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OXIDATION OF 1-NITROSO-1-ALKYLHYDRAZINES

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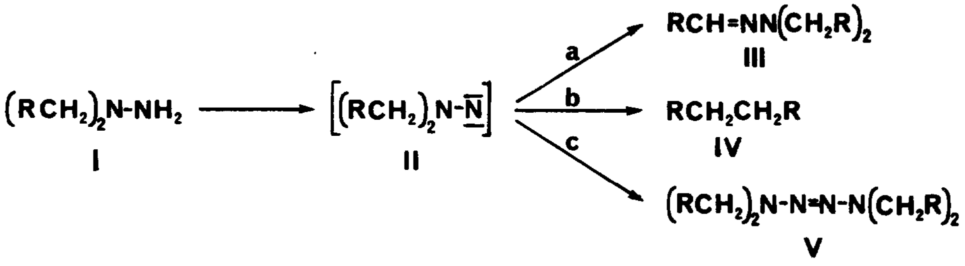
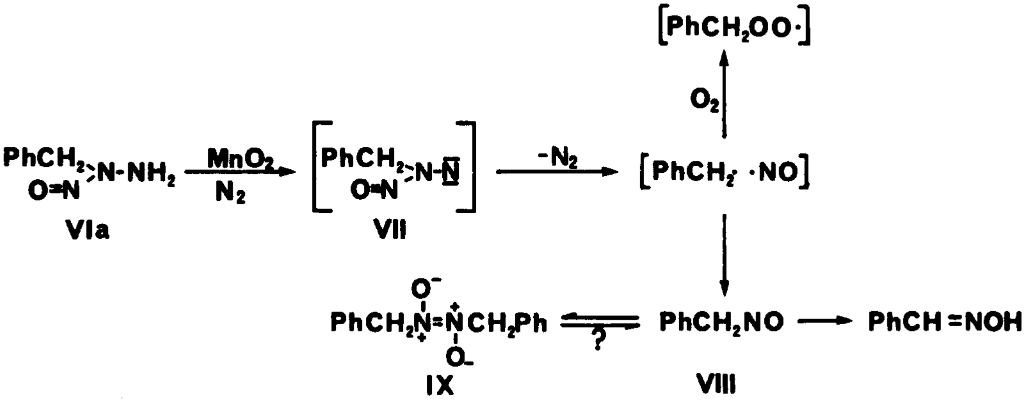
Summary Oxidation of 1-nitroso-1-alkylhydrazines with a variety of oxidizing agents yields the product of coupling of the radical fragments generated by extrusion of nitrogen from the putative N-nitrene intermediate.

N-Nitrenes (II) presumed intermediates of a number of reactions,[1a] can undergo a variety of transformations (Scheme 1).[1] All of these reactions have been investigated and path *b* involving extrusion of nitrogen followed by coupling to the hydrocarbons can become the dominant reaction when the substituent on the nitrogen can cleave as relatively stabilized radicals (e.g. R = Ph). The implied but hitherto unproven suggestion of a radical mechanism for this fragmentation, has to our knowledge never been tested with substituents which might cleave into radicals other than carbon-anchored ones.[2] It was thus of interest to investigate the behavior of N-nitrenes bearing at least one substituent which could cleave as a relatively stable *non-carbon*-centered (dubbed "heteryl") radical. These substituents[3] include *inter alia* nitrogen-centered groups such as NO, NO_2, RN=N, etc. or sulfur-centered groups such as sulfonyl, sulfinyl and thiyl.



Scheme 1

Since the oxidation of 1,1-dibenzylhydrazine (I) has been thoroughly studied,[1,3] 1-nitroso-1-benzylhydrazine (VIa) was selected as the initial substrate for our investigation. The oxidation of VIa in ether with activated MnO_2[4] at room temperature gave 78% yield of benzaldoxime (*syn/anti* mixture)[5a] along with trace amounts of benzaldehyde;[5b] in THF, under nitrogen, a nearly quantitative yield of benzaldoxime (*syn/anti* ratio of 32:1) was obtained (no trace of benzaldehyde) while only a 12% yield of benzaldoxime along with trace amounts of benzaldehyde were obtained in benzene at reflux.[6] The formation of benzaldoxime is economically accounted for by extrusion of nitrogen from the resulting N-nitrene (VII) to give the benzyl radical and nitric oxide; recombination of these two radicals would yield ω-nitrosotoluene (VIII), known to tautomerize to benzaldoxime.[7] Though unlikely, a mechanism involving the formation of $PhCH_2N{=}N{-}N{=}O$ (by migration of either $PhCH_2$ or NO in a *diazene-hydrazone* rearrangement) followed by loss of nitrogen to the same radicals cannot be eliminated from consideration. Oxidation of VIa with lead tetraacetate in methylene chloride at room temperature gave in addition to benzyl acetate (30%), a 42% yield of the dimer of ω-nitrosotoluene (IX), mp. 119-119.5°, along with trace amounts of benzaldehyde.



