in Table II reveals that this is the case. The rates of triplet cleavage appear to correlate well with the stabilities of the product naphthyl radicals. For example, methyl substitution in the position α to the naphthalene in sulfone **2** (**2c**) causes a decrease in activation energy for cleavage, whereas substituion on the benzene side (**2b**) has no effect on the cleavage activation parameters.[21] Similarly, for the β-substituted sulfones, methyl substitution on the benzene side has no effect, whereas substitution on the naphthyl side allows observation of an increased temperature dependence for triplet decay. These observations imply that the transition states for the cleavage reactions are product like. This, in turn, allows an explanation for the reluctance of the β-substituted sulfone triplet states to undergo reaction. Assuming that the A factor for cleavage of sulfone **3a** is the same as that of **2a**, then an increase in activation energy of 2 kcal/mol will decrease the reaction rate by two orders of magnitude. At room temperature under these conditions, the lifetime of the sulfone triplet state will be dominated by the processes which contribute to k_d in eq 2.

The preexponential factors for triplet decay of the β-sulfones and α-methylnaphthalene are typical of those expected if intersystem crossing, or bimolecular quenching reactions are the dominant modes of triplet decay.[22] The A factors for k_r for the α-naphthyl sulfones are typical of those observed for unimolecular cleavage reactions in which the number of degrees of freedom in the transition state are somewhat restricted.[24] For example, they are similar to those observed in isooctane solution for unimolecular loss of CO from phenacetyl radicals.[9]

Knowledge of the intersystem crossing yields for the naphthyl sulfones allows estimation of the extent of singlet-state reactivity. Examination of the data in Table III shows that the sulfone intersystem crossing yields are all less than that of naphthalene (assumed to be 0.8).[14] It is evident that the extent of singlet-state reactivity is not significantly different for the α- or β-substituted sulfones. Indeed, no clear trends in the intersystem crossing yields can be observed. These observations are consistent with the conclusion that the lack of triplet-state reactivity is the origin of the small quantum yields for cleavage of the β-substituted sulfones.

Conclusion

The use of micellar and magnetic field effects has provided information concerning the mechanisms of SO_2 photoextrusion for a variety of aromatic sulfones. Time-resolved optical-absorption experiments provide direct evidence as to the nature of reaction-state multiplicity, the nature of the cleavage step, and the identity of the transient intermediates in these reactions. A correlation is found between the dynamics of the cleavage steps and the energies of the triplet states and stabilities of the intermediate radicals.

Acknowledgment. The authors at Columbia thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this research. The authors at Kansas thank the National Institutes of Health (GM 16611) for financial support. Bogdan Matuszewski acknowledge a leave of absence from A Mickiewicz University, Poznań, Poland.

Registry No. **1b**, 88430-87-9; **2a**, 67168-90-5; **2b**, 88430-88-0; **2c**, 88430-89-1; **3a**, 67168-91-6; **3b**, 88430-90-4; **3c**, 88430-91-5; DBK, 102-04-5; SDS, 151-21-3; acetone, 67-64-1; acetophenone, 98-86-2; 1-(chloromethyl)naphthalene, 86-52-2; 1-methylnaphthalene, 90-12-0.

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(21) The *sec*-phenethyl radical is ca. 2 kcal/mol more stable than the benzyl radical on the basis of hydrocarbon bond-dissociation energies (vide supra, ref 20).

(22) The observed activation parameters for triplet decay are consistent with those previously observed for naphthalene (vide infra, ref 23). The observation of significant temperature dependence for triplet decay in homogeneous solution is usually attributed to impurity quenching (ref 23). In the present case the rate-determining step for the decay of the nonreacting triplets under the present experimental conditions is probably quenching by residual oxygen or other impurities.

