Rates of Decarboxylation of Acyloxy Radicals Formed in the Photocleavage of Substituted 1-Naphthylmethyl Alkanoates

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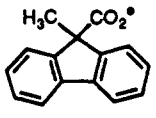
Abstract: Rates of decarboxylation ($k_{CO_2}^R$) have been estimated for the acyloxy radicals **7a–f** formed in the photolysis of substituted 1-naphthylmethyl alkanoates **6a–f**. These rates are based on a proposed mechanism involving initial carbon–oxygen homolytic bond cleavage from the excited singlet state. The products are formed by two competing pathways: electron transfer in the radical pair to give an ion pair and decarboxylation. Measured product yields along with an estimate of the electron-transfer rate (k_{ET}) allow calculation of $k_{CO_2}^R$ as a function of R. The values obtained are the following (R, k (10^9 s^{-1})): CH_3, <1.3; CH_3CH_2, 2.0; $(CH_3)_2CH$, 6.5; $(CH_3)_3C$, 11; $PhCH_2$, 5.0; $PhCH_2CH_2$, 2.3.

Introduction

There have been relatively few estimates of the absolute rates of decarboxylation of acyloxy ($RCO_2^{\bullet}$) radicals because, in general, these reactions are very fast. This is not surprising since carbon dioxide is near the top of an extrusibility[1] scale and the process is exothermic by 39 kJ mol^{-1} (calculated from heats of formation[2]) even for $CH_3CO_2^{\bullet}$. Estimates of $\sim 10^9$ s^{-1} have been made for this rate constant by radical cage effects[3] and chemically induced dynamic nuclear polarization (CIDNP) studies[4] of the thermal decomposition of diacetyl peroxide. For $PhCO_2^{\bullet}$, where the carbon–carbon bond dissociation energy is higher, a value of 2×10^6 s^{-1} in CCl_4 at 24 °C has been recently obtained[5] by laser flash photolysis. If the carbon–carbon bond is weaker, the rate can be much faster; a value of 1.8×10^{10} s^{-1} has been measured[6] in acetonitrile for the fluorenyl compound **1**. Since there are not many carbon-centered radicals that could be more highly stabilized than the 9-methylfluorenyl radical, this study demonstrated that presumably all acyloxy radicals will have a definable, if brief, lifetime.



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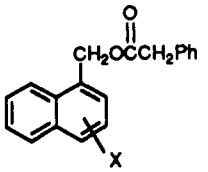
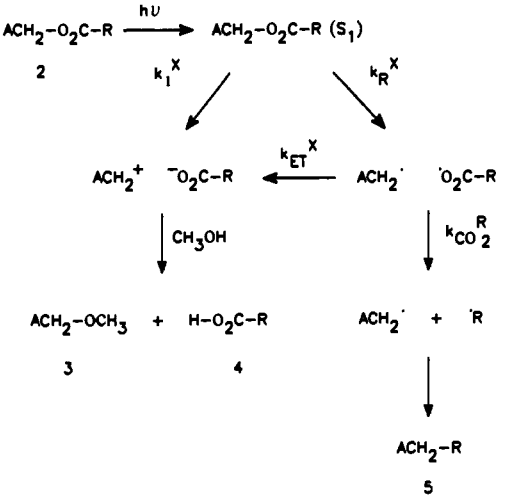


2

Recently we have shown[7] that the singlet excited state of the substituted 1-naphthylmethyl esters **2** in methanol gives the products shown in eq 1 (A = $C_{10}H_{7-n}X_n$). As outlined in Scheme I, the ether **3** and the acid **4** (R = $PhCH_2$) are formed by trapping in methanol of the 1-naphthylmethyl cation and the carboxylate anion, respectively. The hydrocarbon **5** (R = $PhCH_2$) is formed by in-cage coupling of the naphthylmethyl radical and benzyl radical, which is formed by loss of carbon dioxide from the (phenylacetyl)oxy radical. Previous work[8] on the photolysis of

$$\underset{\mathbf{2}}{ACH_2O(O)CCH_2Ph} \xrightarrow[CH_3OH]{} \underset{\mathbf{3}}{ACH_2OCH_3} + \underset{\mathbf{4}}{PhCH_2CO_2H} + \underset{\mathbf{5}}{ACH_2CH_2Ph} \quad (1)$$

Scheme I. The Mechanism of Photolysis of 1-Naphthylmethyl Ester **2** in Methanol (A = $C_{10}H_{7-n}X_n$)



unsubstituted **2** (i.e., X = H) in benzene also reported high yields of **5** along with low yields of out-of-cage dimers. As expected, no nucleophilic trapping products were observed.

