Electron Spin Resonance Spectra of Free Radicals. Part 3.[1] 2,2-Disubstituted 1,3-Dioxolan-4-yl Radicals

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E.s.r. parameters are reported for 11 1,3-dioxolan-4-yl radicals each with two substituents at the 2-position. When the two substituents are different, the β-protons appear non-equivalent, and for some of the radicals selective broadening of the lines with $M = 0$ for the β-protons is observed. The implications of these observations are discussed. Some of the radicals show long-range splittings due to fluorine nuclei. These splittings are discussed in relation to splittings calculated for selected conformations by the INDO MO method.

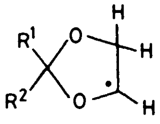
In an earlier paper,[1] we gave an account of the e.s.r. spectrum of the 2-fluoromethyl-1,3-dioxolan-4-yl radical (1; $R^1 = H, R^2 = CH_2F$). Two interesting features of the spectrum were noted; the magnetic non-equivalence of the β-protons, and the unexpectedly large hyperfine splitting due to the fluorine nucleus. The first of these features was interpreted on the supposition of a rapid torsional oscillation of the type shown in Scheme 1 ($R^1 = H, R^2 = CH_2F$).

In this paper, we give details of the e.s.r. spectra of 11 other substituted 1,3-dioxolan-4-yl radicals, which we have generated by hydrogen abstraction from the 4-position of each of the substrates (2)—(12). Some of the e.s.r. spectra show evidence of non-equivalent β-protons, sometimes with selective broadening of the lines with $M_\beta = 0$, and some reveal long-range splittings due to fluorine nuclei. Our discussion is mainly concerned with these features of the spectra.

Experimental

Materials.—The compounds (2)—(6) were prepared by azeotropic removal of water from refluxing solutions of the appropriate ketone, ethylene glycol, toluene-*p*-sulphonic acid, and benzene or toluene. The bromo-substituted precursors of compounds (7)—(9) were prepared by the same method. Compound (7) was generated from the appropriate bromo-substituted precursor by heating with anhydrous silver fluoride, whereas (8) and (9) were generated from their bromo-substituted precursors by heating with anhydrous potassium fluoride in digol.[1] The ketones required to synthesize (10) and (11) were prepared by the Grignard reaction of cyclohexylmagnesium chloride and benzylmagnesium chloride, respectively, with fluoroacetonitrile.[2] These ketones were converted into diethyl acetals using triethyl orthoformate, and the 1,3-dioxolanes (10) and (11) were obtained by acid-catalysed exchange between the acetal and ethylene glycol. To prepare (12), (5) was reduced, using lithium aluminium hydride, to 4-hydroxybutan-2-one ethylene acetal; this was then converted into (12) by known procedures.[1] The identities of the dioxolanes prepared were checked by examining their n.m.r. spectra, and determining their exact molecular masses, as in our earlier work.[1,3] The dioxolanes were freshly purified by preparative g.l.c. before recording the e.s.r. spectra.

E.s.r. Spectra.—Each sample solution consisted of one of the substrates (2)—(12), di-t-butyl peroxide, and in some cases a suitable solvent, such as 2,2-dimethylbutane or toluene. Oxygen was removed by passage of helium, and spectra were recorded during irradiation from a Hg–Xe lamp, using equipment described previously.[3]



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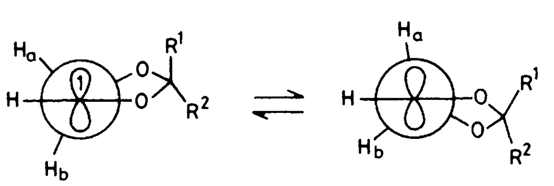
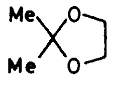


Scheme 1.