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Mechanism of Rearrangement of β-(Acyloxy)alkyl Radicals[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, K1A 0R6 Canada, and the Department of Chemistry, Mount Allison University, Sackville, New Brunswick, E0A 3C0 Canada. *Received July 14, 1983.*
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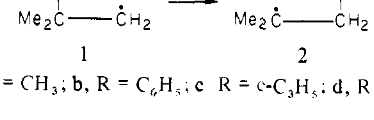
Abstract: Rate constants for the free radical rearrangement, $CF_3C(O)OCMe_2\dot{C}H_2$ (**1d**) → $CF_3C(O)OCH_2\dot{C}Me_2$ (**2d**), have been measured in $CF_2ClCFCl_2$ by kinetic EPR spectroscopy. This reaction is very significantly faster ($k_1^{75\,°C} = 7.0 \times 10^4$ s^{-1}) than the related rearrangement, $CH_3C(O)OCMe_2\dot{C}H_2$ (**1a**) → $CH_3C(O)OCH_2\dot{C}Me_2$ (**2a**) ($k_1^{75\,°C} = 4.5 \times 10^2$ s^{-1}), in hydrocarbon solvents. The potential cyclic intermediate radical, 2-(trifluoromethyl)-4,4-dimethyl-1,3-dioxolan-2-yl (**3d**), does not undergo ring opening to **2d**, at temperatures where the **1d** → **2d** rearangement is very fast. It is concluded that **3d** is not an intermediate in the trifluoroacetoxyl migration. It is also concluded on the basis of the k_1 values for **1a** and **1d** that these rearrangements involve a charge-separated transition state. The **1a** → **2a** rearrangement is very much faster in water ($k_1^{75\,°C} = 2.1 \times 10^4$ s^{-1}) than in hydrocarbon solvents, which provides additional support for a charge-separated transition state.

The mechanism of the 1,2 migration of acyloxy groups in β-(acyloxy)alkyl radicals (**1** → **2**) continues to fascinate chemists.[4-12] We[10] have recently confirmed Beckwith's suggestion[7,8] that at least some **1** → **2** rearrangements do not proceed via an



1 2

a, R = CH_3; b, R = C_6H_5; c R = c-C_3H_5; d, R = CF_3

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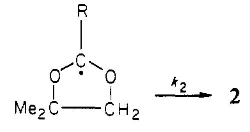
intermediate 1,3-dioxolan-2-yl radical, **3**. Thus, **1a**, **1b**, and **1c**, as well as **3a** and **3b**, were shown by EPR spectroscopy to rearrange to the corresponding **2**. However, radical **3c** underwent an opening of the cyclopropyl rather than the dioxolanyl ring, and hence **3c** could not lie on the **1c** → **2c** reaction path. Detailed kinetic data suggested that the transition state for the **1** → **2** rearrangement was relatively "loose" with C–O bond scission virtually complete before there had been much bond making between the carbonyl oxygen and the primary radical center.[10] We therefore proposed that a charge-separated structure, **4**, played an important role in the **1** → **2** transition state. Suport for this proposal is presented below.



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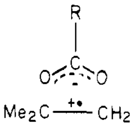


4

We hypothesized that an inductively electron-attracting group R would strongly accelerate the **1** → **2** rearrangement because it should stabilize the transition state **4**, whereas such a group would probably reduce the rate of the **3** → **2** rearrangement because of the general strengthening of σ bonds that is produced by electron withdrawal. As our probe group we chose R = CF_3, i.e., radicals **1d** and **3d**.

We also hypothesized that the **1** → **2** rearrangement should be accelerated by polar solvents since such solvents should also stabilize the transition state **4**. Evidence that such is the case comes from Beckwith and Tindal's[7] observation that the **1a** → **2a** rearrangement was faster than the **3a** → **2a** rearrangement in water, whereas we,[10] working in hydrocarbon solvents, found just the reverse. We have confirmed Beckwith and Tindal's result and have made a quantitative measurement of the rate acceleration of the **1a** → **2a** rearrangement in water. We further hypothesized that a strongly electron-withdrawing R group might, in water, produce sufficient stabilization of the transition state (or even separation of the two ionic fragments) that the isobutylene radical cation would be intercepted by hydroxyl, i.e.,

$$\mathbf{1} \xrightarrow{OH^-} Me_2\dot{C}CH_2OH + RCO_2^-$$

Unfortunately, our attempts to generate **1d** in water were not successful.

