# Radical–Nucleophilic Substitution ($S_{RN}1$) Reactions: Electron Spin Resonance Studies of Electron Capture Processes

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We have probed two of the steps postulated for the radical–nucleophilic substitution ($S_{RN}1$) mechanism for α-substituted aliphatic nitro-compounds [$Me_2C(X)NO_2$] by detecting the intermediates involved by e.s.r. spectroscopy. These two steps are the electron capture by $Me_2C(X)NO_2$ to form radical-anions, and their break-down to yield radicals and anions [equations (1) and (A2) or (B2) in Scheme 1]. A range of radical-anions, $[Me_2C(X)NO_2]^{-\cdot}$ with X = Br, Cl, SCN, $NO_2$, CN, $PO_3Et_2$, $CO_2Et$, COMe, $SO_2Me$, $SO_2Ar$, and Me have been unambiguously identified by e.s.r. spectroscopy and shown to be infinitely long lived at low temperature. Our results indicate that one or more of at least three pathways are followed on the reaction of $Me_2C(X)NO_2$ with electrons: (a) electron-capture to yield a stable radical-anion, $[Me_2C(X)NO_2]^{-\cdot}$; (b) dissociative electron capture to yield $Me_2\dot{C}NO_2$ and $X^-$ (for X= Br, Cl, and SCN); (c) dissociative electron-capture to yield $Me_2\dot{C}X$ and $NO_2^-$ (for X = CN, $NO_2$, $PO_3Et_2$, and $CO_2Et$). The effect of solvent on these processes, and the structure of the radical-anions and the radicals $Me_2\dot{C}NO_2$, $Me_2\dot{C}PO_3Et_2$, and $Me_2\dot{C}CN$ are discussed.

Radical-anions of various aliphatic α-substituted nitro-compounds have been proposed as reactive intermediates in radical–radical-anion chain substitution ($S_{RN}1$) reactions (Scheme 1). The mechanism was termed $S_{RN}1$ (substitution radical–nucleophilic, first order) by Bunnett [1] in his studies on aromatic substrates, while the same mechanism for aliphatic nitro-compounds was elaborated by Russell [2] and Kornblum.[3]

The initiation step [equation (1)] is effected by electron-transfer to the α-substituted nitro-compound by a suitable electron donor; in many cases it is the anion ($A^-$). The initiation is light catalysed, but some reactions have also been thermally or electrochemically induced. Equations (2)—(4) represent the propagation steps of the chain reaction. Inhibition[3b] of these chain reactions by strong electron acceptors (*e.g.* oxygen, *p*-dinitrobenzene) or radical scavengers (*e.g.* oxygen, galvinoxyl, di-t-butyl nitroxide) is now a well established method for determining the $S_{RN}1$ mechanism. The inhibition also provides strong evidence for the intermediacy of the proposed radicals and radical-anions.

Route A [loss of the α-substituent ($X^-$), Scheme 1] has been observed [2,3] for X = I, Br, Cl, $SO_2R$, SR,[4] S(O)R,[4] and SCN [5] and route B (loss of $NO_2^-$) has been observed [2,3] for X = COR, $CO_2R$, CN, $NO_2$, p-$NO_2C_6H_4N_2$,[2,5] and Me.[6]

A growing number of anions have been shown to participate in $S_{RN}1$ reactions with α-substituted nitro-compounds,[2,3] *e.g.* $A^-$ = $R_2CNO_2^-$, $RSO_2^-$, $RS^-$, $N_3^-$, $SO_2^{2-}$,[7] $(RO)_2PO^-$,[8] and carbanions [RC(X)Y with X,Y = $CO_2R$, COR, $SO_2R$, CN, and combinations thereof].

Several mechanistic pathways, related to $S_{RN}1$, which include an initial step of electron transfer to an α-substituted nitro-compound [equation (1)] have been proposed and are shown in Scheme 2 [equation (1) is not shown].

Other proposed mechanisms including these radical-anion intermediates have also been reported, *e.g.* $S_{ET}2$ (substitution, electron transfer, second order),[10] and reduction by dihydrobenzylnicotinamide,[11] trialkyltin hydride,[12] or methanethiolate.[13]

All these mechanisms have an initial step of electron capture by the α-substituted nitro-compound to yield an intermediate radical-anion, with sufficient lifetime to allow reaction with other species. Several groups [14] have however reported their inability to detect these radical-anions [$Me_2C(X)NO_2$ with X = Br, Cl, $NO_2$, and CN] due to their instability. The subsequent 2-nitropropyl radical [equation (A2)] has been observed by e.s.r. spectroscopy [14c,15] but not as a result of breakdown of radical-anions $[R_2C(X)NO_2]^{-\cdot}$. Similarly, some radical-anions $[R_2C(A)NO_2]^{-\cdot}$ resulting from the addition of the 2-nitropropyl radical (generated by the oxidation of the anion of 2-nitropropane) to anions such as $^-NH_2$, $^-SH$, and $Me_2CNO_2^-$ have been observed by e.s.r. spectroscopy.[14c,16]

From the viewpoint of e.s.r. spectroscopy, electron capture by $RNO_2$ (R = alkyl, aryl) molecules to give $R\dot{N}O_2^-$ radical-anions is well established, both in solid-state [17,18] and liquid-phase [14,19] studies. However, substituted radical-anions of the type $[R_2C(X)NO_2]^{-\cdot}$ have not been widely studied.[20]

$$\begin{array}{rcll}
Me_2C(X)NO_2 + e^-(A^-) & \longrightarrow & [Me_2C(X)NO_2]^{\dot{-}} + (A^\cdot) & (1)\\
[Me_2C(X)NO_2]^{\dot{-}} & \longrightarrow & Me_2\dot{C}NO_2 + X^- & (A2)\\
Me_2\dot{C}NO_2 + A^- & \longrightarrow & [Me_2C(A)NO_2]^{\dot{-}} & (A3)\\
[Me_2C(A)NO_2]^{\dot{-}} + Me_2C(X)NO_2 & \longrightarrow & Me_2C(A)NO_2 + [Me_2C(X)NO_2]^{\dot{-}} & (A4)\\
[Me_2C(X)NO_2]^{\dot{-}} & \longrightarrow & Me_2\dot{C}X + NO_2^- & (B2)\\
Me_2\dot{C}X + A^- & \longrightarrow & [Me_2C(A)X]^{\dot{-}} & (B3)\\
[Me_2C(A)X]^{\dot{-}} + Me_2\dot{C}(X)NO_2 & \longrightarrow & Me_2C(A)X + [Me_2C(X)NO_2]^{\dot{-}} & (B4)
\end{array}$$

