Electron Spin Resonance Spectra of Free Radicals. Part 2.[1] Radicals formed by Hydrogen Abstraction from Cyclic and Acyclic Fluoro-acetals

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Free radicals formed during the photolysis of solutions containing di-t-butyl peroxide and fluoro-acetals such as 1,1-diethoxy-2-fluoroethane and substituted 1,3-dioxolanes, have been studied by e.s.r. spectroscopy. Only the radicals formed initially by hydrogen abstraction were detected, although product analysis by g.c.–m.s. indicated that certain of the cyclic radicals rearranged to acyclic species. The e.s.r. parameters are discussed in relation to the preferred conformations of the radicals.

There have been a number of investigations of the e.s.r. spectra of free radicals formed by hydrogen abstraction from acetals and related substances.[2–12] In this work, we have studied radicals (1)—(6), formed similarly during the photolyses of solutions containing di-t-butyl peroxide and fluoro-acetals (see Table). These free radicals differ significantly in their preferred geometries from analogous free radicals without fluoro-substituents, such as those derived from 1,1-dimethoxyethane,[2,7,8] 1,3-dioxolane,[3,4,7,9] and methyl-substituted 1,3-dioxolanes.[3–5,7–10]

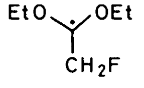
Experimental

Materials.—Fluoroacetaldehyde diethyl acetal was prepared by heating bromoacetaldehyde diethyl acetal with anhydrous KF in digol. 2-Fluoromethyl- and 2-fluoromethyl-4-methyl-1,3-dioxolane were similarly synthesised from the bromo-compounds prepared from bromoacetaldehyde diethyl acetal. 4-Fluoromethyl-2-methyl-1,3-dioxolane[13] was prepared by a standard procedure from the tosylate of the corresponding alcohol. The fluoro-compounds gave the correct $(M - 1)^+$ peaks in the g.c.–m.s. run at 20 eV on an AEI MS30 double-beam mass spectrometer. These compounds were freshly purified (>99% purity) by preparative g.l.c. before running the e.s.r. spectra.

E.s.r. Spectra.—Each sample solution contained an acetal and di-t-butyl peroxide. Usually, it was found advantageous also to include 2,2-dimethylbutane as a solvent, since it was then possible to use lower temperatures without separation of solid. Oxygen was removed by passage of helium, and spectra were recorded during irradiation from a Hg–Xe lamp, using equipment described previously.[1]

Results and Discussion

When di-t-butyl peroxide was photolysed in the presence of 1,1-diethoxy-2-fluoroethane, the e.s.r. spectra recorded between 193 and 253 K were analysed as due to mixtures of radicals (1) and (2). Using 2-fluoromethyl-1,3-dioxolane as substrate, at 183 K the only radical detected was (3). At 233 K, however, the spectrum indicated that both (3) and (4) were present, as shown in the Figure. The other substrates investigated, 2-fluoromethyl-4-methyl- and 4-fluoromethyl-2-methyl-1,3-dioxolane, gave spectra attributable solely to radicals (5) and (6), respectively, under the conditions used in these experiments. All spectra were matched against computer simulated spectra, and the e.s.r. parameters are reported in the Table.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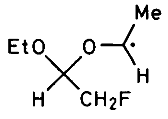
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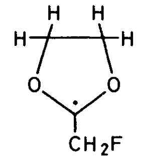
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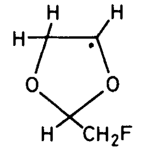
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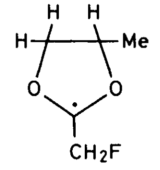
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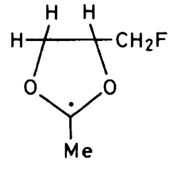
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We consider that product analysis by g.c.–m.s. can be a valuable adjunct to e.s.r. spectroscopy, especially since it is possible for a transient free radical to have an important kinetic effect even though its steady-state concentration may be too low for detection by e.s.r. Following the photolyses of di-t-butyl peroxide–2-fluoromethyl-1,3-dioxolane at 233 K and di-t-butyl peroxide–2-fluoromethyl-4-methyl-1,3-dioxolane–2,2-dimethylbutane at 183 K, analysis by g.c.–m.s. indicated the formation of 2-t-butoxyethyl and 2-t-butoxypropyl fluoroacetate, respectively, as the major products. The former photolysis also yielded 4-butoxy-2-fluoromethyl-1,3-dioxolane as a minor product: this is expected by combination of radical (4) with a t-butoxy radical. To explain the identities of the major products, we speculate that the rearrangements (1) and (2) may occur. Rearrangements of this type are well known, and Perkins and Roberts[14] observed e.s.r. spectra of the rearranged radicals derived from methyl substituted dioxolan-2-yl radicals at 70—80 °C. Our observation that the

