Tetrahedron Letters No. 23, pp 2019 - 2022, 1977. Pergamon Press. Printed in Great Britain.

NOVEL FIVE-CO-ORDINATE PHOSPHORUS SYSTEMS VIA OXIDATIVE ADDITION OF PSEUDOHALOGENS TO ORGANIC PHOSPHITES

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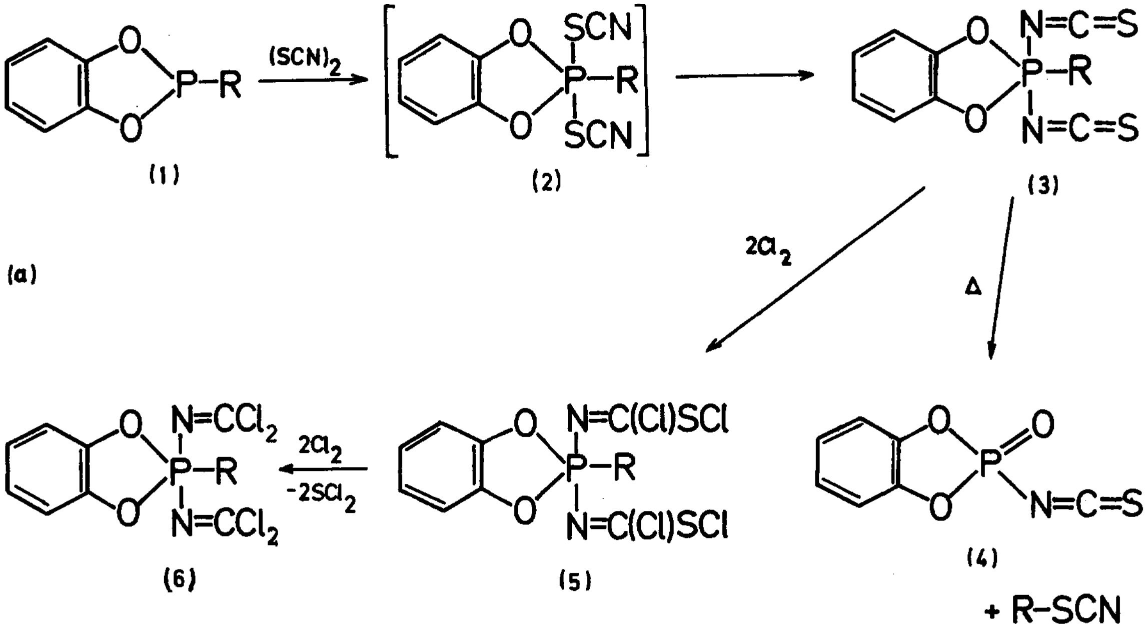
(Received in UK 15 April 1977; accepted for publication 25 April 1977)

Although numerous examples of five-co-ordinate phosphorus compounds with halogens attached directly to the phosphorus atom are known[1,2], there is no evidence for the existance of analogous compounds with pseudohalogens. We report here a successful characterisation of penta-co-ordinate phosphorus structures synthesized by oxidative addition of pseudohalogens to organic phosphites derived from pyrocatechol and phenol. Typical disulphide pseudohalogens such as thiocyanogen $(SCN)_2$ and bis-(diethoxyphosphinyl) disulphide $/(EtO)_2P(O)S/_2$ (7) were employed in this study[3].

Equimolar quantities of the phosphite (1) and the thiocyanogen in EtCl or CH_2Cl_2 solution were allowed to react in a sealed tube at -85°C. ^{31}P NMR spectra showed only the presence of five-co-ordinate compounds with high field chemical shifts. The structure of compounds (3) was evident from their i.r. spectra (R=OEt; OCH_2CMe_3: ν_{NCS} 1980 cm^{-1}; 1975 cm^{-1}). Compounds (3) were stable at -40°C and in the case of R=OPh even at ambient temperature. Warming up of (3) to 20°C resulted in clean decomposition to give the phosphoroisothiocyanidate (4) (R=OEt ^{31}P +7 p.p.m., ν_{NCS} 1985 cm^{-1}) and the corresponding alkylthiocyanate (R=Et ν_{SCN} 2155 cm^{-1}).

