

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

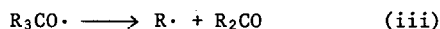
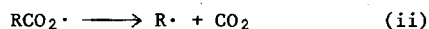
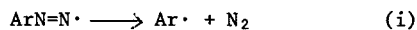
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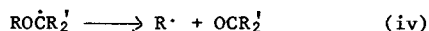
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A new method for the production of nitrogen radicals is described. Essentially, it is a process for removal of $\cdot\text{OH}$ from $=\text{N-OH}$ and is used here to generate oxy- and diazo-iminyls, amidyls and phenyloxydiazinyl ($\text{Ph}\overset{+}{\text{N}}=\overset{-}{\text{N}}$).

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,



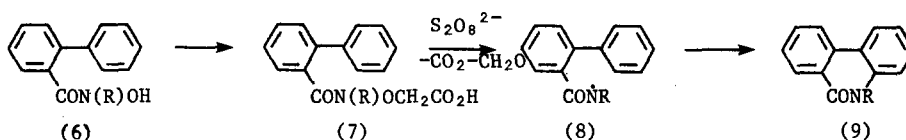
the ease of fragmentation^{1,2} depending on the size and/or nature of the groups R and R'.



However, this fragmentation has not found general use in free radical work although it is a key step in Barton's³ recent novel reduction of $>\text{CHOH}$ to $>\text{CH}_2$. Formation of alkyl radicals ($\text{R}\cdot$) 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.⁴ 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

The sequence of steps used in the production of iminyls [$=\text{NOH} \rightarrow =\text{NOCH}_2\text{-CO}_2\text{H}$ (or $-\text{CO}_3\text{Bu}^t$) $\rightarrow =\text{NOCH}_2\cdot \rightarrow =\text{N}\cdot$] is essentially a method for removal of $\cdot\text{OH}$ from $=\text{N-OH}$. 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.

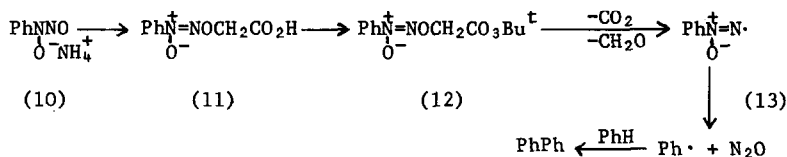
1. Amidyls from hydroxamic acids. Conversion of the *o*-phenylbenzohydroxamic acids (6; R=H and Ph) into the corresponding oxyacetic acids (7; R=H and Ph) followed by oxidation



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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