flections at −162 °C were $a = 23.19$ (2) Å, $b = 11.37$ (1) Å, $c = 16.56$ (1) Å, $V = 4366$ (2) Å^3, $Z = 4$, $d_{calcd} = 1.287$ g cm^{-3}, with space group = *Pnam*.

A total number of 3305 reflections were collected by using standard moving-crystal, moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0 + dispersion, single background time at extremes of scan = 3 s, and aperture size = 3.0 × 4.0 mm. The limits of data collection were $6° \leq 2\theta \leq 45°$. Of the 3305 reflections, 2982 were unique, and the number with $F > 2.33\sigma(F)$ was 2025. It should be pointed out that the crystal was a poor scatterer of X-rays, and of the 3305 measurements, only 2102 has a net count greater than twice the background count.

The structure was solved easily by direct methods and Fourier techniques. During refinement, several atoms in the neopentoxy ligands acquired nonpositive definite thermal parameters. To resolve this problem, we first assumed that the space group was incorrect, and the molecule was placed in the corresponding noncentric space group. While the residuals, as expected, were slightly less in the noncentric space group, the same atoms were nonpositive definite, indicating other problems were responsible. Careful examination of Fourier and difference-Fourier maps indicated that disorder might be present, although attempts to resolve the disorder were unsuccessful. Our final conclusion is that most of the neopentoxy ligands are undergoing large vibratory motion, which may or may not be disorder. This conclusion is supported in part by the large number of reflections that were less than twice their background values (an unusual occurrence for low-temperature data) and experience with other compounds containing the neopentoxy ligand.

The following full-matrix refinement utilized only those data that were observed by using the criteria I (net count) > 2.0 × (background count). The final residuals are $R(F) = 0.093$ and $R_w(F) = 0.109$. The goodness of fit for the last cycle was 2.345, and the maximum Δ/σ was 0.05.

Acknowledgment. We thank the Office of Basic Sciences, Chemistry Division, Department of Energy, the Wrubel Computing Center, and the taxpayers of the State of Indiana for support of this work. M.H.C. is also grateful for a Camille and Henry Dreyfus Teacher–Scholar Grant.

Registry No. $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(HCCH)$, 78736-93-3; $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(MeCCH)$, 78736-94-4; $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(MeCCMe)$, 78750-14-8; $Mo_2(ONe)_6(py)_2(\mu\text{-}HCCH)$, 81987-91-9; $Mo_2(ONe)_6(py)(\mu\text{-}C_4H_4)$, 82010-06-8; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $Mo_2(ONe)_6(py)_2$, 81987-92-0.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (60 pages). Ordering information is given on any current masthead page. The complete structural reports, MSC Reports No. 8066 ($Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}C_2H_2)$) and No. 81018 ($Mo_2(ONe)_6(py)(\mu\text{-}C_4H_4)$), are available, in microfiche form only, from the Indiana University Library.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 38. Rearrangement of β-(Acyloxy)alkyl and β-(Benzoyloxy)alkyl Radicals[1]

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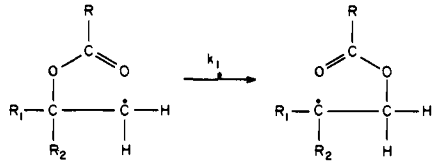
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada, and the Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada. *Received December 28, 1981*

Abstract: Rate constants for the free-radical rearrangement, $RC(O)OCMe_2\dot{C}H_2 \rightarrow RC(O)OCH_2\dot{C}Me_2$, and for the ring-opening reaction, $R\underline{\dot{C}OCH_2CMe_2O} \rightarrow RC(O)OCH_2\dot{C}Me_2$, have been measured by kinetic EPR spectroscopy. In hydrocarbon solvents at 75 °C with R = methyl and phenyl, the 1,2-acyloxy migrations are slower ($k = 5.1 \times 10^2$ s^{-1} and 2.5×10^2 s^{-1}, respectively) than the corresponding 1,3-dioxolan-2-yl ring openings ($k = 7.6 \times 10^3$ s^{-1} and 1.0×10^3 s^{-1}, respectively). The formation of a 1,3-dioxolan-2-yl radical as an intermediate in these two rearrangements could not, therefore, be ruled out. However, with R = cyclopropyl, the rearrangement proceeded normally ($k \approx 1.2 \times 10^2$ s^{-1} at 75 °C), but the corresponding 1,3-dioxolan-2-yl radical underwent opening of the cyclopropyl ring rather than the dioxolanyl ring. Since this process occurred at a much faster rate ($k = 8.7 \times 10^5$ s^{-1} at 75 °C) than the rearrangement, the dioxolanyl radical cannot, in this case at least, be an intermediate in this acyloxy migration. The possible role of charge separation in the transition state for acyloxy migration is considered.