Compounds (3) underwent a smooth reaction with chlorine at -80°C in toluene in a manner typical for compounds containing the isothiocyano group[4].

The reactions were carried out by first treating (3) with the appropriate amount of chlorine to give (5). Without isolation these were treated with another two moles of chlorine yielding (6). The five-co-ordinate structures of (5) and (6) were clearly evident from ^{31}P NMR spectra.



(a)

Table [†] ^{31}P NMR chemical shift[†] and coupling constant[‡] data for phosphoranes (A)

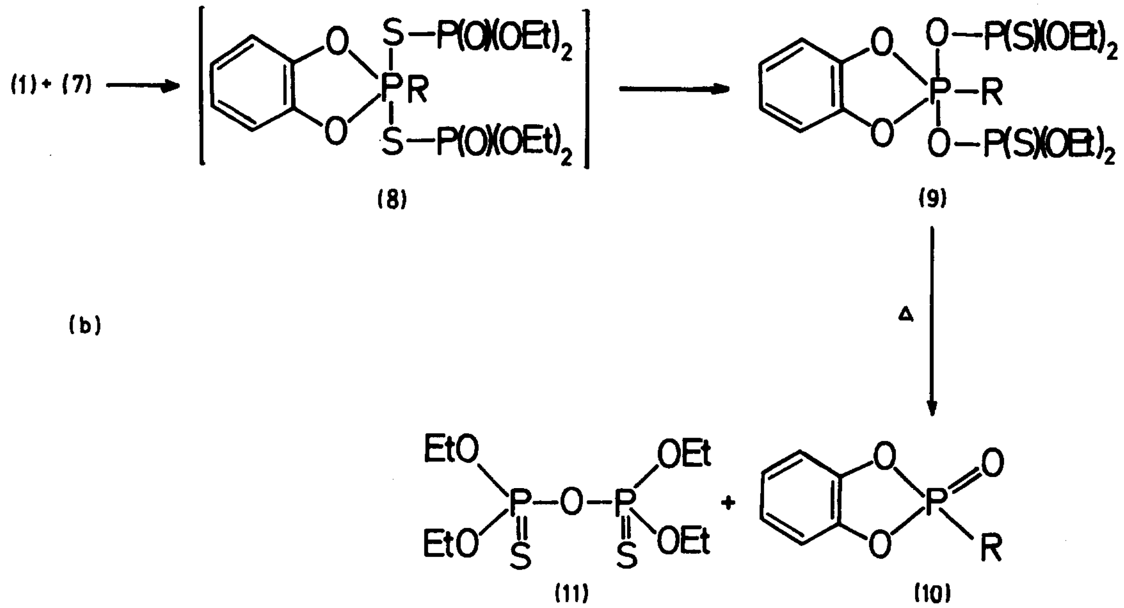
A	3a[*]	3b	3c	5a	5c	6a	6c
δ	+77	+76	+80	+39	+42	+42	+44

A	9a	9b	9d	9e	12c
δ	P^V +61.3(t) P^{IV}-57.8(d)	P^V +69(t) P^{IV}-55.2(d)	P^V +25.5(t) P^{IV}-53.8(d)	P^V +63(t) P^{IV}-55.6(d)	P^V +94.4(t) P^{IV}-52.6(d)
$J_{P^V-O-P^{IV}}$	29	29	51	36	44

[†] ^{31}P chemical shifts, δ, in p.p.m. from H_3PO_4 85%; [‡] coupling constants, J, in Hz; [*] a: R=OEt, b: R=OCH_2CMe_3, c: R=OPh, d: R=Bu^t, e: R=NEt_2

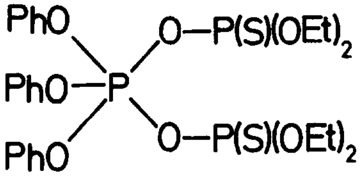
The disulphide (7) treated at -80°C with (1) in CH_2Cl_2 solution gave a new type of phosphorus oligomer containing one central P^V and two adjacent P^{IV} atoms linked by an oxygen bridge.