$A^-$ = anion

Scheme 1

$S_{RN}2$:[9]

$$[Me_2C(X)NO_2]^{\dot{-}} + A^- \longrightarrow [Me_2C(A)NO_2]^{\dot{-}} + X^-$$
$$[Me_2C(A)NO_2]^{\dot{-}} + Me_2C(X)NO_2 \longrightarrow Me_2C(A)NO_2 + [Me_2C(X)NO_2]^{\dot{-}}$$

Oxidative dimerisation (chain):[9]

$$[Me_2C(X)NO_2]^{\dot{-}} + A^- \longrightarrow A^{\bullet} + Me_2CNO_2^- + X^-$$
$$A^{\bullet} + A^- \longrightarrow AA^{\dot{-}}$$
$$AA^{\dot{-}} + Me_2C(X)NO_2 \longrightarrow AA + [Me_2C(X)NO_2]^{\dot{-}}$$

Oxidative dimerisation (non chain):[10]

$$[Me_2C(X)NO_2]^{\dot{-}} \longrightarrow Me_2\dot{C}NO_2 + X^-$$
$$Me_2\dot{C}NO_2 + A^- \longrightarrow Me_2CNO_2^- + A^{\bullet}$$
$$2A^{\bullet} \longrightarrow AA$$

**Scheme 2**

$$[R_2C(X)NO_2]^{\dot{-}} + R_2C(X)NO_2 \rightleftharpoons R_2C(X)NO_2 + [R_2C(X)NO_2]^{\dot{-}} \quad (5)$$
$$[R_2C(X)NO_2]^{\dot{+}} + R_2C(X)NO_2 \rightleftharpoons R_2C(X)NO_2 + [R_2C(X)NO_2]^{\dot{+}} \quad (6)$$

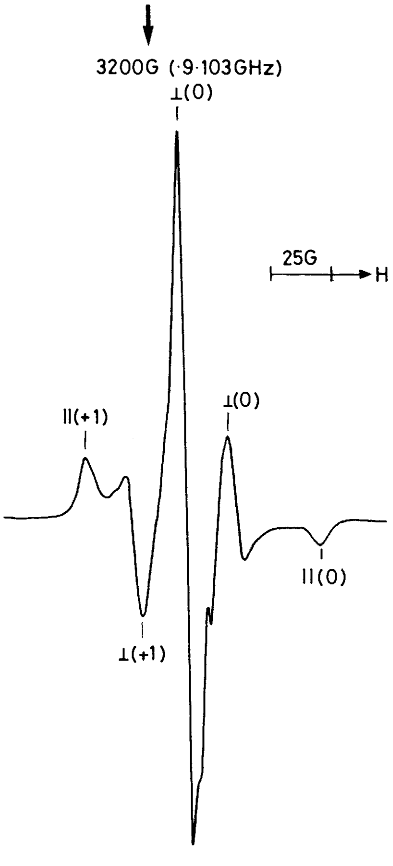


**Figure 1.** First derivative X-band e.s.r. spectrum for a dilute solution of $Me_3CNO_2$ in $CD_3OD$ after exposure to $^{60}Co$ γ-rays at 77 K, and annealing to destroy most of the solvent radicals, showing features assigned to $(Me_3CNO_2)^{-\bullet}$ radical-anions

We know of no other studies on the radiolysis of $R_2C(X)NO_2$ molecules. Radiolysis of unsubstituted nitroalkanes in the pure state results in C–N bond homolysis.[21] In the present study, we have found that pure $R_2C(X)NO_2$ derivatives studied herein behave similarly.[20] Thus neither the primary anions, cations or their breakdown products could be detected by e.s.r. spectroscopy. We suggest that this arises because of efficient charge transfer between adjacent molecules and ions [reactions (5) and (6)].

In either case this mobility, coupled with the coulomb effect, encourages electron-return which gives an excited $R_2C(X)NO_2$ molecule. This may decompose homolytically before falling to the ground-state. In the present study we have used dilute solutions of these compounds in order to avoid such homolyses, and encourage electron-capture.

## Results and Discussion

*Identification of Radicals.*—Identification of $[Me_2C(X)NO_2]^{-\bullet}$ radical-anions depends on recognising the characteristic asymmetric triplet usually present in the spectra as shown in Figure 1. In certain cases, on annealing, these radical-anions become sufficiently mobile to give isotopic features to the spectrum, thus forming a link with liquid-phase studies and establishing that $A_{\parallel}$ and $A_{\perp}$ are of like sign. The derived $^{14}N$ hyperfine coupling constants were not very dependent upon the nature of the group X, which greatly facilitated identification. In certain cases, extra hyperfine splitting was observed. For example the chlorine and bromine derivatives gave spectra exhibiting coupling to $^{35}Cl$, $^{37}Cl$ and $^{79}Br$, $^{81}Br$, the phosphorus derivative spectra showed coupling to $^{31}P$, and the dinitro-compound showed a small coupling to the second $^{14}N$ nucleus. Some examples of spectra showing these characteristics are given in ref. 20 and in Figure 2. It should be stressed that the hyperfine constants derived from such spectra and recorded in Table 1 are not necessarily principal values since, in general, there are no common axes for these interactions. The results suggest that the major $^{14}N$ coupling constants are all close to expectation, which suggests that the powder spectra are dominated by this interaction.

Formation of $Me_2\dot{C}NO_2$ radicals was usually clear-cut since the e.s.r. features for this species were well resolved even at 77 K (Figure 3). In most cases some of the features were distorted by overlap with those from the parent radical-anions or other radicals, but nevertheless, most of the seven characteristic triplets could be detected. Most of the other $Me_2\dot{C}X$ species were also clearly defined by the characteristic 20 G septet from the $Me_2\dot{C}$ unit. Some examples are given in Figure 4.