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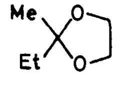

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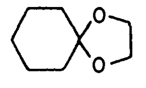

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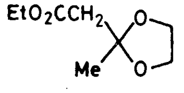

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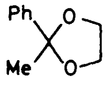

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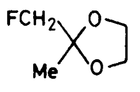

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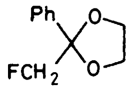

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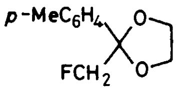

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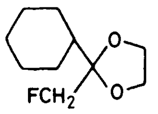

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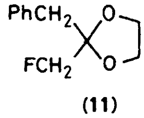

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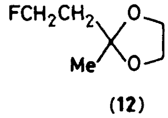


(12)

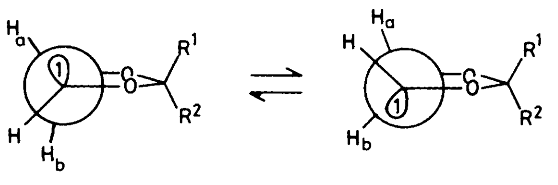
Results and Discussion

As expected, the e.s.r. spectra recorded when di-t-butyl peroxide was photolysed in the presence of the substrates (2)—(12) indicated, in every case, that the radical formed in the largest

Table. E.s.r. data for free radicals of type (**1**)

Substrate	Substituents		Solvent[a]/temp. (K)	g[b]	Hyperfine splitting constants (G)		
	R^1	R^2			$a(\alpha\text{-H})$	$a(\beta\text{-H})$	$a(F)$
2-Fluoromethyl-1,3-dioxolane	H	CH_2F	none/233	2.00319	11.58[c]	25.84; 29.10[c]	2.41[c]
(**2**)	Me	Me	none/283		11.42	27.27	
(**3**)	Me	Et	none/273		11.37	26.61; 28.27[d]	
			DMB/183		11.78	26.39; 29.05[d]	
(**4**)	$-(CH_2)_5-$		none/293		11.40	27.19	
(**5**)	Me	CH_2CO_2Et	none/273	2.003 38	11.80	26.95; 28.80	
(**6**)	Me	Ph	none/283		11.55	24.16; 30.64	
(**7**)	Me	CH_2F	none/273	2.003 29	12.02	27.20; 28.70	2.31
			none/253	2.003 31	12.05	27.00; 29.14	1.73
(**8**)	Ph	CH_2F	DMB/273	2.003 26	11.49	25.79; 30.00	*e*
(**9**)	p-MeC_6H_4	CH_2F	toluene/273	2.003 27	11.32	25.64; 29.98	*e*
(**10**)	C_6H_{11}	CH_2F	none/313	2.003 23	11.30	26.24; 29.14[d]	1.92
			none/243	2.003 28	11.55	26.36; 29.76[d]	1.96
(**11**)	$PhCH_2$	CH_2F	none/293	2.003 19	11.61	27.48; 28.06[d]	1.68
			none/233	2.003 31	11.80	27.55; 28.26[d]	1.61
(**12**)	Me	CH_2CH_2F	none/273		11.71	26.85; 28.46[d]	0.48
			DMB/183		12.20	27.03; 28.83[d]	0.40

[a] DMB = 2,2-dimethylbutane. [b] No entry indicates that g was not determined. [c] Data from ref. 1. [d] Selective broadening of the lines with $M_\beta = 0$ was observed. [e] No splitting attributable to the fluorine nucleus was resolved.



Scheme 2.

steady-state concentration belonged to the general type (**1**). We recorded a large number of spectra at different temperatures and with different solvents, and a selection of e.s.r. parameters for the substituted 1,3-dioxolan-4-yl radicals (**1**) is shown in the Table. With some of the substrates, minority species contributed relatively broad lines of low intensity to the spectra, but these species could not be identified.

β-*Proton Hyperfine Splittings*.—The new results appear to be consistent with the model of torsional oscillation shown in Scheme 1, which was used previously to explain the inequivalence of the β-protons in the 2-fluoromethyl-1,3-dioxolan-4-yl radical. In Scheme 1, attention is focussed on the non-planarity of the dioxolane ring, and the geometry at the α-carbon atom appears planar. However, the magnitudes of the α-proton hyperfine splittings (Table) suggests that the geometry at the α-carbon atom is actually appreciably non-planar.[4] This non-planarity may be due partly to the influence of the neighbouring oxygen atoms, and partly to the steric constraints imposed by a five-membered ring; similar non-planar geometries have been proposed for analogous five-membered heterocyclic radicals.[5] The non-planarity at the carbon centre is emphasised in the alternative Scheme 2, in which for the sake of clarity the dioxolane ring is shown as planar. Both Schemes 1 and 2 represent simplified views: however, our calculations based on standard bond lengths and bond angles seem to indicate that Scheme 2 may be closer to the true situation.

