

A Novel Phosphorus(V) → Phosphorus(III) Rearrangement: A Possible Example of Phenylphosphinidene as a Reaction Intermediate

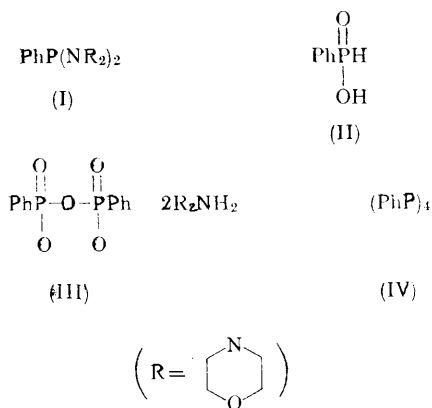
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A RECENT paper¹ claiming the detection of phenylphosphinidene, the phosphorus analogue of phenylcarbene, prompts us to report the results of our study of an entirely novel type of reaction which we feel is best rationalised by the existence of this intermediate.

Reaction of phenylphosphonousbismorpholinamide (I) with phenylphosphinic acid (II) in boiling ethyl acetate, a reaction giving good yields of amides with carboxylic acids,² afforded only the bismorpholinium salt of phenylphosphonic anhydride (III; m.p. 203—205°; 55%), tetraphenylcyclotetraphosphine (IV; m.p.³ 150—152°; 10%), and in some instances, small amounts of morpholinium phenylphosphonate (m.p. 167—170°). Rigid exclusion of moisture and air affected neither products nor yields. Replacement of the amide (I) with phosphoroustrisdimethylamide gave a reduced yield (7—8%) of the phosphine (III) and a small yield of phenylphosphonic anhydride as its monodimethylammonium salt.

A solution of the acid (II; 2 moles) and dicyclohexylcarbodi-imide (1 mole) gave a quantitative precipitate of dicyclohexylurea and a foul-smelling solution of the anhydride (V) (p.m.r. evidence: aromatic multiplet δ 7.4—7.9; P-H multiplets δ 3.05 and 13.05; J_{PH} 600 c./sec.) which reacted with morpholine to give the salt (III; 45%) and the phosphine (IV; 4%).



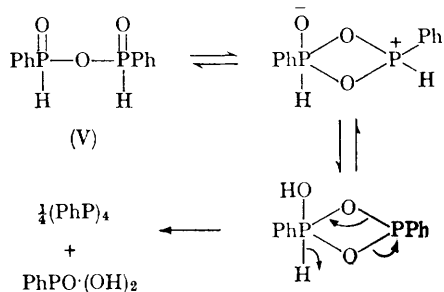
¹ U. Schmidt and C. Osterroht, *Angew. Chem. Internat. Edn.*, 1965, 4, 437.

² R. Burgada, *Bull. Soc. chim. France*, 1963, 2335.

³ J. N. B. Reesor and G. F. Wright, *J. Org. Chem.*, 1967, 22, 385.

A solution of the anhydride decomposed at room temperature, and more rapidly on heating, with disappearance of the P-H multiplets and appearance of a single broad peak (δ 13.8) attributable to POH. Phenylphosphine could not be detected and attempted isolation of the anhydride gave only oils. On a larger scale, decomposition of the anhydride, followed by hydrolysis gave phenylphosphonic acid (60%) and the phosphine (IV; 11%).

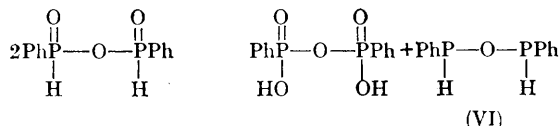
The coincidence of yields by the two methods of preparation strongly suggests that the anhydride



⁴ A. W. Frank, *Chem. Rev.*, 1961, **61**, 389.

is a common intermediate. The mechanism for decomposition of the anhydride is speculative but may proceed as follows:

Alternatively, a disproportionation of two molecules of the anhydride (V) could occur



followed by decomposition of the intermediate (VI). Neither of these reactions has any precedent, but whatever the mechanism it is difficult to escape the conclusion that it must involve the generation of phenylphosphinidene. The only similar type of reaction is the long known⁴ thermally-induced disproportionation of monosubstituted phosphinic acids to primary phosphines and phosphonic acids. The anhydride (V), however, does not induce decomposition of phenylphosphonic acid in boiling benzene.

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