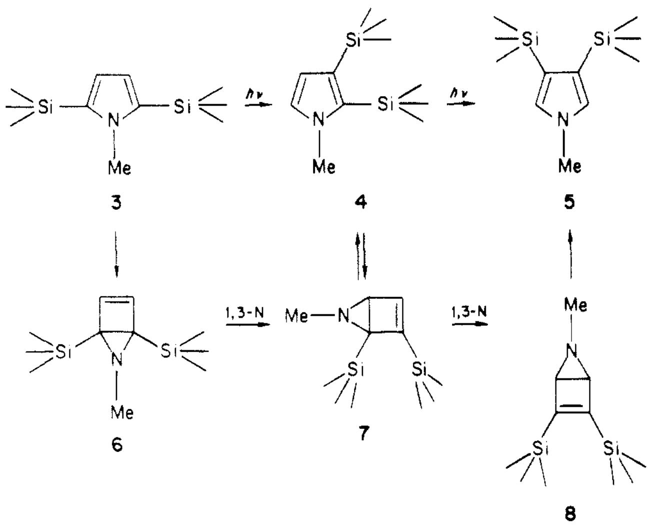
Scheme I



or 920 or Fischer/Victoreen Series 4400 gas chromatograph. GC yields were determined with internal standards and predetermined response factors. All melting points (mp) were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of 2-(Trimethylsilyl)thiophene and 2,5-Bis(trimethylsilyl)thiophene. To 1.05 g (0.025 mol) of freshly distilled thiophene in 125 mL of Et_2O was added 0.026 mol of *n*-butyllithium in hexane at 0 °C. After the mixture was stirred for 1 h at 25 °C, 3.3 mL (0.026 mol) of trimethylchlorosilane was added and stirring was continued for 8 h. Following extraction of the reaction mixture with saturated aqueous NaCl, the organic layer was dried (Na_2SO_4). Removal of the solvent and distillation of the residue (79 °C (35 torr)) afforded pure 2-(trimethylsilyl)thiophene (76%), which was identified by NMR and MS comparison to previously reported spectra.[6] 2,5-Bis(trimethylsilyl)thiophene was prepared in analogous fashion from 1.02 g (0.025 mol) of thiophene, 0.052 mol of *n*-butyllithium, and 0.052 mol (6.6 mL) of trimethylchlorosilane. Distillation (62 °C (15 torr)) afforded 4.3 g (75%) of pure 2,5-bis(trimethylsilyl)thiophene, which was also identified by spectral comparison to those previously reported:[6] UV (CH_3CN) λ_{max} 235 nm (9951).

Preparation of *N*-Methyl-2-(trimethylsilyl)pyrrole (1) and *N*-Methyl-2,5-bis(trimethylsilyl)pyrrole (3). To 5.0 mL (0.056 mol) of *N*-methylpyrrole in 200 mL of Et_2O was added 0.056 mol of *tert*-butyllithium. After the mixture was stirred at 25 °C for 12 h, 6.27 g (0.058 mol) of trimethylchlorosilane was added. Following an additional 2 h of stirring, the crude reaction mixture was extracted with saturated aqueous NaCl, and the organic phase was separated and dried over Na_2SO_4. Removal of the solvent and distillation (70 °C (13 torr)) afforded 4.2 g (48%) of pure **1**, which was identified by comparison of its NMR and IR spectra to those previously reported.[6] In similar fashion, **3** was prepared from 1.5 mL (0.017 mol) of *N*-methylpyrrole, 0.040 mol of *tert*-butyllithium, and 4.5 mL (0.040 mol) of trimethylchlorosilane. Distillation (95 °C (12 torr)) afforded pure **3** as a solid. Recrystallization from hexane gave 1.7 g (44%) of **3**: mp 75–76 °C, lit.[6] mp 76–77 °C. Spectral features matched those previously reported: UV (CH_3CN) λ_{max} 235 nm (10471).