According to Scheme 1 (or 2), in the fast exchange limit, one would expect the two β-protons to appear inequivalent when $R^1 \neq R^2$, and equivalent when $R^1 = R^2$. This is exactly the situation indicated by our analyses of the e.s.r. spectra of the radicals derived from substrates (**2**) and (**4**) (Table). It is possible to distinguish between two factors which may contribute to the inequivalence of the β-protons when $R^1 \neq R^2$. One factor is the influence of R^1 and R^2 on the β-proton splittings, as a result of which the exchange-averaged splitting due to H_a will not be the same as the averaged splitting due to H_b, even if the two interconverting conformations have the same population. The other factor is the influence of R^1 and R^2 on the relative stabilities, and therefore populations, of the two exchanging conformations. It is interesting to note (Table) that the difference between the exchange-averaged β-proton splitting is particularly large when R^1 or R^2 = Ph or p-MeC_6H_4. This may be related to a specific stabilization of one of the conformations in Scheme 2. This explanation would be in line with our interpretation, in the next section of this paper, of the fact that the e.s.r. spectra of the radicals derived from substrates (**8**) and (**9**) did not show evidence of hyperfine splittings attributable to the fluorine nuclei.

In our studies[1] of the 2-fluoromethyl-1,3-dioxolan-4-yl radical we were not able to detect any indication of selective broadening of the lines corresponding to $M_\beta = 0$, and we concluded that torsional oscillation (Scheme 1) was rapid. For a number of the new radicals investigated in this work, selective broadening of the lines with $M_\beta = 0$ *was* observed (Table), although even at the lowest usable temperatures the splitting patterns due to the β-protons resembled the four-line fast-limit pattern far more closely than the eight-line pattern which we would expect in the slow limit. For those radicals which displayed the selective line-broadening effect, the temperature dependence of the effect was as expected from Scheme 1 (or 2), *i.e.* the selective broadening became more pronounced at *lower* temperatures: this is illustrated for one of the radicals in Figure 1.

All our experimental spectra were interpreted with the aid of computer simulations, including the spectra which displayed selective line broadening. A sample simulated spectrum is shown in Figure 1. The spectra with selective line broadening were efficiently simulated by a method which has been described.[6] In these simulations, the values used for the slow-limit hyperfine splitting constants were necessarily guesses, and the populations of the interconverting conformations were assumed to be equal. We are not reporting the parameter values used in our simulations, except for those reported in the caption to Figure 1, because these assumptions are highly unreliable,