The mechanism of formation of the critical intermediates (in this case, the naphthylmethyl cation and radical) that control product distribution in the photochemistry of benzylic compounds with leaving groups has been a subject of much current interest.[7-10] Many factors such as the nature of the leaving group, the structure of the aromatic ring (substituent effects), the multiplicity of the excited state, and the solvent have an effect on the competition between the two pathways. We have suggested that, for the esters **2**, the excited state cleaves exclusively to the radical pair ($k_R^X \gg k_I^X$) and that competition between electron transfer (K_{ET}) and decarboxylation (k_{CO_2}) then controls the product distribution. Since these are all esters of phenylacetic acid, the rate of decarboxylation is a constant (i.e., radical clock[11]) so that the product ratio **3**/**5** = k_{ET}/k_{CO_2} (R = $PhCH_2$) is a measure of k_{ET}. Systematic variation in k_{ET} is possible by variation of the substituents (X), which control the oxidation potential[12] of the 1-naphthylmethyl radical. These rates of electron transfer were well-rationalized by Marcus theory,[13] including the observation of the

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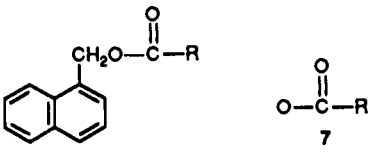
"inverted region", which predicts slower rates of electron transfer as the process becomes prohibitively exoergonic. To our knowledge, this is the first observation of this phenomenon in a caged radical pair.

If this explanation is correct, a second consequence follows. If the rate of electron transfer is kept constant by keeping X constant, then product distribution will be controlled by the rate of decarboxylation. This rate can obviously be systematically varied by changing the carboxylic acid side of the ester. We now report results for the photolysis of the esters **6** that support this idea. As well, we report the first determination of rate constants for the decarboxylation of the radicals **7**.



6

7

6a, 7a: R = CH_3
6b, 7b: R = CH_3CH_2
6c, 7c: R = $(CH_3)_2CH$
6d, 7d: R = $(CH_3)_3C$
6e, 7e: R = $PhCH_2$
6f, 7f: R = $PhCH_2CH_2$

Experimental Section

General Procedure. Ultraviolet (UV) spectra were obtained in methanol on a Varian Cary 219 spectrophotometer. Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were obtained in $CDCl_3$ with TMS as an internal standard on a Nicolet NB 360 spectrometer. Mass spectra were obtained on a Hewlett-Packard 5890 GC/MS with a 5% phenylsilicone capillary column. Infrared spectra were obtained on a Pye Unicam SP 1000 spectrophotometer. Fluorescence spectra were obtained on a Perkin-Elmer MPF 66 spectrophotometer with samples in methanol that were degassed by three freeze–pump–thaw cycles; the optical densities of the samples were always less than 0.2, and quantum yields were obtained relative to a value of 0.21[14] for 1-methylnaphthalene. Fluorescence lifetimes were obtained on the same samples with use of a PRA System 3000 instrument with a hydrogen flash lamp of pulse width 0.8 ns. Microanalysis were by Canadian Microanalytical Service Ltd., Delta, BC, Canada.

Irradiations. Irradiations were done with a 200-W medium-pressure Hanovia mercury lamp in a standard immersion well with a Pyrex filter. Solutions were degassed with a slow nitrogen stream. Progress of the reaction was monitored by HPLC with a Waters system, operating in isocratic conditions (80/20 methanol/water), equipped with a Brownlee Spheri-10 reversed-phase column (25 × 0.46 cm). Detection was at 280 nm. Complete conversion of 200 mg of the esters took about 20 h. Product ratios remained constant throughout the course of the irradiation, and dark samples taken either before or during the irradiation showed no conversion. Yields were obtained by calibrating the HPLC detector with samples of the products of known concentration in methanol.

