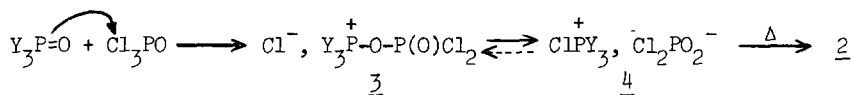


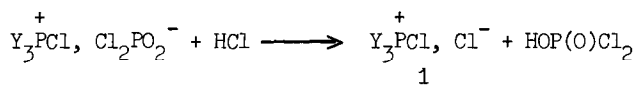
which no developed formula was assigned. The covalent chloride 2 appeared only after heating.

Hence the reaction of HMPT on POCl_3 may be detailed as follows :



We did not try to make clear the mechanism of formation of 2 from 3 or 4.

In a preparative scale, we performed the reaction in CH_2Cl_2 as solvent, adding slowly HMPA on POCl_3 at $\theta < 20^\circ\text{C}$. The reaction is fast. The addition of a solution of anhydrous HCl in ether induced the precipitation of salt 1



whereas the chlorophosphoric acid could be washed out with ether.

Addition of water solution of KPF_6 or KClO_4 to salt 1 gave the chlorophosphonium hexafluorophosphate or perchlorate 6, in almost quantitative yield.

Hence we got the reaction we looked for the preparation of BOP : one molar equivalent of triethylamine was added to the complex 4 followed by gradual introduction of anhydrous hydroxybenzotriazole (dried by azeotropic distillation with benzene) as a triethylammonium salt in CH_2Cl_2 . The O_2PCL_2^- anion does not interfere in this reaction. Just after the addition the reaction mixture was poured into iced water buffered with 1.5 molar equivalent of triethylamine. The organic layer was twice extracted with water, and the aqueous extracts were washed with ether. Then one molar equivalent of KPF_6 solution in water was added inducing the precipitation of the crude BOP (80 %) which could be recrystallised from acetone-ether (M.P. : $145-147^\circ\text{C}$).

----- References and notes

- 1) B. Castro, J.R. Dormoy, B. Dourtoglou, G. Evin, C. Selve and J.C. Ziegler, *Synthesis*, 11, 751 (1976)
- 2) P. Lester, U.S. Pat. 2678335, *Chem. Abst.*, 49, 6300g (1955) cited by H. Normant, *Angew. Chem. Int. Ed.* 12, 1050 (1967)
- 3) M.M. Crutchfield, C.H. Dungan, J.H. Letcher, V. Mark and J.R. Van Wazer, *Topics in Phosphorus Chemistry*, Vol. 5, Intersc. Publ., 347 (1967)
- 4) G.J. Martin, S. Poignant, *J. Chem. Soc. Perkin II*, 1964 (1972)
- 5) H.J. Vetter, *Z. Naturforsch.*, 19b, (1), 72 (1964)
- 6) B. Castro, J.R. Dormoy, *Tet. Lett.*, 47, 4747 (1972)
- 7) ^{31}P NMR spectra were obtained at 36.4 MHz (BRUKER 90 Apparatus with F.T.). Chemical shifts upfield from external H_3PO_4 (10 % in $(\text{CD}_3)_2\text{CO}$) are quoted as negative.

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