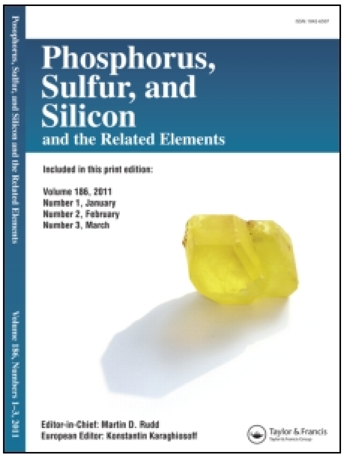


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reaction of Tricoordinate Phosphorus Compounds with Pseudohalogens. Scope and Mechanism

Aleksandra Skowrońska[a]; Ewa Krawczyk[a]; Janusz Burski[a]
[a] Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Boczna 5, łódź, Poland

To cite this Article Skowrońska, Aleksandra , Krawczyk, Ewa and Burski, Janusz(1983) 'Reaction of Tricoordinate Phosphorus Compounds with Pseudohalogens. Scope and Mechanism', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 233 — 236

To link to this Article: DOI: 10.1080/03086648308076009

URL: http://dx.doi.org/10.1080/03086648308076009

Phosphorus and Sulfur, 1983, Vol. 18 pp. 233-236
0308-664X/83/1801-0233/$18.50/0

REACTION OF TRICOORDINATE PHOSPHORUS COMPOUNDS WITH PSEUDOHALOGENS. SCOPE AND MECHANISM

ALEKSANDRA SKOWROŃSKA, EWA KRAWCZYK and JANUSZ BURSKI
Polish Academy of Sciences, Centre of Molecular and
Macromolecular Studies, Boczna 5, 90-362 Łódź, Poland

Abstract The selectivity of sulphur, selenium and oxygen removal from pseudohalogens: phosphorus disulphides 1 and 2, diselenides 3 and oxophosphoranesulphenyl chlorides 4 has been investigated. A mechanistic rationalization is proposed to account for sulphur(selenium)/oxygen extrusion variation as a function of substrates structure and reaction conditions.

As a part of our continuing investigation[1] of nucleophilic displacement reactions on sulphenyl sulphur we have examined the reactions of a number of pseudohalogens: disulphides $>P(O)SSP(O)<$ 1, $>P(S)SSP(S)<$ 2, diselenides $>P(O)SeSeP(O)<$ 3, oxophosphoranesulphenyl chlorides $>P(O)SCl$ 4 and thiocyanogen $(SCN)_2$ 5 with various tricoordinate phosphorus compounds. We have found that pseudohalogens 1,2,3 and 4 are subject to facile desulphurisation, deselenylation and deoxygenation by P(III) derivatives. The experimental data are summarized in the Table. In view of the synthetic and mechanistic implications of these reactions, a detailed investigation of their scope and mechanism was undertaken.

We wish to report that depending on the structure of the tricoordinate phosphorus compound and on the nature of the pseudohalogen these reactions can proceed under very mild conditions predominantly or exclusively via two main paths: path a leading to the desulphurisation or deselenylation products 9 and 10 or path b with the formation of deoxygenation products 13,14 and 13',14' or both pathways are involved simultanously. If the P(III) compounds bear OR groups susceptible to the nucleophilic attack, the products of dealkylation (R=alkyl) or desililation ($R=Me_3Si$) 11 and 12 have also been observed (path c).