Results

Experiments in a Nonpolar Solvent. Radical **1d** was generated in $CF_2ClCFCl_2$ (Freon 113) by UV photolysis directly in an EPR cavity, as follows:

$$CF_3OOCF_3 \xrightarrow{h\nu} 2CF_3\dot{O}$$

$$CF_3\dot{O} + CF_3C(O)OCMe_3 \rightarrow CF_3OH + \mathbf{1d}$$

Table I. EPR Spectral Parameters[a]

radical	T, °C	g	a^H	ref
1a–c	90	2.0029	21.3 (2), 1.17 (6)	10
1d	−30	2.0026	22.4 (2), 1.18 (6)	this work
2a-c	90	2.0028	15.5 (2), 23.1 (6)	10
2d	30	2.0026	12.3 (2), 22.8 (6)	this work
3a	10	2.0032	1.24 (2), 13.11 (3)	10
3d	25	2.0046	1.7 (2), 11.0 (3F)[b]	this work

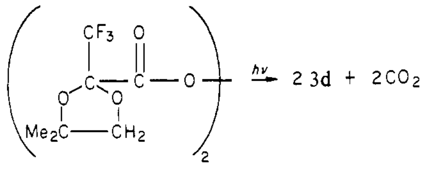
[a] In *tert*-butylbenzene; except **1d**, **2d**, and **3d**, which were measured in $CF_2ClCFCl_2$. Hyperfine splittings are given in Gauss. The numbers in parentheses in the a^H column are the number of equivalent H atoms unless otherwise noted. [b] a^F(3F).

Table II. Kinetic Data for the **1d** → **2d** Rearrangement in $CF_2ClCFCl_2$

T, °C	$10^8\cdot$ [**2d**], M	$10^8\cdot$ [**1d**], M	$10^7\cdot$ $(k_1^{1d}/2k_t^{2d})$, M	$10^{-9\,a}\cdot$ $2k_t^{2d}$, M^{-1} s^{-1}	$10^{-3}\cdot$ k_1^{1d}, s^{-1}
−11	7.0	9.5	1.2	3.7	0.4
−7	6.1	4.4	1.5	3.8	0.6
−7	14.1	9.3	3.5	3.8	0.6
2	18.1	7.3	6.3	4.3	2.7
2	17.2	11.3	4.3	4.3	1.8
2	19.2	11.1	5.2	4.3	2.2
5	16.0	12.3	3.7	4.5	1.7
10	12.7	4.6	4.8	4.7	2.3
18	22.1	6.6	9.6	5.2	5.0
18	13.4	3.5	6.5	5.2	3.4
26	23.4	4.2	15	5.7	8.6
32	19.8	4.2	11	6.2	6.8

[a] Assumed. See text.

Radical **3d** was generated by photolysis of the parent diacyl peroxide in the same solvent. EPR parameters for these and some related radicals are given in Table I.



The rearranged radical **2d** is formed from **1d** in measurable concentrations at temperatures of −11 °C and above (see Table II), whereas **2a** was formed from **1a** in measurable amounts only at 69 °C and above.[10] The **1d** → **2d** rearrangement is therefore significantly faster than the **1a** → **2a** reaction. The rate constant ratios $k_1^{1d}/2k_t^{2d}$ were determined by measuring the absolute concentrations of **1d** and **2d** over a temperature range from −11 to 32 °C and were calculated from the equation[10]

$$k_1^{1d}/2k_t^{2d} = [\mathbf{2d}](([\mathbf{2d}]/[\mathbf{1d}]) + 1)$$

where $2k_t^{2d}$ refers to the rate constant for the bimolecular self-reaction of **2d**.

$$2\,\mathbf{2d} \xrightarrow{2k_t^{2d}} \text{products}$$

Values of $2k_t^{2d}$ were assumed to be the same as those reported[13] for the diffusion-controlled bimolecular self-reaction of *tert*-butyl radicals in an alkane solvent having the same viscosity as $CF_2ClCFCl_2$.[14] These results are given in Table II, and the derived Arrhenius parameters are given in Table III together with those previously determined[10] for the **1a** → **2a** rearrangement in *tert*-butylbenzene.[15] At 75 °C[16] k_1^{1d} is calculated to be 156 times

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(6) Tanner, D. D.; Law, F. C. P. *J. Am. Chem. Soc.* **1969**, *91*, 7535-7537.

