A Novel Carbon–Phosphorus Bond Formation Reaction

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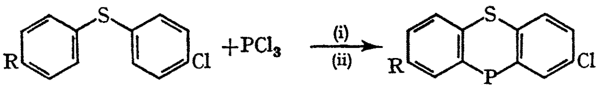
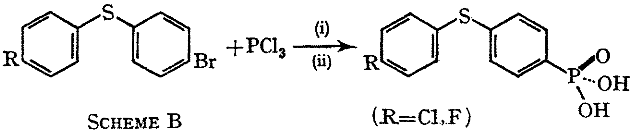
A SERIES of chlorine- and fluorine-containing phenothiaphosphinic acids have been prepared (See Scheme A).[1,2]



R=Me, Cl, F
SCHEME A (i) $AlCl_3$ (ii) hydrolysis

The basic hydrolysis step is accompanied by oxidation.[2,3]

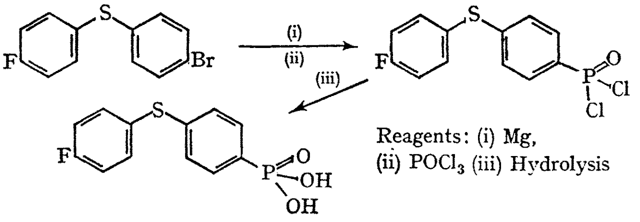


SCHEME B (R=Cl,F)

When bromine was present in either the *para*- or *ortho*-position only a *p*-arylthiophenylphosphonic acid (characterised as its dicyclohexylammonium salt) was isolated (Scheme B).

Absence of absorption near 310 nm. differentiates this type of acid from the phosphinic acids obtained in Scheme A. Treatment of the diazonium fluoroborate of *o*-aminophenyl *p*-chlorophenyl sulphide with phosphorus trichloride in the presence of cuprous bromide followed by reduction with aluminium,[4] and basic hydrolysis of the product gave *o*-(*p*-chlorophenylthio)-phenylphosphonic acid.[3]

The structure of one of the products obtained in accordance with Scheme B was proved as follows:

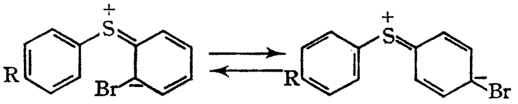


Reagents: (i) Mg,
(ii) $POCl_3$ (iii) Hydrolysis

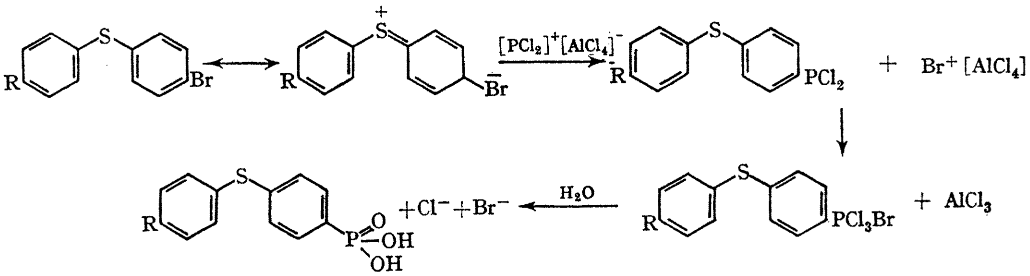
In the reactions represented by Scheme B, the presence of aluminium chloride is essential; it is characteristic that the aromatic bromine is recovered as bromide ion. Whilst the *o*-bromo-derivative loses bromine and yields the same product as the *p*-bromo-isomer, no debromination takes place when the halogen is in the *meta*-position.

The reaction summarized by Scheme B can perhaps be rationalized as follows:

It would be necessary to assume further the following isomerisation reaction:



This mechanism is supported by the observation that the analogous derivatives of diphenyl ether behave similarly.[5]



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[2] I. Granoth, A. Kalir, and Z. Pelah, *Israel J. Chem.*, 1968, **6**, 651.
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[4] L. D. Quin and J. S. Humphrey, *J. Amer. Chem. Soc.*, 1961, **83**, 4124.
[5] I. Granoth, A. Kalir, Z. Pelah, and E. D. Bergmann, unpublished results.