Electron Spin Resonance Spectra of Free Radicals. Part 1. α-Fluoromethylbenzyl Radical and Related Species

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The e.s.r. spectrum of the radical $\mathrm{PhCHCH_2F}$ has been studied for a variety of solvents and over a range of temperature. INDO calculations have been carried out for several conformations of the radical. The evidence suggests that rotation about the $\mathrm{C{-}CH_2F}$ bond is hindered, with one of the rotamers strongly destabilized by steric interaction between the fluorine atom and the phenyl group. E.s.r. spectra of a number of related radicals have also been studied. Rotation of $\mathrm{CH_2F}$ and $\mathrm{CHF_2}$ substituents is hindered, and some of the radicals appear to be significantly non-planar at the radical centre.

We have had a continuing interest [1] in benzylic hydrogen atom abstraction, in which, typically, free radicals of the type $\mathrm{XC_6H_4\dot{C}HCH_2F}$ are formed as reactive intermediates. This paper is an account of an investigation into a related class of transient free radicals (see Table 1), using e.s.r. spectroscopy.

A number of studies are relevant to this work. The e.s.r. spectrum of the benzyl radical itself was first observed some years ago,[2] and has since been the subject of theoretical study [3] as well as further experiment.[4] Fluorinated benzyl radicals have also received attention,[5] and e.s.r. parameters have been reported for the species $\mathrm{Ph\dot{C}HCH_3}$[6] and $\mathrm{Ph\dot{C}(OSiMe_3)CF_3}$.[7] Several β-fluoroalkyl radicals have been studied by e.s.r., including the β-fluoroethyl radical.[8]

Experimental

Materials.—The fluorides $\mathrm{XC_6H_4CH_2CH_2F}$ were prepared as reported.[1] The phenacyl fluorides $\mathrm{XC_6H_4COCH_2F}$ were synthesized by established routes [9] or by fluorinating the appropriate phenacyl bromides by heating with anhydrous KF in digol. β-Bromophenethyl fluoride was prepared as described.[10] The compounds *o*-$\mathrm{MeC_6H_4CHBrCH_2F}$ and *o,p*-$\mathrm{Me_2C_6H_3CHBrCH_2F}$ were synthesized from the appropriate phenacyl fluorides by standard routes. The fluoride $\mathrm{PhCH(OPh)CH_2F}$ was prepared from sodium phenoxide and β-bromophenethyl fluoride. Difluoromethyl phenyl ketone was prepared by a literature method.[11] All new compounds gave satisfactory exact mass measurements, using an AEI MS-30 mass spectrometer. The fluorides used for e.s.r. spectroscopy were generally purified by preparative g.l.c.

Samples.—Sample components were introduced into 4 mm o.d. thin-walled Suprasil tubes which were fitted with serum caps. The samples were deoxygenated by passing a slow stream of helium for 20 min with the aid of two hypodermic needles. Samples were subjected to intense radiation from a 1 kW Hanovia Hg–Xe lamp during the recording of the e.s.r. spectra.

Radicals were generated by known light-initiated reactions, using the following sample compositions: (A) $\mathrm{XC_6H_4CH_2CH_2F}$-di-t-butyl peroxide; (B) $\mathrm{XC_6H_4CHBrCH_2F{-}Bu_3SnH}$–solvent; (C) ketone–di-t-butyl peroxide–$\mathrm{Et_3SiH}$–solvent; (D) ketone–$\mathrm{Bu_3SnH}$–solvent.

Equipment.—A Bruker model 420 e.s.r. spectrometer with a 25 cm magnet was used. The spectrometer was equipped with a Bruker B-NM12 n.m.r. oscillator, an EIP model 350D frequency counter, and a Bruker model B-ST 100/700 variable-temperature unit. The on-line data system has been described elsewhere.[12] For the INDO calculations the University's Univac 1100/11 computer was used.

Results and Discussion

In Table 1 hyperfine splitting constants are reported for 14 benzylic radicals. Also included, for the purpose of comparison, are data for the radical $\mathrm{Ph\dot{C}HCH_3}$.[6] The hyperfine constants were estimated with the help of computer-simulated e.s.r. spectra, calculated to second order. Typical experimental spectra, together with the computer simulations, are shown in Figures 1 and 3. In Figure 3, second-order splittings may be observed in the central multiplet. Similar agreement between experimental and calculated spectra was achieved for the other radicals, and we believe this is good evidence for the accuracy of our assignments. We estimate the errors in the hyperfine splitting constants reported in Table 1 to be not greater than ±0.04 G.