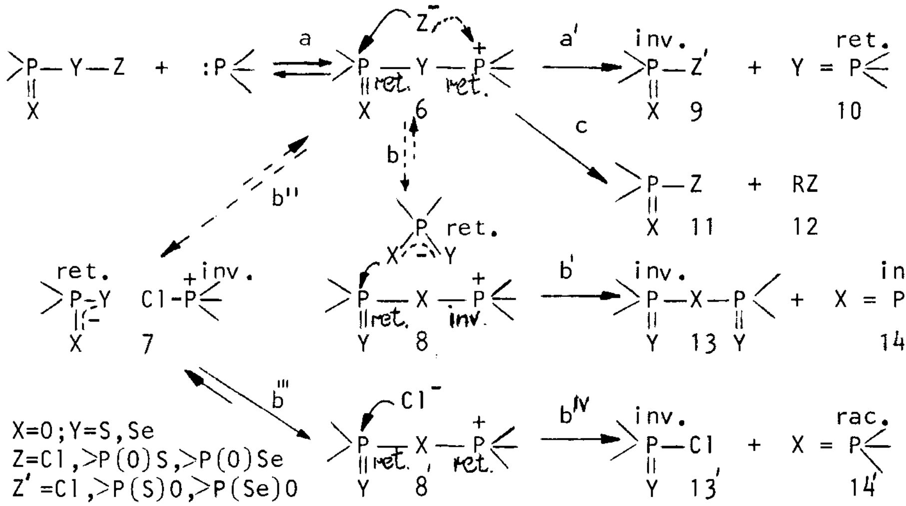
It was of crucial importance to define the intermediates involved, as well as the stereochemical consequences on the P(III) and P(IV) centers. Application of the F.T. ^{31}P NMR at low temperatures provided important information concerning the existence of possible short-lived species in desulphurisation, deselenylation and deoxygenation of pseudohalogens. A thermally labile phosphonium salt 6 with P-S-P or P-Se-P bridge was observed at -100°C in the reaction of 1,2,3 and 4 with selective desulphurisation or deselenylation reagents (see Table). At higher temperatures clean decomposition of 6 into the desulphurisation or deselenylation products occured via nucleophilic attack of the Z^- anion on the phosphoryl center of 6 (step a', Scheme 1). The nature of the deoxygenation process is also clear in spite of its greater complexity. ^{31}P NMR studies revealed that separate stages can be distinguished in the reactions of 1,3 and 4 with deoxygenation reagents. At -100°C the phosphate-phosphonium intermediate 6 was detected (step a, Scheme 1). In the reaction with non-selective reagents some desulphurisation products were also noted along with the intermediate 6. Raising the temperature to -90°C resulted in the formation of a new species, an oxygen bridged thio(seleno)phosphate-phosphonium intermediate 8 (steps b, b''). Subsequent temperature elevation resulted in the decomposition of 8 or 8' to the deoxygenation products by nucleophilic attack of the Z^- anion on the thio(seleno)phosphoryl centre of 8. Transformation of the phosphonium salt 6 into 8 is due to nucleophilic ligand exchange at the phosphonium phosphorus atom (step b) which proceeds according to the SHAB principle with the formation of a stronger phosphorus oxygen bond. In the case of Cl^- anion, ligand exchange takes place twice: $6 \rightleftharpoons 7 \rightleftharpoons 8'$. The structure of phosphonium intermediates 6,8 and 8' is evident from their ^{31}P chemical shifts and coupling constant values [e.g., phosphate-phosphonium salt 6 $R=OCH_2Bu^t$ $\delta P(IV)=5,6$ ppm (d), $\delta P(IV^+)=38,7$ ppm (d), $J_{PSP}=10$ Hz; thiophosphate-phosphonium salt 8 $R=OCH_2Bu^t$ $\delta P(IV)=51,3$ (d), $\delta P(IV^+)=-11,7$ ppm (d), $J_{POP}=23$ Hz].

The intermediacy of species 6,8 and 8' is in accord with stereochemical results, since desulphurisation of pseudohalogens 1 and 4 proceeds with inversion of configuration at the phosphoryl phosphorus atom and with the retention of configuration at the P atom derived from the tricoordinate phosphorus compounds involved. However, deoxygenation of 1 occurs with inversion of configuration at both phosphorus centers, whereas deoxygenation of 4 involved inversion of configuration at P(IV) atom and racemization at P atom derived from tricoordinate derivative. The experimental facts presented above are depicted in Scheme 1.

We found that the competitive reactions involving desulphurisation and deoxygenation can be controlled to favour desulphurisation only. This was accomplished by the addition of boron trifluoride etherate complex in excess to the reaction mixture at -100°C.

Low temperature studies also demonstrated that in addition to substituent structure at both phosphorus atoms, which play an important role in the selectivity of desulphurisation, deselenylation and deoxygenation, also the reaction temperature has a great influence on the ratio of the products formed. For example, when the reaction of trineopentyl phosphite with disulphide 1 was carried out -70°C, the desulphurisation-deoxygenation ratio was 1:3. At -100°C the same reaction gave only desulphurisation products.

Disulphide 1 with triphenylphosphine at -70°C afforded a mixture of products (17% desulphurisation and 73% deoxygenation), whereas at -100°C only deoxygenation products were obtained.



