

Reactions of Trico-ordinate Phosphorus Compounds with Phosphorus Pseudohalogens. Part 2. Pentaco-ordinate Intermediates in the Reaction of *o*-Phenylene Neopentyl Phosphite with Diethoxyoxophosphorane-sulfenyl Chloride

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Reaction between oxophosphoranesulfenyl chloride **1** ($R = R' = \text{EtO}$) and *o*-phenylene neopentyl phosphite **4** takes predominantly the deoxygenation course, yielding the phosphorochloridothioate **7** and the phosphate **8**. Formation of minor products **5** and **6** corresponding to the desulfurization pathway, and low-temperature ^{31}P NMR observations, are rationalized by proposing phosphorane-phosphonium equilibria which are shifted towards phosphorane structures **9**, **13**, **11**. These results supplement our earlier studies on desulfurization and deoxygenation of compound **1** with trico-ordinate phosphorus compounds and add new evidence for phosphonium-phosphorane equilibria.

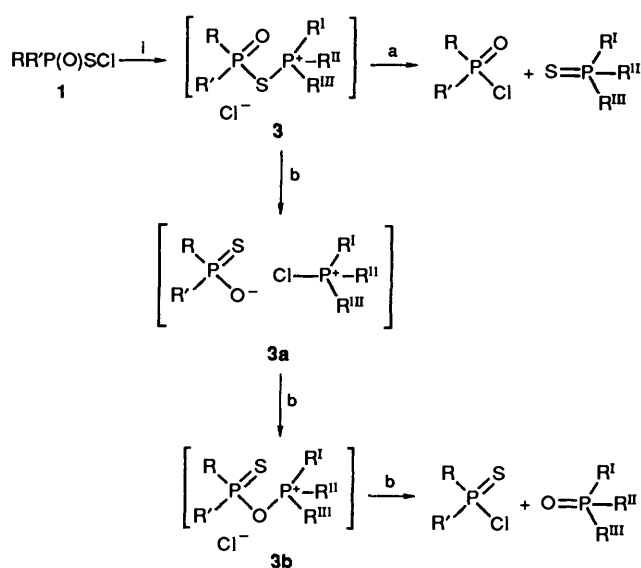
Reactions of trico-ordinate phosphorus compounds with phosphorus pseudohalogens are of synthetic and mechanistic interest. The systematic studies of Michalski and Skowrońska and their colleagues have revealed that disulfides $[\text{RR}'\text{P}(\text{O})\text{S}]_2$, diselenides $[\text{RR}'\text{P}(\text{O})\text{Se}]_2$ and sulfenyl chlorides $\text{RR}'\text{P}(\text{O})\text{S}-\text{Cl}$ react with trico-ordinate phosphorus compounds under conditions comparable to those involving 'true' halogens. Such reactions can be classified as desulfurization, deselenization and deoxygenation, and proceed in many cases with a high degree of chemo- and stereo-selectivity. The selectivity depends greatly on the structure of the P^{III} compound and to some extent on the P^{IV} substrate and reaction conditions.^{1,2}

We have recently described in detail the first part of our studies on desulfurization and deoxygenation of oxophosphoranesulfenyl chlorides **1** by P^{III} compounds. The application of variable-temperature FT ^{31}P NMR spectroscopy has provided information about the existence and structure of short-lived intermediates that are responsible for desulfurization and deoxygenation. The thermally labile phosphonium salts **3** and **3b** have been detected in the reaction of substrates **1** with a variety of trico-ordinate phosphorus compounds $\text{PR}^{\text{I}}\text{R}^{\text{II}}\text{R}^{\text{III}}$ at -100 to -80 °C;⁰ **3a** is a transient species between **3** and **3b**. These intermediates are of decisive importance in the formation of final products, and their mode of decomposition is shown in Scheme 1.^{2e}

Whether a pentaco-ordinate species could be involved in this kind of chemical change is an open question. Therefore we decided to examine the reaction of sulfenyl chloride **1** with a trico-ordinate phosphorus compound containing a ligand which stabilizes the pentaco-ordinate phosphorus species and contains an alkoxy ligand resistant to dealkylation, *e.g.* the neopentoxy group. We anticipated that the presence of a five-membered ring would increase the stability of pentaco-ordinate intermediates.³ Our attempts to verify this assumption in the reaction of compound **1** ($R = R' = \text{EtO}$) with *o*-phenylene neopentyl phosphite **4** have proved successful and will be described in this paper.