There has been a continuing interest in the 1,2 migration of the acyloxy group (**1** → **2**) in β-(acyloxy)alkyl radicals[4] since this reaction has no direct intermolecular analogue. This rearrangement was originally observed during radical addition to the acetate of 2-methylbut-3-en-2-ol.[5] Subsequently, it was detected during the free-radical-induced decarbonylation of $(CH_3)_2C[OC(O)CH_3]CH_2CHO$, which was found to give both $(CH_3)_3COC(O)CH_3$ and $(CH_3)_2CCHCH_2OC(O)CH_3$.[6] It was suggested that the reaction proceeded through the 1,3-dioxolan-2-yl radical, **3a**, which could serve as "a transition state, or an unreactive intermediate".[6] Subsequent kinetic and product studies by Beckwith and co-workers[7,8] led to the conclusion that **3** did not lie on the rearrangement pathway, although labeling experiments with ^{18}O showed a clean inversion of the positions of the two acyloxy oxygens. A cyclic transition state of ill-defined structure,[9] **4**, was proposed.[8]



1 2

a R, R$_1$, R$_2$ = CH$_3$
b R = C$_6$H$_5$; R$_1$, R$_2$ = CH$_3$
c R = cyclo-C$_3$H$_5$; R$_1$, R$_2$ = CH$_3$
d R, R$_1$ = CH$_3$, R$_2$ = C$_6$H$_5$

The evidence that **3** was not involved in these rearrangements came from kinetic studies.[7,8] In the first place, reaction of *tert*-butyl acetate with HO· radicals in water in an EPR spec-

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[1] Issued as N.R.C.C. No. 20476. Part 37: Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 3094–3098.

[2] Mount Allison University.

[3] N.R.C.C.

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[9] Structure **4** differs slightly from the original representation.

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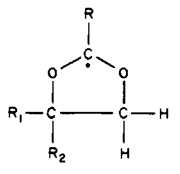

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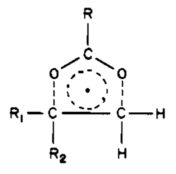
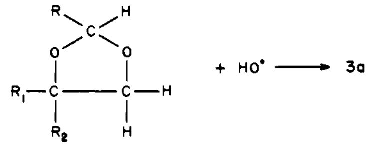


4

trometer at room temperature gave spectra due to both **1a** and **2a**, there being no sign of **3a**.[7]

$$(CH_3)_3COC(O)CH_3 + HO\cdot \rightarrow \mathbf{1a} + \mathbf{2a}$$

However, reaction of 2,4,4-trimethyldioxolane, **5a**, with HO· under similar conditions gave **3a** with no sign of **1a** or **2a**. That is, **1a** rearranges to **2a** in water under conditions where **3a** does not undergo ring opening. Secondly, rate constants for the rearrangement of **1a**, **1b**, and **1d** to the corresponding **2** in benzene were estimated by the tin hydride method[4,10] to be 6.2×10^3 s^{-1} (75 °C), 3.9×10^3 s^{-1} (70 °C), and 4.1×10^4 s^{-1} (70 °C), respectively.[8] It was pointed out that if the rearrangement involved two steps with **3** lying on the reaction path, then the rate of the overall rearrangement of **1** to **2** would be more sensitive to a change in R from methyl to phenyl than to a like change in R_1. That is, the similarity in the rearrangement rates of **1a** and **1b**, plus the faster rearrangement of **1d**, argue in favor of a concerted rearrangement.



5

The recognition of a one-step concerted rearrangement mechanism still leaves some questions unanswered:

(1) What is the essential difference between **3** and **4**? Beckwith[8] suggested that the answer to this question might lie in their different geometries. A cyclic transition state implies a planar geometry for the five annular atoms plus R, whereas EPR studies have shown that the radical centers in 1,3-dioxolan-2-yl and in 2-alkyl-1,3-dioxolan-2-yl and related radicals are pyramidal.[7,11-13] However, the 2-phenyl-1,3-dioxolan-2-yl radical has since been shown to be planar at its radical center,[14] which implies that for the benzoyloxy migration, at least, any difference between **3b** and **4b** is not due simply to geometric factors. This raises the further questions:

(2) Do **3** that are planar at their radical center differ from the corresponding **4**?

