

THIOPHOSPHORYL ADDUCTS OF NITROGEN BASES

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Thiophosphoryl and phenylthiophosphoryl chloride have been shown to form adducts with ethylenediamine and dipyriddy in variable ratios. Similar adducts of pyridine could not be purified. The stoichiometry seems to depend on the number of chlorines attached to phosphorus. In the case of dipyriddy complexes, thiophosphoryl chloride forms the adducts in the ratio 2:5 while phenylthiophosphoryl chloride forms a 1:1 adduct. With ethylenediamine, on the other hand, the ratio with thiophosphoryl chloride is 4:15 and with phenylthiophosphoryl chloride it is 2:5. The adducts have been formulated as ionic substances.

Phosphine oxides and sulphides are known to form complexes with a variety of metallic chlorides where oxygen or sulphur is the donor. Jellinek and Veer have recently reported the adducts of thiophosphoryl chloride with aluminium trichloride, antimony pentachloride and sulphur trioxide where sulphur is the donor. This paper reports the reaction of nitrogen bases like ethylenediamine, dipyriddy and pyridine with thiophosphoryl chloride and phenylthiophosphoryl chloride. They are formed out of the acid-base reactions and have an ionic nature. These adducts seem to be a result of the donor properties of the chloride ion rather than the sulphur attached to phosphorus. The adducts of nitrogen bases like pyridine, picoline and quinoline have been reported by Paol, Malhotra and Singh, but the compounds isolated by them maintain stoichiometry while the compounds reported here are not strictly stoichiometric but seem to be polymeric in nature.

Experimental

Thiophosphoryl chloride was prepared from phosphorus trichloride and sulphur by the Friedel-Crafts reaction and purified by distillation. Phenylthiophosphoryl chloride, ethylenediamine and dipyriddy were of C.P. grade and were used as such.

Ethylenediamine Adducts.—The reaction of thiophosphoryl chloride or phenylthiophosphoryl chloride with ethylenediamine was very vigorous. The reaction was, therefore, carried out in dry ether, with cooling to 5°C. A white precipitate was immediately formed with a nearly quantitative yield. The precipitates were washed with dry ether in a dry box having a nitrogen atmosphere.

Found: C, 19.4; H, 7.5; N, 21.1; Cl, 32.2; P, 7.0; S, 6.8%. $(\text{PSCl}_3)_4[(\text{C}_2\text{H}_4(\text{NH}_2)_2)_{15} \cdot 6\text{HCl} \cdot 9\text{H}_2\text{O}]$ requires: C, 18.4; H, 7.3; N, 21.4; Cl, 32.6; P, 6.3; S, 6.5%. M.p.=162±2° in sealed tube.

Found: C, 29.1; H, 6.8; N, 17.2; Cl, 28.7; P, 7.4; S, 5.5%. $[(\text{C}_6\text{H}_5\text{PSCl}_2)_2][(\text{C}_2\text{H}_4(\text{NH}_2)_2)_5 \cdot 2\text{HCl} \cdot 3\text{H}_2\text{O}]$ requires: C, 31.1; H, 6.8; N, 16.5; Cl, 25.1; P, 7.3; S, 7.5%. M.p.=222±3° (decomp).

The adducts are very hygroscopic and the reaction is strongly exothermic. Mixing the reactants directly gives a mixture of products. The reaction must be carried out under controlled conditions, otherwise impure yellow precipitates are obtained which become gummy on standing.

Dipyriddy Adducts.—The adducts formed by the interaction of thiophosphoryl chloride or phenylthiophosphoryl chloride with dipyriddy were not instantaneously obtained as in the above case. The solution of thiophosphoryl or phenylthiophosphoryl chloride and that of dipyriddy in ether were mixed together at room temperature and allowed to stand for 12 hr in a dry box. White precipitates formed at the end of this period were washed thoroughly with dry ether and dried in vacuum.

Found: C, 50.26; N, 4.5; Cl, 17.9; P, 6.5; S, 5.02%. $(\text{PSCl}_3)_2[(\text{C}_5\text{H}_4\text{N})_2]_5 \cdot 4\text{H}_2\text{O}$ requires: C, 50.3; H, 4.03; N, 11.7; Cl, 17.9; P, 5.2; S, 5.3%. M.p.=60±3° in sealed tube.

Found: C, 50.4; H, 4.6; N, 7.4; Cl, 18.02; P, 6.5; S, 5.5%. $(\text{C}_6\text{H}_5\text{PSCl}_2)(\text{C}_5\text{H}_4\text{N})_2 \cdot \text{H}_2\text{O}$ requires: C, 49.8; H, 3.9; N, 7.3; Cl, 18.4; P, 8.1; S, 8.3%. M.p.=63±2° in sealed tube.

These compounds are also very hygroscopic. The reaction is susceptible to decomposition in a humid atmosphere, particularly when the reaction is carried out without a solvent or in a concentrated solution.

Pyridine Adducts.—An attempt was made to isolate the pyridine complexes by mixing an ethereal solution of thiophosphoryl chloride or

phenylthiophosphoryl chloride with pyridine, at low temperatures (up to -78°C). The white precipitate obtained melted into a gummy liquid immediately on exposure to the atmosphere or on removal of the solvent. Attempts to purify the adducts failed and the product obtained was usually yellow. It was possible to identify the adducts by means of their IR spectra, which in each case showed a shift in the N—H and not in the P=S frequencies.

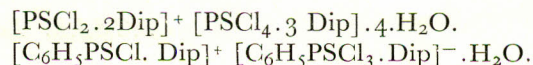
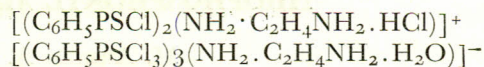
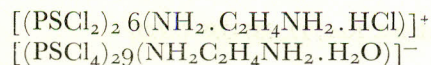
Discussion

The analysis of the products at a glance does not show a neat stoichiometry but it appears that the compounds can be formulated as ionic products. The evidence for such a formulation is obtained from conductivity and IR spectra. The compounds are highly conducting ($\Lambda_m \sim 118.5 \times 10^{-2}$ moles litre $^{-1}$) while the IR vibration corresponding to P=S stretching frequency is either unaltered or moves to a higher frequency. The NH_2 frequency corresponds to a N^+ (quaternary ammonium) vibration as well as to free amino group. The thiophosphoryl adducts of aluminium trichloride and antimony pentachloride prepared by Veer and Jellinek¹ have been shown to form adducts through the thiophosphoryl sulphur. Paul *et al.*³ have isolated thiophosphoryl compounds with pyridine, quinoline and picoline and have formulated the adducts as an ionic product.



It has been suggested by the latter authors that the above organic bases combine with $(\text{PSCl}_2)^+$ and increases the chloride ion concentration.

The following is a speculative formulation but it is interesting to see that both ethylenediamine and dipyridyl form similar compounds. These formulations fit in with the analytical results.



The cation and the anion share the base in an approximate ratio of 2-3. The cation for ethylenediamine adducts has the hydrochloride of the base while the anion carries its monohydrate. The hydrochloride seems to be a result of the hydrolysis of the thiophosphoryl chloride due to the presence of the water molecule in the base. The dipyridyl adducts are rather simple in formulation and the acid-base reaction is clearly demonstrated. The crowding of the bases by more than what stoichiometry demands suggests that the compounds may have a polymeric nature. This aspect is under study.

For the present, however, it is clear that these compounds exhibit the coordinating properties of thiophosphoryl chloride through the chloride ion as the donor which is in contrast with the phosphorylchloride adducts which have oxygen as the donor.

References

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