A Novel Synthesis of Phostones and Deoxophostones (1,2-Oxaphospholanes)

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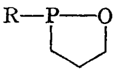
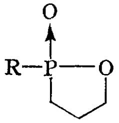
IN a previous report[1] we described the preparation of phosphinothioite (R_2PSR^1) and phosphonodithioite [$RP(SR^1)_2$] esters from primary and secondary phosphines and disulphides. We have now found that secondary phosphines and secondary phosphine oxides containing a 3-hydroxyalkyl group give sulphur-free products whose spectral and chemical properties are consistent with the previously unreported 1,2-oxaphospholanes (I) and the known[2,3] 1,2-oxaphospholane 2-oxides (phostones, II). For example, 3-hydroxypropylphenylphosphine and phenyl disulphide in benzene at 22° after 15 hr. gave 2-phenyl-1,2-oxaphospholane (Ia), (34%) b.p. 112°/0·5 mm. in which both P–H and OH bands were absent in the infrared, whereas bands for P–O–C, P–Ph, and P–CH_2 were present (960, 1435, and 1418 cm.$^{-1}$, respectively). The proton count by n.m.r. gave the aryl : OCH_2 : CH_2 ratio as 5 : 2 : 4 (σ of multiplets relative to Me_4Si were centred at 7·2, 3·95, 1·83 p.p.m.) with a single peak in the 16·2 Mc/sec. ^{31}P spectrum at $-110{\cdot}2$ p.p.m. relative to 85% H_3PO_4. Reaction of (Ia) with sulphur gave the 2-thiono-compound (III), b.p. 152°/0·2 mm. (P–O–C 973 and 799, P–CH_2 1412, P–Ph 1115 and 1439, and a new band at 650 cm.$^{-1}$ which is probably $P \rightarrow S$; proton ratios again were 5 : 2 : 4 at 7·6, 4·45, and 2·36 σ, and the single ^{31}P peak was at $-102{\cdot}4$ p.p.m.) Similarly reaction of 3-hydroxypropylphenylphosphine oxide with phenyl disulphide gave the known[2] phostone (IIa) (84%), b.p. 142°/0·2 mm. (P–O–C 967 and 817, $P \rightarrow O$ 1215, P–CH_2 1413, and P–Ph 1123 and 1442 cm.$^{-1}$; proton ratios for multiplets centred at 7·6, 4·38, and 2·15 σ were 5 : 2 : 4 and ^{31}P n.m.r gave a single peak at $-58{\cdot}4$ p.p.m.).

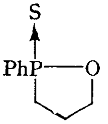
Also prepared were (Ib), b.p. 127°/0·15 mm. (P–O–C 730 and 972, P–CH_2 1423 cm.$^{-1}$; ratio of OCH_2 to all other protons was 2 : 15 with σ centred at 3·95 and 1·9 p.p.m.; the single ^{31}P peak was at $-123{\cdot}1$ p.p.m. and (IIb), b.p. 94°/0·25 mm. ($P \rightarrow O$ 1220, P–O–C 985 and 800, and P–CH_2 1412 cm.$^{-1}$;

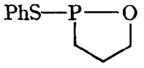
proton $OCH_2:CH_2:CH_3$ ratio was 2:10:3 with multiplets centred at 4·25, 1·9, and 0·95 σ, ^{31}P was at −71·1 p.p.m.).

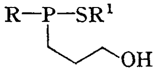
With 3-hydroxypropylphosphine and 2 mol. equivalents of phenyl disulphide, the mixed ester (IV) (22%) b.p. 116°/0·2 mm., was obtained (P–O–C 960, Ph at 1582, and P–CH_2 at 1418 cm.$^{-1}$; proton aryl:$OCH_2:CH_2$ ratio was 5:2:4 at 7·3, 4·18 and 1·8 σ, with the ^{31}P peak at −79·0 p.p.m.).


(Ia) R=Ph
(Ib) R=C_6H_{11}


(IIa) R=Ph
(IIb) R=Bu^n


(III)


(IV)


(V)

Intermediate formation of the thioite ester (V) ($R=C_6H_{11}$, $R^1=n\text{-}C_4H_9$) was shown by carrying out the reaction as usual (dry benzene, room temperature) but removing solvent and thiol at 20—25° under reduced pressure. The infrared spectrum and elemental analysis of the residue were consistent with (V) and vacuum distillation gave (Ib) in 35% yield along with the usual residual glassy resin.

Preparation of ring-substituted 1,2-oxaphospholanes and the use of cyclization reagents other than disulphides will be reported elsewhere. The hydrolytic properties and ring-strain chemistry of these phosphorus(III) compounds are also under study in view of their relationship to the unusually reactive five-membered cyclic esters of various phosphoric acids.[4]

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[4] E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1966, **88**, 3432 and references cited therein.