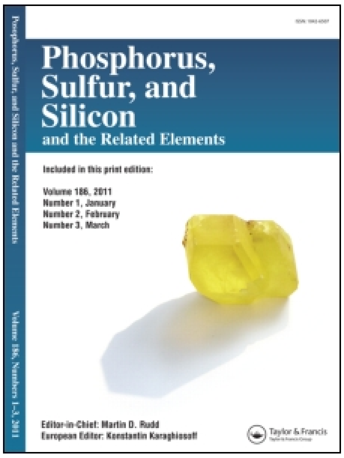

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Gas-Phase Pyrolysis of Tervalent Phosphorus-Oxy and -Thia Heterocycles: A new Approach to Short-Lived Pentavalent Phosphorus Compounds Having Co-Ordination Number 3

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GAS-PHASE PYROLYSIS OF TERVALENT PHOSPHORUS-OXY AND -THIA HETEROCYCLES: A NEW APPROACH TO SHORT-LIVED PENTAVALENT PHOSPHORUS COMPOUNDS HAVING CO-ORDINATION NUMBER 3

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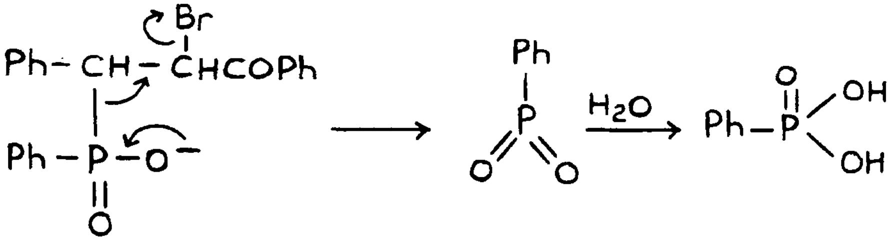
Abstract Generation of short-lived metaphosphonates by thermal fragmentation of cyclic phosphonites and their thia-analogues in the gas phase is described, including an elaboration of the method whereby a monomeric phosphonobenzene is detected unambiguously for the first time by an intra-molecular trapping reaction which also illustrates the considerable potential of such species in the synthesis of phosphorus heterocycles.

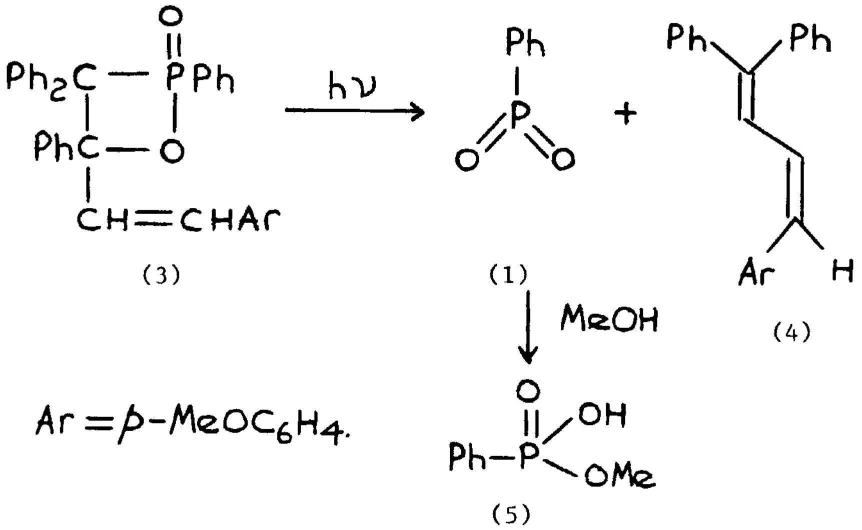
Although short-lived pentavalent phosphorus compounds with co-ordination number 3 have commanded a fair amount of attention in the past few years[1], little information is available concerning aryldioxophosphoranes ('metaphosphonates'). This neglect stems largely from the ease of their trimerisation and polymerisation which not only makes them difficult to detect, but hitherto has precluded their use in preparative chemistry.