Carbon-centred free radicals are known to adopt a variety of geometries between the extremes of planar and tetrahedral. In this connection it is significant to note (Table 1) that $a(\alpha\text{-H})$ varies only slightly among those radicals for which the datum is available, and is in fact close to the value for the benzyl radical itself (16.3 G).[4a] α-Hydrogen splittings are known to depend strongly on the trigonal carbon atom geometry, being negative for planar geometry and positive for tetrahedral geometry.[13] It seems reasonable to conclude therefore that all the radicals in Table 1 for which $a(\alpha\text{-H})$ is available, and the unsubstituted benzyl radical, have closely similar geometry at the trigonal carbon atom. Furthermore, there is little doubt that this geometry is planar. Benzyl itself has always been thought to be planar: [3] the value of $a(\alpha\text{-}^{13}\mathrm{C})$ predicted by INDO calculations on the basis of a planar structure is 32% too large,[4c] but would be even more unsatisfactory on the basis of a non-planar structure.

Our investigation of the radical $\mathrm{Ph\dot{C}HCH_2F}$ (Figures 1 and 2) has been particularly extensive. For the reasons given above, we consider the radical to be planar, or nearly so. It is interesting to compare this radical with $\mathrm{{\cdot}CH_2CH_2F}$, which is also planar. The β-fluorine hyperfine splitting is significantly larger for $\mathrm{Ph\dot{C}HCH_2F}$ (Table 1) than for $\mathrm{{\cdot}CH_2CH_2F}$ (47.6 G [8]), even though the spin density at the α-carbon atom is less; furthermore the temperature coefficient of $a(\beta\text{-F})$ is negative for $\mathrm{Ph\dot{C}HCH_2F}$ (Figure 2) but is positive for $\mathrm{{\cdot}CH_2CH_2F}$.[8] From their detailed study of $\mathrm{{\cdot}CH_2CH_2F}$, Chen *et al.*[8] proposed a four-fold potential barrier to rotation about the $\mathrm{C{-}CH_2F}$ bond, with torsion angles of 90° separating the stable rotamers. It seems that our observations on $\mathrm{Ph\dot{C}HCH_2F}$ can be ex-

Table 1. Hyperfine splitting constants of benzylic radicals

Radical	Method [a]/solvent [b]/ temp. (K)	Hyperfine splitting constants (G)					
		a(α-H)	a(β-H)	a(β-F)	a(H_p)	a(H_o)	a(H_m)
$Ph\dot{C}HCH_3$ [c]	/water/293	16.3	17.9		6.1	4.9	1.7
p-$Bu^tC_6H_4\dot{C}(OSnBu_3)CH_3$	D/DMB/243		13.65			4.59; 4.81	1.51
$Ph\dot{C}HCH_2F$	A/DBP/233	16.15	10.76 [e]	59.20 [d]	5.90	4.92	1.67
p-$MeC_6H_4\dot{C}HCH_2F$	A/DBP/233	*f*	*f*	62.29 [d]		*f*	*f*
p-$Bu^tC_6H_4\dot{C}HCH_2F$	A/DBP/233	16.08	10.00 [e]	61.98 [d]		4.93	1.53
p-$FC_6H_4\dot{C}HCH_2F$	A/DBP/243	16.30	10.30	61.33 [d]	(13.70) [h]	5.05	1.54
o-$FC_6H_4\dot{C}HCH_2F$	A/DBP/233	16.53	11.48	52.90 [d]	5.90	(7.52) [h]; 4.98	1.62
o,p-$Me_2C_6H_3\dot{C}HCH_2F$	B/toluene/233	*g*	*g*	53.50		*g*	*g*
o-$MeC_6H_4\dot{C}HCH_2F$	B/toluene/233	*g*	*g*	49.37	*g*	*g*	*g*
$Ph\dot{C}(OPh)CH_2F$	A/benzene/293		5.14	77.78	5.28	4.69; 4.59	1.53
$Ph\dot{C}(OSiEt_3)CH_2F$	C/benzene/283		5.25 [e]	87.77 [d]	5.25	4.37; 4.62 [i]	1.53
p-$FC_6H_4\dot{C}(OSiEt_3)CH_2F$	C/benzene/278		5.18	90.05 [d]	(11.94) [h]	4.39; 4.74 [i]	1.50
$Ph\dot{C}(OSiEt_3)CHF_2$	C/DMB/243		1.50 [e]	40.78 [d]	5.30	4.42; 4.70 [i]	1.54
$Ph\dot{C}(OSnBu_3)CHF_2$	D/toluene/273		1.54 [e]	40.04 [d]	4.90	4.11; 4.46 [i]	1.50
$Ph\dot{C}(OSiEt_3)CF_3$ [j]	C/benzene/278			22.35	5.05	4.47	1.50