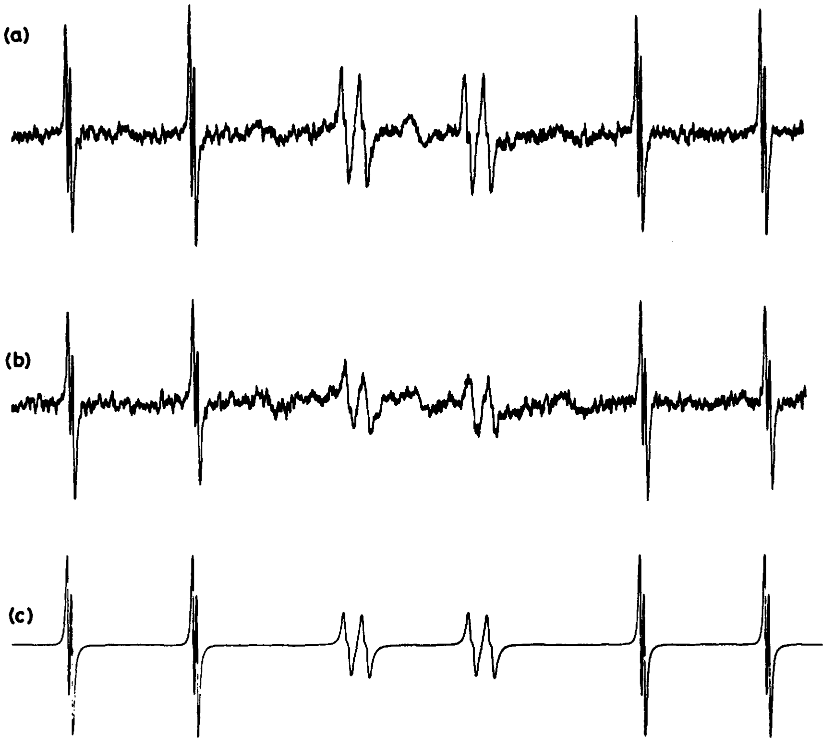


Figure 1. E.s.r. spectra of 2-fluoroethyl-2-methyl-1,3-dioxolan-4-yl radicals. (a) and (b) experimental spectra, recorded using 2,2-dimethylbutane as solvent, at 193 and 183 K respectively. (c) Computer simulation of spectrum (b), assuming slow-limit hyperfine splittings of 29.48 and 25.48 G for one of the hydrogen atoms and 32.18 and 24.58 G for the other, and an exchange rate of 8.16 × 10^7 Hz: other parameters were as given in the Table

even though they enabled us to simulate spectra in excellent agreement with experiment. The differing degrees of selective broadening among the radicals studied could conceivably arise from differing slow-limit hyperfine splittings, or differing exchange rates, or differing populations of the exchanging conformations, or a combination of these factors. Our observations, being confined to the fast-exchange region, do not allow us to distinguish between these possibilities.

Our explanation for the non-equivalence of the β-protons in the spectra of some of the radicals studied, and the temperature-dependent linewidth alternation in the spectra of others, is closely analogous to the explanation which has been offered for similar phenomena observed when a radical or radical ion has a β-CH_2 group adjacent to a chiral centre.[7]

Long-range Fluorine Hyperfine Splittings.—A large body of information is available on long-range splittings due to protons, but considerably fewer examples have been reported of long-range splittings due to fluorine nuclei. However, interesting observations have been made on the radical $(Me_3C)_2\dot{C}CH_2C_6F_5$,[8] for which a hyperfine splitting of 17.6 G was attributed to one of the *ortho*-fluorine nuclei, which was thought to interact with the unpaired electron by a through-space mechanism.

The absolute values of the hyperfine splitting constants which we have assigned to the fluorine nuclei in the previously studied[1] 2-fluoromethyl-1,3-dioxolan-4-yl radical, as well as the free radicals investigated in this work, are shown in the Table. We have carried out INDO molecular orbital calculations[9] for the simplest of these free radicals, namely the 2-fluoromethyl-1,3-dioxolan-4-yl radical. Six conformations were considered, which are shown in perspective in Figure 2. In these conformations, the trivalent carbon atom was assumed to have tetrahedral geometry, and standard bond lengths[10] were used: where possible, standard bond angles[10] were used also,

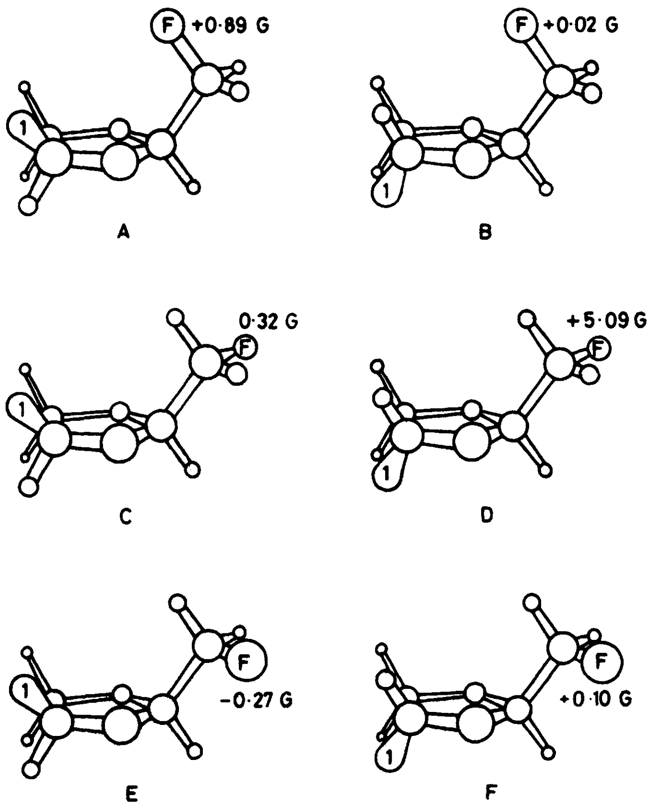
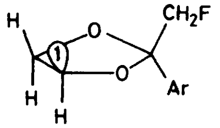


