Electron Paramagnetic Resonance Studies of Electron-capture Processes. *p*-Nitrobenzyl and *p*-Nitrobenzylidene Systems[1]

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Electron paramagnetic resonance spectroscopy has been used to probe the anion radicals formed by electron capture by *p*-nitrobenzyl and *p*-nitrobenzylidene halides and their subsequent decomposition to yield radicals. In the case of the monohalogenated compounds ($ArCH_2X$; Ar = *p*-$NO_2C_6H_4$–; X = F, Cl, Br, I) the anion radicals of the fluoride, chloride and bromide are essentially long-lived over the temperature range used (77 K to *ca.* 160 K) while for the iodide significant decomposition of the anion radical is evident at 77 K. Our results show that the *p*-nitrobenzyl fluoride and chloride anion radicals adopt a conformation in which the halogen atoms are away from the perpendicular site while the *p*-nitrobenzyl bromide and iodide anion radicals prefer a conformation where the halogens are close to the perpendicular or maximum overlap site. In the case of the dihalogenated compounds (ArCHXY; Ar = *p*-$NO_2C_6H_4$–; X = Y = Cl; X = Cl, Y = Br; X = Y = Br; X = F, Y = Br), it is found that increasing halogen substitution destabilizes the anions and facilitates their decomposition to radicals. In the case of $ArCHCl_2$ and ArCHClBr, both the parent anion radicals and the radicals arising from their dissociation are detected at 77 K. In the case of $ArCHCl_2$, the anion radical is the major product and is shown to prefer a conformation in which the lone hydrogen atom is in the perpendicular position with respect to the aromatic ring. In the case of ArCHClBr, the anion radical is detected as the minor product with a conformation in which π–σ overlap involving the NO_2/aromatic π-orbitals and the C–Br σ-orbital has been reduced. The anion radicals of $ArCHBr_2$ and ArCHFBr are not detected at 77 K; only the radicals from bromide ion departure were observed.

We have previously used EPR spectroscopy at low temperature to investigate the anion radicals and radicals postulated as key intermediates in the $S_{RN}1$ reactions of *p*-nitrobenzyl and *p*-nitrocumyl derivatives.[2] We have now extended the study to include other *p*-nitrobenzyl and *p*-nitrobenzylidene derivatives where electron-transfer (ET) processes have also been postulated for some reactions of these substrates, in particular their reactions in basic media.[3–7] For example the reactions of *p*-nitrobenzyl chloride as well as *p*-nitrobenzylidene dichloride with hydroxide ion have been shown by kinetic studies to proceed *via* a mechanism involving electron-transfer as the key step (Scheme 1).[4,5] The key intermediates are the anion radicals formed by electron capture in the rate determining step. The mechanism has been shown to be quite general for various ring-substituted as well as side-chain derivatives, although the nature of the substituents as well as the reaction conditions can also affect the course of these reactions. Thus it has been shown that in the case of ring-substituted derivatives, additional methyl substitution suppresses the ET pathway and diverts the reaction towards solvolysis whereas chlorine substitution causes minimal perturbation and the reaction essentially proceeds *via* the radical pathway.[6] In the case of the various side-chain derivatives the course of the reaction is influenced by both the nature of the halogen substituent and the reaction conditions.[7] To complement the product studies we have carried out EPR studies at low temperature to probe the formation of these anion radicals and their subsequent fate. The EPR method involves generation of the parent anion radicals, $ArCHXY^{\bullet -}$, by direct addition thereby eliminating the formation of $Ar\dot{C}HX$ radicals. It also probes the stability of these anion radicals and their tendency to lose halide ions as in step (3) of Scheme 1.