Results and Discussion

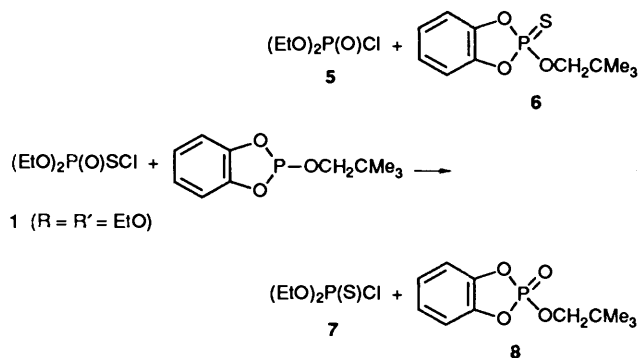
Reaction between diethoxyoxophosphoranesulfenyl chloride **1** ($R = R' = \text{EtO}$) and *o*-phenylene neopentyl phosphite **4** proceeds at temperatures as low as -100 °C. After completion by gradual warming to ambient temperature, the reaction led to two pairs of products: **5**, **6** and **7**, **8** (Scheme 2). The latter pair



Scheme 1 Reagents: *i*, $\text{PR}^{\text{I}}\text{R}^{\text{II}}\text{R}^{\text{III}}$. *a* = desulfurization path; *b* = deoxygenation path

corresponds to a deoxygenation pathway and is dominant. Properties of products **5–8** were found to be the same as those of authentic specimens.

^{31}P NMR studies of the reacting species **1** ($R = R' = \text{EtO}$) and **4** were performed in the temperature range -100 to 10 °C in ethyl chloride. The protocol of the ^{31}P NMR studies was described in detail in our earlier paper.^{2e} The spectra were



Scheme 2

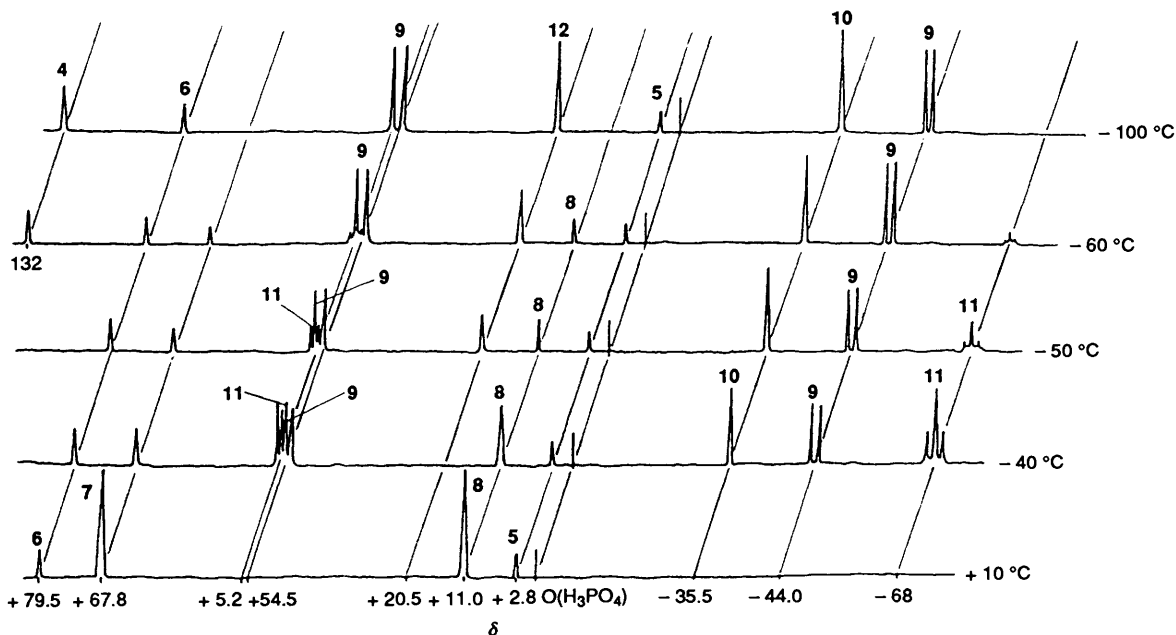
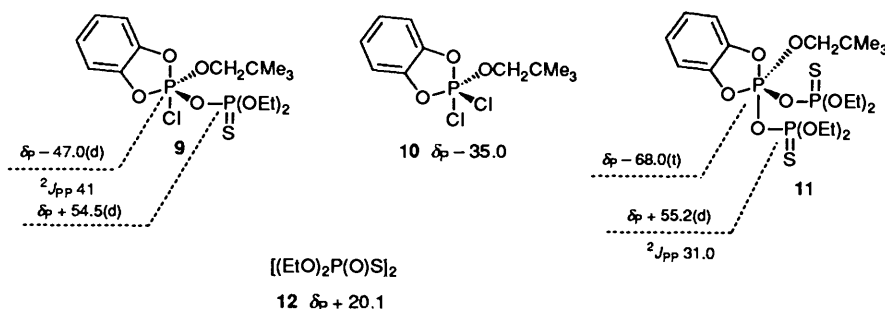


