Electron Paramagnetic Resonance Studies of Electron Capture Processes. Part 8.[1] Radical Anions of *N*-Nitroimines and Nitroalkenes

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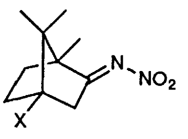
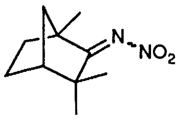
A range of *N*-nitroimines (**1**–**3**) and *N*-nitrofluorene-2-imine (**4**), in dilute solutions of methyltetrahydrofuran and CD_3OD, exposed to ^{60}Co γ-rays at 77 K, gave the corresponding radical anions, detected by EPR spectroscopy. Analysis of the spectra shows that the radical anions of the aliphatic *N*-nitroimines **1**–**3** have the unpaired electron in the π^*-NO_2 molecular orbitals, and that the radical anion of the aromatic *N*-nitroimine **4** is delocalised in the aromatic π molecular orbitals. The EPR spectra of the radical anions of nitroalkenes **5**–**8**, prepared in the solid state by similar methods, have been studied and compared with the radical anions of the *N*-nitroimines. Analysis of the EPR spectra indicates that the unpaired electron in the radical anions of the *N*-nitroimines is more centred on the nitro group than in the nitroalkenes.

N-Nitroimines (nitrimines) have been known for some time[2] but have been little investigated. In aliphatic systems they are generally stable if the imine carbon atom is adjacent to at least one tertiary carbon atom, though exceptions are known.[3] Several examples exist in the steroid and terpenoid fields,[4–6] and in addition, certain aromatic derivatives, exemplified by the *N*-nitroimines of benzophenone and fluorenone, are known.[7]



1; X = H
2; X = Cl



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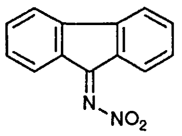

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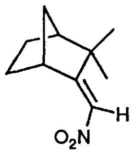

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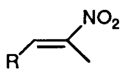
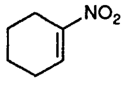


6; R = Me
7; R = Pr^i



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The electron acceptor properties of the nitro group are well documented and indeed it has been described as 'the best known one electron acceptor in organic chemistry'.[8] The radical anions of a wide variety of nitro compounds with C–NO_2 groups have been studied using electron paramagnetic resonance (EPR) spectroscopy.[9] These include nitroarenes,[9,10] nitroalkenes,[9,11] and nitroalkanes.[9,12] Our own studies[13] have included the radical anions of a variety of substituted nitroalkanes, many of which are able to fragment to radicals and anions. The radical anions of *N*-nitroimines, or the EPR spectroscopy of these species, have not been studied before, so far as we can determine from the literature. In this study we report our results of electron addition to *N*-nitroimines, compounds in which the nitro group is attached to a heteroatom. We have also compared the radical anions of the *N*-nitroimines with those nitroalkenes. The radical anions of nitroalkenes have not been previously studied in the solid phase using EPR spectroscopy.

Four *N*-nitroimines **1**–**4**, derived from camphor, 4-chlorocamphor, fenchone, and fluorenone, respectively, were studied and compared with nitroalkenes **5**–**8**. 2,2-Dimethyl-3-nitromethylenebicyclo[2.2.1]heptane (**5**)[14] was chosen as one of the nitroalkenes because it is a close analogue of the *N*-nitroimine derived from fenchone (**3**) and is particularly useful for comparing the radical anions derived from a $C{=}C$-NO_2 group and those from a $C{=}N$-NO_2 group.

Matrix isolation of the radical anions has proved a useful method for studying the EPR spectra of unstable species.[15] The low-temperature technique often allows the observation of first-formed species, and for strongly coupled nuclei anisotropic coupling constants are obtained which can be used to obtain estimates of spin densities. However, lines are broad and in many cases smaller hyperfine splittings are not fully resolved. It has been shown,[15] by using solvents such as CD_3OD and methyltetrahydrofuran (MeTHF), that the major reaction shown by solutes is electron capture. The general technique is fully detailed in the literature.[15]