[a] See Experimental section. [b] DMB = 2,2-dimethylbutane; DBP = di-t-butyl peroxide. [c] Data from ref. 6. [d] Negative temperature gradient. [e] Positive temperature gradient. [f] Resolution not attempted due to the presence of $\cdot CH_2C_6H_4CH_2CH_2F$ radicals. [g] Not resolved due to poor signal to noise ratio. [h] Figures in parentheses apply to ring fluorine atoms. [i] Non-equivalent *ortho*-protons. [j] Similar splittings are reported in ref. 7.

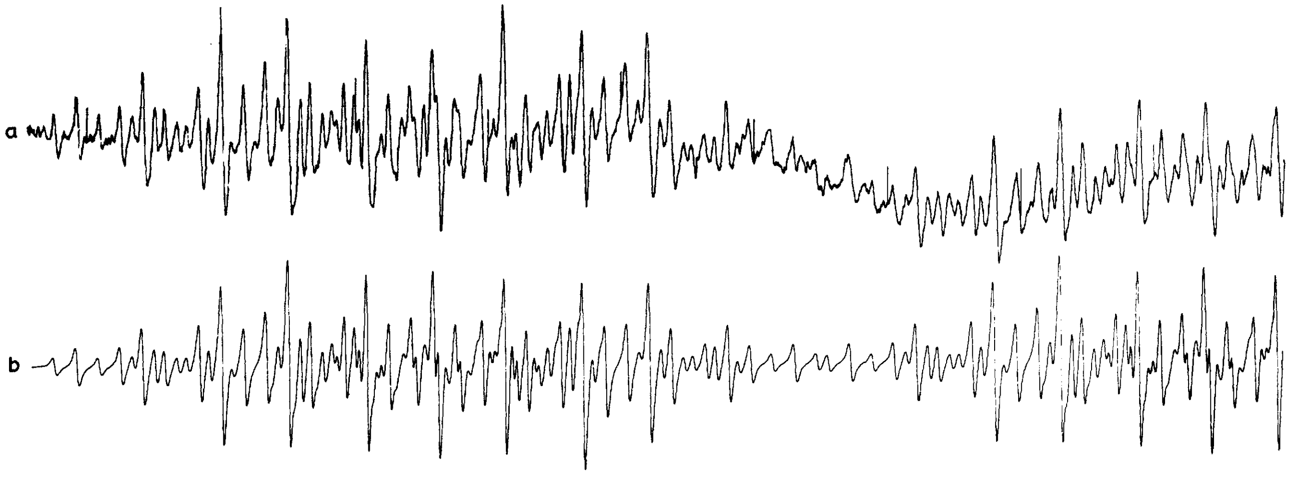


Figure 1. A portion of the e.s.r. spectrum of $Ph\dot{C}HCH_2F$ comprising the low field multiplet and part of the high field multiplet: a, experimental, n.m.r. marks at 10 G intervals; b, simulated

plained on the basis of the following analogous stable rotamers.

We have carried out INDO calculations [14] on these rotamers, using standard bond lengths and angles, and assuming θ 0; some pertinent results are given in Table 2. One would expect the observed hyperfine splittings to be suitably weighted averages of the splittings for the different rotamers; however, the predicted fluorine splittings are probably consistently too large, as noted by other authors.[4b,8,15] Rotamer (2) is predicted to be more stable than (1), as expected from the study of $\cdot CH_2CH_2F$,[8] but (4) is the least stable rotamer, presumably because of steric repulsion between the fluorine atom and one of the *ortho*-hydrogen atoms. This effect does not exist in the analogous conformation of $\cdot CH_2CH_2F$. In view of the relatively low stability of rotamer (4), which is associated with a minimal fluorine hyperfine splitting constant, the rather striking differences between $Ph\dot{C}HCH_2F$ and $\cdot CH_2CH_2F$, as regards a(β-F), are understandable. We have not been able to observe anomalous line broadening with $Ph\dot{C}HCH_2F$ of the type exhibited by $\cdot CH_2CH_2F$.[8] This is possibly because, in our experiments, it was impossible to achieve sufficiently low temperatures, due to the separation of solid phenethyl fluoride.

