Formation of 1-Aza-allyl Radicals from 2-Halogenoalkylamines

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Hydrogen abstraction from 2-halogenoethylamines is followed by dehydrohalogenation to give 1-aza-allyl radicals which show significantly greater spin density at the CH_2 terminus than do allyl radicals.

1- and 2-aza-allyl radicals are the archetypes for all delocalised radicals containing nitrogen and have consequently been sought experimentally and studied theoretically.[1] Several diaza-allyl radicals (1) have been observed by e.s.r. spectroscopy[2,3] and some substituted triazenyl radicals (2) were detected recently.[4,5] Neither the 1-aza-allyl (3) nor the 2-aza-allyl radicals (4) had been observed prior to the present work, although some cyclic and acyclic derivatives of the latter were examined by e.s.r. spectroscopy[6,7] and three 4,4-dimethyloxazolinylmethyl radicals (5) have been reported.[7]

Hydrogen abstraction from primary amines by photochemically generated t-butoxy radicals gives mainly 1-aminoalkyl radicals, $R\dot{C}HNH_2$,[8—10] which can be observed over a wide temperature range by e.s.r. spectroscopy.[11] Some abstraction of the amino hydrogens may occur to give aminyl radicals[12,13] but alkylaminyls are not in general detectable by e.s.r. in solution.[12,14]

The photochemical reaction of 2-fluoroethylamine with di-t-butylperoxide in hydrocarbon solvents gave the e.s.r. spectrum shown in Figure 1.† Two radicals were observable in the range 160 to 290 K, their concentration ratio being 2.5 : 1 at 262 K. The same two radicals were detected when 2-

chloroethylamine was used but the ratio of their concentrations was 1 : 1 at 262 K. It follows that the radicals are not aminoalkyls, $X CH_2 \dot{C}HNH_2$, and very probably do not contain halogen atoms. Computer simulations gave good fits for two radicals each showing spin–spin splittings from four nonequivalent hydrogens and a nitrogen atom. The reaction products were t-butyl alcohol, an intractable polymer, and $FCH_2CH_2 \overset{+}{N}H_3 \bar{F}$ or, in the case of the chloroamine, $ClCH_2CH_2 \overset{+}{N}H_3 \bar{Cl}$, and they indicate the occurrence of a dehydrohalogenation step. Both 2-halogenoethylamines are known to readily dehydrohalogenate in the presence of base to give aziridine[15] and therefore the possibility that the observed radicals were formed by hydrogen abstraction from aziridine was considered. However, t-butoxy radicals are known to abstract the amino hydrogen from aziridine to give 1-aziridinyl radicals (6) which have e.s.r. parameters $[a(4H) = 30.7, a(N) = 12.5 \text{ G}\dagger]$[16] which are quite different to those observed here.

By analogy with other alkylamines the first step in the reaction will be hydrogen abstraction at the carbon atom adjacent to the amino group to give 1-amino-2-halogenoalkyl radicals (7). The reaction medium is quite polar because of the presence of the amine and, after the start of the reaction, of t-butyl alcohol, so that the dipolar form (8) will make a significant contribution. Loss of halide from (8) either followed by proton loss or concerted with proton loss will give 1-aza-allyl radicals (3). We assign the observed spectra to the *anti-* (3a) and *syn*-conformers (3b). The reaction with $FCH_2CH_2ND_2$ showed that the 12.25 G† hyperfine splitting (hfs) of the major conformer corresponded to the hydrogen attached to nitrogen. In allyl radicals *anti*-hydrogens have larger hfs[17] and the complete assignments shown in Table 1† were made on the assumption that this rule holds for aza-allyl radicals. INDO calculations were in satisfactory agreement (see Table 1), and the assignment was further supported by the close correspondence of the hfs to those of the related radicals (5) (Table 1).

The formation of a higher ratio of *anti-* to *syn*-conformers, $[(3a)]/[(3b)]$, from the 2-fluoro- as compared with the 2-chloro-amine can be rationalised by examination of the conformations of the precursor radicals (7). In the preferred conformation of the 2-fluoroethyl radical the fluorine atom is
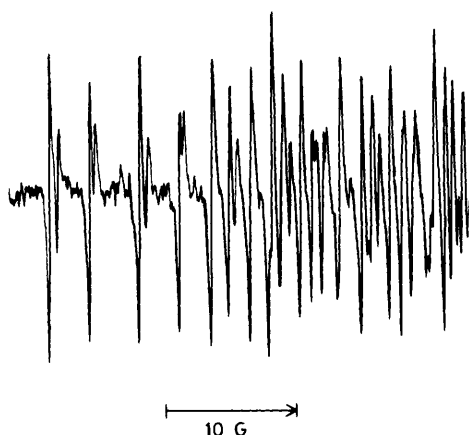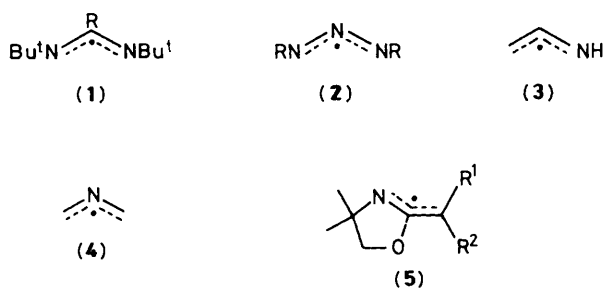