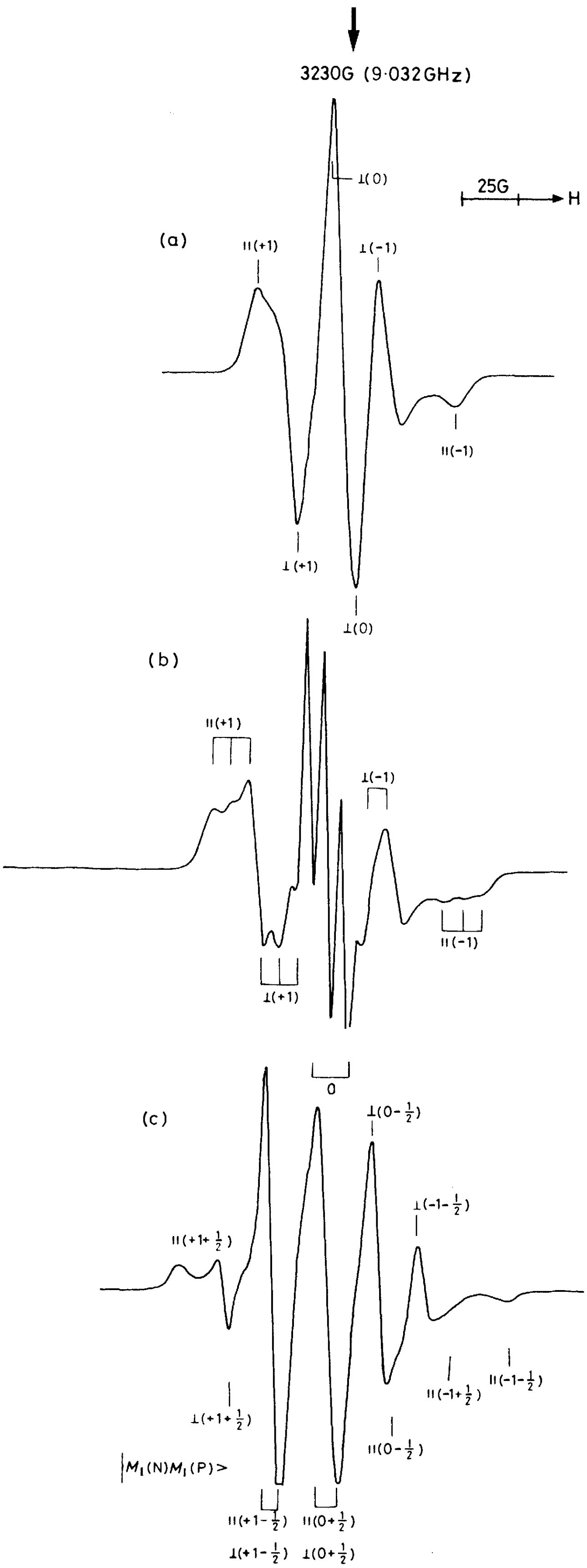


**Figure 2.** First derivative X-band e.s.r. spectra for dilute solutions of various $Me_2C(X)NO_2$ compounds after exposure to $^{60}Co$ γ-rays at 77 K. (a) $Me_2C(CN)NO_2$ in MeTHF after slight annealing to remove signals from solvent radicals, showing features assigned to $[Me_2C(CN)NO_2]^{-\cdot}$ radical-anions. (b) $Me_2C(NO_2)_2$ in $CD_3OD$ after annealing to remove features from $Me_2\dot{C}NO_2$ and solvent radicals, showing features assigned to $[Me_2\dot{C}(NO_2)_2]^{-\cdot}$ radical-anions. (c) $Me_2C(PO_3Et_2)NO_2$ in $CD_3OD$ after annealing to remove signals from other radicals, showing features assigned to $[Me_2C(PO_3Et_2)NO_2]^{-\cdot}$ radical-anions. $^{14}C$ (+1, 0, −1) and $^{31}P$ ($+\frac{1}{2}$, $-\frac{1}{2}$) features are indicated

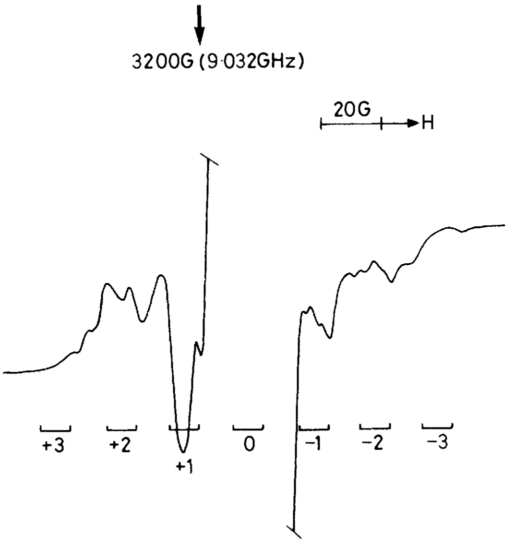


**Figure 3.** First derivative X-band e.s.r. spectrum for a dilute solution of $Me_2C(NO_2)_2$ in $CD_3OD$ after to exposure to $^{60}Co$ γ-rays at 77 K, prior to annealing, showing features assigned to $Me_2\dot{C}NO_2$ radicals (±3, ±2, ±1, 0) superimposed on features for the parent radical-anion and solvent radicals

*Solvent Effects*.—Methanol ($CD_3OD$ was used to avoid signals from $H_2\dot{C}OH$ and $H\dot{C}O$ radicals) and methyltetrahydrofuran (MeTHF) were used because their solutions usually give good glasses, and because dilute solutes usually only react with electrons at 77 K, electron-loss centres being confined to the solvent. For $CD_3OD$ solutions, the central narrow multiplet is due to solvent radicals. For MeTHF solutions a 20G sextet due to solvent radicals dominated the spectra at 77 K. Fortunately these features were lost rapidly on annealing, thereby revealing signals from solute radicals. In most cases it was established that these signals were initially present at 77 K, and were not formed as a result of reactions with solvent radicals. For both solvents, in the absence of solutes, intense violet-blue colours are produced on irradiation which are characteristic of trapped electrons. All solutes used suppressed this colouration. This shows that they all captured electrons efficiently. We conclude that we need only consider electron-capture processes, as is normally the case for these solvents.

In general, two primary solute species were detected, one being the parent radical-anion, $[Me_2C(X)NO_2]^{-\cdot}$, and the other being $Me_2\dot{C}NO_2$ or $Me_2\dot{C}X$, formed by dissociative electron-capture. On annealing, no evidence for conversion of the radical-anions into $R_2\dot{C}NO_2$ or $R_2\dot{C}X$ radicals was obtained at temperatures below the decomposition temperatures of the radical-anions. Indeed, in several cases $[R_2C(X)NO_2]^{-\cdot}$ radical-anions seemed to increase on loss of $R_2\dot{C}NO_2$ or $R_2\dot{C}X_2$ radicals. At temperatures near the glass-softening temperatures the radical-anion spectra were lost, but we cannot tell if this was due to the formation of $R_2\dot{C}X_2$ or $R_2\dot{C}NO_2$ radicals, or simply loss caused by diffusion and reaction.