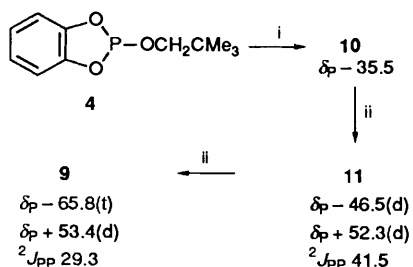
Fig. 1 ^1H -Decoupled ^{31}P NMR spectrum of an equimolar mixture of $(\text{EtO})_2\text{P}(\text{O})\text{SCl}$ **1** and $\text{OC}_6\text{H}_4\text{OPOCH}_2\text{CMe}_3$ **4** in ethyl chloride solution recorded at between -100 and $+10$ $^\circ\text{C}$



monitored at intervals of 10 min and are illustrated in Fig. 1. Only those data which were reproduced in several experiments are included.

In the temperature range -100 to -60 $^\circ\text{C}$ the following compounds **9–12** were recognized as intermediates.

The structures of pentaco-ordinate species **9–11** were deduced from chemical shifts, multiplicity of spectral signals and coupling constants, and were confirmed by independent synthesis as shown in Scheme 3.⁴ ^{31}P NMR data do not give, however, an unequivocal answer concerning the positions of the ligands involved in the trigonal bipyramid. In view of the lack of any spectral difference between the two thiophosphoryl ligands in compound **11** one could assume either that both are situated in equatorial positions or that both might have chemical shifts which are indistinguishable under the experimental conditions. The other possibility is that a fast



Scheme 3 Reagents and conditions: i, Cl_2 , EtCl , -100 $^\circ\text{C}$; ii, $(\text{EtO})_2\text{P}(\text{S})\text{O}^- \text{HNEt}_3$, CH_2Cl_2 , -78 $^\circ\text{C}$

ligand reorganization with respect to the NMR time-scale takes place.