Chen *et al.*[8] reported that a(β-F) for $\cdot CH_2CH_2F$ was sensitive to the nature of the solvent, and they concluded that different solvents had different effects on the relative stabilities

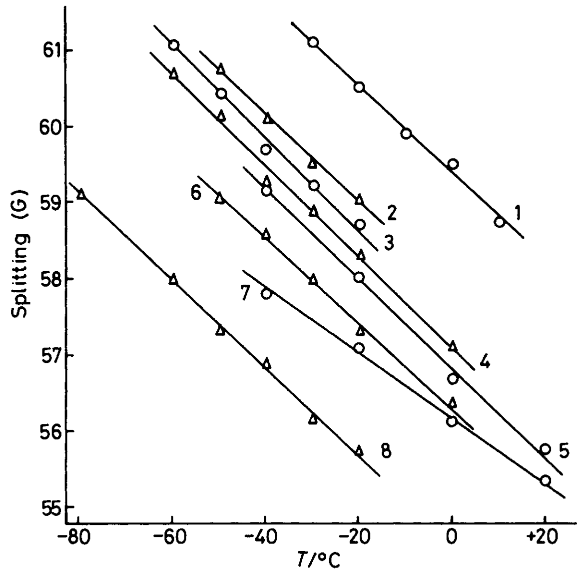
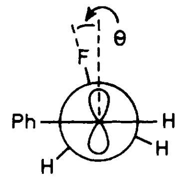


Figure 2. β-Fluorine hyperfine splittings for $Ph\dot{C}HCH_2F$, generated using the $PhCHBrCH_2F$–Bu_3SnH system, in the presence of different solvents (*ca.* 55%) and at different temperatures; 1, anisole; 2, *m*-chlorotoluene; 3, *m*-fluorotoluene; 4, toluene; 5, no solvent, $PhCH_2CH_2F$–DBP system; 6, *p*-t-butyltoluene; 7, t-butylbenzene; 8, 2,2-dimethylbutane



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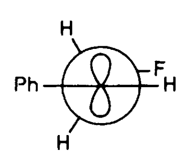

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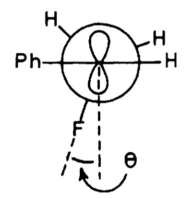

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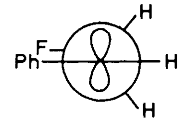

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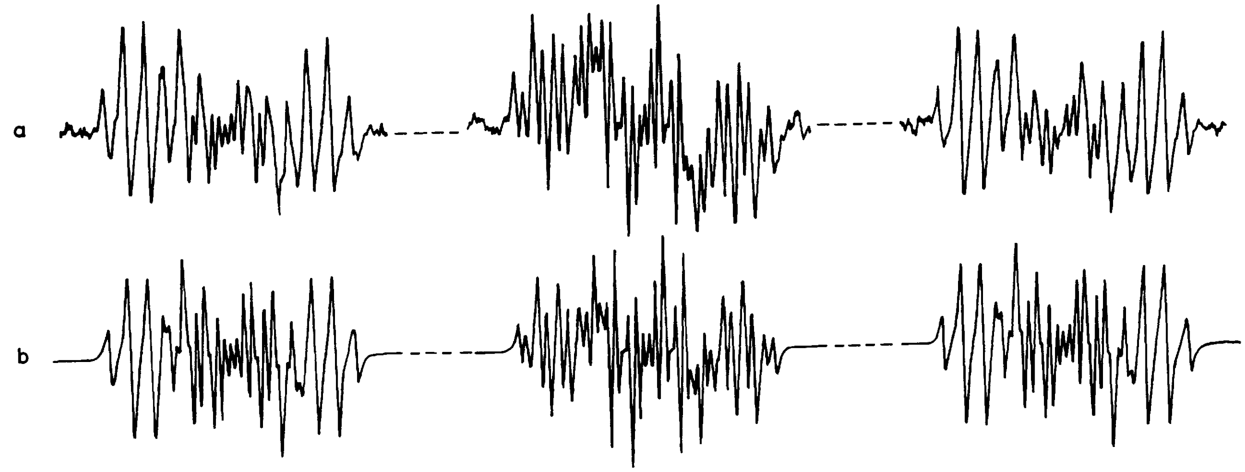