$$\mathrm{ArCHXY} + \mathrm{OH}^- \rightleftharpoons \mathrm{Ar}\bar{\mathrm{C}}\mathrm{XY} + \mathrm{H_2O} \qquad \text{(fast)}$$

$$\mathrm{Ar}\bar{\mathrm{C}}\mathrm{XY} + \mathrm{ArCHXY} \longrightarrow \mathrm{Ar}\dot{\mathrm{C}}\mathrm{XY} + \mathrm{ArCHXY}^{\bullet -} \qquad \text{(slow)}$$

$$\mathrm{ArCHXY}^{\bullet -} \longrightarrow \mathrm{Ar}\dot{\mathrm{C}}\mathrm{HX} + \mathrm{Y}^-$$

$$\mathrm{Ar}\dot{\mathrm{C}}\mathrm{XY} + \mathrm{Ar}\dot{\mathrm{C}}\mathrm{HX} \longrightarrow \xrightarrow{\mathrm{OH}^-} (E \text{ and } Z) - \mathrm{ArCX{=}CXAr}$$

$$2\,\mathrm{Ar}\dot{\mathrm{C}}\mathrm{XY} \longrightarrow (\mathrm{ArCXY})_2$$

$$2\,\mathrm{Ar}\dot{\mathrm{C}}\mathrm{HX} \longrightarrow \xrightarrow{\mathrm{OH}^-} \mathrm{Ar{\equiv}CAr}$$

$$\mathrm{Ar}\dot{\mathrm{C}}\mathrm{HX} + \mathrm{ArCHXY} \longrightarrow \mathrm{ArCH_2X} + \mathrm{Ar}\dot{\mathrm{C}}\mathrm{XY}$$

$$\mathrm{ArCH_2X} \xrightarrow{\mathrm{ROH}} \mathrm{ArCH_2OR}$$

$$(\mathrm{Ar} = p\text{-}\mathrm{NO_2C_6H_4}\text{–}, \mathrm{X} = \mathrm{H \text{ or } Cl}, \mathrm{Y} = \mathrm{Cl})$$

Scheme 1

Results and Discussion

General.—The application of EPR spectroscopy to the study of matrix isolated radical anions and radicals is by now well established as a powerful technique, providing in many instances not only clear identification but also structural and mechanistic information that would be otherwise difficult to obtain.[8,9] As in our previous studies of nitroaromatic derivatives, the parent radical anions display outer parallel features which lead to unambiguous identification.[2,10] One principal advantage of the method is that in the majority of cases it allows the first formed intermediates to be observed. In the present study, not only are the first formed anion radicals clearly seen but in some cases the radicals derived from dissociation of the anion radicals are also evident allowing

Table 1 Relative stability of anion radicals *vs.* radicals for the process $ArCHXY + e \longrightarrow ArCHXY^{\bullet -} \longrightarrow Ar\dot{C}HX$ (or $Ar\dot{C}HY$) + Y^- (or X^-)

Substrate	Anion Radical	Radical	Comments
$ArCH_2F$ $ArCH_2Cl$	Anion radicals exclusive products	Not detected to annealing point	Anion radicals long-lived in matrices over temperature range used
$ArCH_2Br$	Exclusive product	Trace of radical detected on annealing	Slight loss of Br^- on annealing
$ArCH_2I$	Anion radical detected but minor product	$Ar\dot{C}H_2$ radical major product; on annealing, anion radical dissociates to radical	Loss of I^- facile
$ArCHCl_2$	Anion radical seen	$Ar\dot{C}HCl$ radical also present	Anion > radical and anion is stable on annealing
$ArCHClBr$	Present but minor product	$Ar\dot{C}HCl$ and $Ar\dot{C}HBr$ present	Anion unstable, Loss of $Br^- > Cl^-$
$ArCHBr_2$	Detectable but in trace amounts only	$Ar\dot{C}HBr$ radical major product	Anion unstable
$ArCHFBr$	Not detected	$Ar\dot{C}HF$ radical exclusive product	Loss of Br^- facile

Table 2 EPR parameters for *p*-nitrobenzyl and *p*-nitrobenzylidene halide anion radicals $ArCHXY^{\bullet -}$

		^{14}N Hyperfine coupling/G			Halogen hyperfine coupling/G[b] or ^1H hyperfine coupling/G
X,	Y[a]	$A_{\parallel}$	$A_{\perp}$	A_{iso}	
H,	F (MeTHF)	27	*ca.* 0	*ca.* 9	^{19}F 19
	(CD_3OD)	30	*ca.* 0	*ca.* 10	^1H *ca.* 5, ^{19}F 19
H,	Cl	28.5	0 ± 5[c]	*ca.* 9.5	*d*
H,	Br	26.5	0 ± 5	*ca.* 9	$A(^{81}Br) = 26.5$
H,	I	26	0 ± 5	*ca.* 9	^{127}I *ca.* 20 G
Cl,	Cl	28	0 ± 5	*ca.* 9.5	*d*
F,	Br		*e*		
Cl,	Br	*ca.* 27	*ca.* 0 ± 5	*ca.* 9	$A(^{81}Br)$ *ca.* 18 G
Br,	Br		*e*		

[a] Dilute solutions in MeTHF or CD_3OD. [b] $G = 10^{-4}$ T. [c] Not clearly resolved; 5 G is based on simulations. [d] Not resolved. [e] Not detected.