Acetyl chloride, 2,2-dimethylpropanoyl chloride, propanoic anhydride, 1-(1′-naphthyl)ethanal, and 1-naphthylmethanol were obtained from Aldrich and were used without further purification. Pyridine was obtained from Analar and was distilled before use. 2-Methylpropanoyl chloride was prepared from 2-methylpropanoic acid with use of the method of Kent and McElvain.[15] 1-Cyanonaphthalene was synthesized by the method of Friedman and Shechter.[16] 1-(Methoxymethyl)-naphthalene (**8**) was obtained by the procedure of Wright and Platz.[17]

Synthesis of Esters 6a,c–f. To a well-stirred solution of 1-naphthalenemethanol (10 mmol) and 1 mL of pyridine in 50 mL of dry benzene was slowly added the corresponding acid chloride (10 mmol) in 30 mL of benzene at room temperature. The pyridinium hydrochloride salt precipitated, and after all of the acid chloride was added, the solution was stirred overnight. Then 50 mL of water was added, and the two layers were separated. The benzene layer was washed twice with 10% aqueous HCl, once with 5% aqueous NaOH, and finally with water. The organic layer was then dried ($MgSO_4$), filtered, and rotoevaporated to yield the crude ester.

The ester was then column chromatographed over silica gel with 50/50 hexane/methylene chloride as the eluent. The ester fractions were identified by TLC and then combined and concentrated. The esters were distilled under vacuum for purification.

Synthesis of Ester 6b. To a 50-mL round-bottom flask were added 2.96 g (18.7 mmol) of 1-naphthylmethanol and 20 mL of pyridine. Then 2.40 mL (2.36 g, 18.2 mmol) of propanoic anhydride was introduced and the solution heated at 50 °C for 1 day and then stirred at room temperature for 12 h. The solution was poured into 50 mL of ether and washed sequentially with 20% HCl, 5% $NaHCO_3$, and water. The organic layer was dried ($MgSO_4$), filtered, and rotoevaporated to yield the crude ester as a pale yellow oil. The ester was purified as above.

Characterization of Esters. 1-Naphthylmethyl acetate (6a): yield 63%; bp 52–53 °C (0.5 mmHg) [lit.[10] bp 65 °C (1 mmHg)]; UV λ_{max} 265 nm (ϵ 6.54 × 10^3), 275 (6.80 × 10^3), 284 (4.57 × 10^3); IR (neat) 3070, 2980, 1740 (C=O), 1340, 1240 (C–O), 1035, 800, 760 cm^{-1}; ^1H NMR identical with that reported earlier;[10] ^{13}C NMR δ 170.9 (s, C=O), 133.7 (s), 131.5 (s), 131.4 (s), 129.2, 128.7, 127.4, 126.5, 125.9, 125.2, 123.5, 64.5 (t, CH_2O, J = 146.4 Hz), 21.0 (q, $-CH_3$, J = 129.5 Hz); GC/MS, m/z 201 (7, M + 1), 200 (52, M^+), 158 (94), 141 (100), 140 (62), 139 (36), 129 (50), 128 (29), 127 (29), 115 (47).

1-Naphthylmethyl propanoate (6b): yield 65%; bp 86–88 °C (0.5 mmHg); UV λ_{max} 265 nm (ϵ 6.56 × 10^3), 275 (7.26 × 10^3), 284 (5.10 × 10^3); IR (neat) 3015, 2950, 2915, 2870, 1735 (C=O), 1460, 1345, 1265, 1175 (C–O), 1070, 1000, 780, 760 cm^{-1}; ^1H NMR δ 8.00 (d, 1 H, J = 8.05 Hz), 7.82–7.88 (m, 2 H), 7.42–7.55 (m, 4 H), 5.57 (s, 2 H, CH_2O), 2.38 (q, 2 H, CH_2CH_3, J = 7.56 Hz), 1.15 (t, 3 H, CH_2CH_3, J = 7.54 Hz); ^{13}C NMR δ 174.3 (s, C=O), 133.6 (s), 131.5 (s), 129.1, 128.9 (s), 128.6, 127.3, 126.5, 125.9, 125.2, 123.5, 64.4 (t, CH_2O, J = 147.9 Hz), 27.6 (t, CH_2CH_3, J = 127.6 Hz), 9.1 (q, CH_2CH_3, J = 127.3 Hz); GC/MS, m/z 215 (8, M + 1), 214 (48, M^+), 159 (12), 158 (96), 142 (18), 141 (100), 140 (64), 139 (37), 129 (43), 128 (24), 127 (24), 115 (49), 57 (46). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.04; H, 6.59.

