Photolysis of 1-Azidophosphetan Oxides

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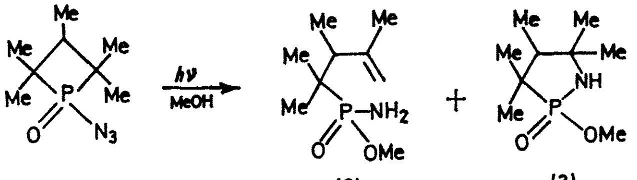
Summary Photolysis of 1-azidophosphetan oxides in methanol gives products resulting from loss of nitrogen and ring opening or ring expansion.

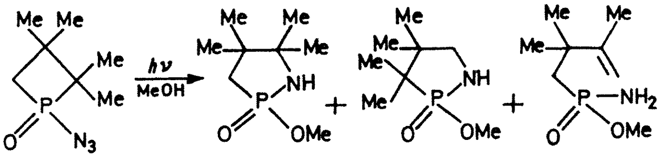
RING expansion and ring opening have previously been observed in several reactions of phosphetans, phosphetan oxides, and phosphetanium salts.[1] 1-Azidophosphetan oxides† (**1**) and (**4**) have now been prepared, and have been found to decompose photolytically with both ring opening and ring expansion.

Azide (**1**), b.p. 80—82°/0·2 mm, ν_{max} 2140 cm^{-1}, was obtained from 1-chloro-2,2,3,4,4-pentamethylphosphetan oxide[2] and sodium azide. The geometry of the azide, which is apparently (n.m.r.) a single isomer, is unknown. Since, however, the chlorine in 1-chloro-2,2,3,4,4-pentamethylphosphetan oxide is *trans* to the methyl group on C-3,[3] and is displaced by various nucleophiles with retention of configuration at phosphorus,[4] it is probable that the azide group in (**1**) is *trans* to the C-3 methyl group.

Photolysis‡ of azide (**1**) in methanol, and chromatography of the reaction product, gave acyclic methyl phosphonamidate (**2**, 16%), m.p. 107—115°, *m/e* 205 (M^+), ν_{max} (KBr) 3330, 3250, 3140 (NH_2), and 1640 cm^{-1} (C=C), τ (C_6H_6) 5·13 (2H, slightly broadened s, $C{=}CH_2$), 5·87 (2H, broad d, *J ca.* 5 Hz, NH_2), 6·44 (3H, d, J_{PH} 10·5 Hz, MeO),



(1) (2) (3)



(4) (5) (6) (7)

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† New compounds gave satisfactory elemental analysis results. Structural assignments were based on n.m.r., i.r., and mass spectra; selected data only are given.

‡ Photolyses were carried out at room temperature in a stirred quartz reaction vessel using a 125 W medium-pressure mercury vapour immersion lamp.

7·13 (1H, m), 8·27 (3H, slightly broadened s, CH_3–C=C), 8·67 (3H, d, J_{PH} 17 Hz), 8·67 (3H, d, J_{HH} 7 Hz), and 8·75 (3H, d, J_{PH} 16 Hz), and a mixture of two compounds, each with a methoxy-group attached to phosphorus [τ (C_6H_6) 6·35 (d, J_{PH} 11 Hz) and 6·38 (d, J_{PH} 11 Hz)]. The spectral properties and elemental analysis of the mixture were consistent with it being the two geometrical isomers of cyclic methyl phosphonamidate (**3**) in a ratio of *ca.* 1:3 (total yield 60%). Repeated crystallisation of the mixture afforded the major isomer of (**3**), m.p. 137—138°, *m/e* 205 (M^+), ν_{max} (KBr) 3170 cm^{-1} (NH), τ (C_6H_6) 6·38 (3H, d, J_{PH} 11 Hz, MeO), 8·20 (1H, m), 8·83 (3H, d, J_{PH} 16 Hz), 8·91 (6H, s), 8·97 (3H, d, J_{PH} 15 Hz), and 9·37 (3H, d, J_{HH} 7 Hz), τ (CCl_4) 4·75 (1H, broad d, *J ca.* 9 Hz, NH).

Photolysis of azide (**4**), b.p. 69—72°/0·15 mm, ν_{max} 2140 cm^{-1}, in methanol gave two products of ring expansion, (**5**), m.p. 65—66°, *m/e* 191 (M^+), ν_{max} (KBr) 3240 cm^{-1}, and (**6**), m.p. 104—107°, *m/e* 191 (M^+), ν_{max} (KBr) 3200 cm^{-1} (total yield 40%), in approximately equal amount, suggesting little preference for migration of primary or tertiary carbon from phosphorus to nitrogen. An acyclic methyl phosphonamidate, m.p. 38—46°, which could not be obtained in a pure state, had spectral properties in accord with structure (**7**) (yield *ca.* 13%).

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[1] J. R. Corfield, M. J. P. Harger, J. R. Shutt, and S. Trippett, *J. Chem. Soc.* (*C*), 1970, 1855 and references therein; J. R. Corfield, M. J. P. Harger, R. K. Oram, D. J. H. Smith, and S. Trippett, *Chem. Comm.*, 1970, 1350.

[2] E. Jungermann, J. J. McBride, R. Clutter, and A. Mais, *J. Org. Chem.*, 1962, **27**, 606.

[3] Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 934.

[4] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465; S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200; Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 938; S. E. Cremer, *Chem. Comm.*, 1970, 616.