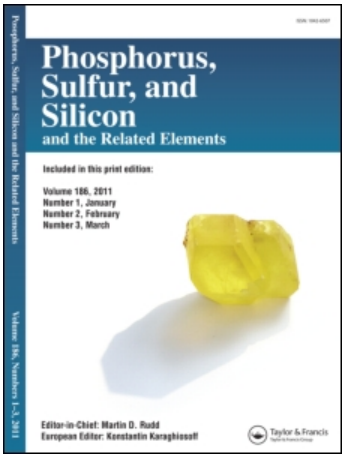

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Observation of a Pentacoordinate Intermediate During the Reaction of N-Chlorodiethylamine and Ethyl 1,2-Phenylene Phosphite

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To cite this Article Denney, Donald B. , Denney, Dorothy Z. and Dimiele, Gina(1978) 'Observation of a Pentacoordinate Intermediate During the Reaction of N-Chlorodiethylamine and Ethyl 1,2-Phenylene Phosphite', Phosphorus, Sulfur, and Silicon and the Related Elements, 4: 1, 125 — 126
To link to this Article: DOI: 10.1080/03086647808079971
URL: http://dx.doi.org/10.1080/03086647808079971

Phosphorus and Sulfur
1978, Vol. 4, pp. 125–126

SHORT COMMUNICATION

Observation of a Pentacoordinate Intermediate During the Reaction of N-Chlorodiethylamine and Ethyl 1,2-Phenylene Phosphite

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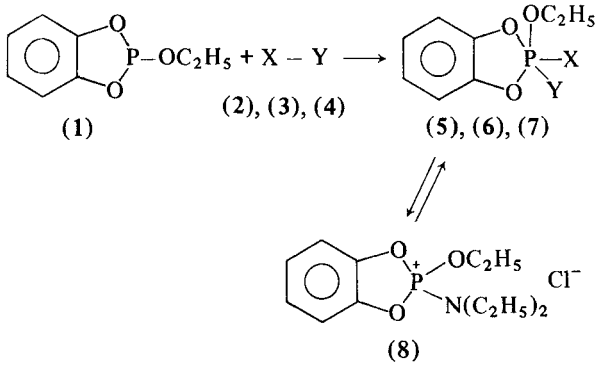
(*Received August 5, 1977*)

It is well known that trisubstituted phosphites react with N-chlorodialkylamines to give an alkyl halide and a phosphoramidate.[1] There have been some studies of the mechanism of this reaction and in a recent report

$$(RO)_3P + R_2NCl \rightarrow (RO)_2\overset{\overset{O}{\|}}{P} \cdot N(R)_2 + RCl$$

it was suggested that a pentacoordinated intermediate $(RO_3)P[N(R)_2]Cl$ is formed during the reaction.[2] The necessity for making this suggestion arose from the observation that when *cis* and *trans*-isomeric cyclic phosphites were allowed to react with N-chlorodiethylamine mixtures of *cis* and *trans*-cyclic phosphoramidates resulted. The stability of the starting materials and products towards isomerization was demonstrated and thus another mode for the loss of stereochemistry had to be proposed. A series of purely ionic reactions cannot account for the loss of stereochemistry, whereas the formation of a pentacoordinated intermediate can. It is interesting to note that under no conditions did the *cis* and *trans*-isomers give the same mixture of phosphoramidates. This result shows that different pentacoordinate intermediates from each isomer were formed and that incomplete interconversion occurred before decomposition.

It is well known that pentacoordinate phosphorus compounds that have one or more 5-membered rings with two oxygens bonded to phosphorus are considerably more stable than their acyclic or larger membered ring counterparts.[3] Recently, ethyl 1,2-phenylene phosphite **1** was allowed to react with chlorine, **2**, at −85°C. The low temperature ^{31}P nmr spectrum showed that, **5**, had been formed as the sole product. Similarly, **3**, was allowed to react with



(2) and (5): X = Y = Cl
(3) and (6): X = C_6H_5S; Y = Cl
(4) and (7): X = $(C_2H_5)_2N$; Y = Cl

1 at −80°C. Under these conditions both, **5** and **6**, were formed.[4]

In view of the above results, it seemed of interest to allow **1** to react with **4** at reduced temperatures. The two reactants at −50°C gave a solution whose ^{31}P nmr spectrum had four major resonances at δ +134.0, +32.6, +18.4 and −38.5 relative to external 85% phosphoric acid. On warming to −15°, the absorption at −38.5 disappeared, that at +18.4 became extremely small while the absorption at +134 decreased in intensity and the absorption at +32.6 increased in intensity. The absorptions at +134 and +32.6 are due to starting material and product respectively.[5] The absorption at −38.5 is undoubtedly due to the pentacoordinate intermediate, **7**. Upfield shifts are characteristic of pentacoordinate intermediates.[6] The absorption at +18.4 is assigned to the phosphonium salt, **8**. Phosphonium salts of this type usually absorb in the same region as their corresponding phosphoryl derivatives.[6]

Although it has been demonstrated that **7** is formed from the reaction of **1** and **4**, it is not possible to comment on its mechanism of formation.

ACKNOWLEDGEMENT

This research has been supported by the National Science Foundation and by the Public Health Service Grant No. CA-10737 from the National Cancer Institute. We also wish to thank the Mobil Chemical Co. for funds which aided in the purchase of nmr equipment.

EXPERIMENTAL

To an 8 mm nmr tube, which was flushed with argon, cooled to −78°C, and which contained 0.17 g (0.001 mol) of ethyl 1,2-phenylene phosphite in 1.8 ml of d-8 toluene, was added 1.56 ml (0.001 mol) of an hexane solution of N-chlorodiethylamine. The reaction mixture was allowed to warm to −50°C slowly. The nmr tube was then introduced into the nmr probe which was cooled to −50°C. The progress of the reaction was monitored at various times and probe temperatures. In a typical experiment, immediately after mixing and warming to −50°C there were observed in the ^{31}P nmr spectrum four major resonances at +134.0, +32.6, +18.4, and −38.5 relative to 85% phosphoric acid. As the probe temperature was raised to -30°C and ultimately to −15°C, the absorption at +18.4 became very small, that at −38.5 disappeared while that at +32.6 continued to grow.

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