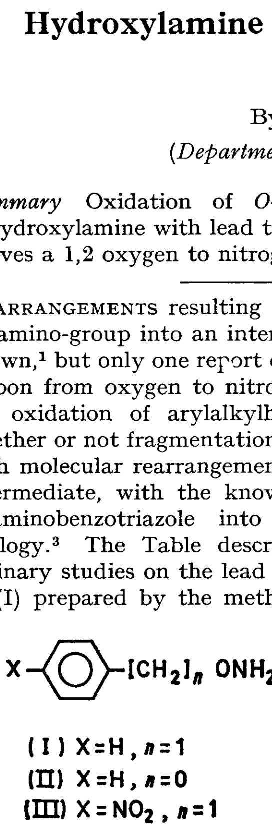
Hydroxylamine Oxidation by Lead Tetra-acetate: *O*-Benzyl- and *O*-Phenylhydroxylamine

By RICHARD PARTCH,* B. STOKES, D. BERGMAN, and M. BUDNIK

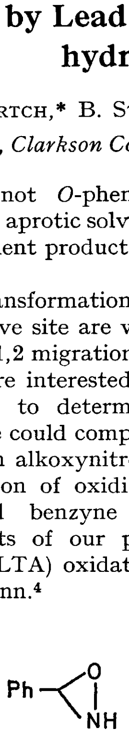
(*Department of Chemistry, Clarkson College of Technology, Potsdam, New York* 13676)

Summary Oxidation of *O*-benzyl- but not *O*-phenylhydroxylamine with lead tetra-acetate, in aprotic solvent gives a 1,2 oxygen to nitrogen rearrangement product.

REARRANGEMENTS resulting from initial transformation of an amino-group into an intermediate reactive site are well known,[1] but only one report deals with the 1,2 migration of carbon from oxygen to nitrogen.[2] We were interested in the oxidation of arylalkylhydroxylamines to determine whether or not fragmentation of nitric oxide could compete with molecular rearrangement, assuming an alkoxynitrene intermediate, with the known fragmentation of oxidized *N*-aminobenzotriazole into nitrogen and benzyne as analogy.[3] The Table describes the results of our preliminary studies on the lead tetra-acetate (LTA) oxidation of (I) prepared by the method of Schumann.[4]



(I) X=H, n=1
(II) X=H, n=0
(III) X=NO$_2$, n=1



(IV)

Only in acetic acid was a measureable amount of gas evolved. At room temperature rapid addition of (I) [τ (CCl$_4$) 2·4 (5H, m), 4·6 (2H, s, absent in D$_2$O), and 5·3 (2H, s)] to the oxidant solution produced a short-lived blue colour. At 70° *ca.* 0·5 mol of gas per mol of (I) oxidized was evolved. Qualitative tests showed that the gas was not nitric oxide. G.l.c. and t.l.c. analysis of the organic residue showed the presence of several neutral products. The major products were identified by i.r. and n.m.r. comparison with authentic samples.

Aprotic solvents such as methylene dichloride or benzene caused a change in the oxidation of (I) to give products retaining the elements of NO. At lower temperatures α-nitrosotoluene dimer[6] [m.p. 118—120°; ν_{max} 1165 cm^{-1}; λ_{max} 294 nm; τ (CDCl$_3$) 2·4 (5H, m), and 4·5 (2H, s)[7] was isolated (60—80%). This is a different dimeric product than that isolated by Carey in the oxidation of *O*-diphenylmethylhydroxylamine.[2]

Rearrangement of (I) to 3-phenyloxaziran (IV) is not a major reaction path since, if it were, benzamide[8] or benzaldehyde[9] would have been major products.

Unlike Brois, in his studies on the LTA oxidation of methoxyamine in the presence of tetramethylethylene, we have been unable to trap the reactive intermediate from (I) with cyclohexene.[10] It is of interest that oxidation of (III) yields mostly *p*-nitrobenzyl alcohol.[2] Data at lower temperatures are needed to determine if oxygen-to-nitrogen migration occurs in this case.[11] Substituent effects have been observed in the homolytic fission of dibenzyl hyponitrite esters. The trend suggests that the *p*-nitro-group would greatly facilitate cleavage of the N–O bond.

Oxidation of the more unstable (II) (1 equiv.) [τ (CDCl$_3$) 2·9 (5H, m) and 4·4 (2H, s, absent in D$_2$O)], prepared by the

TABLE

Solvent	Temp. (°C)	LTA : (I)[a]	Time[b] in min	Major products[c]
C_6H_6	20	1 : 1	10	Benzaldehyde oxime
C_6H_6	20	1·5 : 1	10	Phenylaldazine-*bis*-N-oxide[5]
CH_2Cl_2	20	1 : 1	10	Benzaldehyde oxime
CH_2Cl_2	0	1 : 1	100	α-Nitrosotoluene dimer[6]
$CH_2Cl_2 + C_6H_{10}$ ..	0	1 : 1	100	α-Nitrosotoluene dimer[d]
HOAc	70	1·5 : 1	30	Benzyl acetate
HOAc	0	1 : 1	100	Benzyl alcohol[2]

[a] Mole ratios; [b] Approx. time until lead(IV) was shown to be absent by KI–starch solution; [c] All products had physical and spectral constants comparable with literature data; [d] 50 : 50 CH_2Cl_2–cyclohexene.

method of Bumgardner,[12] by LTA (1 equiv.) in methylene dichloride at 0—25° produced mostly phenol, 0·5 mol. equiv. of gas, and *no* nitrosobenzene. Products were analysed by i.r., n.m.r., and g.l.c. comparison with authentic samples. Control experiments established the stability of nitrosobenzene under the reaction and g.l.c. conditions. We suggest that (II) is oxidatively dimerized to the unknown and presumably very unstable diphenyl hyponitrite.[13] Homolytic fission under the reaction conditions may then produce phenol and nitrogen.

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