Results and Discussion

Interpretation of the Spectra of Nitroalkenes.—The results are given in Table 1, and a typical EPR spectrum is shown in Fig. 1(*a*). For solution in MeTHF, well-defined features characteristic of nitro anions were revealed after annealing above 77 K to *ca.* 140 K to remove signals from solvent radicals. Proton coupling to hydrogen or methyl groups on C(2) (*i.e.* the β-carbon of $C_\beta{=}C_\alpha$-NO_2) of *ca.* 9 G was resolved, but the smaller splitting for C(1) protons was not. From simulation studies, Fig. 1(*b*), we find splittings of *ca.* 2–2.5 G but certainly less than 3 G. For solutions in CD_3OD, features for $^{\bullet}NO_2$ radicals were also detected, and it was not possible to remove central features due to solvent radicals. Hence the overall spectra were poorly defined, but a clear secondary splitting of *ca.* 3 G was displayed on the ± 1 lines, which is assigned to protons associated with C(1). In no case could we resolve any ^{14}N perpendicular splitting, which must, therefore, be small ($<$ *ca.* 5 G). In all cases the glasses were a strong yellow colour after exposure. This is assigned to the radical anions: absence of a violet colour (from 'trapped' electrons) shows that electron capture by the solutes was very efficient.

Interpretation of the Spectra of N*-Nitroimines.*—Again, these were better defined in MeTHF (Fig. 2). In these cases, definite

Table 1 EPR parameters of radical anions formed by electron capture in the radiolysis of nitroalkene solutions at 77 K

		^{14}N Hyperfine coupling/G[a]			
Nitroalkene	Solvent	$A_{\parallel}$	$A_{\perp}$	A_{iso}	^{1}H (G)[a]
2-Nitrobut-2-ene (**6**)	MeTHF	30	0	10	9 (4 H), 2 (3 H)
	CD_3OD	33	0	11	9 (4 H), 3 (3 H)
4-Methyl-5-nitropent-2-ene (**7**)	MeTHF b	30	0	10	9 (1 H), 2 (3 H)
2,2-Dimethyl-3-nitromethylenebicyclo[2.2.1]heptane (**5**)	MeTHF b	30	0	10	—
1-Nitrocyclohex-1-ene (**8**)	CD_3OD and MeTHF	33	0	11	18 (1 H), 9 (1 H), 5 (2 H)
2-Methyl-1-nitroprop-1-ene	CH_3CN[c]	—	—	11.6	9.0 (3 H), 3.2 (1 H)
2,3,3-Trimethyl-1-nitropent-1-ene	CH_3CN[c]	—	—	11.9	8.7 (3 H), 3.5 (1 H)
2,2-Diphenyl-1-nitroethene	CH_3CN[c]	—	—	7.0	3.5 (1 H)
2-C_6D_5-1-Nitroprop-1-ene	CH_3CN[c]	—	—	7.9	9.3 (3 H), 2.8 (1 H)

[a] G = 10^{-4} T. [b] Very poor spectrum in CD_3OD, possibly due to low solubility. [c] Ref. 11.

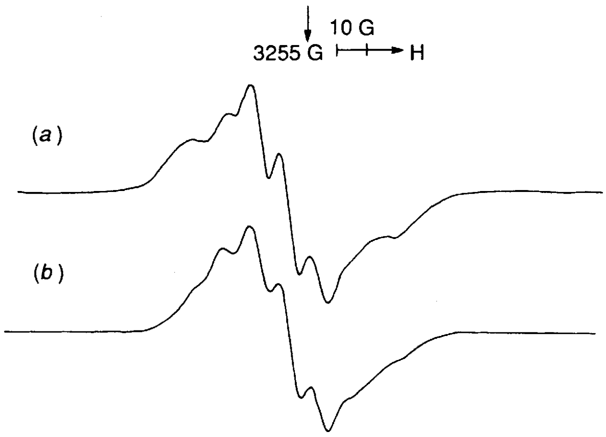


Fig. 1 (*a*) First derivative EPR spectrum of a dilute solution of 1-nitrocyclohex-1-ene in MeTHF after exposure to ^{60}Co γ-rays at 77 K showing features assigned to the radical anion. (*b*) Simulation of the EPR spectrum using the parameters in Table 1.