1-Naphthylmethyl 2-methylpropanoate (6c): yield 50%; bp 115 °C (0.5 mmHg) [lit.[18] bp 127–128 °C (1 mmHg)]; UV λ_{max} 266 nm (ϵ 5.37 × 10^3), 276 (6.08 × 10^3), 284 (4.40 × 10^3); IR (neat) 3030, 2980, 2940, 2880, 1740 (C=O), 1465, 1195 (C–O), 1160, 965, 790, 775 cm^{-1}; ^1H NMR identical with that reported earlier;[17] ^{13}C NMR δ 176.9 (s, C=O), 133.6 (s), 131.6 (s), 131.6 (s), 129.1, 128.6, 127.2, 126.4, 125.8, 125.2, 123.5, 64.5 (t, CH_2O, J = 148.8 Hz), 34.1 (d, $CH(CH_3)_2$, J = 129.7 Hz), 9.0 (q, $CH(CH_3)_2$, J = 127.6 Hz); GC/MS, m/z 229 (10, M + 1), 228 (49, M^+), 158 (79), 142 (32), 141 (100), 140 (46), 139 (37), 129 (24), 128 (23), 127 (24), 115 (79), 71 (24).

1-Naphthylmethyl 2,2-dimethylpropanoate (6d): yield 62%; bp 89–91 °C (0.1 mmHg) [lit.[19] bp 108–110 °C (0.2 mmHg)]; UV λ_{max} 265 nm (ϵ 5.54 × 10^3), 275 (6.47 × 10^3), 284 (4.60 × 10^3); IR (neat) 3060, 2990, 2965, 2920, 2885, 1730 (C=O), 1485, 1285, 1165 (C–O), 800, 780 cm^{-1}; ^1H NMR identical that that reported earlier;[20] ^{13}C NMR δ 178.3 (s, C=O), 133.7 (s), 131.8 (s), 131.6 (s), 129.0, 128.6, 126.9, 126.4, 126.1, 125.8, 125.2, 123.6, 64.6 (t, CH_2O, J = 150.0 Hz), 39.0 (s, $-C(CH_3)_3$), 27.2 (q, $-C(CH_3)_3$, J = 126.7 Hz); GC/MS, m/z 243 (6, M + 1), 242 (32, M^+), 142 (24), 141 (100), 139 (18), 127 (11), 115 (39), 57 (100).

1-Naphthylmethyl phenylacetate (6e): bp 130–132 °C (0.05 mmHg) [lit.[21] bp 212 °C (4–5 mmHg)].

1-Naphthylmethyl phenylpropanoate (6f): bp 137–139 °C (0.05 mmHg[22]).

Synthesis of Alkylnaphthalenes 10a–d. 1-Ethylnaphthalene (**10a**) and 1-propylnaphthalene (10b) were obtained by Wolff–Kishner reduction of 1-(1′-naphthyl)ethanal and 1-(1′-naphthyl)propanone, respectively.[23] 1-(1′-Naphthyl)propanone and 2-methyl-1-(1′-naphthyl)propanone were prepared by reaction of the corresponding Grignard reagent with 1-cyanonaphthalene.[24] 2-Methyl-1-naphthylpropane (**10c**) was obtained via the method of West et al.[25] 2,2-Dimethyl-1-naphthylpropane (**10d**) was prepared as described previously.[26] These hydrocarbons gave ^1H NMR identical with those reported previously.[26–29]