**Table 1.** E.s.r. parameters for $[Me_2C(X)NO_2]^{-\cdot}$ radical-anions

| | | | | *A* Values (G) [a] | | | | *g*-Values | |
|---|---|---|---|---|---|---|---|---|---|
| Group X | Solvent | Radical-anion | Nucleus | $A_{\parallel}$ | $A_{\perp}$ | $A_{iso}$ | 2*B* | $g_{\parallel}$ | $g_{\perp}$ |
| CN | $CD_3OD$ | $[Me_2C(CN)NO_2]^{-\cdot}$ | $^{14}N$ | 47 | 19.2 | 28.5 | 18.5 | 2.0022 | 2.0075 |
| | MeTHF | $[Me_2C(CN)NO_2]^{-\cdot}$ | $^{14}N$ | 45.2 | 18.0 | 27.1 | 18.1 | 2.0021 | 2.0075 |
| SCN | $CD_3OD$ | $[Me_2C(SCN)NO_2]^{-\cdot}$ | $^{14}N$ | 42.4 | 15.2 | 24.3 | 18.1 | 2.0020 | 2.0075 |
| | MeTHF | $[Me_2C(SCN)NO_2]^{-\cdot}$ | $^{14}N$ | 41.0 | 14.6 | 23.4 | 17.6 | 2.0020 | 2.0070 |
| $NO_2$ | $CD_3OD$ | $[Me_2C(NO_2)_2]^{-\cdot}$ | $^{14}N$(i) | 41.2 | 16 | 24.4 | 16.8 | 2.002 | 2.007 |
| | $CD_3OD$ | $[Me_2C(NO_2)_2]^{-\cdot}$ | $^{14}N$(ii) | 7 | 5.5 | 6 | | | |
| | MeTHF | $[Me_2C(NO_2)_2]^{-\cdot}$ | $^{14}N$(i) | 40 | 15 | 23.3 | 16.7 | 2.0022 | 2.0071 |
| | MeTHF | $[Me_2C(NO_2)_2]^{-\cdot}$ | $^{14}N$(ii) | 7 | 5.5 | 6 | | | |
| $PO_3Et_2$ [b] | $CD_3OD$ | $[Me_2C(PO_3Et_2)NO_2]^{-\cdot}$ | $^{14}N$ | | *ca.* 17 | *ca.* 25.3 | 16.7 | 2.002 | 2.0073 |
| | | $[Me_2C(PO_3Et_2)NO_2]^{-\cdot}$ | $^{31}P$ | | *ca.* 57 | *ca.* 55.3 | | 2.002 | 2.0073 |
| | MeTHF | $[Me_2C(PO_3Et_2)NO_2]^{-\cdot}$ | $^{14}N$ | *ca.* 42 [b] | *ca.* 57 | *ca.* 55.3 | | 2.002 | 2.0073 |
| | | $[Me_2C(PO_3Et_2)NO_2]^{-\cdot}$ | $^{31}P$ | *ca.* 64 | *ca.* 57 | *ca.* 55.3 | | 2.002 | 2.0073 |
| $CH_3$ | $CD_3OD$ | $[Me_3CNO_2]^{-\cdot}$ | $^{14}N$ | 48.5 | 18 | 28.2 | 20.3 | 2.0020 | 2.0070 |
| COMe | $CD_3OD$ | $[Me_2C(COMe)NO_2]^{-\cdot}$ | $^{14}N$ | 46 | 17 | 26.7 | 19.3 | 2.0022 | 2.0073 |
| | MeTHF | $[Me_2C(COMe)NO_2]^{-\cdot}$ | $^{14}N$ | 46 | 17 | 26.7 | 19.3 | 2.0022 | 2.0073 |
| $CO_2Et$ | $CD_3OD$ | $[Me_2C(CO_2Et)NO_2]^{-\cdot}$ | $^{14}N$ | 48 | 20 | 29.3 | 18.7 | 2.0024 | 2.0075 |
| | | *c* | $^{14}N$ | *ca.* 33.5 | *ca.* 19 | 23.8 | | 2.0020 | 2.0063 |
| | MeTHF | $[Me_2C(CO_2Et)ON_2]^{-\cdot}$ | $^{14}N$ | 47 | 19 | 28.3 | 18.7 | 2.0023 | 2.0074 |
| $SO_2Me$ | $CD_3OD$ | $[Me_2C(SO_2Me)NO_2]^{-\cdot}$ | $^{14}N$ | 42 | 17 | 25.3 | 16.7 | 2.0020 | 2.0070 |
| $SO_2Ar$ [d] | $CD_3OD$ | $[Me_2C(SO_2Ar)NO_2]^{-\cdot}$ | $^{14}N$ | 41 | 15 | 23.7 | 17.3 | 2,0020 | 2.0070 |
| Cl | $CD_3OD$ | $[Me_2C(Cl)NO_2]^{-\cdot}$ | $^{14}N$ | 40 | $\geqslant 14$ | $\geqslant 22.7$ | | 2.003 | *ca.* 2.10 |
| | | $[Me_2C(Cl)NO_2]^{-\cdot}$ | $^{35}Cl$ | 11 | $0 \pm 2$ | $3.7 \pm 1$ | | | |
| | MeTHF | $[Me_2C(Cl)NO_2]^{-\cdot}$ | $^{14}N$ | 40 | *ca.* 16 | *ca.* 24 | | 2.003 | *ca.* 2.01 |
| Br | MeTHF | $[Me_2C(Br)NO_2]^{-\cdot}$ | $^{14}N$ | *ca.* 40 | *e* | *e* | | 2.005 | *e* |
| | | $[Me_2C(Br)NO_2]^{-\cdot}$ | $^{79/81}Br$ | *ca.* 38 | *e* | *e* | | | |

[a] G = $10^{-4}$ T. [b] These data are probably not principal values. [c] Unidentified species formed from parent radical-anion. [d] Ar = *p*-tolyl. [e] Not resolved or concealed by other features.