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(13) Fischer, H.; Schuh, H.-H. *Helv. Chim. Acta* **1978**, *61*, 2130-2164.

(14) The viscosity of $CF_2ClCFCl_2$ at 30 °C is 0.62 cP. The temperature coefficient of viscosity for the Freon was assumed to be the same as that of an alkane having an equal viscosity at 30 °C.

(15) The use of $CF_2ClCFCl_2$ as a solvent does not appear to affect k_1 significantly. For example, at 75 °C[16] $k_1^{1b} = 2.5 \times 10^2$ s^{-1} in hydrocarbon,[10] while a value of 4.3×10^2 s^{-1} was obtained in the present work in $CF_2ClCFCl_2$ as solvent.

Table III. Rate Constants at 75 °C and Arrhenius Parameters for the Acyloxy Migrations 1a → **2a** and 1d → **2d**

reactn	solvent	T range, °C	log (A/ s^{-1})^a	E_r,^{a} kcal mol^{-1}	$k_1^{75\,°C}$, s^{-1} ^{b}
1a → **2a**	$C_6H_5CMe_3$	70 to 115	13.9 ± 1.1	17.9 ± 1.9	4.5×10^2
1d → **2d**	Freon 113	−11 to 32	11.0 ± 1.0	9.8 ± 1.2	7.0×10^4
1a → **2a**	H_2O	5 to 37	12.3 ± 0.9	12.7 ± 1.2	2.1×10^4

^{a} Experimental values. Errors stated represent one standard deviation. ^{b} Calculated from measured Arrhenius parameters.

Table IV. Kinetic Data for the 1a → **2a** Rearrangement in Water

T, °C	10^8· [**2a**], M	10^8· [1a], M	10^7· (k_1^{1a}/ $2k_t^{2a}$), M	10^{-8} ^{a}· $2k_t^{2a}$,^{a} M^{-1} s^{-1}	10^{-3}· k_1^{1a}, s^{-1}
5	26	38	4.5	4.8	0.22
7	24	25	4.6	5.1	0.23
8	19	35	3.0	5.2	0.16
9	31	32	6.1	5.4	0.33
14	39	29	9.0	6.1	0.55
16.5	30	32	5.9	6.6	0.39
17.5	34	24	8.2	6.7	0.55
23	41	35	8.8	7.8	0.69
31	40	16	14	9.4	1.3
37	48	14	21	11.0	2.3

^{a} Assumed. See text.

as large as k^{1a}. The spectrum due to **3d** could not be detected during the **1d** → **2d** rearrangement although it would certainly be stable toward ring opening at these temperatures. In fact, the **3d** → **2d** reaction must be considerably slower than the **3a** → **2a** reaction since **3d** could be observed at temperatures as high as 120 °C[17] with no sign of **2d**, whereas **2a** is formed from **3a** in detectable concentrations at temperatures of 6 °C and above.[10]

Experiments in Water. Beckwith and Tindall[7] have shown that **1a** and **3a** can be generated in water from their protic parents **1a**H and **3a**H using the Ti^{III}/H_2O_2 couple in a dual flow system. Following the standard procedure[18] separate solutions of titanium(III) ion and hydrogen peroxide were transported by means of a peristaltic pump and were efficiently mixed just before entering the cavity of an EPR spectrometer. The parent acetate or dioxolan were generally added to both solutions in order to maximize their concentrations in the reaction zone.

$$Ti^{III} + H_2O_2 \rightarrow Ti^{IV} + HO^- + HO\cdot$$

$$HO\cdot + RH \rightarrow H_2O + R\cdot$$

With *tert*-butyl acetate as the substrate, we obtained at room temperature a spectrum that showed that radicals **1a** and **2a** were both present. This confirms the original report[7] and indicates that the **1a** → **2a** rearrangement is accelerated in an aqueous solvent.