(3) Can a cyclic intermediate be intercepted? That is, can any **1** → **2** rearrangement be diverted in midcourse?

(4) How do the kinetics for **1** → **2** rearrangements compare with those for the ring opening of related 1,3-dioxolan-2-yl radicals? Beckwith's EPR experiments[7] imply that the **1a** → **2a** rearrangement is faster than the **3a** → **2a** ring opening in water, i.e., that $k_1^{\mathrm{a}} > k_3^{\mathrm{a}}$. This result would appear to be confirmed

$$\mathbf{3} \xrightarrow{k_3} \mathbf{2}$$

by Perkins and Roberts'[15] kinetic EPR measurements, from which they estimate that $k_3^{\mathrm{a}} \approx 7 \times 10^2$ s^{-1} at 72 °C in benzene, which is appreciably less than Beckwith's[8] k_1^{a} value of 6.2×10^3 s^{-1} at 75 °C. However, these two sets of kinetic measurements were not made under identical conditions. Our own results (vide infra) show that k_1^{a} is actually less than k_3^{a} in hydrocarbon solvents—a result that renders mechanistic conclusions regarding the intermediacy of **3a** impossible.

As a start to answering the above questions and to gain a more complete understanding of the 1,2-acyloxy migration, we have measured the rate constants for the **1a**,**b** → **2a**,**b** and **3a**,**b** → **2a**,**b** rearrangement by kinetic EPR spectroscopy. In addition, the cyclopropyl-substituted radicals **1c** and **3c** were studied in order to probe for the intermediacy of **3c** during the rearrangement of **1c**.

Experimental Section

The techniques of kinetic EPR spectroscopy have been described in previous papers in this series.[1]

Materials.[16] 3-Acetoxy-3-methylbutanoic acid was synthesized by two methods. Method 1: *tert*-Butyl 3-hydroxy-3-methylbutyrate[17] was acetylated with acetyl chloride in a mixture of pyridine and chloroform by the usual procedure.[8] The resulting *tert*-butyl 3-acetoxy-3-methylbutyrate distilled at 92 °C (17 mm): NMR δ 1.40 (s, 9 H, $(CH_3)_3C$), 1.50 (s, 6 H, $(CH_3)_2C$), 1.90 (s, 3 H, CH_3CO), and 2.73 (s, 2 H, CH_2). Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.13; H, 9.32. Found: C, 60.92; H, 9.18. The *tert*-butyl group was selectively cleaved by treatment with hydrogen chloride in methylene chloride or with trifluoroacetic acid.[17] The resulting 3-acetoxy-3-methylbutanoic acid (hygroscopic) gave NMR peaks at δ 1.50 (s, 6 H, $(CH_3)_2C$), 1.93 (s, 3 H, CH_3CO), 2.86 (s, 2 H, CH_2) and 10.2 (s, 1 H, COOH). Method 2: 4-Hydroxy-4-methyl-1-pentene was acetylated with acetic anhydride in the presence of triethylamine and (dimethylamino)pyridine[18] to yield 4-acetoxy-4-methyl-1-pentene: bp 38–40 °C (16 mm); NMR δ 1.40 (s, 6 H, $(CH_3)_2C$), 1.93 (s, 3 H, CH_3CO), 2.50 (d, 2 H, CH_2, allylic), 4.83–5.20 (m, 2 H, $=CH_2$), and 5.33–6.13 (m, 1 H, $-CH=$). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.89; H, 9.87. This compound was oxidized with potassium permanganate in water–benzene with hexadecyldimethylethylammonium bromide and the phase transfer technique[19] to yield the required 3-acetoxy-3-methylbutanoic acid.

3-(Benzoyloxy)-3-methylbutanoic was synthesized by method 2. The intermediate unsaturated ester, 4-(benzoyloxy)-4-methyl-1-pentene, was separated from starting reagents (4-hydroxy-4-methyl-1-pentene and benzoic anhydride) by chromatography on silica gel with pentane eluant: NMR δ 1.60 (s, 6 H, $(CH_3)_2C$), 2.66 (d, 2 H, CH_2), 4.90–5.30 (m, 2 H, $=CH_2$), 5.36–6.15 (m, H, $-CH=$), and 7.32–8.20 (m, 5 H, C_6H_5). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.31; H, 7.82. Oxidation[19] of this unsaturated ester yielded the required acid, which crystallized on refrigeration: NMR δ 1.72 (s, 6 H, $(CH_3)_2C$), 3.02 (s, 2 H, CH_2), 7.25–8.30 (m, 5 H, C_6H_5), and 11.0 (s, 1 H, COOH).