General Procedure for Photolysis. All solvents were previously distilled from LAH under a nitrogen atmosphere. Irradiations were typically carried out on two scales: NMR and preparative. In a quartz NMR tube sealed with a septum were placed 50 μL of the material being irradiated and 750 μL of pentane. After degassing with a stream of argon, the sample was positioned adjacent to the water-cooled, quartz immersion well of a 450-W Hanovia mercury arc lamp and irradiated. The reaction progress was monitored by ^{1}H NMR and IR. Preparative scale reactions were performed with a 200-mL capacity reaction vessel that jacketed the quartz immersion well. Into the reaction vessel was placed 150 mL of pentane and 1.5 mL of the material being photolyzed. After degassing with argon for 20 min, the solution was irradiated with a 450-W Hanovia lamp. The reaction progress was monitored with ^{1}H NMR, GC, and IR. After irradiation was complete, the photolysate was transferred to a 250-mL flask, via a double-tipped needle, and the pentane removed under vacuum to leave 3–5 mL of residue. Low-temperature irradiations were performed by cooling the NMR tube or reaction vessel with a dry ice/2-propanol bath.

Irradiation of *N*-Methyl-2-(trimethylsilyl)pyrrole (1). Pyrrole **1** (1.39 g) in 150 mL of degassed pentane was irradiated for 50 min. ^{1}H NMR and GC analysis of the yellow photolysate revealed trace amounts of unreacted **1** and clean formation of only one product that was isolated by preparative GC (10-ft 15% SE-30). Based on its spectral data, this product was identified as **2**: 84%; NMR (CCl_4) δ 0.03 (s, 9 H), 3.45 (s, 3 H), 6.03 (t, 1 H, J = 2 Hz), 6.42 (m, 2 H); ^{13}C NMR δ -0.1, 35.4, 113.4, 122.9, 127.3; IR (neat) 3100, 2960, 1510, 1420, 1245, 1130, 840 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 153 (22), 138 (100), 94 (6.2), 73 (2.4), 69 (13), 59 (11); calculated for $C_8H_{15}NSi$ 153.09738, measured 153.09730. Irradiation of **1** (50 μL) also afforded exclusive formation of **2**.

Irradiation of *N*-Methyl-2,5-bis(trimethylsilyl)pyrrole (3). Pyrrole **3** (50 μL in 600 μL of pentane) was entirely consumed after 50-min irradiation, and two products, identified as **4** and **5**, were cleanly formed. Continued irradiation resulted in complete disappearance of **4** with a concomitant increase in the amount of **5**. A repeat of this reaction on a larger scale (0.50 g of **3**, 150 mL of pentane, 35 min of irradiation) allowed isolation of **4** and **5** by preparative GC (10-ft 20% OV101). **4**: 39%; NMR (CCl_4) δ 0.22 (s, 9 H), 0.35 (s, 9 H), 3.70 (s, 3 H), 6.05 (d, 1 H, J = 3 Hz), 6.58 (d, 1 H, J = 3 Hz); IR (neat) 3100, 2960, 1505, 1410, 1250, 1155, 1110, 945 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 225 (20), 210 (100), 194 (27), 147 (27), 138 (39), 73 (22); calculated for $C_{11}H_{23}NSi_2$ 225.13691, measured 225.13728. **5**: 41%; NMR (CCl_4) δ 0.21 (s, 18H), 3.71 (s, 3H), 6.58 (s, 2H); IR (neat) 3100, 2960, 1515, 1420, 1245, 1150, 1135, 1095 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 225 (30), 210 (100), 194 (23), 184 (12), 147 (56), 128 (77), 73 (42); calculated for $C_{11}H_{23}NSi_2$ 225.13691, measured 225.13651. Compound **4** (ca. 20 mg) in 400 μL of pentane was placed in a quartz NMR tube, degassed with argon, and irradiated for 1 h. Analysis of the photolysate with ^{1}H NMR indicated clean conversion (ca. 50%) to **5** had occurred. No other products were observed.