Scheme 2

Although a control experiment[8] showed that benzaldoxime is oxidized to benzaldehyde by MnO_2, the formation of benzaldehyde as the major product of the oxidation of VIa in THF in the *presence* of oxygen, suggests the generation of benzyl radical as intermediate which is then intercepted by oxygen to yield benzylperoxy radical, thence eventually to benzaldehyde.[9] Support for the formation of benzyl radicals from these oxidations came from the oxidation of

VIa with nickel peroxide in benzene; in addition to IX (17%) and benzaldoxime (as its oxidized dimer benzaldazine bis N-oxide[10]), bibenzyl, evidently the result of coupling of two benzyl radicals, was formed along with other minor unidentified products. Oxidation of VIa with yellow mercuric oxide in ether gave dibenzylmercury as the sole product; however, the instability of the mercury derivative precluded its isolation in yield greater than 16% yield;[11] the formation of dibenzylmercury is best understood in terms of trapping of the benzyl radicals by the mercury generated in the oxidation step.[12] In none of these oxidations could an absorption ascribable to toluene be detected in the nmr spectrum of the reaction mixture.

In order to determine if activation by the benzyl group was necessary for the fragmentation, 1-nitroso-1-isobutylhydrazine (VIb) was prepared[13] and oxidized with MnO_2 in ether. In this case not only was isobutyraldoxime (51%, *syn/anti* ratio ∿ 1:1) obtained but in addition the dimer of 2-methylnitrosopropane (14%, m/e 174)[14] was also characterized [nmr($CDCl_3$): δ 4.16 (4H, d, J = 7.0 Hz), 2.45(2H, m, J = 7.0 Hz) and 1.03(12H, d, J = 7.0 Hz)]. The total yield of coupled product amounted to 65%; a minor unidentified product could be detected by nmr and tlc. This result suggests that the presence of the nitroso substituent is sufficient to trigger the elimination of nitrogen. We are continuing our investigation of the effect of other "heteryl" groups on this process.

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2. There is one example which has a hetero atom substituent on the nitrogen. However, since the hetero atom is incorporated into a ring, this may not represent a true test of this type of system [C. L. Bumgardner, K. J. Martin and J. P. Freeman, J. Am. Chem. Soc., 85, 97 (1963)].
3. G. Koga and J.-P. Anselme, J. Org. Chem., 35, 970 (1970). A fourth path [addition to multiple bonds (C. W. Rees and coworkers)] is observed only

with certain N-nitrenes substituted with electron-withdrawing substituents; formation of adducts with sulfoxides is also known.

4. A. J. Fatiadi, Synthesis, 65 (1976).
5. a) By nmr; b) by tlc.
6. At room temperature, the oxidation was inconveniently slow and decomposition of the substrate became a problem. The reasons for this solvent effect are not obvious since the lead tetraacetate oxidation of VIa occurred readily in methylene chloride.
7. So far we have been unable to obtain evidence for the intermediacy of ω-nitrosotoluene. In one experiment, a deep *blue* colored solution was obtained. However, attempts to isolate the dimer or to repeat this experiment were unsuccessful. This may not be too surprising since a number of reagents, *including* nitric oxide [D. Forrest, B. G. Gowenlock and J. Pfab, J. Chem. Soc., Perkin I, 516 (1979)] can react with and/or isomerize nitrosoalkanes.
8. $\mathrm{PhCH{=}NOH} \xrightarrow{\mathrm{MnO_2,\ O_2}} \mathrm{PhCH{=}NOH}\ (50\%) + \mathrm{PhCHO}\ (50\%)$

   $\mathrm{PhCH{=}NOH} \xrightarrow[\mathrm{H_2O}]{\mathrm{MnO_2,\ N_2}} \mathrm{PhCH{=}NOH}\ (95\%) + \mathrm{PhCHO}$ (traces by tlc)
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12. H. H. Sisler, M. A. Mathur, S. R. Jain and R. W. King, J. Org. Chem., 45, 1329 (1980); J. Grimshaw and J. J. Ramsey, J. Chem. Soc., B, 60 (1968).
13. Pale yellow solid, mp. 78.5-79.5° from ether. Anal. Calcd. for $C_4H_{11}N_3O$: C, 41.01; H, 9.47; N, 35.87. Found: C, 40.95; H, 10.23; N, 35.95; nmr ($CDCl_3$): δ 6.1 (2H, bs, exchangeable), 3.95 (2H, d, J = 7.0 Hz), 2.27 (1H, m, J = 7.0 Hz) and 0.97 (6H, d, J = 7.0 Hz).
14. B. G. Gowenlock and J. Trotman, J. Chem. Soc., 1670 (1956); the ratio of oximes to nitroso dimer seems to be highly variable from run to run.

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