FRAGMENTATION OF OXYALKYL RADICALS: A NEW GENERAL ROUTE TO NITROGEN RADICALS

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A new method for the production of nitrogen radicals is described. Essentially, it is a process for removal of 'OH from =N-OH and is used here to generate oxy- and diazo-iminyls, amidyls and phenyloxydiazinyl (Ph $\stackrel{+}{N}$ = $\stackrel{+}{N}$).

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Alkyl and aryl radicals are frequently produced by fragmentation of a precursor radical with loss of a small stable molecule. The following well-known examples (eq.i-iii) are illustrative. Fragmentation of oxyalkyl radicals (eq. iv) also falls into this category,

$$ArN=N \cdot \longrightarrow Ar \cdot + N_2$$
 (i)

$$RCO_2 \cdot \longrightarrow R \cdot + CO_2$$
 (ii)

$$R_3CO \cdot \longrightarrow R \cdot + R_2CO$$
 (iii)

the ease of fragmentation^{1,2} depending on the size and/or nature of the groups R and R'.

$$RO\dot{C}R_2' \longrightarrow R^2 + OCR_2'$$
 (iv)

However, this fragmentation has not found general use in free radical work although it is a key step in Barton's recent novel reduction of CHOH to CH2. Formation of alkyl radicals (R·) is not a prime requirement for the fragmentation (iv) to proceed, and we have recently shown that iminyl radicals can be generated in this way. The precursor iminoxyalkyl radicals were generated by three routes; oxidative decarboxylation of iminoxyacetic acids with persulphate, thermolysis of the corresponding t-butyl peresters, and oxidation of oxime methyl ethers with di-t-butyl peroxide (eq. v). Using these methods several new reactions of

$$R_{2}C=NOCH_{2}CO_{2}H$$

$$\downarrow S_{2}O_{8}^{2}-$$

$$R_{2}C=NOCH_{2}CO_{3}Bu^{t}\longrightarrow R_{2}C=NOCH_{2}\longrightarrow R_{2}C=N\cdot + CH_{2}O$$

$$hv \uparrow Bu^{t}_{2}O_{2}$$

$$R_{2}C=NOMe$$
(v)

iminyls have been established, e.g., intramolecular aromatic substitution, intramolecular hydrogen abstraction, and intramolecular addition to C=C. A wide range of precursor acids is available so that iminyls can be generated which are difficult to form in other ways. Thus the diazo-iminyls (1; Ar=Ar'=Ph; Ar=Ph, Ar'=p-To1; Ar=p-To1, Ar'=Ph; Ar=Ph and Ar'=p-MeOC₆H₄) have been generated from the appropriate acids and/or from their

peresters. These radicals are much shorter-lived than diphenyliminyl, and unlike the latter could not be detected by e.s.r. when generated from the peresters in hot benzene. They readily fragment to are nonitrile and aryl (via aryldiazinyl) radicals. The latter react with the solvent benzene in the perester decompositions and can be "spin-trapped" by reaction with t-nitrosobutane. The minor products (3) and (4) probably arise from the imine (2) the former by reaction with formaldehyde.

Fragmentation and hydrogen abstraction are also the main reaction paths of the benzyloxyiminyl (5) as indicated by the formation of benzonitrile and benzaldehyde (fragmentation),

PhCN + [PhCH₂O·]
$$\longrightarrow$$
 PhCHO

PhCH₂O PhCH₂O

PhCH₂O

PhCH₂O

PhCH₂O

PhCONH₂ + PhCO₂CH₂Ph

(5)

and benzamide and benzyl benzoate (hydrogen abstraction followed by hydrolysis of the imine). The e.s.r. spectrum of the iminyl generated by thermolysis of the perester was weak, and no proton hyperfine coupling was detected. Spin trapping with t-nitrosobutane gave an intense spectrum of benzoyl t-butyl nitroxide, the benzoyl radicals arising from the benzaldehyde by reaction with t-butoxyl.

The sequence of steps used in the production of iminyls $[=NOH \rightarrow =NOCH_2-CO_2H \text{ (or }-CO_3Bu^t)$ $\rightarrow =NOCH_2 \cdot \rightarrow =N \cdot]$ is essentially a method for removal of $\cdot OH$ from =N-OH. Hence, extension of the method to the production of other nitrogen radicals (and indeed other hetero radicals) seemed feasible. The generality of the method has now been established by its use in the production of two other types of nitrogen radical.

Amidyls from hydroxamic acids. Conversion of the o-phenylbenzohydroxamic acids
 (6; R=H and Ph) into the corresponding oxyacetic acids (7; R=H and Ph) followed by oxidation

with persulphate gave the corresponding phenanthridones (8; R=H and Ph) in ∿65% yield.

Intramolecular aromatic substitution is a known⁶ reaction of amidyls and cyclisation of the amidyls (9; R=H and Ph) has been achieved previously by oxidation of the corresponding amides with several oxidising agents, including persulphate.

2. Phenyloxydiazinyl from "cupferron". Treatment of "cupferron" (10) with bromoacetic acid gave the oxyacetic acid (11) whose t-butyl perester (12) on thermolysis in benzene gave

carbon dioxide, formaldehyde and nitrous oxide. Fragmentation of the intermediate oxyalkyl radical is considered to proceed as before but the intermediate oxydiazinyl radical (13) was too short-lived to be detected by e.s.r., readily fragmenting to phenyl and nitrous oxide. The participation of phenyl radicals was indicated by the isolation of biphenyl and confirmed by spin trapping using t-nitrosobutane.

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