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Table I. Results for the Photolysis of the Esters **6** in Methanol at 20 °C

compd	ϕ_F	τ_s, ns	**8**,[a] %	**10**,[a] %	I/R	$k_{CO_2} \times 10^{-9}$,[b,c] s^{-1}
6a (R = CH_3)	0.14	41	98	ND	>20[d]	<1.3 (±0.2)
6b (R = CH_3CH_2)	0.14	40	93	6	13	2.0 (±0.3)
6c (R = $(CH_3)_2CH$)	0.13	40	80	6	4.0	6.5 (±0.8)
6d (R = $(CH_3)_3C$)	0.14	39	71	9	2.4	11 (±2)
6e (R = $PhCH_2$)[e]	0.14	39	84	16	5.2	5.0 (±0.8)
6f (R = $PhCH_2CH_2$)[f]	0.14	41	92	7	12	2.3 (±0.4)

[a] Estimated error ±2%. Yields are corrected for unreacted starting material. [b] Assuming $k_{ET} = 2.6 \times 10^{10}$ s^{-1}. [c] Errors in parentheses are calculated assuming ±2% in the determination of product yields and ±10% error in the measured rate of decarboxylation of **1**. [d] Assuming 5% of **10** would have been detected. [e] The yields of phenylacetic acid were 80% (HPLC) and 58% (isolated). [f] The yield of phenylpropanoic acid was 42% (isolated).[22]

Results and Discussion

Photolysis of the esters **6a–6f** again gave, as expected, three major products: the methyl ether **8**, the carboxylic acids **9a–9f**, and the hydrocarbon coupling products **10a–10f** (eq 2 (N = $C_{10}H_7$)). The yields are given in Table I. Since no attempt was made to determine the yields for the low molecular weight carboxylic acids **9a–9d**, which have no UV detectable chromophore, yields are only available for **9e** and **9f** (footnote in Table I). In general, mass balance is excellent.

$$\underset{\textbf{6a–6f}}{NCH_2O(O)CR} \xrightarrow[CH_3OH]{} \underset{\textbf{8}}{NCH_2OCH_3} + \underset{\textbf{9a–9f}}{RCO_2H} + \underset{\textbf{10a–10f}}{NCH_2R} \quad (2)$$

However, determining the yield of the products derived from the decarboxylation pathway is not straightforward for these substrates. This is because the yield of the radical coupling product **10** is significantly lowered for the highly branched aliphatic cases **10c** and **10d**. The reason is the well-established fact that highly branched alkyl radicals give increased amounts of disproportionation (D) relative to combination (C) (eq 3).[30] For instance,

$$NCH_2^{\bullet} + {}^{\bullet}C(CH_3)_3 \rightarrow \textbf{10d} + NCH_3 + CH_2{=}C(CH_3)_2 \quad (3)$$

for reaction with alkoxy radicals in decalin at 30 °C, the relative values for D/C ratios are 1.0 (CH_3CH_2), 7.7 ($(CH_3)_2CH$), and 77 ($(CH_3)_3C$).[31] To our knowledge, values of D/C have not been determined for the specific radical pairs involved in this work. Note that, in the previous study,[7] disproportionation was not possible since the two radicals involved were 1-naphthylmethyl and benzyl (R = $PhCH_2$) (Scheme I). As well, small amounts of out-of-cage radical products like 1,2-dinaphthylethane are always detectable by HPLC.

On the other hand, quantifying the yield of the products derived from the ionic pathway is straightforward since the methyl ether **8** is the same for all substrates and gives a peak on the HPLC traces that is well-resolved from the others. Therefore, we have chosen to assume that all of the material not accounted for by the yield of **8** has reacted by a pathway involving decarboxylation of the alkanoyloxy radicals **7**. It follows that the ratio of the two pathways ($k_{ET}(X = H)/k_{CO_2}$ = yield of **8**/(100 − yield of **8**) is I/R. These values ar given in Table I. Calculation of the rates of decarboxylation requires only the knowledge of $k_{ET}(X = H)$, provided the reasonable assumption is made that this rate constant is independent of the structure of R. An estimation of $k_{ET}(X = H) = 2.6 \times 10^{10}$ s^{-1} has been made by us previously[7] for R = $PhCH_2$. The k_{CO_2} values obtained this way are listed in Table I.