Quantitative measurements of the rate constant ratios $k_1^{1a}/2k_t^{2a}$ in water were determined in the usual way[10] by measuring the absolute concentrations of **1a** and **2a**. Measurements were made over a temperature range from 5 to 37 °C, and the results are given in Table IV. Values of $2k_t^{2a}$ were estimated by comparison with the rate constants reported by Lehni and Fischer[19] for the bimolecular self-reaction of the $(CH_3)_2\dot{C}OH$ radical in water. Concentrations of **1a** and **2a** were determined under conditions (flow rate, reagent concentration, etc.) designed to reduce the intensities, and hence the concentrations, of the radicals that give rise to the two single-line EPR signals in Ti^{III}/H_2O_2 systems[18,20] to negligible levels. The flow system was then switched, without stopping the pump, from the two reservoirs containing Ti^{III} and H_2O_2 with added *tert*-butyl acetate to two different reservoirs containing Ti^{III} and H_2O_2 with isopropyl alcohol which was present in an amount equal to that of the *tert*-butyl acetate in the preceding experiment (see Experimental Section). Since the rate of hydroxyl radical production remains the same in the two experiments we can write:

$$d[\dot{O}H]/dt = 2k_t^{Me_2\dot{C}OH}[Me_2\dot{C}OH]^2 = 2k_t^{(1a+2a)}[(\mathbf{1a} + \mathbf{2a})]^2$$

The value of $2k_t^{(1a+2a)}$ can be assumed to be equal to that of $2k_t^{2a}$ since the two radicals are of similar size and should have similar diffusion coefficients. Therefore,

$$2k_t^{2a} = 2k_t^{Me_2\dot{C}OH}\frac{[Me_2\dot{C}OH]^2}{[(\mathbf{1a} + \mathbf{2a})]^2}$$

Four measurements in the temperature range 8–23 °C gave a mean value of 0.61 for the ratio $[Me_2\dot{C}OH]^2/[(\mathbf{1a} + \mathbf{2a})]^2$. This value was combined with the kinetic results of Lehni and Fischer[19] to calculate the $2k_t^{2a}$ values that are listed in Table IV. Arrhenius parameters for the **1a** → **2a** rearrangement in water are given in Table III.

At room temperature we found, as Beckwith and Tindal[7] had reported, that reaction of the dioxolan **3a**H with the Ti^{III}/H_2O_2 couple gave only radical **3a**. This contrasts with our previous result in hydrocarbon solvents in which **2a** could be observed at measurable concentrations at temperatures >6 °C.[10] However, both **3a** and **2a** could be observed in the aqueous system at temperatures somewhat above ambient. The EPR spectra were not of good quality, and for this reason the rate constant ratio $k_2^{3a}/2k_t^{2a}$ was estimated from the measured concentrations of **3a** and **2a** at only a single temperature, 55 °C. Combination of the estimated rate constant ratio with the 55 °C value for $2k_t^{2a}$, which was estimated as indicated above, yielded $k_2^{3a} = 9.6 \times 10^2$ s^{-1} for the **3a** → **2a** rearrangement in water at this temperature. Comparison with the value previously found for this ring-opening reaction in hydrocarbon solvent, viz.,[10] $k_2^{3a} = 1.9 \times 10^3$ s^{-1} at 55 °C, implies that the reaction rate is reduced slightly in water. Certainly, ring opening of **3a** in water is significantly slower than the **1a** → **2a** rearrangement in the same solvent ($k_1^{1a} = 6.9 \times 10^3$ s^{-1} at 55 °C).

Under a variety of conditions, *tert*-butyl trifluoroacetate in the Ti^{III}/H_2O_2 flow system gave only the singlets[20] that are found in the absence of a reactive substrate, rather than the expected rearranged radical **2d** or the radical $Me_2\dot{C}CH_2OH$[21] formed by interception of an intermediate isobutylene radical cation by OH^-. It would appear that *tert*-butyl trifluoroacetate is too insoluble in water to give an observable EPR spectrum. Unfortunately, the addition of some potential cosolvents gave radicals derived from the cosolvent (e.g., methyl from dimethyl sulfoxide).

