. Nevertheless, satisfactory results are obtained. We noticed that when **1** is used for the titration of PhLi, the end point is not sharp. This fact is probably due to the lower basicity of PhLi compared to the other alkyllithium reagents. Thus although **1** is not suitable for titration of PhLi, good results are obtained with reagent **2**. In all titrations attempted thus far, with the sole exception of PhLi and **1**, good agreement was found between this method and other commonly used analytical procedures.

Experimental Section

Tetrahydrofuran was distilled from sodium/benzophenone, and dichloromethane was distilled from CaH_2 prior to use. Organolithium reagents were purchased from Aldrich Chemical Co. and Janssen Chemicals. Compounds **1** and **2** were synthesized as describe below. *o*-Toluidine, *o*-benzylaniline, and pivaloyl chloride were purchased from Aldrich Chemical Co. and were not purified

Table I. Comparative Titrations of Organolithium Reagent[i]

RLi	1	2	ref 2	ref 7	ref 3	ref 10	total base[k]	nom value
BuLi[a]	1.64	1.65	1.71	1.61	1.69	1.65	1.87	1.60[g]
BuLi[b]	2.37	2.35	2.38	2.36	2.49	2.29	2.50	1.60[g]
sBuLi[c]	1.31	1.30	1.24	1.32	1.09	1.20	1.46	1.30[g]
tBuLi[a]	1.88	1.87	1.90	1.88	1.61	1.62	2.09	1.70[g]
tBuLi[d] + tBuOLi	1.88							
MeLi[e]	1.42	1.47	1.48	1.49	1.51	1.46	1.56	1.60[h]
MeLi[f]		1.43	1.50	1.51	1.68		1.86	1.60[h]
PhLi		0.94	1.05	0.95	1.04	0.89[j]	2.05	2.00[g]

[a] New bottle without any sediment. [b] The bottle had previously been opened and some solvent had evaporated. [c] New bottle, brown solution. [d] One equivalent of tBuOLi was added to the THF solution containing the reagent 1. [e] Clear solution, the bottle has been opened and used, no sediment. [f] *Old bottle but never opened and containing a lot of sediment.* [g] From Aldrich C^{ie}. [h] From Janssen C^{ie}. [i] Average of three determinations. [j] The end point was not very clear. [k] Titration using 0.1 N hydrochloric acid solution with phenolphthalein as indicator after hydrolysis of 5-mL aliquot of the organolithium solution by 10 mL of distilled water.

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