**Table 2.** E.s.r. parameters for radicals formed by dissociative electron capture in the radiolysis of $Me_2C(X)NO_2$ solutions at 77 K

| | | | | *A* Values (G) [a] | | | *g*-Values | |
|---|---|---|---|---|---|---|---|---|
| Group X | Solvent | Radical | Nucleus | $A_{\parallel}$ | $A_{\perp}$ | $A_{iso}$ | $g_{\parallel}$ | $g_{\perp}$ |
| Cl | $CD_3OD$ or MeTHF | $Me_2\dot{C}NO_2$ | $^{14}N$ | 4.3 | <4 | <4 | 2.003 | 2.003 |
| | | | $^{1}H$ | 21 | 21 | 21 | | |
| Br | $CD_3OD$ or MeTHF | $Me_2\dot{C}NO_2$ | $^{14}N$ | 4.3 | <4 | <4 | 2.003 | 2.003 |
| | | | $^{1}H$ | 21 | 21 | 21 | | |
| SCN | $CD_3OD$ or MeTHF | $Me_2\dot{C}NO_2$ | $^{14}N$ | 4.3 | <4 | <4 | 2.003 | 2.003 |
| | | | $^{1}H$ | 21 | 21 | 21 | | |
| $NO_2$ | $CD_3OD$ or MeTHF | $Me_2\dot{C}NO_2$ | $^{14}N$ | 4.3 | <4 | <4 | 2.003 | 2.003 |
| | | | $^{1}H$ | 21 | 21 | 21 | | |
| CN | $CD_3OD$ or MeTHF | $Me_2\dot{C}CN$ | $^{14}N$ | 11 | 0 | 3.7 | 2.003 | 2.003 |
| | | | $^{1}H$ | 20 | 20 | 20 | | |
| $PO_3Et_2$ | $CD_3OD$ | $Me_2\dot{C}PO_3Et$ | $^{31}P$ | | | *ca.* 50 | *ca.* 2.003 | 2.003 |
| | | | $^{1}H$ | | | *ca.* 21 | | |
| COMe | $CD_3OD$ or MeTHF | *b* | | | | | | |
| $CO_2Et$ | $CD_2OD$ | $Me_2\dot{C}CO_2Et$ | $^{1}H$ | | | 21.5 | 2.0025 | 2.003 |
| $SO_2Me$ | $CD_3OD$ or MeTHF | *b* | | | | | | |
| $SO_2Ar$ [c] | $CD_3OD$ or MeTHF | *b* | | | | | | |

[a] G = $10^{-4}$ T. [b] Only radical-anions detected. [c] Ar = *p*-tolyl.

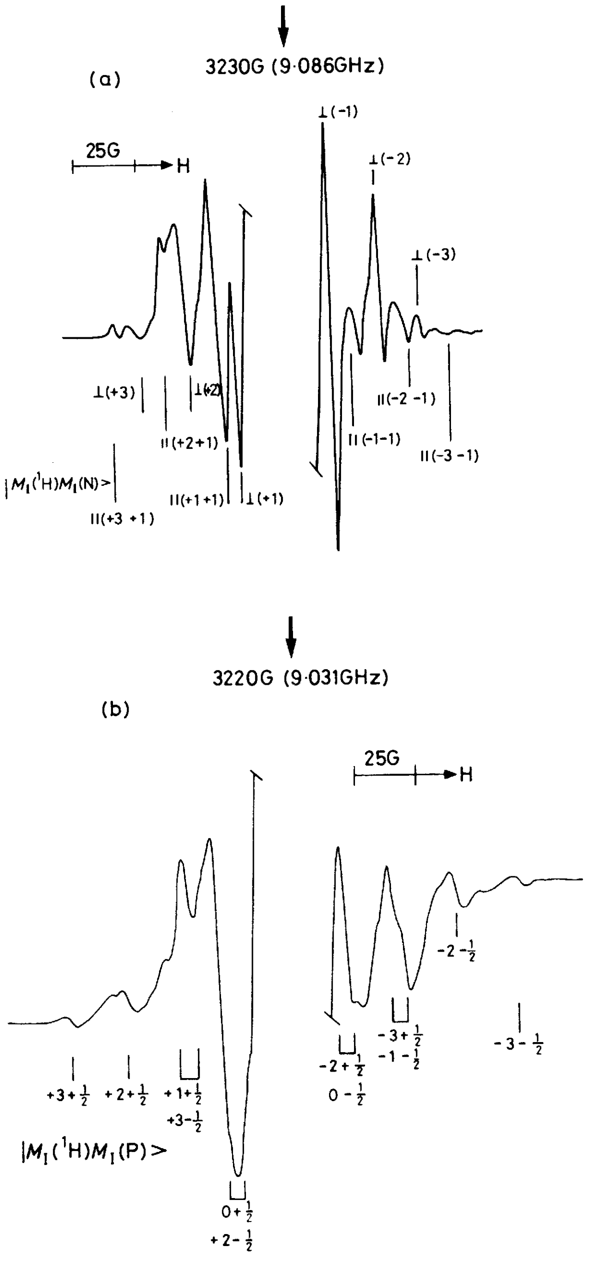
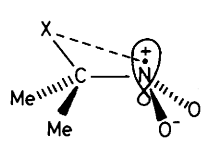


**Figure 4.** First derivative X-band e.s.r. spectra for dilute solutions of $Me_2C(CN)NO_2$ and $Me_2C(PO_3Et_2)NO_2$ in $CD_3OD$ after exposure to $^{60}Co$ γ-rays, prior to annealing, showing features assigned (a) to $Me_2\dot{C}CN$ radicals (±3, ±2, ±1, 0) superimposed on features for the radical-anions and solvent radicals and (b) to $Me_2\dot{C}PO_3Et$ radicals (±3, ±2, ±1, 0) (+½, −½) superimposed on features for the parent radical-anions and probably some $Me_2\dot{C}NO_2$ features

In all cases, the relative initial yield of radical-anions to neutral radicals ($R_2\dot{C}X$ or $R_2\dot{C}NO_2$) was greater for the ether matrix than for the alcohol matrix. It also varied with the nature of X, but not in any clearly defined pattern. Generally, the initial yield of neutral species was about equal to that for the radical-anions, but for X = $SO_2Me$, $SO_2Ar$, COMe, and CN, the radical-anions dominated [it is difficult to be precise, because of overlapping spectra and differing degrees of anisotropy]. In some cases, especially of the $PO_3Et_2$ derivative, there were possible indications of the presence of both $Me_2\dot{C}NO_2$ and $Me_2\dot{C}X$, but generally only one set of features was clearly identifiable. The major dissociation products detected are indicated in Table 2.