$$(3) \longrightarrow \underset{(3R)}{FCH_2COOCH_2CH_2\cdot} \qquad (1)$$

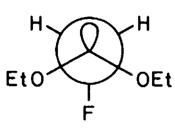
$$(5) \longrightarrow \underset{(5R)}{FCH_2COOCH_2\dot{C}HMe} \qquad (2)$$

Figure. (a) E.s.r. spectrum recorded at 233 K during irradiation of a solution of 2-fluoromethyl-1,3-dioxolane in di-t-butyl peroxide. (b) Simulated spectrum for a mixture of radicals (3) and (4) in the molar ratio 2.2 : 1

Table. Data from e.s.r. spectra

			Hyperfine splitting constants (G)					
Substrate	Radical	T/K	a(α-H)	a(β-H)	a(β-F)	a(γ-H)	other a(F)	g
$FCH_2CH(OEt)_2$	(1)	193		22.80	29.50 [b]			2.002 53
	(2)	193	14.12	22.30		1.44 (1 H)		2.003 19
$FCH_2CH\text{-}OCH_2CH_2O$	(3)	183		23.28	32.22 [b]	0.71 (2 H) [c]		2.002 53
	(4) [a]	233	11.58 [b]	25.84 [b]; 29.10 [b]		1.18 (1 H)	2.41	2.003 19
$FCH_2CH\text{-}OCHMeCH_2O$	(5)	183		23.26	32.45 [b]	0.70 (2 H) [c]		2.002 54
$MeCH\text{-}OCH(CH_2F)CH_2O$	(6)	213		13.92		0.97 (2 H); 0.64 (1 H)	0.25	2.002 98

[a] For this spectrum only, 2,2-dimethylbutane was *not* used as solvent. [b] Negative temperature coefficient. [c] Temperature invariant.



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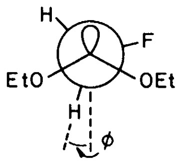


(8)

major products of the photolyses at relatively low temperatures appeared to be derived from the rearranged radicals is unexpected, since it suggests that the rearrangement reactions compete effectively with biradical termination reactions involving the unrearranged radicals. If this is so, why do the rearranged radicals not contribute significantly to the e.s.r. spectra? A possible explanation is that the rearranged radicals induce the decomposition of di-t-butyl peroxide, as shown for radical (3R) in equation (3). Induced decomposition

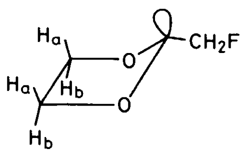
$$\text{(3R)} + \text{Me}_3\text{CO}_2\text{CMe}_3 \longrightarrow \text{FCH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{OCMe}_3 + \text{Me}_3\text{CO}\cdot \quad (3)$$

of di-t-butyl peroxide by free radicals has been reported previously.[15] Reactions of this type can explain the fact that the steady-state concentrations of the rearranged radicals were too low for detection, and are consistent with the identities of the major reaction products. Similar reactions were evidently not effective in suppressing the rearranged radical concentrations in the experiments of Perkins and Roberts. In their experiments, however, the rearrangement gave tertiary radicals, which one might expect to be less reactive towards the peroxide than the primary and secondary radicals (3R) and (5R).