Discussion

Our present results lend support to our original suggestion[10] that the 1,2-acyloxy migration proceeds via a charge-separated transition state, **4**, and provide further evidence in support of Beckwith and Tindal's original proposal that the dioxolanyl radical, **3**, does not lie on the reaction path. Specifically, in nonpolar solvents the rate of the **1** → **2** rearrangement is markedly accelerated when acetoxy is replaced by (trifluoromethyl)acetoxy and, since the ring opening of the trifluoromethyl-substituted dioxolanyl, **3d**, is much slower than the **1d** → **2d** rearrangement, it is clear that **3d** is not an intermediate in the (trifluoromethyl)acetoxy migration. Furthermore, the rate of the acetoxy migration is greater in water than in hydrocarbon solvents. For this rearrangement the change to water as solvent decreases both the Arrhenius preexponential factor and the activation energy—

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(16) The temperature used for comparison in ref 10.

(17) During continuous UV irradiation of the diacyl peroxide in a sealed tube in $CF_2ClCFCl_2$ as solvent.

(18) Dixon, W. T.; Norman, R. O. C. *J. Chem. Soc.* **1963**, 3119–3124.

(19) Lehni, M.; Fischer, H. *Int. J. Chem. Kinet.* **1983**, *15*, 733–757.

(20) Jefcoate, C. R. E.; Norman, R. O. C. *J. Chem. Soc. B* **1968**, 48–53 and references cited therein.

(21) The EPR spectrum of this radical can be distinguished from that due to $Me_2\dot{C}CH_2OC(O)CH_3$.[7,22]

(22) Gilbert, B. C.; Norman, R. O. C.; Williams, P. S. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1401–1405.

(23) Trifluoroacetic acid has a pK_a value of 0.23.

just as would be expected for a reaction in which the transition state was more highly solvated than the reactant. As a corollary, the decreased rate of the **3a** → **2a** ring opening in water implies that this reaction proceeds through a transition state that is less solvated than the reactant.

Additional support for a charge-separated transition state in the **1** → **2** rearrangement comes from a single experiment with *tert*-butyl cyanoacetate. We reasoned that the greater acidity of cyanoacetic acid ($pK_a = 2.45$) compared with acetic acid ($pK_a = 4.75$) should accelerate the rearrangement of the primary alkyl radical. As was expected, *tert*-butyl cyanoacetate in the Ti^{III}/H_2O_2 system at room temperature gave only the rearranged radical $Me_2\dot{C}CH_2OC(O)CH_2CN$ ($a^H(6H) = 23.25$ G, $a^H(2H) = 12.50$ G).

Finally, CF_3 groups are generally believed to flatten a neighboring radical center on carbon.[24,25] This would suggest that **3d** is more planar at C-2 than **3a**. Evidence that may favor this suggestion is provided by the high *g* factor for **3d** relative to **3a**. That is, the more planar radical center would allow increased electron delocalization onto the neighboring oxygen atoms of the dioxolan ring, which, since oxygen has a higher spin orbit coupling than carbon, should enhance *g*.[26] However, the planarity, or otherwise, of the radical center has only a small effect on k_2 since **3b**, which is planar, undergoes ring opening only slightly more slowly than **3a**.[27]

Experimental Section

General Procedures. The steady-state EPR technique in which radicals are generated directly in the EPR cavity by UV photolysis in nonpolar solvents in evacuated quartz tubes has been described previously.[10] For the Ti^{III}/H_2O_2 flow system the two solutions were pumped from reservoirs (after degassing by bubbling with nitrogen) by means of a peristaltic pump into a two-way tube appropriately positioned in the cavity of the spectrometer. The two solutions were flowed at equal rates that were in the range 50 mL/min. One solution contained 7.5 mL/L of 20% (w/v) titanous chloride and the other 0.75 mL/L of 30% H_2O_2. For the *tert*-butyl acetate experiments this compound was added at 5 mL/L to both solutions, while for the isopropyl alcohol experiments the isopropyl alcohol was added at 10 mL/L only to the H_2O_2 solution. In the variable-temperature experiments the liquid from the room-temperature reservoirs were passed through heat exchangers before entering the mixer, and the temperature of the stream flowing from the cavity was measured.