(1)

*Aspects of Mechanism.*—As stressed above there are good reasons for assuming that the only radiation process that we need to consider for the substrates in dilute solutions is electron-capture. Our inability to detect break-down of the parent radical-anions [equations (A2) or (B2) in Scheme 1] shows the initial formation of $Me_2\dot{C}X$ or $Me_2\dot{C}NO_2$ radicals is a ' hot ' process. We suggest that initial electron addition occurs on the planar nitro-group and that relaxation proceeds *subsequently*, involving either bond-stretching, giving $Me_2\dot{C}X$ or $Me_2\dot{C}NO_2$ or bond-bending, giving the stable radical-anion, $[Me_2C(X)NO_2]^{-\cdot}$. The e.s.r. results show conclusively that these radical-anions are pyrimidal at nitrogen (see below), and we suggest that this relaxation stabilises the unit, thereby inhibiting dissociation. Although we have not detected subsequent dissociation at low temperature, there can be no doubt that it occurs at room temperature.

We do not wish to imply that this trichotomy of reaction (loss of $NO_2^-$, loss of $X^-$, or radical-anion formation) is normal in liquid-phase electron-transfer processes. These differ from the present process in that suitable relaxation must occur during electron-transfer. It is probable that this is predominantly the bending mode so that the ground-state radical-anion is smoothly formed as transfer occurs. In that case dissociation occurs after ground-state radical-anion formation. Nevertheless, we believe that our results properly reflect the tendency for the radical-anions to lose $X^-$ or $NO_2^-$ on dissociation. In fact, they tie in well with deductions from liquid-state studies.[2,3] Thus, for X = CN, we get $Me_2\dot{C}CN$ formation, and liquid-phase results indicate loss of $NO_2^-$ ions.[3] For X = $CO_2Et$, we see the spectrum of $Me_2\dot{C}(CO_2Et)$ radicals, and again loss of $NO_2^-$ has been observed.[3] For X = Cl and Br we see the spectrum of $Me_2\dot{C}NO_2$ and loss of $Cl^-$ and $Br^-$ is expected. We predict that for X = SCN the $SCN^-$ anion should be lost preferentially, but for X = $PO_3Et_2$ it should be $NO_2^-$ that is lost. Initial results show that $SCN^-$ is indeed lost in preference to $NO_2^-$ in the liquid phase.

It is interesting to consider the detailed pathway responsible for loss of $X^-$ from the parent radical-anion. Our results (see below) suggest that when X = Cl, Br, $PO_3Et_2$, $SO_2R$, and SCN, structure (1) is strongly favoured, with significant delocalisation into the C–X σ-bond. Evidence for this in $R_2\dot{C}$–$C(X)R_2$ systems has been presented previously.[22] This structure heads smoothly to the required transition state for loss of $X^-$. For the planar radical-anion, loss of $NO_2^-$ is orbitally ' forbidden ', but for the pyramidal radical-anion this becomes allowed, with σ-delocalisation into the C–N bond. So in this case we now postulate some bending prior to bond stretching. Solvent assistance by protic solvents would be expected to favour loss of $NO_2^-$ rather than $X^-$. In our studies, however, there was no clear evidence that loss of $NO_2^-$ is favoured when methanol rather than MeTHF is used as solvent, which may mean that there is little development of solvation prior to bond breakage.

We must also consider the possibility of anion return [the reverse of equations (A2) or (B2)], especially since an important step in the $S_{RN}1$ substitution process [equations (A3) or (B3)] is, in effect, anion return. In our view, this may well occur in our systems. Thus we know that the radical-anions do not dissociate in the 77—*ca.* 170 K range apart from the initial dissociation of ' hot ' anions.

The $Me_2\dot{C}X$ and $NO_2^-$ or $Me_2\dot{C}NO_2$ and $X^-$ species are formed, and probably remain, in a rigid solvent cage, so that return is greatly facilitated. This would give ground-state radical-anions which could then remain stable. For methanolic solutions return would be strongly opposed by anion solvation. One of us has established that solvation of small anions is rapid in methanol glasses at 77 K.[23] Hence for methanolic solutions return is less probable than for MeTHF solutions. We propose that this is the best way of understanding the higher yield of the parent anions in MeTHF compared with methanol. It may also explain the apparent slight growth in intensities of the radical-anion features on annealing, as the $Me_2\dot{C}NO_2$ or $Me_2\dot{C}X$ radicals were lost. Indeed in those cases for which only radical-anions were detected, it is possible that dissociation occurred, followed by efficient back-reaction.

The stability of the radical-anions observed by e.s.r. spectroscopy correlates well with behaviour in liquid-phase reactions. $PhSO_2^-$ adds easily to $Me_2\dot{C}NO_2$, but only leaves slowly[3b] from the radical-anion, suggesting that anion return is important. $Br^-$ and $Cl^-$ will not add[24] to $Me_2\dot{C}NO_2$, but leave rapidly from the radical-anion.[3b] $Br^-$ leaves more rapidly than $Cl^-$ in $S_{RN}1$ reactions; this is also indicated by the relative stability of the radical-anions as shown by the e.s.r. spectra {*i.e.* $[Me_2C(Br)NO_2]^{-\cdot}$ cannot be observed in $CD_3OD$ but $[Me_2C(Cl)NO_2]^{-\cdot}$ is sufficiently stable}. Thiocyanate[5] adds easily but is also easily lost. Cyanide,[24] nitrite,[24] and diethyl phosphite[8] add relatively easily to $Me_2\dot{C}NO_2$, and nitrite[11] leaves slowly from the radical-anions of $Me_2C(CN)NO_2$ and $Me_2C(NO_2)_2$.

The pioneering study of Norman and his co-workers[14c,16] on various α-chloronitroalkanes is related to the present work. They studied liquid-phase reduction, using $R_2\dot{C}OH$ radicals as reducing agents. Although $[R_2C(Cl)NO_2]^{-\cdot}$ radical-anions were not detected, they did observe the alkylated analogues, $R^1_2C(Cl)\dot{N}O_2R^2$, and the radicals, $R_2\dot{C}NO_2$. The isotopic $^{35}Cl$ and $^{14}N$ hyperfine coupling constants for the former radicals (*ca.* 4 and 25 G, respectively) are close to those given in Table 1 for $[Me_2C(Cl)NO_2]^{-\cdot}$. This encourages us to believe that our interpretation of the complex solid-state spectrum is correct. It also establishes that our choice of signs for the parallel and perpendicular hyperfine components is correct. It is interesting to note that their $R_2\dot{C}NO_2$ radicals in the presence of ammonia or $HS^-$ ions gave the radical-anions $[R_2C(NH_2)NO_2]^{-\cdot}$ and $[R_2C(SH)NO_2]^{-\cdot}$ thereby establishing the efficiency of reactions (A3) and (B3) in Scheme 1 for the particular substrates.