The pyramidal geometry of trigonal carbon atoms with two alkoxy-substituents is well established,[3-5,7-9,10,16] and the e.s.r. spectrum of $\text{Me}\dot{\text{C}}(\text{OMe})_2$ has been discussed in terms of the likely preference of the radical for staggered conformations.[7,8] Of the three staggered, or approximately staggered, conformations of radical (1), (7), and (8) represent two energetically distinct conformations. We have discussed several free radicals which are thought to prefer conformations analogous to (7) previously.[1] They are characterized by relatively large values of a(β-F) and small values of a(β-H). In contrast, the observed values of these parameters for radical (1) provide evidence that the preferred conformations resemble (8), and not (7). However, we can only speculate on the value of ϕ; INDO calculations could be used to estimate the angle, but we doubt if these calculations are sufficiently accurate to give a meaningful answer. For a suitable value of ϕ, torsional motion in one direction leads to a diminution in a(F), and in the other direction to an increase in a(F); whether one would expect a positive or negative temperature coefficient for a(F) depends not only on the precise value of ϕ, but also on the detailed angular dependence of a(F), and so it is difficult to draw any definite conclusion from the observed negative temperature coefficient.

Starting from conformation (8), clockwise rotation of C_α through $(240-2\phi)°$ gives a conformation of unchanged energy, but with the two β-protons exchanged. Therefore, at sufficiently low temperatures, one might expect a broadening of the central components of the triplets due to the β-protons. In our experiments, we have not been able to observe any such selective broadening.

The e.s.r. spectra of radicals (3) and (5) resemble that of radical (1) in the magnitudes of the splittings due to the β-nuclei, and also in showing no detectable selective broadening within the triplets due to the β-protons; therefore it seems likely that the radicals have similar conformational preferences with regard to the C_α–C_β bond.



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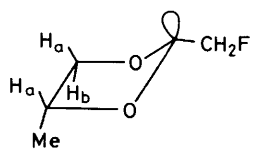


(10)

An interesting feature of the e.s.r. spectrum of radical (3) concerns the splitting due to the γ-protons. Over the temperature range 183—273 K, a constant splitting due to two equivalent γ-protons was observed, with no resolvable splitting due to the remaining two γ-protons. This contrasts with the observations of Gaze and Gilbert [7] on the 2-methyl-1,3-dioxolan-2-yl radical, for which at low temperatures two of the γ-protons had a splitting constant of 1.45 G and the other two had a splitting constant of 1.00 G. Evidently, substituting fluorine for one of the methyl hydrogens in 2-methyl-1,3-dioxolan-2-yl has a significant effect on the preferred conformation. That γ-proton hyperfine splittings in this type of free radical are sensitive to the precise geometry is supported by INDO calculations.[7,8] Gaze and Gilbert [7,8] were able to identify conformations of 1,3-dioxolan-2-yl and related free radicals for which the hyperfine splittings constants calculated by the INDO method differed, in absolute magnitude, from the experimental splittings by not more than a few tenths of a gauss. For some of the radicals it was deduced from the e.s.r. spectra that the non-equivalent γ-protons had splitting constants of the same sign, and the INDO results were consistent with this feature also. We do not consider that the accuracy of the INDO method in calculating hyperfine splitting constants is such that conformations identified in this way are necessarily meaningful. The approximations involved in using INDO calculations to estimate long-range splittings have been discussed,[17] as also have the limitations of calculations at this level of approximation when determining the conformations of five-membered rings by minimizing the total energy.[18]

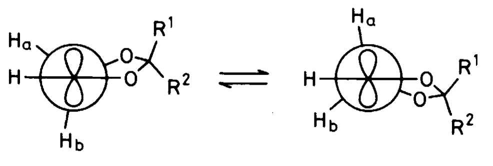
This is not to deny the value of INDO calculations in interpreting e.s.r. data, provided the approximations of the method are taken into account. For the radical (3), we deduce from the observed equivalences among the γ-protons that, on an appropriate time scale, the ' average conformation ' corresponds to the envelope conformation (9). From INDO calculations for the 1,3-dioxolan-2-yl radical (ref. 7, Table 3) it appears that the measurable γ-proton splitting belongs to the protons H_a, and the immeasurably small splitting to the protons H_b. This conclusion seems to be supported by the e.s.r. data for radical (5), discussed below.

