Reduction of 2-Hydroxyethyl Disulphide to Ethylene Sulphide by Phosphines and Secondary Phosphine Oxides

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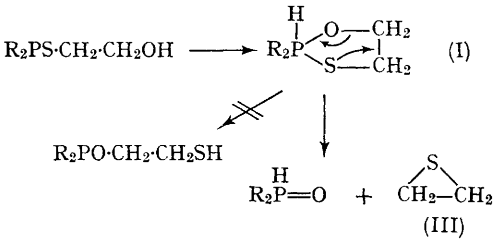
IN the preceding Communication, we reported the intramolecular transesterification of 3-hydroxyalkyl-substituted thioite esters of phosphorus to give 1,2-oxaphospholanes. The esters were formed by direct reaction of the P–H group with a disulphide.[1] It was of interest to determine whether the presence of a hydroxyl group on the disulphide, which would then be positioned three atoms from phosphorus in the thioite ester, would lead to an intramolecular rearrangement *via* a presumed 1,3,2-oxathiaphospholane (I, eq. 1). What in fact was observed was oxidation of phosphorus. For example, stirring diphenylphosphine oxide (0·054 mole) and 2-hydroxyethyl disulphide (II) (0·054 mole) at 30—40° for 20 hr. followed by brief heating to 120° (10 min.) and crystallization of the mixture from hexane–propan-2-ol gave diphenylphosphinic acid in 65·5% yield (m.p. 189—192°, lit.[2] 194—195°; infrared spectrum identical with an authentic sample).

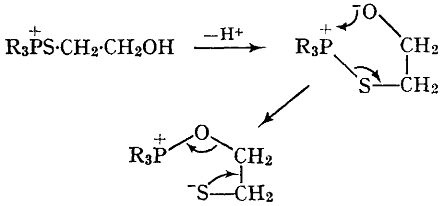
Since the only source of oxygen was the alcohol group of (II), we speculated that ethylene sulphide (III) might be a product of the reaction. Accordingly, di-isobutylphosphine (0·49 mole) and (II) (0·36 mole) in the presence of hydroquinone (1·0 g.) were mixed at room temperature and warmed at 65° to permit collection of 4·4 g. of liquid of b.p. 53–61°/1 atm. whose infrared spectrum indicated ethylene sulphide (lit.,[3] b.p. 55—56°). The liquid solidified (polymerized) on standing and the elemental analysis of this solid was satisfactory for $(CH_2CH_2S)_x$. Also isolated by vacuum distillation were 2-mercaptoethanol, (IV), (95%), di-isobutylphosphine oxide (73%; b.p. 71—75°/0·2 mm.), and di-isobutylphosphinic acid (23%; b.p. 131–136°/0·2 mm.).

Oxidation of two tertiary phosphines was also carried out. Triphenylphosphine (0·10 mole) and (II) (0·10 mole) reacted exothermically in the absence of solvent. Distillation after heating at 40—50° for 30 min. gave 1·9 g. (32%) of (III), 7·9 g. (100%) of (IV), and 23·0 g (83%) of triphenylphosphine oxide (m.p. 152—153·5° from ethyl acetate, lit.,[4] m.p. 153°). Cyclohexyldiphenylphosphine (0·12 mole) and (II) (0·12 mole) also reacted exothermically to give (III) (58%), (IV) (92%) and cyclohexyldiphenylphosphine oxide (74%; m.p. 164—165° from acetone–water;

(1)



(2)



lit.,[5] m.p. 165°). We feel that a reasonable mechanism for this reaction can be depicted in terms of a synchronous intramolecular rearrangement of (I) propelled by the formation of the phosphoryl group and favourable attack of an incipient mercaptide ion at saturated carbon. The formation of a quinquevalent phosphorus intermediate is most compelling with tertiary phosphines since a stepwise reaction would entail separation of charge between the phosphonium and mercaptide ions (eq. 2).

Satisfactory elemental analyses and infrared spectra were obtained for all compounds. Extension of this reaction to the syntheses of substituted ethylene sulphides will be reported in the future.

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[3] "Handbook of Chemistry and Physics", Chem. Rubber Publ. Co., 1963.
[4] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **1942**, **64**, 2982.
[5] L. Horner, P. Beck, and V. Toscano, *Chem. Ber.*, **1961**, **94**, 1317.