Irradiation of *N*-(Trimethylsilyl)pyrrole.[7] *N*-(Trimethylsilyl)pyrrole (50 μL in 750 μL of pentane) was irradiated for 1 h. Precipitation of a large amount of a yellow polymer was observed. Analysis of the photolysate by NMR and GC indicated only unreacted starting material. No further photolyses of *N*-(trimethylsilyl)pyrrole were attempted.

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged.

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The Benzoyloxy Radical: Attempted Photochemical Generation for Kinetic Studies and Some Relative Rate Constants[1]

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Benzoyl peroxide has been used for many years as a thermal initiator for the free-radical polymerization of vinyl

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Table I. Spin Trapping of Benzoyloxy and Phenyl Radicals by PBN in Freon 113 at 55 °C

10^2[PBN], M	$10^9(d[BA]/dt)_{t\to0}$,[a] M s^{-1}	$10^9(d[PA]/dt)_{t\to0}$,[b] M s^{-1}	$10^9(d[BA] + d[PA])/dt_{t\to0}$, M s^{-1}	$(d[BA]/dt)_{t\to0}/(d[PA]/dt)_{t\to0}$	k_2/k_1, M^{-1}
1.25	3.67	2.59	6.26	1.42	(114)[c]
3.13	5.61	1.34	6.95	4.19	(134)[c]
4.69	6.31	0.88	7.19	7.17	153
6.25	6.42	0.69	7.11	9.30	149
13.5	6.80	≤0.35[d]	≤7.15	(19.4)[e]	(144)[e]

[a] BA; a^N = 13.25 G, a^H = 1.5 G. [b] PA; a^N = 14.38 G, a^H = 2.25 G. [c] Not reliable because not all radicals are spin trapped. [d] Too small for accurate measurement. [e] Calculated assuming $(d[PA]/dt)_{t\to0} = 0.35 \times 10^{-9}$ M^{-1} s^{-1}.

monomers.[3] There is, in consequence, extensive literature dealing with the relative reactivities of various substrates toward the benzoyloxy radical and the reactivities of substrates relative to the rate of benzoyloxy decarboxylation.[4] Direct kinetic measurements on benzoyloxy are almost entirely confined to CIDNP investigations of the decarboxylation reaction.[5]

$$\mathrm{PhCO_2\cdot \rightarrow Ph\cdot + CO_2} \qquad (1)$$

The rate of this process appears to depend on the method of radical generation[5d,6] as well as on the nature of the solvent.[7] The CIDNP data with suitable peroxide precursors of $\mathrm{PhCO_2\cdot}$ yield $k_1 \sim 1 \times 10^8$ s^{-1} both at 130 °C[5a] and at 100 °C[5b] for thermolytic generation and $k_1 > 7 \times 10^9$ s^{-1} at room temperature for direct photolytic generation,[5d] while for photosensitized generation k_1 would appear to have intermediate values.[6] The thermal CIDNP k_1 values are reasonably consistent with the results of various competitive experiments at lower temperatures if we assume a "normal"[8] preexponential factor for a bond-scission reaction of $10^{16\pm1}$ s^{-1}. That is, the activation energy for reaction 1 has been estimated to be ca. 13.6 kcal/mol in a competitive addition of benzoyloxy to styrene,[9] and competitive spin trapping[10] experiments have indicated that $k_1 \sim 5 \times 10^5$ s^{-1} at 40 °C[11] and $\leq 2.5 \times 10^5$ s^{-1} at room temperature.[12]