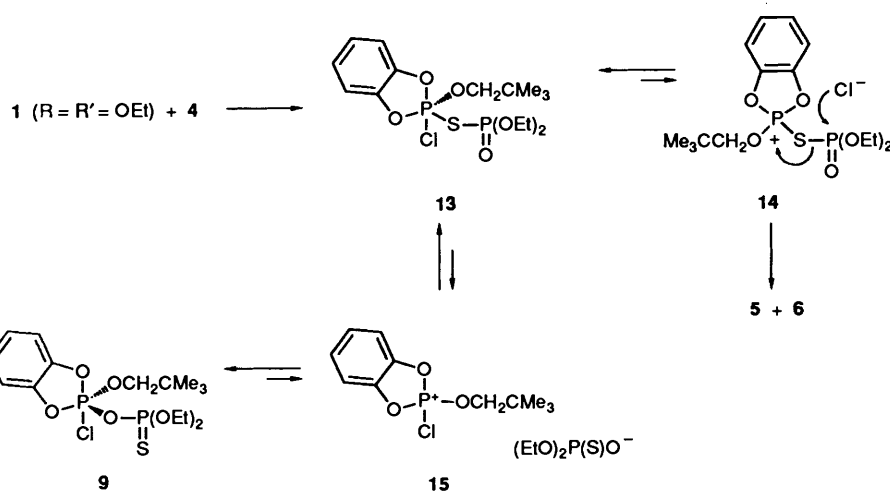
The dichlorophosphorane **10**, prepared by oxidative addition of elemental chlorine to the phosphite **4**, was allowed to react stepwise with the triethylammonium salt of *O,O*-diethylhydrogen thiophosphate. The phosphoranes **9** and **11** are formed at -78 $^\circ\text{C}$ in CH_2Cl_2 solution with some degree of selectivity. The spectroscopic data of all pentaco-ordinate species obtained in this way are almost identical with those observed in the reacting system.

The rational explanation for the chemical changes which take place between -100 and -60 $^\circ\text{C}$ in the reacting system requires the very reasonable assumption that the first step in the reaction is the formation of a phosphorus–sulfur bond leading to the phosphorane **13** (Scheme 4).

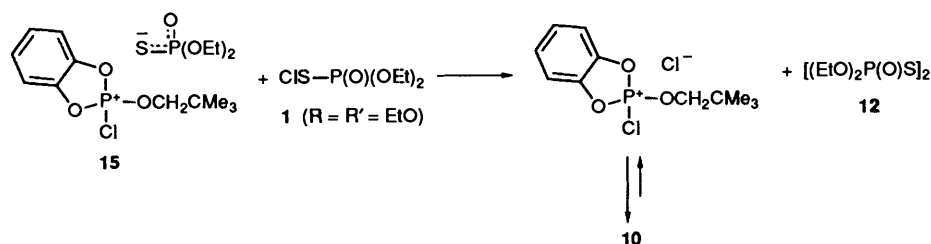
Ionization of intermediate **13** to give the phosphonium salt **14** and its subsequent decomposition into compounds **5** and **6** gives a satisfactory explanation for the desulfurization pathway. Isomerization of intermediate **13** to give the dominant phosphorane **9** is most likely to proceed *via* the phosphonium salt **15** which recombines to form product **9** by 'hard–hard' interaction. Formation of the phosphorane **10** and the disulfide **12** can be explained by the reaction of sulfenyl chloride **1** ($\text{R} = \text{R}' = \text{EtO}$), still present in the reaction medium, with the phosphonium salt **15** (Scheme 5).

The appearance of a new electrophilic species—the disulfide **12**—allows reaction with the unchanged phosphite **4** at -60 $^\circ\text{C}$ to give the phosphorane **11** (Scheme 6).