3-(Cyclopropylcarboxy)-3-methylbutanoic acid was synthesized by method 2. 4-Hydroxy-4-methyl-1-pentene was acylated with cyclopropanecarbonyl chloride in the presence of triethylamine and (dimethylamino)pyridine to yield 4-(cyclopropylcarboxy)-4-methyl-1-pentene: bp 64–66 °C (6 mm); NMR δ 0.60–1.30 (m, 5 H, cyclopropyl), 1.40 (s, 6 H, $(CH_3)_2C$), 2.53 (d, 2 H, CH_2, allylic), 4.80–5.25 (m, 2 H, $=CH_2$), and 5.45–6.15 (m, 1 H, $-CH=$). Oxidation of this compound as before yielded the required acid: NMR δ 0.69–1.39 (m, 5 H, cyclopropyl), 1.56 (s, 6 H, $(CH_3)_2C$), 2.89 (s, 2 H, CH_2), and 10.7 (s, 1 H, COOH).

The substituted acids were converted into their corresponding diacyl peroxides by known procedures.[20,21] The diacyl peroxides were purified immediately before use by preparative TLC or column chromatography on silica gel; the required peroxides were located on the chromatograms with a *N*,*N*-dimethyl-*p*-phenylenediamine spray. The diacyl peroxides were further identified by their NMR spectra, which all lacked COOH absorption.

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Table I. EPR Spectral Parameters[a]

radical	T, °C	g	a^H
1a–c	90	2.0029	21.3 (2), 1.17 (6)
2a–c	90	2.0028	15.5 (2), 23.1 (6)
3a	10	2.0032	1.24 (2), 13.11 (3)
3b	−50	*b*	6.8 (1), 1.0 (2) 1.7 (2), 5.3 (2)[c]
3c	−85	2.0031	6.03 (1)
6	−39	2.0027	0.64 (1), 21.86 (2) 29.50 (2)

[a] In hydrocarbon solvents; see text. Hyperfine splittings are given in gauss. The numbers in parentheses in the a^H column refer to the number of equivalent hydrogen atoms. Parameters for 1a–c and for 2a–c are the same within experimental error. [b] Not measured. [c] These hfsc's were estimated by spectral simulation.

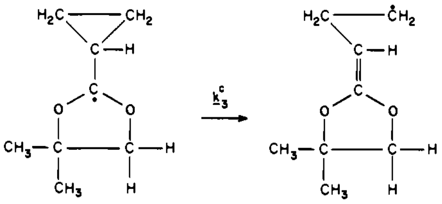
1-Bromo-2-(cyclopropylcarboxy)-2-methylpropane was synthesized by acylation of isobutylene bromohydrin[22] with cyclopropanecarbonyl chloride. The resulting product distilled at 90–96 °C (15 mm): NMR δ 0.65–1.30 (m, 5 H, cyclopropyl), 1.53 (s, 6 H, $(CH_3)_2C$), and 3.75 (s, 2 H, CH_2Br). Anal. Calcd for $C_8H_{13}BrO_2$: C, 43.46; H, 5.93; Br, 36.14. Found: C, 43.49; H, 5.73; Br, 36.13.

The required substituted 1,3-dioxolanes were synthesized by condensation of isobutylene glycol with the appropriate aldehyde. 2,4,4-Trimethyldioxolane has been prepared previously.[15] 2-Phenyl-4,4-dimethyl-1,3-dioxolane, from benzaldehyde and isobutylene glycol, distilled at 73–74 °C (1.3 mm): NMR δ 1.39 (s, 6 H, $(CH_3)_2C$), 3.65–3.92 (m, 2 H, CH_2), 5.93 (s, 1 H, CH), and 7.20–7.70 (m, 5 H, C_6H_5). 2-Cyclopropyl-4,4-dimethyl-1,3-dioxolane from the condensation of cyclopropanecarbaldehyde[23] and isobutylene glycol was separated by preparative VPC: NMR δ 0.33–0.80 (m, 5 H, cyclopropyl), 1.27 and 1.35 (2 s, 6 H, $(CH_3)_2C$), H_A 3.60, H_B 3.78, (J_{AB} = 4 Hz, 2 H, CH_2), 4.51 (d, 3 Hz, 1 H, CH). The last two substituted dioxolanes are new compounds, but they were not available in sufficient amounts for elemental analysis.