We began work with the hope of obtaining some reliable kinetic data for the benzoyloxy radical by the technique of laser flash photolysis. Although it seemed likely that the direct photolysis of benzoyl peroxide at room temperature would not yield benzoyloxy radicals that were sufficiently long-lived for study[13-15] (i.e., if any $\mathrm{PhCO_2\cdot}$ were produced, they would not be in their ground state), it did seem possible that radicals of sufficient lifetime might be generated by a photosensitized decomposition of the peroxide. However, a kinetic study of the quenching of various triplet sensitizers by benzoyl peroxide[17] showed that such processes are too slow to produce radicals in the kinetically required "instantaneous"[18] manner. We therefore prepared 4,4′-dibenzoylbenzoyl peroxide,[19] $(4\text{-}\mathrm{C_6H_5COC_6H_4CO_2})_2$. In contrast to the related intermolecular system (i.e., benzoyl peroxide plus benzophenone) this particular peroxide has been shown to photolyze with a quantum yield approaching unity.[19] We hoped that this intramolecular sensitization would yield thermalized (ground-state) (4-benzoylbenzoyl)oxy radicals in an "instantaneous"[18] process. In the event, and using what appeared to be the optimum experimental conditions (308-nm laser photolysis of a rapidly flowing 2×10^{-3} M solution of 4,4′-dibenzoylbenzoyl peroxide in benzene at room temperature), we obtained only a transient ($\tau \sim$ 1.0–1.5 μs) absorption that was very similar to that due to benzophenone triplet.[20] This spectrum (which we believe must be due to a benzophenone type impurity in the peroxide since it seems unlikely that self-quenching could be so inefficient[19] and since the flow system removes all reaction products from the path of the laser beam between pulses) masked any absorption due to the (benzoyl-

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[3] Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957.

[4] For a comprehensive survey of kinetic data on benzoyloxy and related radicals, see: Scaiano, J. C.; Howard, J. A. in "Landolt-Börnstein. New Series. Radical Reaction Rates in Liquids"; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Part d, pp 127–141. For some more recent measurements of relative rate constants for benzoyloxy radical reactions, see e.g.,: Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 1573–1588.

[5] (a) Schwerzel, R. E.; Lawler, R. G.; Evans, G. T. *Chem. Phys. Lett.* **1974**, *29*, 106–109. (b) Den Hollander, J. A. *Chem. Phys.* **1975**, *10*, 167–184. (c) Poranski, C. F., Jr.; Moniz, W. B.; Sojka, S. A. *J. Am. Chem. Soc.* **1975**, *97*, 4275–4283. (d) Nedelec, J. Y.; Lefort, D. *Tetrahedron* **1980**, *36*, 3199–3203.

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[8] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

[9] Bevington, J. C.; Toole, J. *J. Polym. Sci.* **1958**, *28*, 413–420. See also: Suehiro, T.; Ishida, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1692–1695. This paper gives $E_1 - E(\mathrm{PhCO_2\cdot + Ph_3C\cdot})$ = 12.9 kcal/mol, the radical coupling reaction being expected to have an apparent activation energy of ca. 2 kcal/mol.

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[11] (a) Janzen, E. G.; Evans, C. A.; Nishi, Y. *J. Am. Chem. Soc.* **1972**, *94*, 8236–8238. (b) Janzen, E. G.; Evans, C. A. *Ibid.* **1975**, *97*, 205–206.

[12] Gilbert, B. C.; Holmes, R. G. G.; Marshall, P. D. R.; Norman, R. O. C. *J. Chem. Res., Synop.* **1977**, 172; *J. Chem. Res., Miniprint* **1977**, 1949–1973.

[13] Kitamura, A.; Sakuragi, H.; Yoshida, M.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1981**, *53*, 1393–1398.

[14] (a) The direct laser flash photolysis of benzoyl peroxide at room temperature has been shown to yield kinetically identifiable phenyl radicals rather than benzoyloxy radicals, see: Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609–3614. On the other hand, there are also reports that benzoyloxy and related aroyloxy radicals can be trapped (generally, though not always, at low temperatures) by the direct photolysis of appropriate peroxide precursors in solution. See, e.g.: (b) Nakata, T.; Tokumaru, K.; Simamura, O. *Tetrahedron Lett.* **1967**, 3303–3308. (c) Saltiel, J.; Curtis, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 2056–2058. (d) Cookson, P. G.; Davies, A. G.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1976**, 289–290. (e) Lunazzi, L.; Placucci, G.; Grossi, L. *J. Chem. Soc., Perkin Trans. 2* **1982**, 875–880. (f) Takahara, S.; Kitamura, A.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1983**, 1315–1318. (g) Takahara, S.; Urano, T.; Kitamura, A.; Sakuragi, H.; Kikuchi, O.; Yoshida, M.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 688–697 and references cited. (h) Benzoyloxy can also be observed by EPR spectroscopy following low-temperature photolysis of suitable peroxide crystals. See, e.g.: Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729–6743. McBride, J. M.; Merrill, R. A. *Ibid.* **1980**, *102*, 1723–1725.

