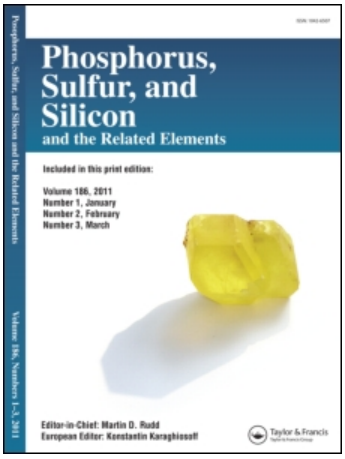

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The Reaction of Thiolates with Elemental Phosphorus

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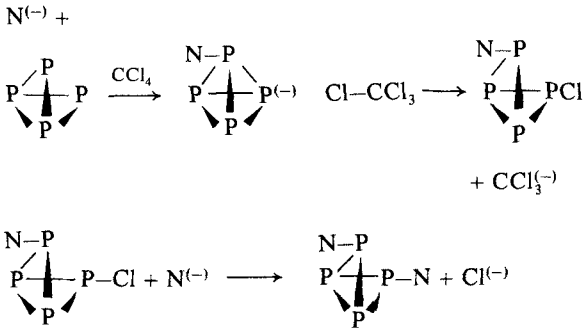
Sodium alkanethiolates react rapidly with elemental phosphorus in tetrachloromethane to give high yields of trialkyl phosphorothioites when the thiolate is used in excess.

There is much interest in the direct synthesis of organophosphorus compounds from the element as such methods would have considerable advantages over more classical procedures.[1] The main difficulties are the insolubility of elemental phosphorus, the very low nucleophilic reactivity of phosphorus incorporated in highly strained rings, and the extreme reactivity of the phosphide ion produced by initial nucleophilic attack.

We have developed a general synthetic method[2] involving the combined attack of nucleophile, e.g. RO^-, RS^-, $R^1R^2NH^2$, on phosphorus, and electrophilic capture of the released phosphide ion by a positive halogen compound, in particular tetrachloromethane, viz.,



The significance of the method is that the phosphide ion released in the initial reaction reacts rapidly with tetrachloromethane, in preference to a proton of the conjugate acid NH, to give a chloro-compound which reacts rapidly with the nucleophile. Repetition of this series of reactions leads to a tri-substituted product in high yield.

We find that thiolate ions, in the presence of thiol, react over a period of 24 h in an excess of tetrachloromethane with white phosphorus in the form of a fine sand, to give high yields of the corresponding trialkyl phosphorotrithioite:

$$P_4 + 6RS^- + 6RSH + 6CCl_4 \longrightarrow 4P(SR)_3 + 6CHCl_3 + 6Cl^-$$

Because of the side reaction between sodium alkanethiolate and carbon tetrachloride,[3] the reaction does not proceed to completion when stoichiometric quantities are used. For this reason two equivalents of thiolate were used. The product formation in a typical reaction of ethanethiol is shown in Table I. Similar results were obtained for other alkanethiols, but benzenethiol failed to react.

The side products, diethyldisulphide and triethyl trithio-orthoformate, are formed by reaction of thiolate ions with tetrachloromethane,[3] and this,

TABLE I

Product composition[a] in the reaction of sodium ethanethiolate with white phosphorus in tetrachloromethane at 25°

Time (hr)	$CHCl_3$ mol	EtSSEt mol	$CH(SEt)_3$ mol	$P(SEt)_3$ mol
3	0.02	0.002	0	0.004
5	0.03	0.002	0.001	0.010
24	0.05	0.010	0.004	0.028
48	0.07	0.021	0.005	0.031

Initial amount of P_4 0.008 mol; theoretical yield of $P(SEt)_3$ = 0.032 mol. Maximum yield of $P(SEt)_3$ = 86%.

[a] Analysis of the reaction mixture was performed by g.l.c.

together with the reaction on phosphorus, leads to high yields of trichloromethane.

Intermediate phosphorus compounds are detected by ^{31}P nmr spectroscopy, when a stoichiometric amount of thiolate is used. Diethyl phosphorochloridodithioite may be produced by reaction of an intermediate dithiophosphide ion on tetrachloromethane, viz.,

$$(EtS)_2P{-}\underset{\displaystyle SEt}{\underset{|}{P}}{-}P(SEt)_2 + EtS^{(-)} \longrightarrow (EtS)_2P^{(-)} + (EtS)_2P{-}\underset{\displaystyle SEt}{\underset{|}{P}}{-}P(SEt)_2$$

$$(EtS)_2P^{(-)} + CCl_4 \longrightarrow (EtS)_2P{-}Cl + CCl_3^{(-)}$$

Diethyl trichloromethylphosphorodithioite, which is also detected, arises from the reaction of the trichloromethyl carbanion with diethylphosphorochloridodithioite.

In the presence of an excess of ethanethiolate, these processes are suppressed, and hence high yields of trialkyl phosphorotrithioite are found.

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