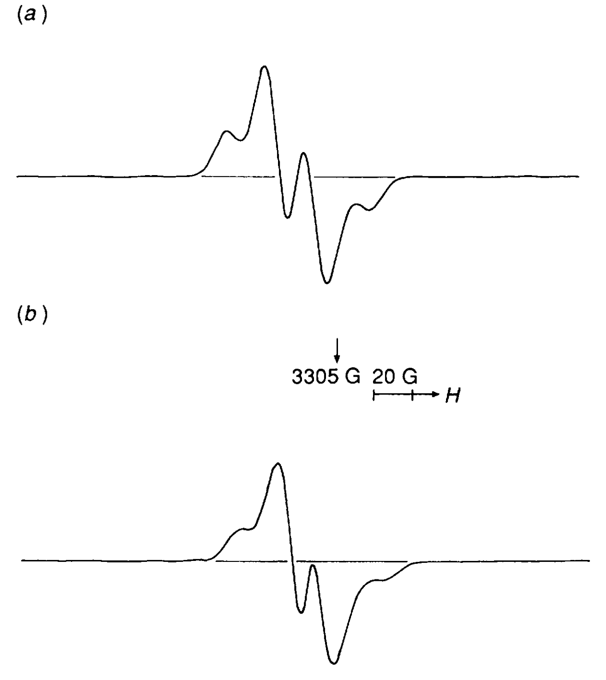


Fig. 1 (*a*) First derivative X-band EPR spectrum for the anion radical of $NO_2C_6H_4CH_2F$ after electron addition to the parent molecules in dilute solution in CD_3OD. (*b*) Computer simulation using the hyperfine parameters in Table 2 with $g_{\parallel} = 2.002$ and $g_{\perp} = 2.004$.

an estimate of the relative stability of a series of related anion radicals. The comparative stability of anion radicals *vs.* radicals for the process in eqn. (1) in the series of related nitrobenzylic

$$ArCHXY \xrightarrow{e} ArCHXY^{\bullet -} \longrightarrow Ar\dot{C}HX \text{ (or } Ar\dot{C}HY) + Y^- \text{ (or } X^-) \quad (1)$$

halides is shown in Table 1. It can be seen that for the monosubstituted derivatives (*p*-nitrobenzyl halides), the anion radicals are all formed. The anion radicals of the fluoride and chloride are stable once trapped and persist even to the annealing point. For the bromide, there is only a slight loss of Br^- on annealing. In contrast, in the case of the iodide although the anion radicals are observed, considerable decomposition of the anion radicals is evident even at 77 K; on further annealing the anion radical dissociates to the radical, a feature that was missed in a previous study.[2] The present result provides the EPR spectrum of the *p*-nitrobenzyl radical which has not previously been reported (*vide infra*). The present data is also in accord with that of other studies on the relative rates of dissociation of *p*-nitrobenzyl anion radicals which are in the order I > Br > Cl > F, an order that also correlates with the C–halogen bond strength.[11–13] In the case of the dihalogenated derivatives (*p*-nitrobenzylidene dihalides), anion radicals are detected for all substrates except ArCHFBr. In the case of *p*-nitrobenzylidene dichloride ($ArCHCl_2$), both the anion radical and the radical are observed at 77 K with radical predominating. The anion radical is also stable on annealing. Progressive bromine substitution appears to destabilize the anion radicals as is evident from the observation that on going from $ArCHCl_2$ to ArCHClBr and $ArCHBr_2$ the amount of the anion progressively diminishes with concurrent increase in the corresponding radical. In the case of ArCHFBr, the anion is not detected at all and the radical is the exclusive product.