[15] After this work was completed, a report appeared[16] that photolytically generated benzoyloxy radicals had been observed by a time-resolved EPR technique and that they had a lifetime of 0.25 μs at 20 °C.

[16] Yamauchi, S.; Hirota, N.; Takahara, S.; Sakuragi, H.; Tokumaru, K. *J. Am. Chem. Soc.* **1985**, *107*, 5021–5022.

[17] Ingold, K. U.; Johnston, L. J.; Lusztyk, J.; Scaiano, J. C. *Chem. Phys. Lett.* **1984**, *110*, 433–436. For a related study, see: Misawa, H.; Kitamura, A.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1167–1168.

[18] The laser experiments are carried out on the nanosecond time scale.

[19] Leffler, J. E.; Miley, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 7005–7012.

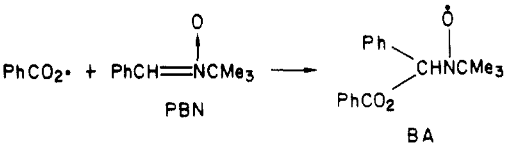
[20] This absorption showed maxima at ~320 nm (strong) and ~530 nm (weak); the former left a residual absorption, i.e., did not decay completely. Addition of the triplet quencher, piperylene, reduced τ to ≤20 ns and left a weak absorption with maxima at ~320 and ~420 nm with lifetimes of microseconds. Even if this residual absorption were due to (benzoylbenzoyl)oxy or to the expected[14b-g] benzene adduct radical, [(benzoylbenzoyl)oxy]cyclohexadienyl, it was too weak to be used to carry out quantitative kinetic investigations.

benzoyl)oxy radical or to the cyclohexadienyl radical that is expected to be formed by addition of this radical to benzene.[14b-g]

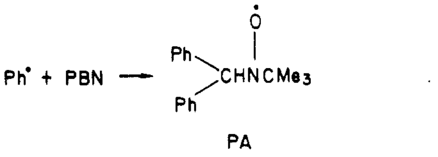
Our failure to generate kinetically identifiable benzoyloxy radicals by laser flash photolysis led us to measure relative reactivities for two benzoyloxy radical–molecule reactions by the technique of kinetic electron paramagnetic resonance (EPR) spectroscopy. The two reactions studied were chosen originally in the hope that they would serve as "standards" for determining k_1.

Results

Spin Trapping with PBN. In one of the pioneering kinetic applications of the EPR spin-trapping technique, Janzen et al.[11a] reported that during the thermal decomposition of benzoyl peroxide in the presence of *N-tert*-butyl-α-phenylnitrone (PBN) both benzoyloxy spin adducts, BA, and phenyl spin adducts, PA, were formed.



(2)



(3)

Janzen's brief report gives $k_2/k_1 = 123\ \mathrm{M}^{-1}$ at 40 °C in benzene.[11a] Our own, somewhat more detailed, study of this competition yields a k_2/k_1 ratio at 55 °C in good agreement with Janzen's result.