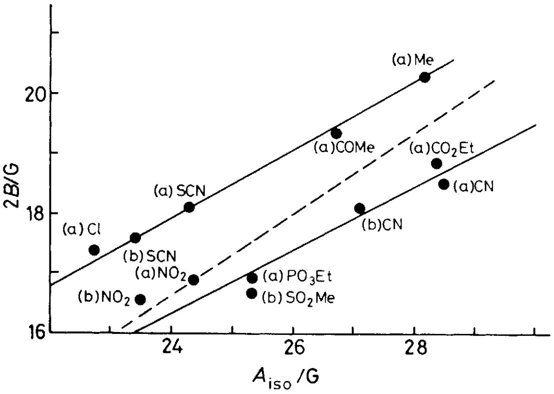


**Figure 5.** Relationship between the isotropic $^{14}N$ hyperfine coupling ($A_{iso}$) and the anisotropic coupling ($2B$) for a range of $[Me_2C(X)NO_2]^{-\cdot}$ radical-anions. The dashed line is the proportional line discussed in the text: (a) in $CD_3OD$, (b) in MeTHF. The full lines span the data

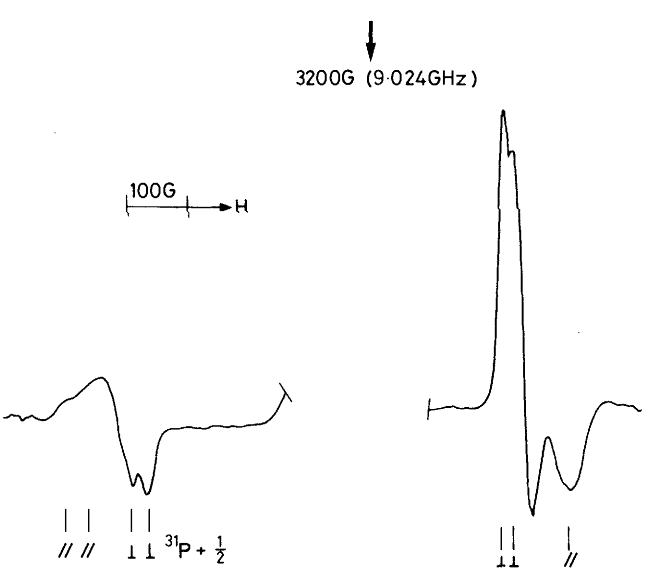


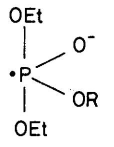
**Figure 6.** First derivative e.s.r. spectrum for $Me_2C(PO_3Et_2)NO_2$ in $CD_3OD$ after exposure to $^{60}Co$ γ-rays at 77 K, showing $M_I(^{31}P) = \pm\frac{1}{2}$ overlapping features assigned to phosphoranyl and phosphoryl radicals

*Aspects of Structure.*—As has been stressed before[18] the $^{14}N$ hyperfine parameters for the parent radical-anions clearly established their pyramidality at nitrogen. In the present examples, the isotropic coupling corresponds to *ca.* 5% 2*s* character and the purely anisotropic coupling ($2B$) corresponds to *ca.* 57% 2*p* character, as estimated by the usual procedure.[25] This gives a *p*/*s* ratio of *ca.* 11. For planar π-radicals such as $NH_3^{+\cdot}$ this is usually in the region of 30, so we feel that deviation from planarity, though small, is well established. This probably increases slightly as the spin-density on nitrogen increases, as can be qualitatively gauged from Figure 5. As the $2B$ term (a measure of 2*p* character on nitrogen) increases, $A_{iso}$ also increases, but at a rate faster than predicted for a fixed deviation from planarity.

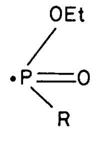
Despite this pyramidality, the large coupling to $^{31}P$ in the $[Me_2C(PO_3Et_2)NO_2]^{-\cdot}$ radical-anion suggests that there is still a tendency for the radical-anions to adopt the normally preferred conformation (1) as was found previously for planar carbon-centred radicals.[22] The results (Table 1) can be used to derive approximate orbital populations, but it must be borne in mind that the powder spectra do not provide accurate data in this case. The results suggest *ca.* 5.6% spin density on phosphorus (1.3% 3*s* + 4.3% 3*p*), which is less than we found for various $R_2\dot{C}–C(PL_3)R_2$ radicals (*ca.* 15%), but is certainly quite reasonable.

The isotropic coupling for $[Me_3CNO_2]^{-\cdot}$ (*ca.* 28 G in methanol) is greater than the values (25—26 G) reported for alkyl derivatives in liquid-phase studies.[14c,26] Since this species was formed in high yield at 77 K, there can be no doubt about identity. We therefore suggest that there is a relatively large temperature effect on $A_{iso}$, but we have not attempted to study this in any detail.

The species with large $A(^{31}P)$ formed from $Me_2C(PO_3Et_2)NO_2$ (Figure 6) are surely the phosphoranyl radical (2) and the phosphoryl radical (3), the latter being formed by loss of $EtO^-$ ions. The two species were formed in roughly equal yields, as was found in our studies of phosphate esters.[27]



(2)



(3)

Radical (2) had $A_{\parallel}$ *ca.* 830 G, but $A_{\perp}$ could not be estimated accurately. Radical (3) had $A_{\parallel}$ *ca.* 550 G but $A_{\perp}$ could not be estimated. These values are in reasonable accord with expectations for such species.[28]

In one case [$Me_2C(CO_2Et)NO_2$] the radical-anion spectral features were converted on annealing into new features (Figure 7). Judging from the high-field feature, these changes indicate the formation of a new nitrogen-centred radical, with parameters given in Table 1. We suggest that this is a nitro radical-anion, with modified structure, but there is no further evidence and we can do no more than speculate about possible modifications.