Before discussion of these values, two points should be made.

First, as described previously,[7] all the rate constants reported are anchored to a single radical-clock reaction, the rate of decarboxylation of **1** in acetonitrile. Any error in this value leads to an error in all the others but not to any change in the relative order of reactivity. Even the assumption that the value obtained for **1** in acetonitrile can be used for the results obtained here in methanol may be in error. Although radical reactions are not usually very sensitive to solvent effects, the rate of decarboxylation of the (4-methoxybenzoyl)oxy radical has been shown to decrease by more than a factor of 20 on changing the solvent from carbon tetrachloride to acetonitrile.[5]

Second, for substrates like **6e**, we have observed[32] that intramolecular charge transfer can occur for appropriately substituted aromatic rings. This results in lower quantum yields of fluorescence and shorter lifetimes. As well, these intramolecular exciplexes are reactive and give products resulting from the equivalent[33] of homolytic carbon–oxygen bond cleavage of the ester. Any product formed by this pathway would clearly decrease the yield of the ether **8** and lead to erroneous values of I/R. However, the esters **6e** and **6f**, having aryl rings on the carboxylic acid side, have quantum yields of fluorescence ($\phi_f = 0.14$) and singlet lifetimes ($\tau_s = 40$ ns) identical with those of the aliphatic carboxylic acid esters (Table I). Therefore, there is no significant interaction between the two chromophores for **6e** and **6f**.

The rates of decarboxylation of $RCO_2^{\bullet}$ as a function of R only span a factor of about 10. This is much smaller than, for instance, the range for the rates of decarbonylation of RCO, which vary by a factor of 10^7 for the same substituents.[34] This is not surprising since the decarboxylations are exothermic (vide supra), whereas the decarbonylations are endothermic by 60 kJ mol^{-1} for R = CH_3 and only became mildly exothermic for R = $PhCH_2$ at −5 kJ mol^{-1}. Moreover, the rate range is chemically sensible since the values are all between those estimated[3,4] for the acetyloxy radical (10^9 s^{-1}) and measured[6] for the fluorenyl compound **1** (1.8×10^{10} s^{-1}). However, the relatively large estimated error (Table I) combined with the small total range in the rate constants means that there could be difficulties in interpreting the order.

Despite this caution, the order of reactivity observed for the decarboxylation gives us confidence that the method is giving reasonable values. For instance, the order as a function of R is $CH_3 < CH_3CH_2 < (CH_3)_2CH < (CH_3)_3C$ in agreement with all bond dissociation energy expectations.[35] Moreover, the two very different primary radical cases **6b** (R = CH_3CH_2) and **6f** (R = $PhCH_2CH_2$) give, within experimental error, the same value.

Recently, Skell and May[36] have reported relative values for the decarboxylation of aliphatic acyloxy radicals formed by the low-temperature photolysis of acyl hypobromites. They conclude that the order of increasing rate of decarboxylation is $(CH_3)_3C < (CH_3)_2CH < CH_3CH_2$ and that "... rates do not increase with increasing stability of the radical formed in this decarboxylation process". As well, they report results that indicate that two different states (designated π and σ_a) of the acyloxy radicals are formed depending on the method of generation and that both states show the same order for the decarboxylation rate. Ab initio MO calculations[37] suggest that a possible reason for this order is that the transition state for these exothermic processes is early so that there is little development of radical character on the incipient alkyl radical. However, the transition state does have considerable opening of the O–C–O bond angle to about 140° from the initial 120°, and steric hindrance of the more bulky alkyl groups might therefore raise the energy of this transition state.

A reviewer of a preliminary form of this paper has suggested that there is reason to question the experimental results of Skell and May. Their work relied on the assumption that acyloxy radicals would be trapped by hydrogen abstraction from cyclohexane in competition with decarboxylation. However, more

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recent laser flash photolysis results[5] indicate that this rate constant ($\sim 1 \times 10^6$ M^{-1} s^{-1} for the benzoyloxy radical in CCl_4) would be too slow to compete with the very fast decarboxylation rates for alkanoyloxy radicals.