X=O;Y=S,Se
Z=Cl,>P(O)S,>P(O)Se
Z'=Cl,>P(S)O,>P(Se)O

Scheme 1

On the basis of the experimental results presented here, the key intermediate in desulphurisation as well as deoxygenation process is the phosphonium salt 6 with the P-S-P or P-Se-P bridge. Such a salt has electrophilic centres at phosphoryl and phosphonium phosphorus atoms. Depending on the electronic and steric factors of substituents at both phosphorus atoms and the reaction conditions, the nucleophilic attack of the counter-ion may occur on the phosphoryl or on the phosphonium centre or on both centres simultanously. Therefore, the selectivity of desulphurisation, deselenylation and deoxygenation depends on the relative rates of nucleophilic substitution on both phosphorus atoms.

Finally we wish to report that the following reactions of pseudohalogens with P(III) derivatives are noteworthy from the synthetic point of view:

a/ Reaction of disulphides 1 and diselenides 3 with triphenylphosphine at -100°C occurs via path b, Scheme 1 and can be considered as an alternative method for the synthesis of dithio- and diselenopyrophosphates RR'P(X)OP(X)RR', X=S,Se.

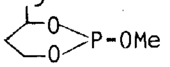
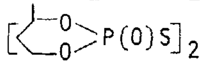
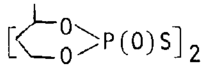
b/ Reaction of diselenides 3 with dialkyltrimethylsilyl phosphite proceeds exclusively via path c, Scheme 1 with the formation of sym. selenopyrophosphates RR'P(O)SeP(O)RR'. This reaction provides a unique approach to such a class of phosphorus anhydrides.

c/ The efficient synthesis of acyl, phosphoryl and thiophosphoryl isothiocyanates including optically active ones in the reaction of thiocyanogen with mixed anhydrides 15 is of special interest.

$$>P{-}OA + (SCN)_2 \longrightarrow >P(O)NCS + A{-}N{=}C{=}S$$

15 $>P=C_6H_4O_2P$; $A=RC(O)-$, $RR'P(O)-$, $RR'\overset{*}{P}(S)-$

TABLE. Desulphurisation, deselenylation[a] and deoxygenation[b] of pseudohalogens 1,2,3,4

P(IV) compounds	P(III) compounds	a%	b%
$[(EtO)_2P(O)S]_2$	$(Me_2N)_3P$	100	
$[(EtO)_2P(O)S]_2$	$(Bu^tCH_2O)_3P$	25	75
$[(EtO)_2P(O)S]_2$	Ph_3P	17	83
$[(EtO)_2P(O)S]_2$	 cis	15	21
 t,t	$(Bu^tCH_2O)_3P$	100	
 t,t	Ph_3P	10	90
$[Bu^t(MeO)P(O)S]_2$	Ph_3P		100
$[(EtO)_2P(S)S]_2$	$(Me_2N)_3P$	100	
$[(EtO)_2P(S)S]_2$	$(Bu^tCH_2O)_3P$	100	
$[(Bu^tCH_2O)_2P(O)Se]_2$	$(Me_2N)_3P$	100	
$[(Bu^tCH_2O)_2P(O)Se]_2$	$(Bu^tCH_2O)_3P$	100	
$[(Bu^tCH_2O)_2P(O)Se]_2$	Ph_3P		100
$(EtO)_2P(O)SCl$	$(Me_2N)_3P$	100	
$(EtO)_2P(O)SCl$	$(Bu^tCH_2O)_3P$	100	
$(EtO)_2P(O)SCl$	Ph_3P		100[x]
$(EtO)EtP(O)SCl$	$(PhO)_3P$	10	90

[x] reaction was carried out at -100°C

REFERENCES

1. J. Michalski and A. Skowrońska, J.Chem.Soc. C. 703 (1970); B. Krawiecka, J.Michalski, J.Mikołajczak, M.Mikołajczyk, J. Omelańczuk and A. Skowrońska, J.Ch.S., Chem.Commun., 630 (1974); J. Omelańczuk, P. Kiełbasiński, J. Michalski, J. Mikołajczak, M. Mikołajczyk and A. Skowrońska, Tetrahedron 31, 2809 (1975); E. Krawczyk, J. Michalski, M. Pakulski and A. Skowrońska, Tetrahedron Letters 2019 (1977); A. Skowrońska, E. Krawczyk, Phosphorus and Sulphur 9, 189 (1980); J. Burski, J. Kieszkowski, J. Michalski, M. Pakulski and A. Skowrońska, Tetrahedron, in press.