Figure 3. The e.s.r. spectrum of $Ph\dot{C}(OSnBu_3)CHF_2$, with the multiplets moved together for presentation purposes: a, experimental; b, simulated

of the stable rotamers. Our investigation of $Ph\dot{C}HCH_2F$ has also revealed that *a*(β-F) is markedly solvent dependent (Figure 2). In Table 2 the INDO-predicted dipole moments of the rotamers (1)—(4) are reported. Evidently rotamers (1)—(3) do not differ greatly in dipole moment, but the dipole moment of rotamer (4) is substantially less. Hence one would expect solvents of high dielectric constant to favour rotamers (1)—(3) relative to rotamer (4), and thus lead to increased values for *a*(β-F). As Figure 2 shows, this qualitative prediction is borne out by experiment.

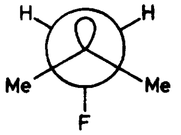
Considering other radicals of the type $Ar\dot{C}HCH_2F$ (Table 1) a point of interest is that *a*(β-F) is significantly reduced when there is a fluorine or methyl substituent in an *ortho*-position. At present, we are unable to offer a convincing explanation for this phenomenon.

The substituent $OSiEt_3$ has a tendency to induce non-planarity in carbon-centred free radicals.[16] Although fluorine hyperfine splittings of α-CF_3 groups have been used as an indication of the geometry at the carbon centre,[8,15,16] it is difficult to apply this criterion to the radical $Ph\dot{C}(OSiEt_3)CF_3$ (Table 1), because of uncertainty about the distribution of unpaired spin density. However, there are certain reasons to believe that the radicals with $OSiEt_3$ or $OSnBu_3$ substituents (Table 1) are to some extent non-planar. For example, the hyperfine splittings due to the nuclei of the aromatic substituents are significantly smaller than the corresponding splittings in the planar $Ar\dot{C}HR$ radicals (Table 1), indicating reduced delocalization of unpaired spin density into the aromatic substituents. The radicals $Ph\dot{C}(OSiEt_3)CH_2F$ and *p*-$FC_6H_4\dot{C}(OSiEt_3)CH_2F$ resemble $Me_2\dot{C}CH_2F$ [17] in their small values of *a*(β-H) and large values of *a*(β-F), and it seems likely that they prefer conformations closely analogous to the non-planar conformation (5) proposed for $Me_2\dot{C}CH_2F$.[17] Data for the radical $Ph\dot{C}(OPh)CH_2F$ (Table 1) seem to indicate that the substituent OPh also induces non-planarity at the free radical centre, but is less effective than $OSiEt_3$.

A conspicuous feature of the e.s.r. data for the radicals $Ph\dot{C}(OSiEt_3)CHF_2$ and $Ph\dot{C}(OSnBu_3)CHF_2$ (Table 1) is that the β-proton splittings are unusually small. Similarly small β-proton splittings have been observed [18] in a number of radicals thought to be locked in conformations in which

Table 2. Important parameters from INDO calculations for $Ph\dot{C}HCH_2F$ in three different conformations

Parameter	Conformation (1) and (3) (θ 0)	(2)	(4)
a(α-H)/G	−16.61	−16.69	−15.91
a(β-H)/G	10.74; 11.21	52.95	53.15
a(β-F)/G	264.32	0.62	−15.19
a(*p*-H)/G	−5.45	−5.16	−5.20
a(*m*-H)/G	3.47; 3.49	3.32; 3.32	3.34; 3.40
a(*o*-H)/G	−6.18; −6.21	−5.89; −5.86	−5.94; −6.87
Dipole moment (D)	2.014	2.140	1.468
Binding energy (a.u.)	−8.3654	−8.3756	−8.3488



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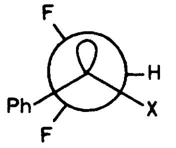

(6)

the C−H$_β$ bond is orthogonal to the singly occupied orbital at the α-carbon atom. We are led to conclude that the radicals $Ph\dot{C}(X)CHF_2$ ($X = OSiEt_3$ or $OSnBu_3$) have a pronounced preference for conformations of type (6). Evidence for hindered rotation about the $C_α$−CHF_2 bond in (6) was obtained from observed[19] linewidth alternation in the spectrum of the *p*-$Bu^tC_6H_4\dot{C}(OSiEt_3)CHF_2$ radical.

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