Figure 2. Six conformations of the 2-fluoromethyl-1,3-dioxolan-4-yl radical, drawn in perspective by using a computer program.[12] The h.f.s. constants for the fluorine nuclei, calculated by the INDO method, are shown



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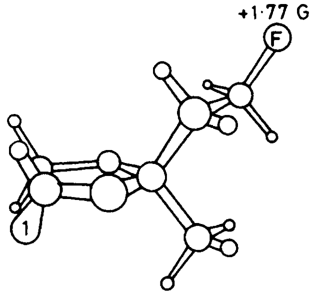

Figure 3. The 2-fluoroethyl-2-methyl-1,3-dioxolan-4-yl radical in a conformation expected to maximize the through-bond hyperfine interaction involving the fluorine nucleus. The h.f.s. constant for the fluorine nucleus, calculated by the INDO method, is shown

but this was not always feasible for the bond angles constrained by the dioxolane ring, which was taken to be planar. The splitting constants due to fluorine, as calculated by the INDO method, are inserted in Figure 2.

Among the conformations shown in Figure 2, the through-space interaction between the unpaired electron and the fluorine nucleus is maximized in conformation A, whereas the through-bond interaction would be expected to be favoured in conformation D, which approximates as closely as allowed by the constraints of the ring to the 2.5V scheme.[11] Evidently, the through-bond interaction is better able to explain the observed hyperfine splittings due to fluorine. On steric considerations, one would expect conformations D and F to be the most stable. If these conformations are assumed to have equal probabilities and to interconvert rapidly on the e.s.r. time scale, and if other conformations have negligibly small probabilities, on average $a_F = 2.6$ G is calculated. This value is remarkably close to the observed value of 2.41 G (Table). Several authors have commented[3] that the INDO method, as usually parameterized,[10] sometimes appears to give fluorine hyperfine coupling constants which are too large. In spite of this, one may tentatively suggest that the observations are not inconsistent with the assumptions made concerning the conformational equilibrium of the radical.

Considering the other radicals with $R^2 = CH_2F$, presumably the variations in the magnitudes and the temperature coefficients of a_F are related to the influence of R^1 on the relative stabilities of the different conformations. A particularly intriguing observation is that, with R^1 = Ph or p-MeC_6H_4, the e.s.r. spectra showed no evidence for splitting due to the fluorine nuclei. We speculate that conformations of type **(13)** may be favoured. The expected value of a_F would then approximate to the mean of the splittings for conformations C and E, in view of the fact that the conformation analogous to A is expected to be relatively unstable for steric reasons. This mean splitting is close to zero, in conformity with the observations. Steric interactions alone do not seem to provide a convincing explanation for the relative stability of **(13)**, and we consider it may be necessary to entertain the possibility of some more specific interaction, possibly between the unpaired electron and the π electrons of the aryl group. In this connection, we note that the lines of the spectra recorded with substrates **(8)** and **(9)** were uniformly rather broader than expected by comparison with the other spectra: this might conceivably be a consequence of unresolved splittings due to the aromatic protons.

The decrease in a_F when the substituent CH_2F is replaced by CH_2CH_2F (Table) seems to be roughly of the expected magnitude for a predominantly through-bond interaction mechanism, by comparison with data on long-range proton splittings.[11] The radical derived from substrate **(12)** is shown in Figure 3 in a conformation expected to maximize the through-bond interaction between the unpaired electron and the fluorine nucleus. For this conformation the value of a_F calculated by the INDO method was +1.77 G. This is considerably larger than the observed values, no doubt reflecting the fact that a_F is smaller for the other conformations important in the conformational equilibrium of the radical.

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