

Cyclopropylbenzyl Radical Clocks

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Cyclopropylbenzyl radicals formed by pulse radiolysis of cyclopropylbenzyl benzoates undergo ring-opening rearrangements with absolute rate constants $(0.5-4) \times 10^5 \text{ s}^{-1}$ in hexane at room temperature.

Ring-opening of cyclopropylmethyl radical (**1**) to the but-3-enyl radical [equation (1), $R^1 = R^2 = H$] has been used extensively as a radical clock.¹ The rate of rearrangement k depends upon substituents. Ring-opening of radical (**2**) ($R^1 = H$, $R^2 = Me$)² is slower than that of primary radical (**1**).¹ The $\sim 40 \text{ kJ mol}^{-1}$ resonance stabilization energy of benzylic radicals³ suggests that k would be even lower for cyclopropylbenzyl radicals, but the rate of rearrangement of a benzylic radical has not been established. We report that cyclopropylbenzyl radicals may be observed at room temperature by transient absorption techniques. Direct observation of these radicals under ambient conditions obviates an extrapolation of the rate constants from low temperature measurements.¹ The absolute rate constants k found for benzylic radicals (**3**)–(**7**) correlate with Creary's σ^* parameter.⁴

The 1-cyclopropyl-1-phenylethyl radical (**8**) ($R^1 = Ph$, $R^2 = Me$), when formed by hydrogen atom transfer to α -cyclopropylstyrene, has been observed to rearrange according to equation (1) in competition with hydrogen atom abstraction from transition metal hydrides.⁵ Alkyl radicals are also produced effectively by pulse radiolysis of alkyl esters of carboxylic acids.⁶ Pulse radiolysis of benzhydryl benzoate in hexane under a nitrogen atmosphere affords absorptions near 330 nm, which are characteristic of the diphenylmethyl radical⁷ [Figure 1(a)]. The radical decays via second-order processes to form coupling products.⁶ Pulse radiolysis of 1-cyclopropyl-1-phenylethyl benzoate⁸ under similar conditions affords transient absorption bands appearing between 300 and 400 nm [Figure 1(a)] due to (**8**) which undergo first-order decay. The analogous 4-fluorobenzoate and acetate esters produce an identical species upon radiolysis in hexane or in alcohol solution. Cyclization of the 4-phenylpent-3-enyl

radical, the reverse of equation (1), was not observed on this timescale and must occur at least about an order of magnitude slower than the ring-opening process.⁹ Therefore, the rate constant $k = (3.6 \pm 0.3) \times 10^5 \text{ s}^{-1}$ determined from the decay of (**8**) corresponds to the rearrangement of equation (1), and clearly the rate of this process is much smaller than that for (**1**) or (**2**).[†]

Similarly, transient absorptions of the 1-cyclopropyl-1-phenylmethyl radical (**3**) and its derivatives (**4**)–(**7**) are observed following pulse radiolysis of the corresponding benzoates. Both the absorption spectra [Figure 1(a)] as well as the rate constants for rearrangement depend upon the substitution of the phenyl group [Figure 1(c) and Table 1]. A correlation is evident between substituent effects on equation (1) and the Creary σ^* values⁴ (Table 1). A negative slope (-1.3) of the correlation results from k representing destruction of the benzylic radical, whereas the σ^* scale was developed for a reaction in which benzylic radicals were generated.⁴ Evaluation of the absolute rates for cyclopropylbenzyl rearrangements by use of the σ^* correlation enables use of these radicals as tunable clocks in competition experiments.

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Table 1. Rates of cyclopropylmethyl rearrangement.

Radical	λ_{mon}^a	k/s^{-1}^a	$-\log(k_X/k_H)$	σ^*^b
(1) $\text{CH}_2(\text{C}_3\text{H}_5)^c$	—	2.1×10^8	—	—
(2) $\text{MeCH}(\text{C}_3\text{H}_5)^d$	—	7×10^6	—	—
(3) $\text{PhCH}(\text{C}_3\text{H}_5)$	350	2.7×10^5	0.00	0.00
(4) $4\text{-MeC}_6\text{H}_4\text{CH}(\text{C}_3\text{H}_5)$	350	2.1×10^5	0.11	0.11
(5) $4\text{-ClC}_6\text{H}_4\text{CH}(\text{C}_3\text{H}_5)$	380	2.0×10^5	0.13	0.12
(6) $4\text{-MeOC}_6\text{H}_4\text{CH}(\text{C}_3\text{H}_5)$	400	1.4×10^5	0.28	0.24
(7) $4\text{-PhC}_6\text{H}_4\text{CH}(\text{C}_3\text{H}_5)$	330	0.5×10^5	0.7	0.46
(8) $\text{PhCMe}(\text{C}_3\text{H}_5)$	350	3.6×10^5	—	—
(8) $\text{PhCMe}(\text{C}_3\text{H}_5)^e$	350	3.9×10^5	—	—