Results

Photolysis in the cavity of an EPR spectrometer of the appropriate diacyl peroxides in hydrocarbon solvents at room temperature gave rise to the spectra of the primary alkyl radicals **1a–c**.[24,25] Radical **1c** was also generated by photolysis of a *tert*-butylbenzene solution of 1-bromo-2-(cyclopropylcarboxy)-2-methylpropane, di-*tert*-butyl peroxide, and triethylsilane.[24,25] At temperatures above ca. 70 °C **1a–c** all underwent rearrangement to the tertiary alkyl radicals **2a–c**, respectively. No spectra due to the dioxolanyl radicals **3a–c** could be detected at any temperature. The EPR parameters for these radicals are reported in Table I.

Photolysis of hydrocarbon solutions of di-*tert*-butyl peroxide and the appropriate dioxolanes at low temperatures in the EPR spectrometer yielded the spectra of the dioxolanyl radicals **3a–c**. At higher temperatures the dioxolane rings of both **3a** ($T > 6$ °C) and **3b** ($T > 55$ °C) opened to give **2a** and **2b**, respectively. However, at all temperatures above −74 °C, it was the cyclopropane ring of radical **3c** that opened, forming the primary alkyl radical, **6**. This behavior is typical of cyclopropylcarbinyl radicals.[4,26] Even at temperatures as high as 100 °C, the only radical observed in this system was **6**. The EPR parameters for these radicals are also given in Table I.



3c 6

Rate constants for the rearrangements of **1a–c** to **2a–c**, respectively, of **3a** and **3b** to **2a** and **2b**, respectively, and of **3c** to **6** were measured by the steady-state EPR procedure.[4,27] In this method, the temperature for the reaction under investigation is adjusted until both the unrearranged radical, U, and the rearranged radical, R, can be observed simultaneously. The usual assumptions[4,27] lead to the kinetic expression:

$$k_r/2k_t^R = [R]([R]/[U] + 1)$$

where k_r and $2k_t^R$ are the rate constants for the reactions

$$U \xrightarrow{k_r} R$$

$$2R \xrightarrow{2k_t^R} \text{molecular products}$$

The bimolecular self-reactions of relatively small, sterically unhindered, alkyl radicals are diffusion-controlled processes,[27–29] and hence values of $2k_t^R$ are related to the viscosities, η, of the medium in which the reaction occurs. Accordingly, values of $2k_t^R$ were estimated from Schuh and Fischer's[29] highly reliable measurements of the rate constants for the bimolecular self-reaction of *tert*-butyl radicals, $2k_t^{Me_3C}$, in a wide variety of solvents. The temperature dependence of the viscosity of isooctane[30] is similar to that of *n*-octane, a solvent for which $2k_t^{Me_3C}$ values are available,[29] and hence these data were used directly. The temperature dependence of the viscosity of *tert*-butylbenzene[31] was found to lie between that for *n*-decane and *n*-dodecane, and hence the averaged $2k_t^{Me_3C}$ values for these two solvents were employed to represent $2k_t^R$. For cyclopropane as solvent, rate constants for the self-reaction of *n*-hexyl radicals[32] were used to represent $2k_t^R$. However, these data were subject to relatively large experimental errors, which are necessarily propagated into the values of k_r.

The measured rate constants for the various rearrangements are reported in detail as supplementary material. The derived Arrhenius parameters are summarized in Table II. For the **1c** → **2c** rearrangement, poor signal-to-noise ratios in the EPR spectra precluded a study of the temperature dependence on this reaction.

Discussion

The rate constant for the acetoxy migration **1a** → **2a** at 75 °C (5.1×10^2 s^{-1}; see Table II) is much smaller than the rate constant for the ring opening, **3a** → **2a**, of the potential intermediate, **3a**, at this temperature (viz., 7.6×10^3 s^{-1}), and so no mechanistic conclusions can be drawn regarding the intermediacy of **3a** in the **1a** → **2a** rearrangement. In this respect, our results contrast with Beckwith's earlier study of these two reactions in an aqueous medium.[7] Our rate constant for the **1a** → **2a** reaction is appreciably less than the value of 6.2×10^3 s^{-1} at 75 °C obtained by Beckwith by using the tin hydride method,[8] a result which can be attributed to the procedure used by Beckwith to calculate his rate constant.[33] For the **3a** → **2a** reaction our rate constant is in reasonable agreement with Perkins and Roberts'[15] value of 7×10^2 s^{-1} at 72 °C in view of the fact that these workers used a smaller value for $2k_t^R$[35] than that used herein.