As our solvent we chose Freon 113, $CF_2ClCFCl_2$. This solvent should be unreactive toward $PhCO_2\cdot$ radicals and is known to be relatively unreactive toward phenyl.[14a] To trap all the radicals formed from benzoyl peroxide, Janzen et al.[11a] found that the PBN concentration had to be ≥0.075 M at 40 °C. However, at 40 °C and at such PBN concentrations we found that the [BA]/[PA] ratio was rather too large for accurate measurement. Experiments were therefore carried out at 55 °C, where reaction 1 is noticeably faster, using 1.1×10^{-2} M benzoyl peroxide and various PBN concentrations (see the Experimental Section). Measurement of the initial rates of growth of each spin adduct, i.e., of $(d[BA]/dt)_{t\to0}$ and $(d[PA]/dt)_{t\to0}$, were made and are reported in Table I. The sum of the initial rates of growth of the two spin adducts reaches a constant level of ca. $7.15 \times 10^{-9}\ \mathrm{M\ s^{-1}}$ at [PBN] ≥ 0.047 M (see Table I). This implies that all the radicals formed from the benzoyl peroxide are trapped by the PBN. Dividing this growth rate by the benzoyl peroxide concentration yields a rate constant of $6.5 \times 10^{-7}\ \mathrm{s^{-1}}$ for the thermal decomposition of benzoyl peroxide (to produce two benzoyloxy radicals) at 55 °C. This rate constant is in satisfactory agreement with literature data.[11a]

At PBN concentrations where all radicals are trapped and where the ratio of the initial rates of formation of BA and PA can be accurately determined, a simple kinetic analysis yields the relation

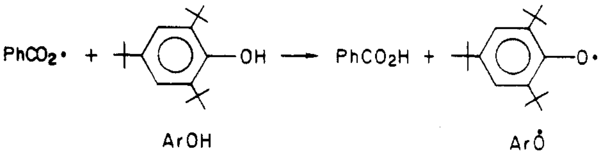
$$\frac{k_2}{k_1} = \frac{1}{[\mathrm{PBN}]}\,\frac{(d[\mathrm{BA}]/dt)_{t\to0}}{(d[\mathrm{PA}]/dt)_{t\to0}}$$

The mean value of k_2/k_1 calculated from the results obtained at the two concentrations where these conditions apply is $151\ \mathrm{M}^{-1}$, a value in good agreement with the estimate of Janzen et al. at 40 °C.[11a]

Table II. Spin Trapping of Benzoyloxy by 6.25×10^{-2} M PBN in the Presence of ArOH in Freon 113 as Solvent at 55 and 33 °C

	55 °C		33 °C	
10^2[ArOH], M	$10^9(d[BA]/dt)_{t\to0}$, M s^{-1}	k_4/k_2	$10^{10}(d[BA]/dt)_{t\to0}$, M s^{-1}	k_4/k_2
0	6.42		1.77	
0.63	3.92	6.35	0.78	12.6
1.56	2.53	6.13	0.45	11.7

Competition between PBN and ArOH for Benzoyloxy Radicals. Although PBN was not a suitable "probe"[14a] for benzoyloxy radicals in laser flash-photolysis experiments,[21] it can be employed in competitive EPR experiments to search for other potential benzoyloxy probes, using thermally generated radicals. We chose 2,4,6-tri-*tert*-butylphenol, ArOH, as the reagent to compete with PBN. This phenol, which also turned out not to be a suitable probe for laser flash experiments,[22] yields the persistent phenoxyl radical, ArO·. The EPR spectrum of ArO· does not interfere with the outside lines of the two PBN spin adduct spectra, nor does this radical add to PBN.[23]



(4)

Competitive experiments were carried out at 55 °C and also at 33 °C in Freon 113 using 1.1×10^{-2} M benzoyl peroxide as the benzoyloxy source. Two different concentrations of ArOH were employed. The PBN concentration was kept at 6.25×10^{-2} M since this is sufficient to trap all the radicals produced from the decomposition of benzoyl peroxide at 55 °C, with 90% of the trapped radicals being benzoyloxy (see Table I). Presumably an even higher percentage of benzoyloxy will be trapped at 33 °C. Initial rates of growth of the BA spin adduct were measured. The results are given in Table II. Values of k_4/k_2 were calculated from the relation

$$\frac{(d[\mathrm{BA}]/dt)_{t\to0}{}^{0}}{(d[\mathrm{BA}]/dt)_{t\to0}{}^{[\mathrm{ArOH}]}} = 1 + \frac{k_4[\mathrm{ArOH}]}{k_2[\mathrm{PBN}]}$$

In this equation, the superscripts 0 and [ArOH] refer to rates of growth in the absence and presence of ArOH. In deriving this equation, we have ignored the small fraction (10%) of benzoyloxy radicals that decarboxylate (at 55 °C) in the absence of ArOH. This fraction will be further decreased by the addition of the ArOH.