The parent phenyldioxophosphorane ('phosphonobenzene') (1) was first reported in 1882 by Michaelis and Rothe[2] who believed it to have been formed in the reaction of benzenephosphonic acid with benzenephosphonic dichloride, but almost eighty years later it was shown[3] that the product was the trimer of (1) rather than (1) itself. In 1921 Conant and Pollack[4] observed the spontaneous decomposition of the phosphinate anion (2) in aqueous solution, but only now with the advantage of hindsight



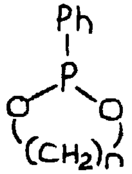
(2) (1)

does the question arise of whether this reaction proceeds by way of phosphonobenzene (1). More recently, Regitz and Eckes[5] showed that photolysis of the 1,2 λ^5-oxaphosphetane (3) in methanol produces the 1,3-diene (4) and the mono-methyl ester (5) and suggested that (5) arose <u>via</u> the monomeric phosphonobenzene (1)



which is trapped by methanol, but the evidence is tenuous since spontaneously formed oligomers of (1) also react with methanol to give (5)[3]. We now describe (i) a genuinely simple and novel way of generating highly reactive metaphosphonate intermediates by thermal fragmentation of cyclic phosphonites and their thia-analogues in the gas phase, and (ii) an elaboration of this method whereby a monomeric phosphonobenzene is detected unambiguously for the first time by an intramolecular trapping reaction. Sigal and Loew[6] have tried to prepare phosphonomesitylene by the pyrolysis of the corresponding phosphinate, but the only products obtained were polymer and mesitylenephosphonic acid.

The origin of this work lies in our observation that flash vacuum pyrolysis (FVP) of cyclic phosphonites (6: n = 3 or 4) yields the corresponding phosphinic acid (7) which rearranges



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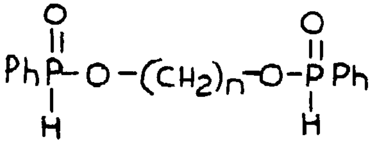

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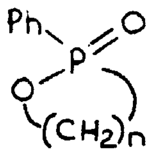
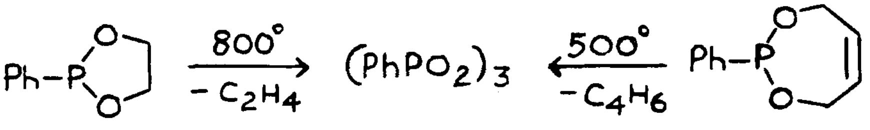


(8)

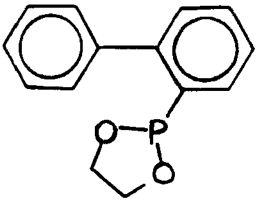
at higher temperatures to a phostone (8)*. FVP of the five-membered analogue (9) under similar conditions (800°C and 0.01 mmHg), resulted in loss of ethylene and the almost quantitive formation of trimeric phosphonobenzene (10) which could also be obtained by thermal elimination of 1,3-butadiene from 2-phenyl-5,6-dehydro-1,3,2-dioxaphosphepane (11) at 500°C.



(9) (10) (11)

The identity of trimer (10) was confirmed by analytical and [FAB] mass spectral data, and in particular, by comparison of its complex ^{31}P-n.m.r. spectrum with that of an authentic sample prepared from the reaction of benzenephosphonic acid with benzenephosphonic dichloride[2].

Expected trapping of the highly reactive monomer (1) by introduction of suitable cycloaddends, e.g. dimethyl acetylenedicarboxylate, tetracyanoethylene, etc. within the pyrolysis zone failed to occur, but indirect evidence for its intermediacy in these reactions was obtained by thermal fragmentation of 2(o-biphenylyl)-1,3,2-dioxaphospholane (12) in the gas-phase at 600-800°C in the usual way[8]. Under these conditions, pyrolysis resulted in the almost quantitative formation of 5-hydroxydibenzophosphole 5-oxide (14; m.p. 252-255°C; lit.[9] 253-257°C) which is the anticipated trapping product of monomeric (13) by the adjacent phenyl ring. Since insertion into an aromatic ring requires the intervention of a powerful electrophilic species, we believe the formation of (14) from (12) constitutes the first reliable evidence for the existence of a phosphonobenzene as a true intermediate.



