

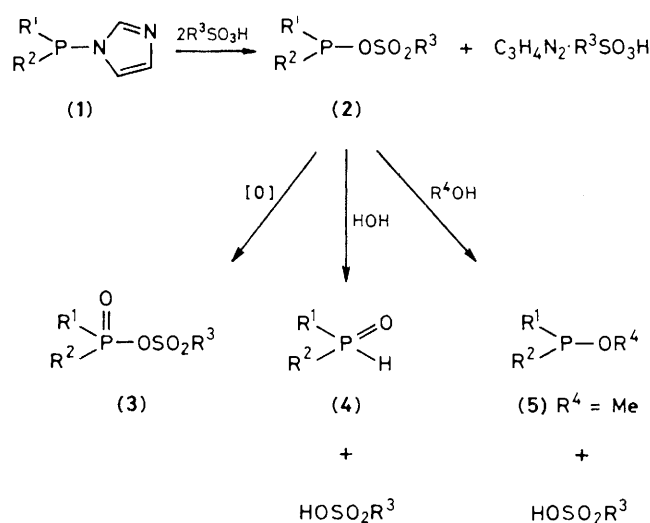
Phosphino Sulphonates, a Type of P^{III}-anhydride and Their Isomerisation into Phosphinoyl Sulphinates: a Novel Rearrangement in Phosphorus–Sulphur Chemistry

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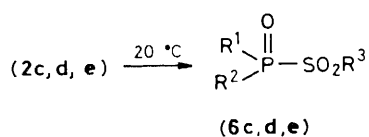
The imidazolides (1) react smoothly with RSO₃H to afford a novel class of trico-ordinate phosphorus anhydride, the phosphino sulphonates (2); under suitable structural circumstances the compounds (2) undergo a novel type of rearrangement, (2) → (6), which provides the first example of a phosphinoyl sulphinate structure (6).

General methods leading to the phosphinoyl sulphonates (3) have been described only recently.¹ In pursuing our studies on phosphorus acid anhydrides we report the synthesis of a new class of P^{III}-anhydride, *i.e.* the phosphino sulphonates (2). The anhydrides (2) were prepared by the reaction of sulphonic acid (2 mol) with the imidazolides (1) at –60 °C in methylene chloride solution (Scheme 1). The ³¹P n.m.r. spectra of the reaction mixture showed that the anhydrides (2) were the only reaction product, and had chemical shifts characteristic of trico-ordinate phosphorus.† More detailed investigations showed that the anhydrides (2) were readily oxidized by air to the phosphinoyl sulphonates (3). The latter were identical with the anhydrides (3) described in our previous paper.¹ Hydrolysis of (2) afforded well-characterized phosphine oxides or their structural analogues (4), and reaction with alcohols led to the trico-ordinate phosphines (5) in quantitative yield.



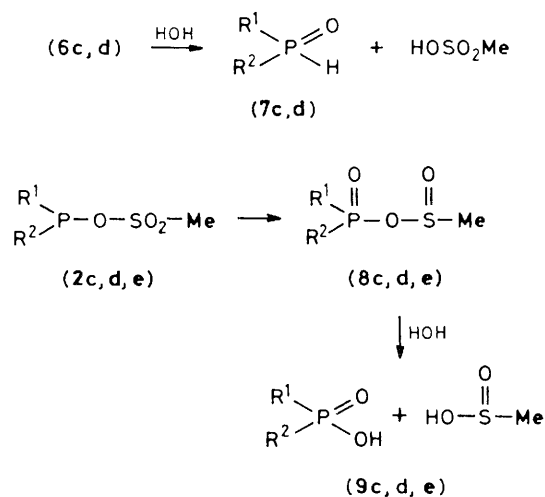
- a; R¹ = R² = OEt, R³ = Me
 b; R¹ = R² = PrⁿO, R³ = Me
 c; R¹ = R² = Ph, R³ = Me
 d; R¹ = Ph, R² = Bu^t, R³ = Me
 e; R¹ = OMe, R² = Bu^t, R³ = Me

Scheme 1

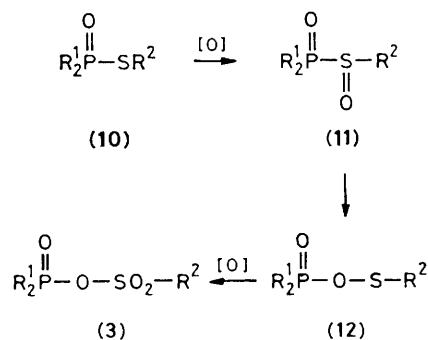


However, the most interesting observation was made when the anhydrides (2) were left to warm up gradually to ambient temperature. No change of structure was noted in the case of (2a, b), and other anhydrides bearing two alkoxy-groups at the phosphorus atom. In contrast (2c–e) isomerized to give the phosphinoyl sulphinates (6c–e). This observation has led to the discovery of a new rearrangement in phosphorus chemistry and revealed a novel class of organophosphorus compound (6) containing a direct P–S bond.² The structure of (6) was confirmed by ³¹P n.m.r. spectroscopy† showing absorption in the region which is characteristic for P^{IV} compounds and by identification of the appropriate phosphine oxides (7) as products of hydrolysis.

The quantitative formation of diphenylphosphine oxide in the above reaction is significant because it excludes the anhydride (8) as an alternative isomeric structure to (6). If



Scheme 2



Scheme 3

† ³¹P N.m.r. data: δ (2a) 134.6, (2b) 132.9, (2c) 123.9, (2d) 145.2, (2e) 141.1, (6c) 32.0, (6d) 53.4, (6e) 34.1, (7c) 22.6 (*J*_{P–H} 515 Hz), and (7d) 47.2 p.p.m. (*J*_{P–H} 446 Hz).

(2) had isomerised to (8) and not to (6), the subsequent reaction of (8) with water should have led to the diphenylphosphinic acid (9) (Scheme 2). It is of interest to note that the phosphinoyl sulphinates (6) undergo slow oxidation by air to give the anhydrides (3). The oxidation of (6), leading to the anhydride (3) may either involve insertion of oxygen into the P-S bond of (6) or oxidation of the P^{III} anhydride (2) as a component of the possible equilibrium $(6) \rightleftharpoons (2)$.³ This observation is relevant to the recent studies of Casida and Segall⁴ on the oxidative conversion of the phosphinoyl sulphide (10) by peracids as a model for the enzymatic oxidation of phosphinoyl sulphides. The following hypothetical steps have been suggested (Scheme 3): formation of the sulphoxide (11), its isomerization into the phosphinoyl sulphenate (12), and its subsequent oxidation into (3). Our work strongly suggests a different sequence of events,

involving formation of (11), its oxidation to the phosphinoyl sulphinate (6) and finally to (3).

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References

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- 2 Somewhat similar behaviour was observed in the case of the acylphosphines $RC(O)PR_2$; E. Lindner and J. C. Wurhmann, *Chem. Ber.*, 1981, **114**, 2272.
- 3 For analogy see: J. Michalski, W. Stec, and A. Zwierzak, *Chem. Ind. (London)*, 1965, 347; J. F. Lutsenko and M. V. Proskurnina, *Usp. Khim.*, 1978, **47**, 1648.
- 4 Y. Segall and E. J. Casida, 'Phosphorus Chemistry,' A.C.S. Symposium Series 171, 1981, p. 337-340; Y. Segall and E. J. Casida, *Tetrahedron Lett.*, 1982, 139.