(1)   (2)   (3)

(4)   (5)

10 G

† 1 G ≡ 0.1 mT.

$$XCH_2CH_2NH_2 \xrightarrow{-HX} \overset{\triangle}{NH} \xrightarrow{Bu^tO\cdot} \overset{\triangle}{N\cdot}$$

X = F, Cl

(6)

$$XCH_2CH_2NH_2 \xrightarrow{Bu^tO\cdot} X CH_2\dot{C}HNH_2 \longleftrightarrow X CH_2\bar{C}H\overset{+\bullet}{N}H_2$$

(7)   (8)

$$\downarrow -X^-$$

$$[CH_2 \overset{\bullet\bullet}{=\!=\!=} CH\overset{+}{N}H_2] \xrightarrow{-H^+} (3)$$
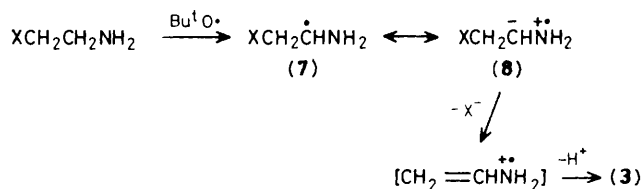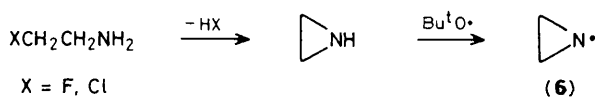
Table 1. E.s.r. parameters of 1-aza-allyl radicals.[a]

Radical	Temp./K	$H^{1\text{-}anti}$	$H^{1\text{-}syn}$	H^2	H^3	N
				hfs/G		
(3a)	206	17.75	16.85	3.05	12.25[c]	6.75
		[−16.03	−15.67	6.06	−13.38	9.25][b]
(3b)	206	17.65	16.75	2.85	11.60	6.60
		[−15.84	−15.69	5.89	−12.80	9.73][b]
(5), $R^1 = R^2 = H$[d]	250	19.4	18.0	—	—	6.1

[a] The g-values of both aza-allyl radicals were 2.003 ± 0.001. [b] INDO calculations with C–C and C–N bond lengths from MNDO–CI calculations (ref. 1). [c] $a(D^{3\text{-}anti}) = 2.05$ G. [d] See ref. 6.

(3a)

(3b)

(9)

(10)
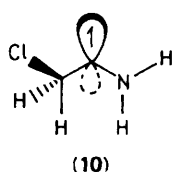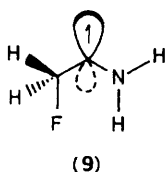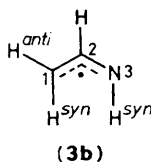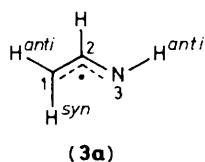
in the nodal plane of the p-orbital containing the unpaired electron (SOMO) whereas in the preferred conformation of the 2-chloroethyl radical the chlorine atom eclipses the SOMO.[18] By analogy, the preferred conformations of the 2-fluoro- and 2-chloro-1-aminoethyl radicals will be (9) and (10) respectively. Loss of HF from (9) to give the *anti*-1-aza-allyl radical (3a) is stereoelectronically favoured, whereas in (10) HCl loss can occur almost equally readily to give (3a) or (3b).

The e.s.r. parameters of 1-aza-allyl radicals indicate greater spin density on the CH_2 group than in allyl radicals for which $a(H^{1\text{-}anti}) = 14.8$ and $a(H^{1\text{-}syn}) = 13.9$ G†[17] *i.e.* radicals (3) have the unpaired electron more localised on the CH_2 group with significant double bond character in the CH=NH bond. This is in good agreement with the theoretical predictions of Dannenberg[1] and suggests that 1-aza-allyl radicals should react regioselectively at the C-terminus.

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