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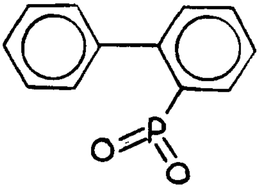

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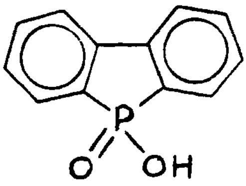

(14)

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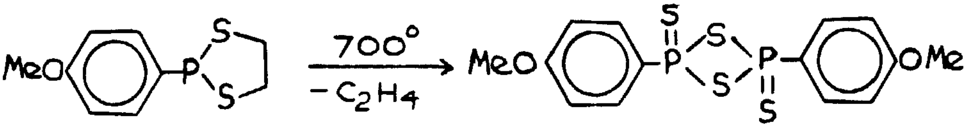
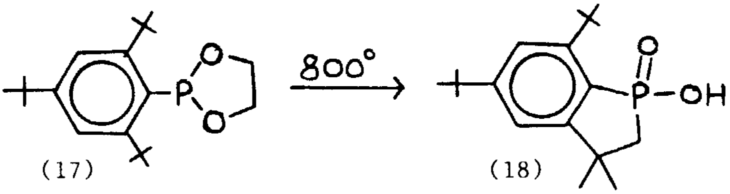
*Mathey and Thavard[7] have shown that 2-phenyl-1,3,2-dioxaphosphorinane (6; n = 3) undergoes the same rearrangement upon heating in toluene at 250°C for 24h.

We have also shown that short-lived three-co-ordinate P(V) compounds possessing a P=S or P=N bond are also accessible by the same method, e.g. the dimer (16) of *p*-methoxyphenylthionophosphine sulphide, otherwise known as Lawesson's reagent, in 80% yield. The thiation properties of (16) are well known[10], but its mode of formation from anisole and P_4S_{10} appears not to be general[11]. Work is now in hand to moderate the reactivity of (16) by changing the nature of the aryl group.



(15) (16)

Finally, we report that FVP of the tri-t-butyl analogue (17)[12] leads to insertion of the PO_2 moiety into a neighbouring methyl group to give the cyclic product (18; 100%).



(17) (18)

REFERENCES

1. For a recent review, see: M. Regitz and G. Maas, Top Curr. Chem., 97, 71 (1981).
2. A. Michaelis and F. Rothe, Ber. Dtsch. Chem. Ges., 25, 1747 (1882); see also A. Michaelis, Liebigs Ann.Chem., 293, 193 (1896); 294, 1 (1896); 315, 43 (1901), for similar reactions involving aryl-substituted derivatives.
3. E. Cherbuliez, B. Baehler, F. Hunkeler and J. Rabinowitz, Helv. Chim. Acta, 44, 1812 (1961).
4. J.B. Conant and S.M. Pollack, J.Am.Chem.Soc., 43, 1665 (1921).
5. M. Regitz and H. Eckes, Tetrahedron, 37, 1039 (1981) and references therein.
6. I. Sigal and L. Loew, J.Am.Chem.Soc., 100, 6394 (1978).
7. F. Mathey and D. Thavard, J.Organometal.Chem., 117, 337 (1976).
8. S. Bracher, J.I.G. Cadogan, I. Gosney and S. Yaslak, J. Chem. Soc. Chem. Commun., 1983, in press.
9. L.D. Freedman and G.O. Doak, J.Org.Chem., 21, 238 (1956).
10. H. Hoffmann and G. Schumacher, Tetrahedron Lett., 2963 (1967); see also S. Lawesson, American Chemical Society Symposium Series N°. 171, 279 (1981) and references therein.
11. H.Z. Lecher, R.A. Greenwood, K.C. Whitehouse and T.H. Chao, J. Am. Chem. Soc., 78, 5018 (1956).
12. With A.H. Cowley and M. Pakulski.