(b)



(8) (9) (11) (10)

Structure (9) was assigned to the product on the basis of its ^{31}P NMR spectrum, which after ^{1}H decoupling showed a triplet for the P^{V} atom due to the splitting by the two magnetically equivalent P^{IV} phosphorus atoms, and a doublet due to the splitting of P^{IV} atom by the P^{V} atom at δ^{31}P -55.5 p.p.m. indicative of the presence of a $\geqslant$P=S structure. Also, it was demonstrated that the five-co-ordinate structure (12) is formed in the reaction of (7) with triphenyl phosphite.



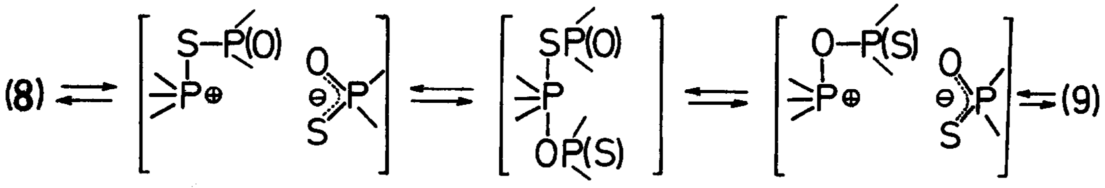
(12)

The ^{31}P NMR spectrum for (12) is analogous to those described for compounds (9). However, in this case the reaction mixture after warming to ambient temperature was more complex. Major components corresponded to products (10) and (11), minor ones were: unsym-tetraethyldithiopyrophosphate $(EtO)_2P(S)SP(O)(OEt)_2$, unsym-tetraethylmonothiopyrophosphate $(EtO)_2P(S)OP(O)(OEt)_2$ and triphenylthiophosphate $(PhO)_3PS$.

The data presented here clearly indicate the penta-co-ordinate nature of structures (3);(5);(6);(9) and (12); they do not give, however, an unambiguous answer concerning the positions of ligands in the trigonal bipyramid involved. In view of a lack of spectral differences between pseudohalogen ligands one could either assume that both are situated in an equatorial position or a fast ligand exchange takes place below the NMR time scale. It is of interest to note that an introduction of a group with a known tendency to occupy an equatorial position[5], such as tert-butyl and dialkylamino, did not induce any essential difference in the ^{31}P NMR spectra. Therefore another possibility should also be considered: in spite of different spatial arrangements the pseudohalide ligands may have ^{31}P NMR shifts and i.r. ν_{NCS} frequencies indistinguishable under the experimental conditions used.

The first step in the oxidative addition of pseudohalogens to phosphites is of particular interest. Although the concerted addition[6] with the formation of a phosphorus-sulphur bond is formulated in schemes (a) and (b) the alternative two-step process involving phosphonium salt formation cannot be ruled out. It seems most likely that isomerisation of structures (2) and (8) into the corresponding isomers (3) and (9) proceeds via equilibria between "phosphorane" and "phosphonium" species.

(c)



A scheme describing the conversion of (2) into (3) would be of the same nature. The return of ion pairs to P^{V} structures proceeds according to SHAB principle with the formation of the stronger phosphorus-oxygen or phosphorus-nitrogen bonds. The isomerisation postulated is reminiscent of isomerisations of sym.-monothiopyrophosphates and phosphinylthiocyanates discovered in this laboratory[7,8].

Acknowledgements. This work was supported by the Polish Academy of Sciences, Research Project MR-12.1.3.1.

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