Discussion

At 55 °C our competitive EPR experiments yield $k_2/k_1 = 151\ \mathrm{M}^{-1}$ and $k_4/k_2 = 6.24$. Absolute upper limits can be put on the individual rate constants by assuming that reaction 4 has no activation energy and a preexponential factor that is "normal"[8] for a hydrogen atom transfer, i.e.,

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(21) In an attempt to use PBN as a "probe"[14a] for benzoyloxy radicals in 308-nm laser flash-photolysis experiments at concentrations in Freon 113 where, in the thermal experiments, it trapped all the benzoyloxy radicals before they decarboxylated, we have found that essentially all the light was absorbed by the PBN.

(22) The growth of the absorption due to ArO· could be readily monitored in the laser flash-photolysis experiment when generated by 337-nm photolysis of a di-*tert*-butyl peroxide/Freon 113 solution of ArOH. However, an attempt to observe the growth of this absorption using 337 nm and triphenylene to sensitize the decomposition of benzoyl peroxide was unsuccessful.

(23) Certain other potential probes gave radicals (e.g., PhS· and cyclohexadienyl) that added to PBN.

$10^{8.5\pm0.5}$ M^{-1} s^{-1}. However, such an assumption will cause the rate constants to be overestimated because preexponential factors for hydrogen atom abstraction from OH groups by oxygen-centered radicals are always found to be considerably smaller than $10^{8.5\pm0.5}$ M^{-1} s^{-1}.[24-33] Indeed, it is highly unlikely that the preexponential factor for reaction 4 would be as large as 10^8 M^{-1} s^{-1}, a value as low as 10^6 M^{-1} s^{-1} (or even 10^4 M^{-1} s^{-1}) being more in line with values that have been reported for hydrogen atom abstraction by oxygen-centered radicals, XO·, from ArOH and similar hindered phenols and for the reverse reactions between ArO· and XOH.[26,27,29,33,34] Nevertheless, to be on the safe side, we take $k_4 \le A_4 \le 10^8$ M^{-1} s^{-1}, which yields $k_2 \le 1.6 \times 10^7$ M^{-1} s^{-1} and $k_1 \le 1 \times 10^5$ s^{-1}. In connection with this *upper* limit on k_1 for *thermalized* benzoyloxy radicals at 55 °C in a hydrocarbon solvent we note that *if* the 308-nm photolysis of benzoyl peroxide gave benzoyloxy radicals, these radicals have $k_1 \ge 10^8$ s^{-1} at room temperature.[14a,35] There can be no doubt that the thermolysis and photolysis of benzoyl peroxide do not yield the same chemical species.

Experimental Section

Materials. Benzoyl peroxide, PBN, and ArOH were commercial materials that were purified by recrystallization before use. 4,4′-Dibenzoylbenzoyl peroxide was prepared by literature methods[36] from 4-benzoylbenzoic acid (Aldrich) and was also purified by several recrystallizations, mp 161 °C, lit.[19] mp 159–160 °C. Freon 113 was purified by refluxing for a few hours over $CaCO_3$ and distillation.

Kinetic EPR Procedures. A stock solution containing 0.03 M benzoyl peroxide in Freon 113 was mixed, 3:5 (v/v), with a Freon 113 solution containing a known concentration of PBN in a quartz EPR tube. This solution was degassed on a high vacuum line by several freeze–thaw cycles, filled with nitrogen at 760 torr, sealed, and placed in a 55 °C water bath for ca. 5–10 s and then in the preheated (to 55 °C) cavity of a Varian E-104 EPR spectrometer. Growth of the BA and PA signals was monitored by repetitive scanning of appropriate lines in their spectra and comparison of these spectra with those obtained by simulation for various BA/PA ratios. Absolute radical concentrations were determined by double integration followed by calibration against a solution containing a known concentration of the diphenylpicrylhydrazyl free radical.[37] The experiments with ArOH were carried out in essentially the same manner.