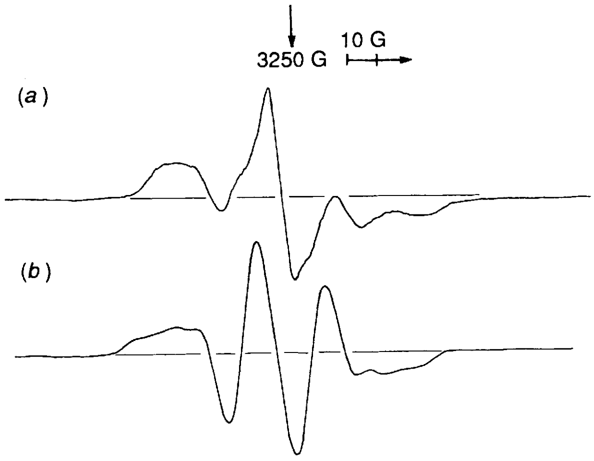


Fig. 2 (*a*) First derivative EPR spectrum of a dilute solution of (*E*)-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptane-2-imine (**1**) in MeTHF after exposure to ^{60}Co γ-rays at 77 K showing features assigned to the radical anion. (*b*) Simulation of the EPR spectrum using the parameters in Table 2.

Table 2 EPR parameters of radical anions formed by electron capture in the radiolysis of *N*-nitroimine solutions at 77 K

	^{14}N Hyperfine coupling/G[a,b]				
N-Nitroimine	$A_{\parallel}$	$A_{\perp}$	A_{iso}	2*B*	1 H (G)[a,b]
Camphor (**1**)	39	17	24.3	14.7	7 (1 H)
Chlorocamphor (**2**)	39	17	24.3	14.7	7 (1 H)
Fenchone (**3**)	43	19	27	16	—

[a] G = 10^{-4} T. [b] Results were about the same for MeTHF and CD_3OD.

perpendicular (^{14}N) features were resolved, the spectra closely resembling those for saturated nitroalkane radical anions.[12,13,15] For solutions in CD_3OD the resolution was better but features from $^{\bullet}NO_2$ and solvent radicals made interpretation more difficult. In the case of the *N*-nitroimine of camphor (**1**) and its chloro derivative (**2**) a well-defined doublet splitting of *ca.* 7 G was observed. This is assigned to an axial proton [*endo*-H at C(3)]. The other proton [equatorial, *exo*-H at C(3)] gave no resolved splitting.

The EPR spectrum of the radical anion of *N*-nitrofluorene-2-imine (**4**) showed a singlet in both MeTHF and CD_3OD, *i.e.* the unpaired electron is mainly in an aromatic π* molecular orbital rather than the nitro π* molecular orbital. Therefore, electron capture by the aromatic ring system is preferred over the nitro group. The nitro group is conjugated to the aromatic system and may simply indicate complete delocalisation of the unpaired electron. On annealing no clear features could be distinguished.

Discussion.—Our results for the radical anions of the nitroalkenes agree reasonably well with those of Berndt *et al.*,[11] for similar species in fluid solution. Using our ^{14}N parallel data and his isotropic coupling, perpendicular splittings of *ca.* 3 G are predicted, which fall within our experimental error. The coupling of *ca.* 2 G for C(1) protons (α-H) using MeTHF is less than his (*ca.* 3 G) but for CD_3OD solutions we obtain 3 G. Reasons for this difference are not clear to us.

There is a remarkable difference between our results for the $C{=}C{-}\dot{N}O_2^-$ system and the $C{=}N{-}\dot{N}O_2^-$ system. For the former, $A_{\perp}$ is very small, the isotropic coupling is low, and the p:s ratio, estimated for the calculated 2s- and 2p-characters on nitrogen (*ca.* 27) shows that the $-\dot{N}O_2$ units must be planar. Indeed they are the only $R{-}\dot{N}O_2^-$ species that we have discovered that seem to be planar.