For the 2-methyl-1,3-dioxolan-2-yl radical at temperatures of 223 K and above, all four γ-protons appeared equivalent.[7] The introduction of the fluoro-substituent in radical (3) has the effect of reducing the rate of inversion, so that even at 273 K the four γ-protons do not appear equivalent.*

The e.s.r. spectrum of radical (5) resembles that of (3) in showing resolvable splitting by only two of the γ-protons. We propose that (10) is the appropriate time-averaged conformation. In this conformation, the methyl substituent is less sterically hindered than if it replaced one H_a, when significant repulsions involving the unpaired electron may be expected. Continuing this line of thought, we consider that alkyl substituents at the 4- and 5-positions may have the effect of reducing the inversion rate at the free radical centre, a point not mentioned by Gaze and Gilbert in their discussions [7,8] of this class of free radical. We note that the e.s.r. spectrum of the 4-methyl-1,3-dioxolan-2-yl radical showed splitting by two γ-protons of one type and one of another type at all temperatures investigated.[7] Unlike Gaze and Gilbert,[7] we think that this non-equivalence among the γ-protons may possibly be a consequence of relatively slow inversion at the radical centre.

With regard to radical (6) (Table), $a(\beta\text{-H})$ has returned to the 'normal' range for radicals of this type.[7] The γ-proton splittings are significantly different from the values reported [7] for the 2,4-dimethyl-1,3-dioxolan-2-yl radical, emphasizing again the extreme sensitivity of these splittings to the precise geometry of the radical. The magnitude of the fluorine splitting is within the expected range.

The e.s.r. spectrum of radical (4) shows evidence of non-equivalent β-protons, for which we present the following explanation. Radicals of this type with substituents R^1 and R^2 ($R^1 \neq R^2$) at the 2-position may exist in two enantiomeric conformations. Considering one of these (enantiomer A, say), the allowed oscillation about the C_α–C_β bond may be represented as follows. If R^1 and R^2 were the same, $a(H_a)(12) = a(H_b)(13)$ and $a(H_b)(12) = a(H_a)(13)$. However, since $R^1 \neq R^2$, these equalities do not apply: in the slow oscillation limit the β-protons cause splitting into eight lines of equal intensity, if (12) and (13) are assumed to be equally stable, and in the fast oscillation limit the β-protons cause splitting into four lines of equal intensity. At intermediate rates of oscillation, alternating linewidths are observed. Of course, enantiomer B gives an identically superimposable spectrum. The situation is similar to that which applies when a chiral centre is adjacent to a β-CH_2 group.[19,20] For radical (4) at 233° the splitting due to the β-protons approximates to the fast limit (Figure). Each of the values of $a(\beta\text{-H})$ reported in the Table actually represents an average splitting.



(12) (13)

We intend to report on the e.s.r. spectra of other 1,3-dioxolane-4-yl radicals in a later paper, when we will discuss long-range splittings of the type shown by radical (4).

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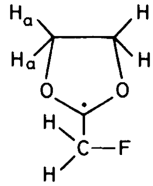
* A referee has suggested that the non-equivalence of the γ-protons might arise in the manner suggested by structure (11).



(11)

We consider this unlikely for two reasons. First, the difference in magnitude between the splitting constants for H_a and H_b (*ca.* 0.6 G, taking the unresolved splitting to be 0.1 G) seems too large to be plausibly explained in this way. Second, for H_a and H_b to appear non-equivalent by this mechanism, 180° reorientations of the CH_2F group would have to be less frequent than *ca.* 1.7×10^6 Hz. We doubt if the barrier to rotation is as large as this implies, and if it were selective broadening of the central components of the triplets due to the β-protons would be expected; as mentioned above, no such selective broadening was detected.