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Table II. Rate Constants at 75 °C and Arrhenius Parameters for the Acyloxy Migrations 1a–c → 2a–c, the Dioxolanyl Ring Openings 3a,b → 2a,b, and Cyclopropyl Ring Opening 3c → 6

			experimental values[a]		recommended values		
reaction	R	temp range, °C	log (A/s^{-1})	E, kcal mol^{-1}	log (A/s^{-1})	E, kcal mol^{-1}	$k^{75\,°C}$/s^{-1}
$RCOOCMe_2\dot{C}H_2$ ↓ $RCOOCH_2\dot{C}Me_2$	CH_3 (1a)	70–115	13.9 ± 1.1	17.9 ± 1.9	13.2[b]	16.8	5.1×10^2
	C_6H_5 (1b)	69–108	12.6 ± 1.8	16.3 ± 3.0	13.2[b]	17.3	2.5×10^2
	c-C_3H_5 (1c)	93	*c*	*c*	13.2[b]	17.8[d]	1.2×10^{2}[d]
$R\dot{C}OCMe_2CH_2O$ ↓ $RCOOCH_2\dot{C}Me_2$	CH_3 (3a)	6–54	10.6 ± 0.4	11.3 ± 0.6	13.0[e]	14.6	7.6×10^3
	C_6H_5 (3b)	55–90	13.7 ± 0.9	17.2 ± 1.4	13.0[e]	16.0	1.0×10^3
$CH_2CH_2CH\dot{C}OCMe_2CH_2O$ ↓ $\dot{C}H_2CH_2CH{=}COCMe_2CH_2O$	c-C_3H_5 (3c)	(−74)–(−49)	9.1 ± 1.2[f]	7.2 ± 1.2[f]	12.5[g]	10.5	8.7×10^5

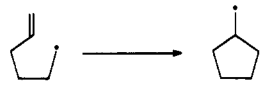
[a] The errors stated represent one standard deviation. [b] Average of results for 1a,b → 2a,b. [c] Not measured. [d] Based on a measured value for $k_r = (4.5 \pm 0.2) \times 10^2$ at 93 °C. [e] See text and ref 37. [f] Includes errors involved in the measurement of $2k_t$.[32] [g] Reference 26.

The benzoyloxy migration **1b** → **2b** occurs at a rate similar to (or possibly slightly slower than) the acetoxy migration, as found originally by Beckwith.[8] As would be expected, the ring opening of the 2-phenyl-substituted dioxolan-2-yl radical, **3b**, is appreciably slower (viz., 1.0×10^3 s^{-1} at 75 °C) than the ring opening of the 2-methyl-substituted radical, **3a**. Nevertheless, the ring opening of **3b** is substantially faster than the benzoyloxy migration **1b** → **2b**, and so, once again, no firm mechanistic conclusions can be drawn regarding the intermediacy of a dioxolan-2-yl radical.

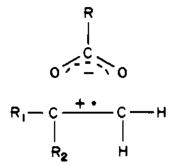
Mechanistic conclusions can, however, be derived from the behavior of the cyclopropyl-substituted radicals. The cyclopropylcarboxy migration **1c** → **2c** occurs normally (k = ca. 1.2×10^2 s^{-1} at 75 °C), but in the 2-cyclopropyl-substituted dioxolan-2-yl radical, **3c**, it is the cyclopropyl ring that opens. Since this ring opening is much faster (8.7×10^5 s^{-1} at 75 °C) than the **1c** → **2c** rearrangement, it is clear that **3c** does not lie on the reaction pathway for this rearrangement. In this instance, therefore, our results totally support Beckwith's conclusion[7,8] that dioxolan-2-yl radicals are not intermediates in acyloxy migrations. Incidentally, the opening of the cyclopropane ring of **3c** is considerably slower than the cyclopropylmethyl → 3-butenyl rearrangement,[26,36] but fortunately it was still sufficiently rapid for our purpose. The reduced rate for **3c** can be attributed to stabilization of the radical by the two neighboring oxygen atoms.

The steady-state EPR method for measuring rate constants for radical rearrangements can normally be applied only over a rather limited temperature range, and for this reason Arrhenius parameters are considerably less reliable than the rate constants themselves. Thus, for the dioxolane ring-opening reactions **3a,b** → **2a,b**, the Arrhenius preexponential factors would be expected to be ca. 10^{13} s^{-1}.[37] No large difference in A factors is expected to arise from the different ground-state geometries of **3a** (nonplanar)[7,11-13] and **3b** (planar).[14] The experimental A factor for the **3a** → **2a** reaction is almost certainly low, which means that the activation energy is also low. The A factor for the **3b** → **2b** reaction may be somewhat high.

