Reactions of Phosphinothioylidene (R–$\ddot{\text{P}}$=S) as Intermediate

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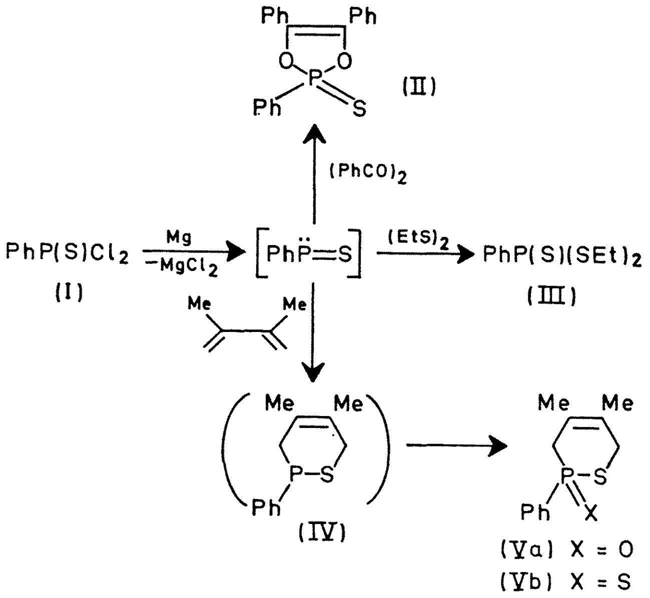
Summary Dechlorination of phenylphosphonothioic dichloride with magnesium in the presence of 2,3-dimethylbutadiene, benzil, and diethyl disulphide gave 1,2-thiaphosphorin, 1,3,2-dioxaphospholene, and phosphonotrithioate derivatives, respectively, and the formation of these products was explained in terms of the intermediacy of phenylphosphinothioylidene (Ph$\ddot{\text{P}}$=S).



WE report some reactions which suggest the intermediacy of phosphinothioylidene (R$\ddot{\text{P}}$=S). Phenylphosphonothioic-dichloride (I) was dechlorinated with an equimolar amount of magnesium in the presence of benzil in tetrahydrofuran (THF) at room temperature to form 2,4,5-triphenyl-1,3,2-dioxaphospholene 2-sulphide (II), m.p. 126·5—127°, almost quantitatively; the structure of (II) was established by the analytical and spectral data: ^{31}P n.m.r. ($CHCl_3$, 85% H_3PO_4 as external standard) δ −104 (t, J_{PH_o} 15·6 Hz), M^+ 350. In the mass spectrum, the peak 140, $(PhPS)^+$ itself, was observed though not predominant.

The dichloride (I) was dechlorinated similarly in diethyl disulphide to give diethyl phenylphosphonotrithioate (III) in a 41% yield (b.p. 109—117°/0·05 mmHg). ^{31}P n.m.r. (neat) δ −80·5 (sp, $J_{PSCH} = J_{PH_o}$ 15·8, $J_{PH_m} = J_{PH_p}$ 3·4 Hz), M^+ 262.

These results suggest that phenylphosphinothioylidene generated, like phosphinidene,[1,2] was trapped by benzil and diethyl disulphide through a 1,4-cycloaddition to both oxygen atoms and an insertion to the S–S bond, respectively.

In an atmosphere of nitrogen (I) was added dropwise to a solution containing 2,3-dimethylbutadiene, THF, and suspended magnesium with stirring, and the mixture was stirred at 50° overnight to complete dechlorination. Products obtained were 4,5-dimethyl-2-phenyl-3*H*,6*H*-1,2-thiaphosphorin 2-oxide (Va; m.p. 85·5—86°) and 2-sulphide (Vb; m.p. 61—62°) in 21 and 22% yields respectively. Their formation is most reasonably explained by the Diels–Alder-type reaction product (IV) of phenylphosphinothioylidene with 1,3-diene as for the thionitroso-compound,[3] followed by the oxidation during isolation and the sulphurisation with unchanged dichloride (I) during reaction. The spectral data of thiaphosphorins (Va) and (Vb) were as follows; (Va): i.r. (KBr) 1205 cm^{-1} ($\nu_{P=O}$), ^{1}H n.m.r. (CCl_4) δ 1·77(s, 5-Me), 1·97(d, 4-Me, J_{PH} 5 Hz), 2·4—4·0(m, 2 × CH_2), and 7·4—8·0(m, Ph), M^+ 238. (Vb): ^{1}H n.m.r. (CCl_4) δ 1·68(s, 5-Me), 1·93(d, 4-Me, J_{PH} 5 Hz), 2·7—3·9(m, 2 × CH_2), and 7·2—8·0(m, Ph), M^+ 254. Very recently (Vb) has been synthesised by another route.[4]

These reactions did not occur in the absence of magnesium under the same conditions.

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