Data for the radical $Me_2\dot{C}NO_2$ show that the extent of $\pi$-delocalisation is small. Thus the methyl proton coupling is *ca.* 91% of the value for t-butyl radicals. The fact that the coupling to $^{14}N$ is almost isotropic shows that it stems primarily from spin-polarisation of the C–N $\sigma$-electrons rather than from $\pi$-delocalisation, since the latter would give a strongly anisotropic contribution. The isotropic coupling, corresponding to *ca.* 1% of 2*s* population, is typical of such spin-polarisation.[29] Russell and Bridges [30] also concluded that delocalisation onto the $NO_2$ group is small. Similarly the data for $Me_2\dot{C}CN$ show that delocalisation is small. The isotropic coupling to $^{31}P$ for $Me_2\dot{C}$–$PO_3Et_2$ (Table 2) is somewhat higher than is usually observed for $\alpha$-phosphorus,[31] but still corresponds to only *ca.* 1.3% 3*s* character which remains well within the expected range for spin-polarisation in the C–P $\sigma$-bond. This again implies almost no delocalisation.

*Conclusions.*—We have unambiguously identified a range of $[Me_2C(X)NO_2]^{-\cdot}$ radical-anions by their e.s.r. spectra. These were too stable for us to follow loss of $X^-$ or $NO_2^-$ by e.s.r. spectroscopy. Fortunately, however, dissociative electron-capture occurred at 77 K during the initial process of electron addition and the propensity to lose $X^-$ or $NO_2^-$ could therefore be gauged. Back reaction between $X^-$ or $NO_2^-$ and $R_2\dot{C}NO_2$ or $R_2\dot{C}X$ radicals is inferred but not proven.

The results agree with results from liquid-phase studies of $S_{RN}1$ reactions when the experiments overlap, *i.e.* $X^-$ leaves where X = Br, Cl, SCN, and $SO_2R$, but $NO_2^-$ leaves when X = COR, $CO_2R$, CN, and $NO_2$. The structure of the radical-anion (location of the added electron density) does not appear to influence the direction of break-down. The radical-anion proceeds smoothly with reorganisation of the $\pi^*$- and $\sigma^*$-orbitals to the required transition state for loss of $X^-$ or $NO_2^-$, and crossing between occupied and unoccupied orbitals does not take place. Factors such as bond strength and nucleofugal properties must play the major role in influencing which group leaves from the radical-anion.

Hence, we have probed two of the steps [equations (1) and (A2) or (B2) in Scheme 1] postulated for the $S_{RN}1$ substitution process by directly detecting the intermediates involved. We are currently trying to probe the anion recombination processes [equation (A3) or (B3) in Scheme 1] in a more direct manner. Our present evidence suggests that the radical-anions break down more slowly than the resulting radicals react, suggesting that step (A2) [or (B2)] in Scheme 1 is the rate-determining step in the $S_{RN}1$ process.

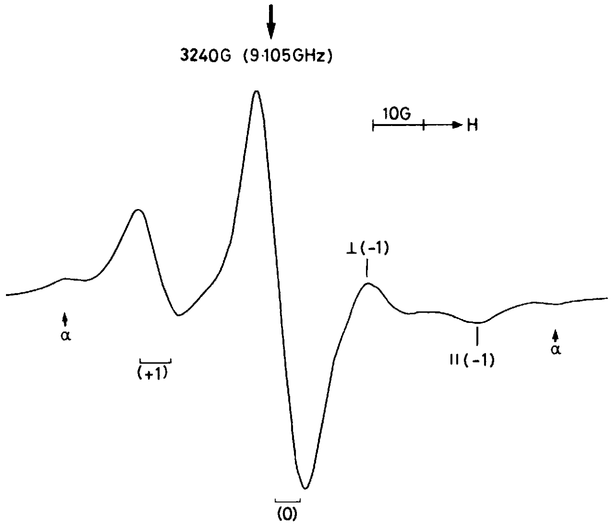


**Figure 7.** First derivative e.s.r. spectrum for $Me_2C(CO_2Et)NO_2$ in $CD_3OD$ after exposure to $^{60}Co$ $\gamma$-rays at 77 K and extensive annealing to remove most of the features ($\alpha$) assigned to the radical-anion $[Me_2C(CO_2Et)NO_2]^{-\cdot}$, showing features for an unidentified nitrogen-centred radical

Finally, it is of interest to compare these results with the theoretical considerations of Bigot *et al.*[32] Their *ab initio* calculations on the radical-anion of $ClCH_2NO_2$ suggest that it 'cannot be considered as an intermediate species, since it dissociates spontaneously to $Cl^-$ and $\cdot CH_2NO_2$.' Our results demonstrate, perhaps even more conclusively, that the radical-anion of $Me_2C(Cl)NO_2$ is not only a genuine intermediate, but indeed is infinitely long-lived at low temperatures. The two methyl groups may confer some slight extra stability, but since most mechanistic studies have involved the dimethyl derivative, we suggest that our results are more pertinent.

## Experimental

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

*Materials.*—2-Bromo- and 2-chloro-2-nitropropane were prepared [33] by halogenation of the sodium salt of 2-nitropropane. 2,2-Dinitropropane and 2-cyano-2-nitropropane were prepared by the method of Urbanski [24] (oxidative addition of the anion of 2-nitropropane to nitrite and cyanide respectively). 2-Nitro-2-thiocyanatopropane was prepared by a modified route of the Urbanski [24] method and will be fully reported in the near future.

2-Methyl-2-nitropropane [34] was prepared by oxidation of t-butylamine with aqueous potassium permanganate.

Ethyl 2-methyl-2-nitropropionate was prepared [35] by reaction of ethyl 2-bromo-2-methylpropionate with sodium nitrite in dimethyl sulphoxide. 2-Methyl-2-nitrobutan-3-one was prepared [35] similarly from 2-bromo-2-methylbutan-3-one.

Diethyl 1-methyl-1-nitroethyl phosphonate was prepared [18,*]

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* W. R. B. thanks Professor G. A. Russell for kindly providing extra experimental details.

by an $S_{RN}1$ reaction of 2-chloro-2-nitropropane and the anion of diethyl phosphite in THF. 1-Methyl-1-nitroethyl *p*-tolyl sulphone was prepared[36] by an $S_{RN}1$ reaction of 2-bromo-2-nitropropane with the sodium salt of toluene-*p*-sulphinic acid. 1-Methyl-1-nitroethyl methyl sulphone was similarly prepared by the method of Kornblum[36] in 14% yield after 2 h reaction time. The sulphone was purified by recrystallisation from ethanol to yield *crystals*, m.p. 82—84° (Found: C, 29.0; H, 5.5; N, 8.4; S, 19.0. $C_4H_9NO_4S$ requires C, 28.75; H, 5.6; N, 8.4; S, 19.15%).

All materials exhibited correct m.p.s or b.p.s and satisfactory spectral data.

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