Identification of Anion Radicals and Radicals.—The EPR spectra obtained from dilute solutions of the *p*-nitrobenzyl and *p*-nitrobenzylidene halides showed features which could be assigned to the parent anion radicals; all the parent anion radicals showed outer parallel features which led to unambiguous identification (Table 2, Fig. 1) The EPR spectrum of the anion radical of *p*-nitrobenzyl fluoride consists of a set of parallel features exhibiting hyperfine coupling to ^{14}N. One major doublet splitting of about 19 G is attributed to ^{19}F, and a

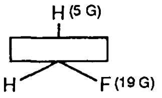
Table 3 EPR parameters for radicals ($Ar\dot{C}HX$) formed by dissociation of anion radicals ($ArCHXY^{\bullet-}$)

X	^1H Hyperfine coupling/G[a]	Halogen hyperfine coupling/G $A_{\parallel}$	$A_{\perp}$	A_{iso}
H	15			
F	16 (1 H), *ca.* 5 (2 H)	136	*ca.* 0	*ca.* 45
Cl	*ca.* 18	*ca.* 18[b]	[c]	—
Br[d]	*ca.* 15	90[b]	[c]	—

[a] G = 10^{-4} T. [b] Very broad features, therefore large errors. [c] *x* and *y* features not resolved, but splitting must be small. [d] From ArCHClBr and $ArCHBr_2$.

minor splitting of *ca.* 5 G is attributed to ^1H. This was just resolved for solutions in CD_3OD, but not for MeTHF solutions. The ^{14}N parallel coupling of *ca.* 29 G is characteristic of *p*-substituted nitroaromatic radical anions.[2,14,15] The proton splitting of 5 G is assigned to one of the two β protons. The other proton coupling was not resolved and must be ⩽ *ca.* 3 G. The isotropic data for this radical anion[16] show that the β protons have on average equal splittings of 1.75 G, the average ^{19}F splitting being 25.73 G. In the solid state, one proton coupling has increased and the ^{19}F coupling has decreased. Thus an asymmetric conformation is clearly favoured, with one of the β protons lying close to the plane of the anion radical. As in the case of the chloride, no dissociation of the anion radicals was observed on annealing to the softening point in either MeTHF or CD_3OD indicating that they are infinitely long-lived in solid matrices over the temperature range used. In the case of *p*-nitrobenzyl iodide, exposure of a dilute solution to ^{60}Co γ rays at 77 K gave an EPR spectrum which showed the presence of both the parent anion radical and the radical derived from it indicating considerable dissociation of the anion radical even at this temperature. The anion radical showed hyperfine coupling to ^{14}N and ^{127}I, $A\,(^{127}I)_{max}$ = *ca.* 20 G as before. However, in contrast to the previous results, dissociation of the parent anion radical was observed on annealing in CD_3OD resulting in loss of features due to the anion radical near the softening point and a corresponding increase in the intensity of the signal due to the corresponding radical. These results are similar to those obtained for the 5-nitrofurfuryl halide series where dissociation of the anion radical was observed only for the iodide derivative.[14] In the case of the *p*-nitrobenzylidene dihalides, both the parent anion radicals and the radicals were observed, indicating lowered stability of the anion radicals on increasing halogen substitution at the benzylic carbon. Thus in the case of *p*-nitrobenzylidene dichloride ($ArCHCl_2$), both the anion radical and the radical were detected at 77 K with the anion radical predominating. The anion radical showed hyperfine coupling to ^{14}N but coupling to the chlorine was not observed. Furthermore the anion radical was stable on annealing. On progressive substitution by the larger bromine atom as in ArCHClBr, destabilization of the anion radical becomes more pronounced; the anion radical is now the minor product while both the radicals ArCHCl and ArCHBr derived from its decomposition are clearly in evidence. The anion radical showed hyperfine coupling to ^{14}N and a coupling of *ca.* 18 G, assigned to bromine. Coupling to chlorine was not resolved. With substitution by two bromine atoms as in $ArCHBr_2$, the effect on anion radical stability is even more pronounced; the anion radical is now hardly detectable being present only in trace amounts so that no reliable data could be obtained. In the case of the fluorobromo derivative (ArCHFBr), the anion radical is not detected at all and only the radical is observed. The EPR parameters of the various *p*-nitrobenzyl radicals arising from dissociation of the parent anion radicals are shown in Table 3. The data are all close to the results expected.