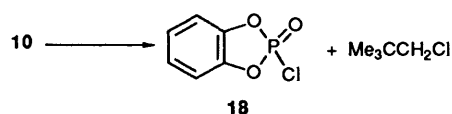
This kind of oxidative addition, which has been discussed in



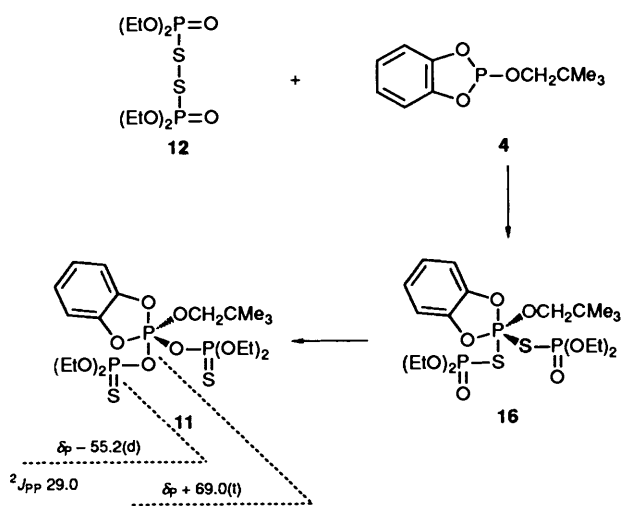
Scheme 4



Scheme 5

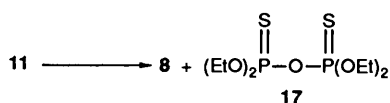


Scheme 8 Reaction condition: -30 °C



Scheme 6

our earlier work, involves formation of a primary phosphorane **16** and its subsequent multistep isomerization to the phosphorane **11**.⁵ Compound **11** prepared independently according to Scheme 3 decomposes thermally at -30 °C into the phosphate **8** and the dithiopyrophosphate **17** (Scheme 7).⁴ Under



Scheme 7 Reaction condition: -30 °C

similar circumstances the dichlorophosphorane **10** decomposes into *o*-phenylene phosphorochloridate **18** and neopentyl chloride (Scheme 8).^{2a,b} We were puzzled that our attempts to

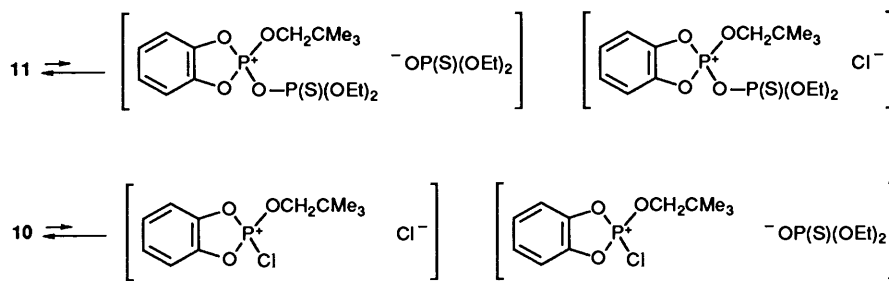
find evidence for compounds **17** and **18** were futile. Therefore we assume that both phosphoranes **11** and **10** react below -30 °C *via* counterion exchange among phosphonium species, present in the system, to give the phosphorane **9**. This somewhat complex interaction is shown in Scheme 9.

The chemical changes presented in Scheme 9 give an additional amount of the phosphorane **9** which is the key intermediate in the deoxygenation pathway *via* compound **19** (Scheme 10).

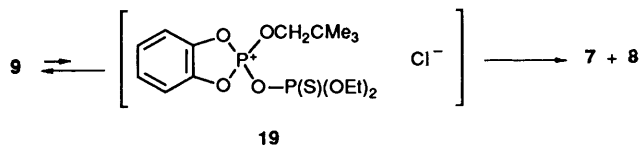
Conclusions.—The reaction between compound **1** (R = R' = EtO) and the phosphite **4** proceeds mainly *via* a deoxygenation pathway and is most likely to involve fast equilibria between the intermediate phosphoranes and the corresponding phosphonium salts. Observation of minor products formed by the desulfurization pathway provides a strong argument that the primary phosphorane **13** containing a P-S-P bridge must be formed as primary intermediate. The reactions summarized in Scheme 1 and our present observations are fully analogous. Therefore phosphonium intermediates presented in Scheme 1 are likely to involve phosphorane-phosphonium equilibria shifted towards the phosphonium species, while the present case involves equilibria shifted towards the phosphorane structure.

