Degradation of Halogenophosphazenes to a New Phosphorane System

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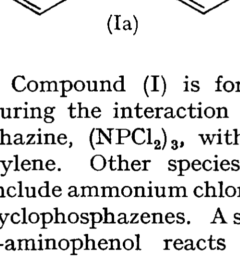
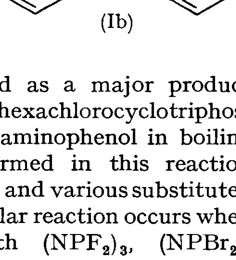
A HIGHLY unusual degradation reaction between *o*-aminophenol and halogeno-triazatriphosphorines (phosphonitrilic halides) leads to the synthesis of a novel penta- or hexa-co-ordinate phosphorus species, (Ia) or (Ib).



(Ia)



(Ib)

Compound (I) is formed as a major product during the interaction of hexachlorocyclotriphosphazine, $(NPCl_2)_3$, with *o*-aminophenol in boiling xylene. Other species formed in this reaction include ammonium chloride and various substituted cyclophosphazenes. A similar reaction occurs when *o*-aminophenol reacts with $(NPF_2)_3$, $(NPBr_2)$, $(NPCl_2)_4$, or $(NPCl_2)_n$ (*n ca.* 15,000).

Compound (I) is a white or pale pink, crystalline solid, m.p. 232—238° (decomp.). The evidence on which its structure is based is as follows. Microanalysis and mass spectrometric data were fully consistent with the proposed structure (Ia) or (Ib): proton n.m.r. spectra (60 Mc./sec.; deuterioacetone) τ 3·37 (strong m, aromatic protons) 6·51 (br s, NH_2 protons), and 2·53 [d, from NH protons, d presumably arising from coupling with ^{31}P (J 22 c./sec.)]. Integration indicated NH : NH_2 : aryl-proton ratios of 0·7 : 1 : 5·5. The low ratio of NH protons may arise from NH exchange with deuterium from the solvent, although in tetrahydrofuran solvent the NH to aryl proton ratio was 1 : 7, again somewhat lower than expected. These data clearly indicate that structure (Ia) predominates in solution, and this is confirmed by the absence of ^{31}P-splitting of the NH_2 proton signals. A ^{31}P spectrum in acetone solvent showed one peak with a shift of $+46·3 \pm 1$ p.p.m. relative to triethylphosphate.† This value is more consistent with a penta-co-ordinate than with a hexa-co-ordinate structure.

The u.v. spectrum of (I) in dioxan was consistent with structure (Ia): 291 sh (log ϵ 4·13), 286 (4·17), 262 sh (3·47), 248 sh (3·95), and 236 nm. (4·34).

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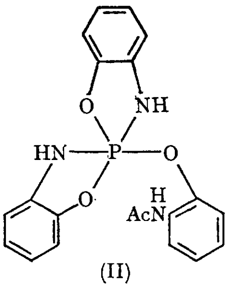
† We are indebted to Dr. J. E. Lancaster of American Cyanamid for the ^{31}P measurements. A Varian DP 60 unit operating at 16·2 Mc./sec. was employed for this work.

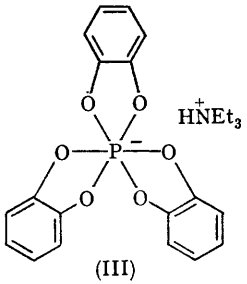
I.r. solution spectra in acetone, dioxan, benzene, and dimethyl sulphoxide provided unambiguous evidence for the presence of NH groups in the 3418—3470 cm.$^{-1}$ region. Weaker aryl–NH_2 bands were also observed in the 3200—3420 cm.$^{-1}$ region in benzene. The remainder of the solution spectrum was also consistent with structure (Ia). However, the i.r. spectrum of Nujol mulls of solid (I) showed a sharp, medium intensity peak at 3392 cm.$^{-1}$, which was attributed to NH groups, together with a very weak, broad band at 3215 cm.$^{-1}$. This latter band was indicative of only minor contributions from NH_2-units but was consistent with the presence of the $^{+}NH_2$-group;[1] which was confirmed by the absence of a strong NH_2-deformation band at 1640 cm.$^{-1}$ and the presence of a minor NH_2-peak at 1580 cm.$^{-1}$. Thus, there is some marginal evidence that structure (Ib) may be present in the solid state.

The reactions of (I) also confirmed its structure. For example, in solution the compound underwent reactions expected of (Ia). Thus, treatment with acetyl chloride yielded an acyl derivative, m.p. 218—220°, of structure (II). I.r., ^{1}H n.m.r., and mass spectrometry confirmed the structure of this species. The ^{31}P spectrum showed one peak at +46 p.p.m., relative to triethyl phosphate.

Compound (I) closely resembles (III), which was reported previously as a product formed from the almost instantaneous reaction of $(NPCl_2)_3$ or tris(*o*-phenylenedioxy)cyclotriphosphazene with catechol and triethylamine.[2] However, there is no evidence that the direct interaction of catechol and $(NPCl_2)]$ in the absence of base yields a species comparable to (I).



(II)



(III)

In the penta-co-ordinate structure (Ia), the "free" *o*-aminophenoxy-ligand probably occupies an equatorial position, since this would allow both O–P–N bond angles to approach 90°. The driving force for the ready formation of (I) from a phosphazene may be the bond angle minimization at phosphorus which occurs in this process. In structure (Ia), a free NH_2-group is present rather than an OH-group. This is an important result for the interpretation of substitution mechanisms at penta-co-ordinate phosphorus.

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[1] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964, p. 282.

[2] H. R. Allcock, *J. Amer. Chem. Soc.*, 1963, **85**, 4050; *ibid.*, 1964, **86**, 2591.