Structure of Anion Radicals.—The nitrogen, hydrogen and halogen hyperfine coupling constants for the various *p*-nitrobenzyl and *p*-nitrobenzylidene anion radicals are shown in Table 2. Comparison of the isotropic and anisotropic coupling constants (^{14}N) with those estimated for unit orbital populations give the apparent p:s ratio of *ca.* 19 indicating that the nitro group, as in the case of the nitrobenzene anion radical, is nearly planar.[10] The observed ^1H and ^{19}F coupling in the case of $ArCH_2F$ and the absence of any coupling to chlorine in the case of $ArCH_2Cl$, suggest that the anion radicals of *p*-nitrobenzyl fluoride and chloride prefer a conformation (**1** and **2** respectively) where the halogen atoms try to avoid the out-of-plane or maximum overlap site. As the halogen atoms become progressively bigger, as in the bromide and iodide, steric factors begin to dictate and there is some preference for the perpendicular site, a site that also allows hyperconjugation (in the reverse sense) to occur (**3** and **4**). This is supported to some extent by the observed small but significant coupling to bromine and iodine in the case of *p*-nitrobenzyl bromide and iodide anion radicals. (Since these are electron excess molecules, we expect the halogens to avoid π-overlap provided steric factors are not dominant.) The hyperfine coupling to the bromine and iodine nuclei in $ArCH_2Br^{\bullet-}$ and $ArCH_2I^{\bullet-}$ suggest that there is considerable π–σ overlap between the π-SOMO and the C–Br and C–I orbitals which, considering the anionic nature of these species, probably involves the σ* C–halogen orbital as we have suggested previously.[2] We have also postulated previously[2] that if this form of the SOMO is accepted, it is likely that only one anion radical is possible; separate structures with the unpaired electron either in an aromatic or NO_2 π* SOMO, or in a C–halogen σ* SOMO being extreme valence forms of the actual structure, a concept that has important implications when considering the mechanism of anion radical dissociation (*vide infra*). In the ArCHXY series where there are now two halogen substituents on the benzylic carbon some significant results emerge. For *p*-nitrobenzylidene dichloride ($ArCHCl_2$), the EPR spectrum of the anion radical shows hyperfine coupling to ^{14}N but unfortunately no resolved coupling to chlorine or ^1H was observed. A conformation that is consistent with this observation is that shown in **5** in which the lone hydrogen atom is in the out-of-plane or maximum overlap site which is also one where hyperconjugation can occur. Since the primary anion radical is stable, it is possible that the main structure adopts conformation **5** with one hydrogen in the out of plane site, leaving the species with the alternative structure **6** which has one chlorine near the plane of the anion radical as unstable anions which readily dissociate. In the case of ArCHClBr, where one chlorine atom has been replaced by bromine, the anion radical is detected as the minor product while both the radicals $Ar\dot{C}HCl$ and $Ar\dot{C}HBr$ are also present. The observed decreased ^{81}Br coupling of 18 G (compared to $ArCH_2Br$) suggests that π–σ overlap has been reduced, indicating that the anion radical now adopts conformation **7**. The radicals $Ar\dot{C}HCl$ (from departure of Br^-) and $Ar\dot{C}HBr$ (from departure of Cl^-) probably originate from radical anions of different conformations and, as in the case of dichloride, the radical anions in these conformations are unstable at the temperature used and are consequently not detected. With substitution by two bromine atoms, as in $ArCHBr_2$, the resultant instability of the anion radical is most pronounced and it is detected only in trace amounts; the main species



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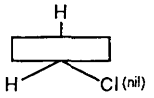

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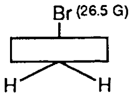

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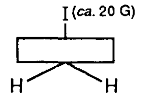

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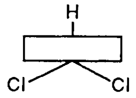
observed in this case is the radical $\mathrm{Ar\dot{C}HBr}$. In the case of ArCHFBr, the anion radical was not detected; only the corresponding radical was seen.