Acknowledgment. L.G. thanks the Consiglio Nazionale delle Ricerche and NATO for a fellowship.

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(34) Although two measurements only 22 °C apart do not define reliable Arrhenius parameters, the results in Table II (viz., $E_2 - E_4 \approx 6.0$ kcal/mol, $\log (A_2/A_4) \approx 3.2$) also suggest that A_4 is considerably less than A_2, the latter being expected to have a "normal"[8] value of $10^{8.5\pm0.5}$ M^{-1} s^{-1}.

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Base-Induced Coupling–Condensations of Phenyl *p*-Toluenesulfonate and of *N*-Methyl-*p*-toluenesulfonanilide[1]

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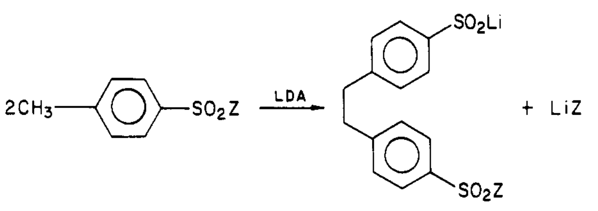
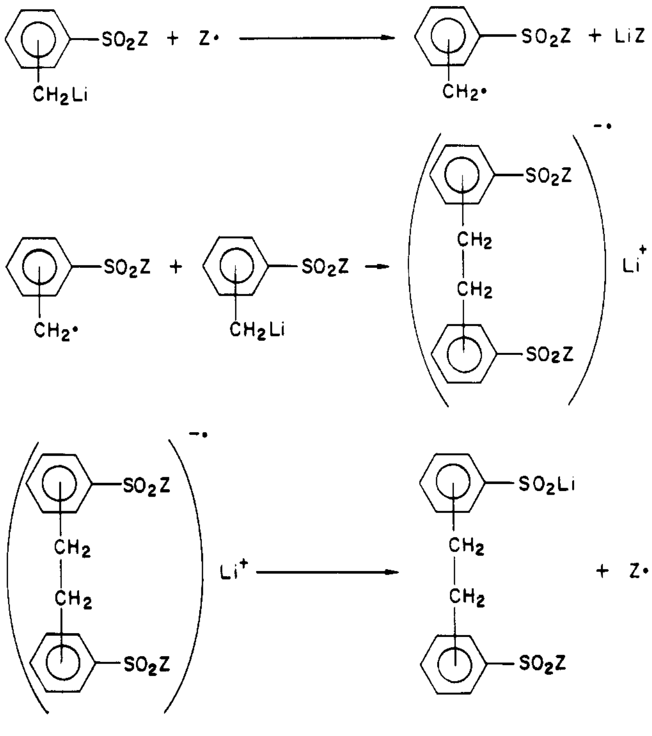
The novel base-induced coupling–condensation reaction[2] of aryl *o*-methylarenesulfonates and of *o*-methylarenesulfonanilides has been extended to para-oriented analogues.



Z = OC_6H_5, $N(CH_3)C_6H_5$

Having discarded several "anionic" mechanisms,[2] and inasmuch as a radical-coupling mechanism is precluded by the absence of symmetrical coupling products, a tentative but highly reasonable sequence for these coupling–condensation reactions is a chain mechanism[3] involving an electron-transfer step and radical and radical-anion intermediates.



Experimental Section

All reactions were carried out under nitrogen atmosphere. The IR spectra were recorded on a Beckmann IR-33. The 60-MHz ^1H NMR spectra were recorded on a Varian A-60A spectrometer and the 90-MHz ^1H NMR spectra on a Perkin-Elmer R32. The 20-MHz ^{13}C NMR spectra were recorded on a Varian CFT-20. All NMR chemical shift data are reported in ppm, employing tetramethylsilane (Me_4Si, δ 0) as an internal standard. Mass

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[1] Abstracted from: Lu, J.-j. Ph.D. Thesis, Purdue University, 1980.

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