Finally, the rate constant obtained for the decarboxylation of the (phenylacetyl)oxy radical **7e** (R = $PhCH_2$) obtained from **6e** seems surprisingly low. All estimations of bond dissociation enthalpies[35] and reaction rates would place this value higher than that for **7d** (R = $(CH_3)_3C$). An explanation for this observation comes from results on the rates of decarbonylation of RCO radicals. A plot[34] of the logarithm of these rates as a function of R versus calculated bond dissociation enthalpies is linear for alkyl groups, except that benzyl derivatives fall significantly below the line. However, the frequency factors for these substrates are also somewhat lower, suggesting that there is an unfavorable entropy effect in the transition state for decarbonylation. This effect is a result of the requirement that the phenyl ring assume a conformation allowing overlap with the breaking σ bond and conjugation with the developing radical center. For the case of the decarboxylation reactions where the process is more exothermic and the enthalpies of activation are undoubtably very low, the energy of the transition state may be dominated by this entropic effect. The lowering of the rate now puts **7e** slower than **7c**.

We are currently extending this approach to measure rates of decarboxylation for other cases.

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Photolysis of Azoalkanes. Reactions and Kinetics of the 1-Cyclopropylcyclopentane-1,3-diyl Biradical and the 1-Cyclopropylcyclopentyl Radical

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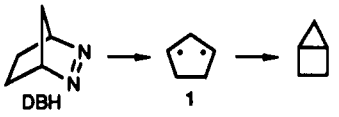
Abstract: The cyclopropylcarbinyl (CPC) rearrangement rates of 1-cyclopropylcyclopentyl (**10a**) and 1-cyclopropylcyclohexyl (**10b**) radicals to yield **34a,b** are found to be 1.45×10^7 and 1.1×10^7 s^{-1} at 24.7 °C, respectively. These values, which are based on thiophenol trapping of **10a,b**, are 6–9 times slower than that of the parent cyclopropylmethyl radical. Ring closure of homoallylic radical **34a** proceeded at a rate of 5.5×10^4 s^{-1}, which is 7 times faster than that of 3-butenyl. No 1,5-hydrogen shift was found in **34a**. The triplet 1,3-biradical **6T** analogous to **10a** was produced by triplet-sensitized photolysis of 1-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**11**). Biradical **6T** rearranges to **9*E*** and **9*Z***, the latter of which undergoes rapid intramolecular disproportionation to **46*Z***. On account of its geometry, the *E* isomer cannot lead directly to a stable product; hence, it recloses to **6T** ($k_{ra} = 1.2 \times 10^5$ s^{-1}), but, interestingly, not to **6S**. If the CPC rearrangement rate of **6T** is taken to equal that of **10a**, we calculate from the product distribution that the lifetime of **6T** is 59 ns. This figure is only half the lifetime of the parent cyclopentane-1,3-diyl (**1**), showing that the perturbing effect of cyclopropyl is similar to that of methyl.

A number of photoreactions proceed via localized biradicals, intermediates that have become a recent focus of mechanistic study.[1] Because deazatation is often a clean and efficient reaction, cyclic azoalkanes[2] are an appealing source of biradicals. As illustrated by the photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH),[3] biradicals can lead to products not easily prepared by alternate routes. Triplet-sensitized irradiation of such bicyclic azoalkanes affords triplet biradicals (designated as T) whose lifetime is a topic of current interest.[1] While a number of triplet biradicals have been observed by ESR or transient UV spectroscopy, ambient-temperature study of biradicals lacking a chromophore requires such methods as photoacoustic calorimetry,[4] oxygen trapping,[5] or CIDNP.[6]



Another approach to the study of biradicals is the free radical clock technique, wherein one or both of the radical centers is functionalized with a group capable of rapid rearrangement. From the product distribution and the rearrangement rate, which is assumed to equal that of an analogous monoradical, one can deduce the lifetime of the biradical. Several years ago, we em-

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