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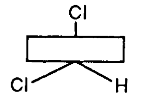

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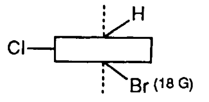

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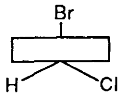

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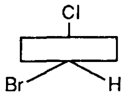

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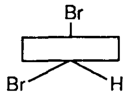

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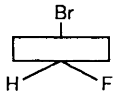

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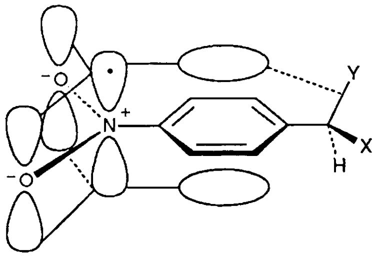

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Relative Stability and Dissociation of Anion Radicals.—We have previously proposed that dissociation of *p*-nitrobenzyl (as well as 5-nitrofurfuryl) anion radicals proceeds by smooth reorganization of molecular orbitals to the required transition state for loss of the halide ion.[2,14,15] This is supported by the observed small but significant hyperfine coupling to the halogen atom in the case of *p*-nitrobenzyl bromide **3** and iodide **4** which establish that there is considerable overlap between the NO_2/aromatic π^* orbitals and the C–halogen σ^* orbitals as represented in structure **12**. In the case of the fluoride and chloride, our results indicate that the preferred conformation for these anion radicals is **1** and **2**, *i.e.* one where the halogen atom is not in the perpendicular site. Consistent with this is the observation that the anion radicals in this conformation are stable on annealing whereas the anion radicals of the bromide and iodide dissociate to the corresponding radicals on annealing. These observations lend further support to our proposal that dissociation involves a transition state as shown in structure **12** where the departing group is suitably oriented with respect to attaining maximum orbital overlap. From the results obtained we can conclude that for the monohalogenated derivatives, there are two stable conformers in many cases in the frozen solutions, one having a halogen substituent close to the out-of-plane site and the other having the halogen close to the in-plane site. On electron addition, the former loses halide ion spontaneously whilst the other anions are stable. In the case of the dihalogenated derivatives the solid-state results indicate that there are at least two conformers in the frozen solutions. The one having a halogen close to the out-of-plane limit will again lose halide ion spontaneously, whilst any conformer having hydrogen in this site will be stable as the anion radical. For *p*-nitrobenzylidene dichloride, replacement of a hydrogen by chlorine is reported to weaken the C–halogen bond strength and facilitate anion radical decomposition in $\mathrm{ArCHCl_2}^{\bullet -}$.[12] In agreement with this, some dissociation of the anion radical was evident at 77 K in contrast to *p* nitrobenzyl chloride anion radical which was stable over the temperature range used. In agreement with our proposal concerning the transition state for loss of halide ion, the primary radical anion **5** with hydrogen in the out-of-plane site is stable and does not dissociate at temperatures below the decomposition temperature of the anion radical while the radical $\mathrm{Ar\dot{C}HCl}$ which is already present at 77 K is probably derived from the radical anion **6** which has one of the chlorine atoms positioned near the maximum overlap site, conducive to attaining the transition state for dissociation *via* smooth reorganization of molecular orbitals. Unfortunately this species was not detected at 77 K. It is likely that its suitable conformational disposition with respect to halide ion expulsion coupled with the effect of the additional chlorine substituent in decreasing the C–hal bond strength causes it to be unstable and facilitated its decomposition. In the case of ArCHClBr, the anion radical was detected only as a minor product with a small coupling (18 G) to bromine consistent with structure **7** while the radicals $\mathrm{Ar\dot{C}HCl}$ and $\mathrm{Ar\dot{C}HBr}$, which are clearly in evidence at 77 K, probably originate from facile decomposition of anion radicals with halogen at the out-of-plane site (*e.g.* **8** and **9**) which were consequently not detected (Fig. 2). In the case of $ArCHBr_2$ where there are now two bulky bromine substituents on the α-carbon, the anion radical is detected only in trace amounts, the major product being the radical. It is likely that in this case the predominant conformation trapped is **10**. The anion radical in this conformation would have the bromine atom ideally poised for expulsion and would thus be expected to undergo facile decomposition to the radical which is what was indeed observed. In the case of ArCHFBr only the radical was detected