Materials. *tert*-Butyl acetate was available commercially (Aldrich) and 2,4,4-trimethyldioxolane from our previous study.[10] *tert*-Butyl trifluoroacetate was prepared by the method of Bourne et al.[28] The diacyl peroxide of 2-carboxy-2-(trifluoromethyl)-4,4-dimethyl-1,3-dioxolane, i.e., the precursor of **1d**, was synthesized as follows:

A mixture of 1-bromo-2-hydroxy-2-methylpropane[29] and methyl (trifluoromethyl)pyruvate[30] in pentane was reacted in the presence of anhydrous potassium carbonate in a modification of the published procedure[31] until the formation of 2-carbomethoxy-2-(trifluoromethyl)-4,4-dimethyl-1,3-dioxolane was optimized (4 days) according to GLC analysis (10 ft × 1/8 in. 8% Carbowax on Chromosorb W, He flow rate 30 cm^3/min at 100 °C). This product was separated from starting compounds by preparative GLC on a 10 ft × 3/8 in. 5% OV 101 column: He flow rate, 150 cm^3/min at 100 °C. [NMR δ 1.45 (s, 6 H, $(\mathrm{C}H_3)_2\mathrm{C}$), 3.82 (s, 3 H, $\mathrm{OC}H_3$), 3.92 (m, 2 H, $\mathrm{C}H_2$). Anal. Calcd for $C_8H_{11}O_4F_3$: C, 42.11; H, 4.86; F, 24.98. Found: C, 43.06; H, 5.08; F, 24.67.] This methyl ester was hydrolyzed by stirring with 10% aqueous potassium hydroxide until the oily layer had disappeared (approximately 2 h). The alkaline solution was extracted with ethyl ether; then the aqueous layer was chilled in ice and acidified with hydrochloric acid and the product extracted several times with ethyl ether. The ether extract was dried with anhydrous sodium sulfate and then evaporated under reduced pressure to leave an oily residue. [NMR δ 1.45 (s, 6 H, $\mathrm{C}\,(\mathrm{C}H_3)_2$), 3.92 (m, 2H, $\mathrm{C}H_2$), 7.04 (s, 1 H, $\mathrm{COO}H$, exchanged with D_2O).] This acid, which is hydroscopic, was dried by azeotropic distillation of the water with benzene and converted to the diacyl peroxide by known procedures.[32,33]

Note Added in Proof. We have been informed that ab initio MO calculations on a prototype 1,2-acyloxy migration support a dipolar transition state analogous to that of **4** (S. Saebo, A. L. J. Beckwith and L. Radom, private communication).

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Registry No. 1a, 33888-00-5; **1d**, 88635-50-1; **2a**, 82064-87-7; **2d**, 88635-51-2; **3d**, 88635-52-3; 1-bromo-2-hydroxy-2-methylpropane, 38254-49-8; methyl trifluoropyruvate, 13089-11-7; 2-carbomethoxy-2-(trifluoromethyl)-4,4-dimethyl-1,3-dioxolane, 88635-53-4; 2-carboxy-2-(trifluoromethyl)-4,4-dimethyl-1,3-dioxolane, 88635-54-6.

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(26) This effect does not occur when there is only one oxygen atom adjacent to the radical center, e.g., for $CH_3\dot{C}HOH$ and $CF_3\dot{C}HOH$ the *g* values were found to be 2.00330 and 2.00339, respectively.

(27) At 75 °C: $k_2^{3a} = 7.6 \times 10^3$ s^{-1}, $k_2^{3b} = 1.0 \times 10^3$ s^{-1}.[10]

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