^a Absorption band (nm) monitored for decay ($k \pm 25\%$) of radical in hexane at $22 \pm 1^\circ\text{C}$. ^b See ref. 4. ^c See ref. 1. ^d At 0°C . ^e Measured in alcohol solution.

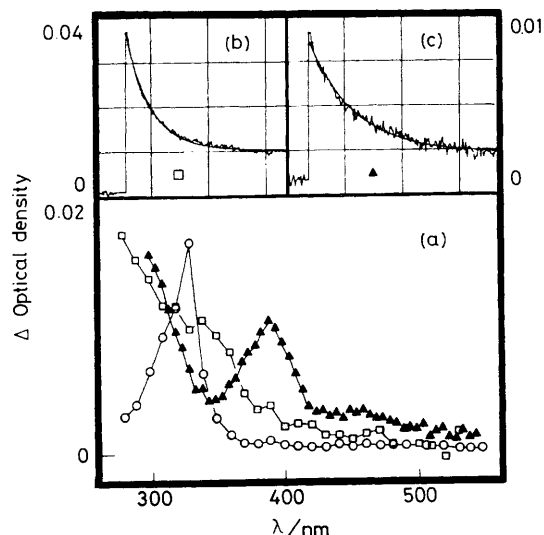
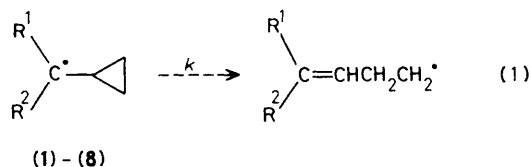


Figure 1. (a) Difference transient absorption spectra of benzhydryl benzoate (circles), 1-cyclopropyl-1-phenylethyl benzoate (squares), and cyclopropyl(*p*-methoxyphenyl)methyl benzoate (triangles) in hexane 3.7 μs following a 250-ns pulse of electrons. Insets show first-order fits to observed decays of (b) radical (**8**) at 320 nm (6 $\mu\text{s}/\text{division}$) and (c) radical (**6**) at 410 nm (11 $\mu\text{s}/\text{division}$).

[†] The differential baselines in Figure 1b,c do not return to zero, and small residual absorptions remain after the benzylic radicals have decayed. Other radicals may be formed (such as cyclohexadienyl radicals from the phenylbutenyl radicals), therefore rates were determined from decays monitored for ~ 2 half-lives.

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References

- 1 B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 7024; D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317; L. Mathew and J. Warkentin, *J. Am. Chem. Soc.*, 1986, **108**, 7981.
 - 2 A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1473.
 - 3 M. Rossi and D. M. Golden, *J. Am. Chem. Soc.*, 1979, **101**, 1230; D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.
 - 4 X. Creary, M. E. Mehrsheikh-Mohammadi, and S. McDonald, *J. Org. Chem.*, 1987, **52**, 3254; X. Creary, *ibid.*, 1980, **45**, 280.
 - 5 R. M. Bullock and E. G. Samsel, *J. Am. Chem. Soc.*, 1987, **109**, 6542.
 - 6 J. Masnovi and J. Maticic, *J. Am. Chem. Soc.*, 1988, **110**, 5189.
 - 7 A. Bromberg, K. H. Schmidt, and D. Meisel, *J. Am. Chem. Soc.*, 1984, **106**, 3056.
 - 8 Benzoates were prepared from the alcohols using KH and benzoyl chloride; S. Sarel, E. Breuer, S. Ertag, and R. Salamon, *Isr. J. Chem.*, 1963, **1**, 451.
 - 9 A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, *J. Am. Chem. Soc.*, 1980, **102**, 1734.
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