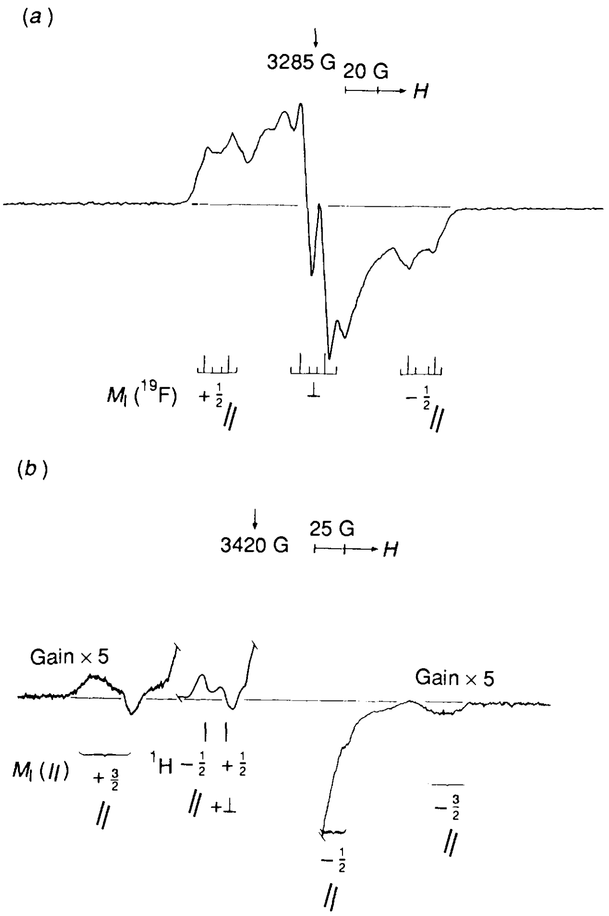

Fig. 2 (*a*) First derivative X-band EPR spectrum for $NO_2C_6H_4\dot{C}HF$ radicals formed by electron addition to $NO_2C_6H_4CHFBr$ in CD_3OD at 77 K. The central region of the spectrum contains weak solvent features and possibly some contribution from the parent anion radicals. (*b*) First derivative X-band EPR spectrum for a dilute solution of $NO_2C_6H_4CHBr_2$ in MeTHF after exposure to ^{60}Co γ-rays at 77 K, and annealing to *ca.* 120 K, showing features for the $\mathrm{Ar\dot{C}HBr}$ radical. The $\frac{3}{2}$ and $\frac{1}{2}$ bromine hyperfine features are indicated. The doublet splitting of *ca.* 15 G is assigned to the α-proton and is not the ^{79}Br–^{81}Br separation.

indicating extremely facile loss of Br^-. We suggest that in this case, since fluorine is small by comparison to the other halogens, the predominant conformation of the anion radical is **11**, *i.e.* one conducive to dissociation. In addition to this factor fluorine substitution must have further facilitated anion radical decomposition since the *p*-nitrobenzyl bromine anion radical **3** is detected. One possible reason could be that fluorine substitution significantly decreases the C–Br bond strength thus facilitating anion radical dissociation. Our present results not only confirm those of Neta *et al.*[11–13] but further extend the order of stability of α-halogenated 4-nitrotoluene anion radicals which is as follows: $ArCH_2F \sim ArCH_2Cl > ArCH_2Br > ArCHCl_2 > ArCH_2I > ArCHClBr > ArCHBr_2 > ArCHFBr$. In conclusion we have shown that the various *p*-nitrobenzyl and *p*-nitrobenzylidene halides can accept electrons to form the respective anion radicals which subsequently dissociate to the corresponding radicals. The results provide additional support for the intermediacy of these anion radicals invoked in a number of reactions of the parent substrates.[3–5,7]

Experimental

EPR Spectroscopy.—Degassed samples were irradiated as dilute solutions (*ca.* 1% v/v) in methyltetrahydrofuran or methanol (CD_3OD was used to avoid overlap with solvent radical features). They were frozen as small beads in liquid nitrogen and irradiated at 77 K in a Vickrad ^{60}Co γ-ray source at doses of up to 1 Mrad. EPR spectra were measured on a Varian E109 spectrometer. Samples were annealed to selected temperatures or until significant changes occurred in the EPR spectra, and recooled to 77 K for study.

Materials.—*p*-Nitrobenzyl chloride and *p*-nitrobenzyl bromide were commercial samples. The preparation of the other compounds are described in the preceding paper.[7]

Acknowledgements

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