Experimental

Solvents and commercial reagents were purified and dried by conventional methods before use. ³¹P NMR spectra were recorded on a JEOL JNM-FX 60 FT spectrometer operating at 24 MHz. Positive chemical-shifts values were downfield from



Scheme 9



19

Scheme 10

external 85% H_3PO_4 . J -Values are given in Hz and signals are singlets unless indicated otherwise. The purity of products was determined from integrated ^{31}P NMR spectra. Variable-temperature spectra were monitored at intervals of 10 °C and 10 min and were recorded on solutions containing the compounds (0.5–1 mmol) in ethyl chloride (2.5 cm^3).

O,O-Diethylhydrogen thiophosphate⁶ and neopentyl *o*-phenylene phosphite⁷ **4** [85%, b.p. 54–56 °C (0.4 mmHg); δ_{P} 132 (Found: C, 58.0; H, 6.4; P, 14.1. Calc. for $\text{C}_{11}\text{H}_{15}\text{O}_3\text{P}$: C, 58.4; H, 6.6; P, 13.7%)] were synthesized by known methods. Diethoxyoxophosphoranesulfonyl chloride **1** was prepared by treatment of *O,O*-triethyl thiophosphate⁸ or *O,O*-diethyl *O*-trimethylsilyl thiophosphate⁹ with an equimolar amount of sulfuryl dichloride.

Reaction of Diethoxyoxophosphoranesulfonyl Chloride 1 with Neopentyl *o*-Phenylene Phosphite 4.—A solution of compound **4** (4.52 g, 20 mmol) in methylene dichloride (25 cm^3) was added dropwise at –20 °C to a stirred solution of sulfonyl chloride **1** (4.1 g, 20 mmol) in methylene dichloride (30 cm^3) under dry argon. The reaction mixture was then allowed to warm slowly to ambient temperature and was stirred for 10 min. After evaporation of the solvent, the crude reaction mixture was analysed by ^{31}P NMR spectroscopy and was found to contain the following compounds: diethyl phosphorochloridate **5** (4.2%), δ_{P} 3.6 (lit.,¹⁰ 3.5); *O*-neopentyl *O,O*-phenylene thiophosphate **6** (4%), δ_{P} 81 (lit.,¹¹ 80.5); *O,O*-diethyl phosphorochloridothioate **7** (46%), δ_{P} 68 (lit.,^{1c} 67.5); and neopentyl *o*-phenylene phosphate **8** (45.8%), δ_{P} 11.2 (lit.,¹⁰ 10). The structures of the products were additionally confirmed by comparison with authentic samples.

Reaction of 2,2-Dichloro-2-neopentoxy-1,3,2-benzodioxaphosphole 10 with *O,O*-Diethyl Hydrogen Thiophosphate in the Presence of Triethylamine.—A solution of diethyl hydrogen thiophosphate (1.86 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in methylene dichloride (10 cm^3) was added at –80 °C to a solution of compound **10** (1.48 g, 5 mmol), freshly prepared from neopentyl *o*-phenylene phosphite **4** and chlorine at –100 °C, in ethyl chloride (10 cm^3). The reaction mixture, analysed by ^{31}P NMR spectroscopy, showed the presence of unchanged substrate **10** (66% recovery), δ_{P} –35.5 (lit.,^{2b} –34.5);

the phosphorane **9**⁴ (5%), δ_{P} –46.5 (d) and 52.3 (d), J 41.5; and compound **11**⁴ (29%), δ_{P} –65.8 (t) and 53.4 (d), J 29.3. The reaction mixture was stirred at –80 °C for 2 h and the ^{31}P NMR spectrum recorded at that temperature then revealed the presence of only the phosphorane **11**. Raising of the temperature to –30 °C resulted in the formation of *sym*-dithiopyrophosphate **17** (50%), δ_{P} 51.8 [lit.,¹² 60.1 (P_4O_6)] and of neopentyl *o*-phenylene phosphate **8** (50%), δ_{P} 11.0.

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