The preexponential factors for the acetoxy, **1a** → **2a**, and benzoyloxy, **1b** → **2b**, migrations are in better agreement with each other, with a mean value of ca. $10^{13.2}$ s^{-1}. Despite the uncertainties in measuring Arrhenius parameters by the EPR method, an A factor of $10^{13.2}$ s^{-1} is extraordinarily high for a radical cyclization yielding a 5-membered ring.[38,39] For example,[38] the A factor for the cyclization of the 5-hexenyl radical to the cyclopentylmethyl radical is accurately known and has a value of only $10^{10.37}$ s^{-1}.



A concerted rearrangement through a transition state like **4**[40] requires that three internal rotations in the starting radical **1** be "frozen". The A factors would therefore be expected to be ca. 10^{11} s^{-1}.[37] If we assume that the much greater values found experimentally are, indeed, significant, then the transition state must be relatively "loose". This would imply that C–O bond scission is virtually complete before there has been much bond-making between the carbonyl oxygen and the primary alkyl radical center. We tentatively propose, therefore, that charge separation in canonical structures such as **7** plays an important role in the **1** → **2** transition state.



7

If the acyloxy migration did involve appreciable charge separation in the transition state, it would help to explain why Beckwith found the **1a** → **2a** rearrangement to be faster than the **3a** → **2a** reaction in water, whereas we, working in hydrocarbon solvents, find just the opposite. That is, polar solvents should stabilize structures such as **7** and hence should lower the barrier for the **1** → **2** rearrangement without greatly affecting the barrier for the **3** → **2** reaction. Of course, we do not mean to imply that complete charge separation occurs. For one thing, the clean inversion of the ^{18}O label observed by Beckwith[8] would not have occurred. For another, in the aqueous system[7] the production of a free 2-methylpropene radical cation from **1a** would have led to its quenching by the solvent and the production of the 2-(hydroxymethyl)prop-2-yl radical, **8**.

$$[(CH_3)_2C{=}CH_2]^{+\cdot} + H_2O \rightarrow \underset{\mathbf{8}}{(CH_3)_2\dot{C}CH_2OH} + H^+$$

This did not occur.[7] Radical **1a** and **8** show similar but quite distinguishable EPR spectra.[7]

Various experimental tests of our hypothesis that **7** makes an important contribution to the **1** → **2** transition state can be envisaged. We are currently exploiting some of the more obvious.

Acknowledgment. The kinetic EPR data was obtained by L. R. C. B. while on sabbatical leave at the N. R. C. C. We thank

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[35] Taken to be 2×10^9 M^{-1} s^{-1} at this temperature. See, however, footnote on p 81 of ref 15.

[36] The Arrhenius equation for the cyclopropylmethyl → 3-butenyl reaction can be represented by log (k/s^{-1}) = 12.48 − 5.94/θ, where θ = 2.3 RT kcal/mol,[26] which yields $k = 5.6 \times 10^8$ s^{-1} at 75 °C.

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[40] It has been suggested[34] that the **1** → **2** rearrangement is analogous to a pericyclic reaction (5 atoms + 5 electrons).

Dr. R. Sutcliffe and D. Lindsay for their advice and technical assistance. This research was supported in part by a grant to L. R. C. B. from the National Science and Engineering Research Council of Canada.

Registry No. **1a**, 33888-00-5; **1b**, 82064-85-5; **1c**, 82064-86-6; **2a**, 82064-87-7; **2b**, 82064-88-8; **2c**, 82064-89-9; **3a**, 33887-88-6; **3b**, 82064-90-2; **3c**, 82064-91-3; **6**, 82064-92-4; 3-acetoxy-3-methylbutanoic acid, 44983-17-7; *tert*-butyl 3-acetoxy-3-methylbutyrate, 82064-93-5; 4-hydroxy-4-methyl-1-pentene, 624-97-5; 4-acetoxy-4-methyl-1-pentene, 926-22-7; 3-(benzoyloxy)-3-methylbutanoic acid, 82064-94-6; 3-(cyclopropylcarboxy)-3-methylbutanoic acid, 82064-95-7; cyclopropanecarbonyl chloride, 4023-34-1; 4-(cyclopropylcarboxy)-4-methyl-1-pentene, 82064-96-8; 1-bromo-2-(cyclopropylcarboxy)-2-methylpropane, 82064-97-9; 2-phenyl-4,4-dimethyl-1,3-dioxolan, 52129-02-9; 2-cyclopropyl-4,4-dimethyl-1,3-dioxolan, 82064-98-0.

