

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

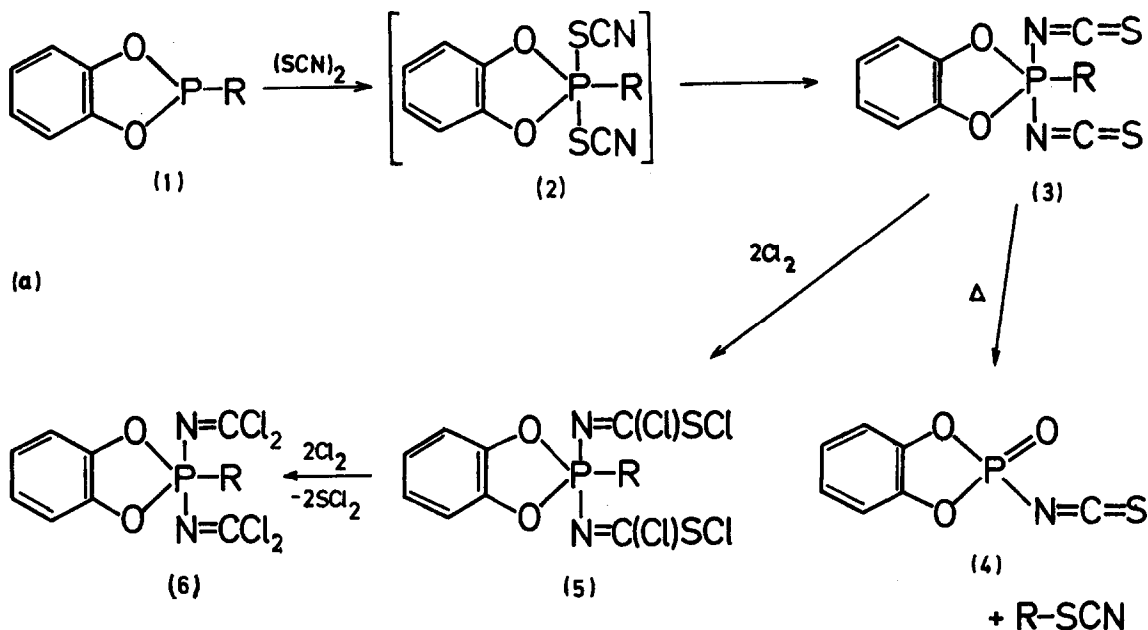
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(Received in UK 15 April 1977; accepted for publication 25 April 1977)

Although numerous examples of five-co-ordinate phosphorus compounds with halogens attached directly to the phosphorus atom are known<sup>1,2</sup>, there is no evidence for the existence 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)<sub>2</sub> and bis-(diethoxyphosphinyl) disulphide / (EtO)<sub>2</sub>P(O)S/<sub>2</sub> (7) were employed in this study<sup>3</sup>.

Equimolar quantities of the phosphite (1) and the thiocyanogen in EtCl or CH<sub>2</sub>Cl<sub>2</sub> solution were allowed to react in a sealed tube at -85°C. <sup>31</sup>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<sub>2</sub>CMe<sub>3</sub>: ν<sub>NCS</sub> 1980 cm<sup>-1</sup>; 1975 cm<sup>-1</sup>). 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 <sup>31</sup>P +7 p.p.m., ν<sub>NCS</sub> 1985 cm<sup>-1</sup>) and the corresponding alkylthiocyanate (R=Et ν<sub>SCN</sub> 2155 cm<sup>-1</sup>). Compounds (3) underwent a smooth reaction with chlorine at -80°C in toluene in a manner typical for compounds containing the isothiocyano group<sup>4</sup>. 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 <sup>31</sup>P NMR spectra.



**Table**  $^{31}\text{P}$  NMR chemical shift<sup>†</sup> and coupling constant<sup>‡</sup> data for phosphoranes (A)

A	3a <sup>*</sup>	3b	3c	5a	5c	6a	6c
$\delta$	+77	+76	+80	+39	+42	+42	+44
A	9a	9b	9d	9e	12c		
$\delta$	$\text{P}^{\text{V}}$ +61.3(t) $\text{P}^{\text{IV}}$ -57.8(d)	$\text{P}^{\text{V}}$ +69(t) $\text{P}^{\text{IV}}$ -55.2(d)	$\text{P}^{\text{V}}$ +25.5(t) $\text{P}^{\text{IV}}$ -53.8(d)	$\text{P}^{\text{V}}$ +63(t) $\text{P}^{\text{IV}}$ -55.6(d)	$\text{P}^{\text{V}}$ +94.4(t) $\text{P}^{\text{IV}}$ -52.6(d)		
$J_{\text{P}^{\text{V}}-\text{O}-\text{P}^{\text{IV}}}$	29	29	51	36	44		

<sup>†</sup> $^{31}\text{P}$  chemical shifts,  $\delta$ , in p.p.m. from  $\text{H}_3\text{PO}_4$  85%; <sup>‡</sup>coupling constants,  $J$ , in Hz; \*a: R=OEt, b: R= $\text{OCH}_2\text{CMe}_3$ , c: R=OPh, d: R= $\text{Bu}^t$ , e: R= $\text{NEt}_2$

The disulphide (7) treated at  $-80^\circ\text{C}$  with (1) in  $\text{CH}_2\text{Cl}_2$  solution gave a new type of phosphorus oligomer containing one central  $\text{P}^{\text{V}}$  and two adjacent  $\text{P}^{\text{IV}}$  atoms linked by an oxygen bridge.

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