In marked contrast, the $-NO_2$ units for the $C{=}N{-}\dot{N}O_2^-$ species have p/s ratios (*ca.* 10) that are actually less than those for typical $R{-}NO_2^-$ species (R = alkyl) (*ca.* 11).[12] We ascribe

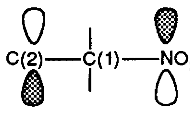
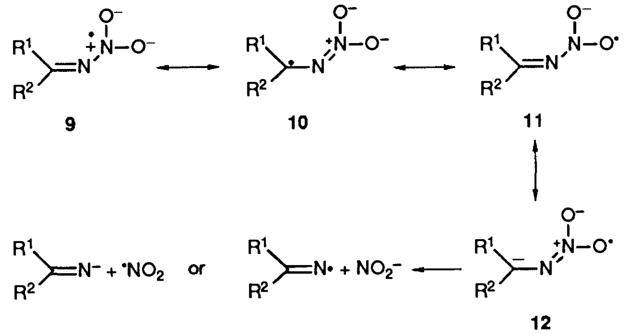


Fig. 3

the difference to the effect of changing one of the nitrogen ligands from carbon to nitrogen. The increase in negativity is expected to induce greater bending on electron addition. Thus, for example, for $^{\bullet}NO_3{}^{2-}$ radicals, p/s ratios of *ca.* 8 are found.

This increased pyramidality results from a greater admixture of 2s character with the wave function on nitrogen, and this should induce a shift of spin density onto the nitrogen unit. For both types of radical an 'allylic' structure is expected, with a node close to the 'central' atom, as in Fig. 3. This is, of course, only an approximation, but it fits the fact that protons associated with C(2) have much greater coupling constants than those for C(1). The fall in coupling for the β-proton in the camphor *N*-nitroimine (**2**) is marked, relative to those for the $C{=}C{-}\dot{N}O_2{}^-$ species, especially since this must be an equatorial proton which is expected to give a large splitting. It is difficult to quantify this result, but qualitatively, this is a clear shift of spin density away from the outer carbon (β) (of $C_\beta{=}C_\alpha{-}NO_2$) towards the $-NO_2$ unit.

Dissociation of N-*Nitroimine Radical Anions.*—Dissociation of the radical anions of *N*-nitroimines is predicted to yield nitrite anions and iminyl radicals ($R^1R^2C{=}N$) (Scheme 1). Iminyl radicals[16] are unusually stable due to very strong hyperconjugation and therefore dissociation would give thermodynamically favourable products. Features in the EPR spectra due to iminyl radicals are easy to observe. However, no features assignable to iminyl radicals were observed in any of the spectra indicating that at the temperatures of the study (77–*ca.* 150 K) dissociation does not take place. However, for the spectra in CD_3OD, features for $^{\bullet}NO_2$ were observed suggesting that in methanol the alternative dissociation (Scheme 1) to yield $^{\bullet}NO_2$ and imine-anions is possible.



Scheme 1

Consideration of the canonical forms **9**–**12** (Scheme 1), of the radical anions of *N*-nitroimines and the deductions from the EPR spectra indicate considerable double bond character for the N–N bond and therefore it is not surprising that dissociation as shown in Scheme 1 does not take place. No dissociation of the corresponding $C{-}NO_2$ bond in the radical anions of nitroalkenes has been observed in our solid or liquid phase studies at 300 K.[9,11] However, the presence of $^{\bullet}NO_2$ in the CD_3OD spectra is possibly of significance.

Experimental

EPR Spectroscopy.—De-gassed samples were irradiated as dilute solutions (*ca.* 1% v/v) in methanol (CD_3OD was used to avoid overlap with solvent features) or MeTHF. They were frozen as small beads in liquid nitrogen and irradiated at 77 K in a Vickrad ^{60}Co γ-ray source to 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.—The *N*-nitroimines of camphor, 4-chlorocamphor, fenchone, and fluorenone; (*E*)-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptane-2-imine (**1**),[5] (*E*)-4-chloro-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptane-2-imine (**2**),[5] (*E*)- and (*Z*)-1,3,3-trimethyl-*N*-nitrobicyclo[2.2.1]heptane-2-imine (**3**),[6] and *N*-nitrofluorene-2-imine (**4**),[7] respectively, were prepared by literature methods. The nitroalkenes (*E*)-2,2-dimethyl-3-nitromethylenebicyclo[2.2.1]heptane (**5**),[14] (*Z*)-2-nitrobut-2-ene (**6**),[17] (*Z*)-4-methyl-5-nitropent-2-ene (**7**)[17] and 1-nitrocyclohex-1-ene (**8**)[18] were prepared by literature methods.

Acknowledgements

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