Supplementary Material Available: Tables of kinetic data (5 pages). Ordering information is given on any current masthead page.

Characterization of the 1:1 Charge-Transfer Reaction between Decamethylferrocene and 2,3-Dichloro-5,6-dicyanoquinone (DDQ): Structure of the DDQH$^-$ Anion[1]

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Abstract: The 1:1 charge-transfer reaction of decamethylferrocene (DMeFc) and 2,3-dichloro-5,6-dicyanoquinone (DDQ) results in a heterosoric stacked complex of [DMeFc$^{+}\cdot$][DDQH$^-$] composition where the DDQH$^-$ anion has a structure intermediate between the quinoid and benzenoid states. The crystal structure of the 1:1 complex [DMeFc$^{+}\cdot$][DDQH$^-$] has been determined by single-crystal X-ray diffraction. The material crystallizes in the orthorhombic space group, *Pbna*, with unit cell parameters a = 17.027 (3) Å, b = 14.497 (4) Å, c = 10.616 (1) Å, V = 2620.4 (14) Å^3, Z = 4, ρ_c = 1.40 g cm^{-3}. The data were collected on a four-circle Syntex P2$_1$ diffractometer, and the structure was solved by direct methods and refined with Fourier and full-matrix least-squares techniques. The final R_F was 0.054 for 2409 independent reflections where $F^2_{\text{obsd}} > \sigma F^2_{\text{calcd}}$. The crystal structure consists of heterosoric stacks of alternating DMeFc$^{+}\cdot$ and DDQH$^-$ ions along the c axis. Each ion has C_2 symmetry, the DDQH$^-$ ion being disordered. The planar DDQH$^-$ anion and C$_5$Me$_5$ rings of the DMeFc$^{+}\cdot$ ion are separated by 3.564 Å. The angle between the C$_5$ and DDQH$^-$ plane is 3.33°. The structure of the DDQH$^-$ ion is intermediate between the quinoid and benzenoid states with C═C bond distances of 1.368 (5) and 1.384 (4) Å and C–C bond distances of 1.454 (3) and 1.445 (3) Å. The C═O, C—Cl, and C≡N distances are 1.237 (3), 1.732 (2), and 1.101 (3) Å, respectively. The DMeFc$^{+}\cdot$ is ordered, and the C$_5$Me$_5$ rings are staggered by 26° with the methyl groups directed away from the Fe atom and out of the C$_5$Me$_5$ plane by 0.30–0.74 Å. The average Fe–C, C–C, and C–Me bond distances are 2.096 (2), 1.422 (3), and 1.505 (3) Å, respectively. The spin susceptibility at room temperature is 5.00 × 10^{-3} emu/mol or 3.5 μ_B for fully oriented samples ($g_\parallel$ of DMcFe$^{+}\cdot$ parallel to the magnetic field). This is consistent with a $S = {}^1/_2$ DMeFc$^{+}\cdot$, which possesses $g_\perp$ = 1.92 and $g_\parallel$ = 4.002. The magnetic susceptibility fits the Brillouin function for all temperatures studied (≥1.80 K) and for magnetic fields up to 8 T. There is no evidence for exchange coupling among the DMeFc$^{+}\cdot$ spins, in contrast to the behavior observed for (DMeFc$^{+}\cdot$)(TCNQ$^{-}\cdot$). Comparison of the magnetic properties of these two compounds demonstrates the important role of the presence of a spin on the acceptor molecule in mediating the exchange interaction between DMeFc$^{+}\cdot$ units.

We have recently characterized several major products formed from the charge-transfer reaction of decamethylferrocene (DMeFc) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) that have interesting chemical and physical properties.[5-8] In these charge-transfer reactions involving TCNQ, the resulting electron-rich TCNQ$^{-}\cdot$ radical anion shows structural differences when compared to the unperturbed neutral TCNQ molecule. These differences are predominantly manifested in the lengthening of the exocyclic carbon–carbon double bonds with charge transfer of electron density from the donor to acceptor.[8b] The exact amount of charge transferred, however, is difficult to ascertain from any bond length correlation.[8b,c]

The analogous charge-transfer reaction of ferrocene and 2,3-dichloro-5,6-dicyanoquinone (DDQ) was initially described as forming a phenoxy radical ion.[9] This reaction was of interest because of the comparable strength of DDQ (electron affinity, $E_A \sim 3$ eV)[11] as an organic electron acceptor when compared to TCNQ[9,10] (E_A = 2.8 eV).[11] No direct structural information was available as to the nature of the phenoxy radical ion, which was postulated and later reformulated to be the hydroquinonide

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