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ALPHATIC NITROSO COMPOUNDS PART II.[1]
REDUCTIVE REARRANGEMENT WITH TRIALKYL PHOSPHITES.

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The reduction of aromatic nitro and nitroso compounds by tervalent phosphorus appears to proceed through an aryl nitrene.[2] Alphatic gem-chloro-nitro and nitroso compounds are reduced to oxime derivatives,[3] and Beckmann rearrangements of such derivatives, with ring expansion, have been observed.[4] These reactions involve the Cl-C-NO group as a whole and resemble the Perkow reaction. In the light of these developments we wish to report on the corresponding reduction of monofunctional aliphatic nitroso monomers.

When 2,4,4-trimethyl-2-nitrosopentane was treated with an equimolar amount of triethyl phosphite in boiling benzene, the blue colour faded after ca. 40 minutes. After further heating (to a constant g.l.c. pattern) and evaporation, the mixture (ν_{max} 1660 cm^{-1}) was hydrolysed with warm dilute sulphuric acid. Alumina chromatography of the organic layer yielded acetone (2,4-dinitrophenylhydrazone*) and methyl neopentyl ketone (2,4-dinitrophenylhydrazone, M^{+}294, m.p. 98-100°; reported[5] 100°) along with triethyl phosphate (i.r., g.l.c. and t.l.c.). From the basified aqueous layer, methylamine was obtained by distillation (phenylthiourea, M^{+}222, m.p. 133-135°; reported[6] 134.5°)

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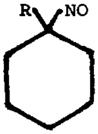
* m.p. undepressed by authentic sample.

With similar conditions and work-up, 1-ethylnitrosocyclohexane (1, R = Et) yielded cyclohexanone (2,4-dinitrophenylhydrazone*) and, from the aqueous acidic layer, ethylamine (picrate*), and a base, b.p. 63-65°/7 mm (reported[7]: 60-63°/15 mm), ν_{max} 1720, 1667 cm^{-1} identical with 7-ethyl-3,4,5,6-tetrahydro-2H-azepine (2, R = Et, b.p., i.r., g.l.c.) prepared for comparison[7]. A similar base, homogeneous on g.l.c., with $M^{\oplus}$ 179 and ν_{max} 1705, 1658 cm^{-1} was obtained from (1, R = cyclohexyl) and assigned the corresponding structure (2, R = C_6H_{11}).



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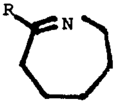

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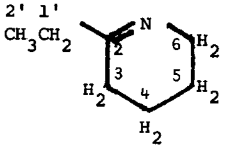

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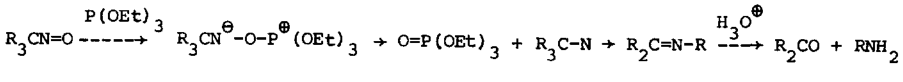
1-Ethylnitrosocyclopentane with triethyl or trimethyl phosphite yielded cyclopentanone (2,4-dinitrophenylhydrazone*), ethylamine (picrate*) and poor yields of a base which rapidly polymerised. The mass spectrum contained strong peaks due to contaminant trimethyl phosphate and phosphite (140, 125, 124 a.m.u.) and strong peaks at 111, 110 (due in part to trimethyl phosphate), 96, 83, 82, 68 and 55 a.m.u., along with weak peaks at 53.5, 52.5, 46.6, 40.4 a.m.u. and m* 83 (111 → 96). The base with difficulty gave a picrate, m.p. 93-95° (ethanol), in whose mass spectrum all the above masses from 111 a.m.u. downwards appeared, along with the few prominent peak of picric acid. The mass spectra of amine picrates in general reproduce faithfully the mass spectrum of the parent amine.[8] The n.m.r. spectrum of the picrate was in good accord with the structure 3 of the base:- $\delta = 1.3$ (3H, t, $J = 7$ Hz, C(2')-H_3);

δ=2.0 (4H, m, $C(4)\text{-}H_2$ and $C(5)\text{-}H_2$); δ=2.8 (4H, m, $C(3)\text{-}H_2$ and $C(1')\text{-}H_2$) δ=3.85(2H, broad s, $C(6)\text{-}H_2$). The labile base prepared** for comparison by the Schmidt rearrangement of 1-ethylcyclopentanol[9] had the same mass spectrum (major fragments, characteristic $\frac{m}{2e}$ peaks and m* 83 a.m.u.) but we failed to isolate the picrate(reported[9] m.p. 95-96°).

Phosphorus trichloride reacted very slowly with 2,4,4-trimethyl-2-nitrosopentane; besides starting material the nitro compound was obtained. (A similar reaction was observed with other acid reagents, eg. sulphuric acid and boron trifluoride[1a]). The order of reactivity $P(OR)_3 > PCl_3$ indicates an initial nucleophilic attack on nitrogen or oxygen. The rearrangements indicated by the products we describe are 1,2-alkyl shifts of the nitrene 4, (or its possible precursor 5). An analogous rearrangement in the pyrolysis of t-butyl azide has been observed[10]. The azomethine link (ν_{max} 1660 cm^{-1}) first formed by migration of either alkyl group, is hydrolysed to the amines and ketones isolated, but survives in the heterocyclic products. Further work on this rearrangement is under way.



$$R_3CN{=}O \xrightarrow{P(OEt)_3} R_3CN^{\ominus}\text{-}O\text{-}P^{\oplus}(OEt)_3 \rightarrow O{=}P(OEt)_3 + R_3C\text{-}N \rightarrow R_2C{=}N\text{-}R \xrightarrow{H_3O^{\oplus}} R_2CO + RNH_2$$

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** by Mr. Z. Cohen

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