New Catalysts for the Preparation of Phosphonitrilic Chlorides

By J. EMSLEY* and P. B. UDY
(*Department of Chemistry, King's College, Strand, London, W.C.2*)

THE phosphonitrilic chlorides are easily prepared by heating phosphorus pentachloride and ammonium chloride in a solvent. *sym*-Tetrachloroethane, chlorobenzene, and nitrobenzene have been used for this purpose and the reaction times in these solvents are about 7, 30, and 6 hr. respectively. Yields of the cyclic and linear phosphonitrilic chlorides are in the ratio of about 70:30% in *sym*-tetrachloroethane and chlorobenzene,[1] and 20:80% in nitrobenzene.[2] Anhydrous metal chlorides such as zinc chloride, cobalt chloride, *etc.*, act as catalysts for the reaction and reduce the times to about a third of those in noncatalyzed reactions.[3] Quinoline has also been reported to act as a catalyst for the reaction in chlorobenzene, reducing the time taken to about 8 hr.[4]

We now report that phosphorus oxychloride is a good catalyst, and reagents which are capable of producing this in the reaction mixture by reaction with PCl_5 are also capable of catalyzing the reaction. Thus water itself is the simplest catalyst and if this is added to a mixture of PCl_5

TABLE

Catalyst	Mole ratio PCl_5 : catalyst	Cyclic products (%)	Linear products (%)	Reaction time (hr.)
None	—	61	39	7
H_2O	1 : 0·06	89	11	3½
$POCl_3$	1 : 0·10	87	13	3½
P_2O_5	1 : 0·06	93	7	3
H_2SO_4	1 : 0·05	83	17	3½
$Ca(OH)_2$	1 : 0·10	89	11	3¼
$MgSO_4,H_2O$ ..	1 : 0·10	54	46	1½
$MgCl_2,6H_2O$ ..	1 : 0·02	69	31	4
$CuCl_2,2H_2O$ ..	1 : 0·05	48	52	4

and NH_4Cl in *sym*-$C_2H_2Cl_4$ the reaction is complete after 3½ hr.

A more interesting feature of these catalysts is their ability to increase the yields of the cyclic phosphonitrilic chlorides relative to the linear compounds. Details of several catalysts and the yields of products are given in the Table. In all cases the $PCl_5 : NH_4Cl$ mole ratio was 1 : 1·10 and the solvent was *sym*-$C_2H_2Cl_4$. In the absence of interfering metal salts the yields of cyclic compounds are of the order of 90%. When certain metal salts are present this falls to 70% or less. As yet the mechanism by which $POCl_3$ acts as a catalyst is unknown nor is its ability to help in ring closure reactions understood. During the course of the reaction the $POCl_3$ is slowly carried off in the hydrogen chloride evolved and can be trapped out of the gas stream.

The logical extension of this discovery was to use pure phosphorus oxychloride as a solvent for the reaction. However this procedure resulted in increased reaction times, due no doubt to the lower refluxing temperature at which the reaction was carried out, ($POCl_3$ b.p. 108°; *sym*-$C_2H_2Cl_4$ b.p. 146°).

(*Received, May 17th,* 1967; *Com.* 484.)

---

[1] L. G. Lund, N. L. Paddock, J. E. Proctor, and H. T. Searle, *J. Chem. Soc.*, 1960, 2542.
[2] M. A. Glushkova, M. M. Ershova, and Yu. A. Buslaev, *Zhur. neorg. Khim.*, 1965, **10**, 1943.
[3] N. L. Paddock and H. T. Searle, B.P. 905,315/1962 (*Chem. Abs.*, 1963, **58**, 14143g).
[4] S. M. Zhivukhin, V. B. Tolstoguzov, and M. M. Levitskii, *Zhur. neorg. Khim.*, 1961, **6**, 2414.