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Nucleophilic Substitutions on Hexachlorocyclotriphosphazene Using 18-Crown-6 Ether Complexes

E. J. WALSH, E. DERBY and J. SMEGAL

The Pennsylvania State University, Shenango Valley Campus, Sharon, Pennsylvania 16146, U.S.A.

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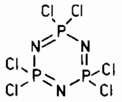
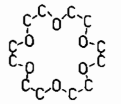
Many nucleophilic substitution reactions on hexachlorocyclotriphosphazene, (I), are very slow.[1]



I

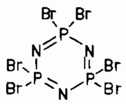
The rates of these reactions are especially slow if carried out as a two phase system. In an effort to decrease the times of these reactions and also to prepare some previously unknown substituted phosphazenes 18-Crown-6, (II), was used as a catalyst.[2-6]



II

It was found that the potassium salts of fluoride and thiocyanide readily substituted the chlorine on I in either benzene, acetonitrile, or tetrahydrofuran (THF) to yield either hexafluoro or hexaisothiocyanato cyclotriphosphazene. The reactions were complete, 85% yield, in approximately one hour at reflux. Although both these products have been prepared previously the times of reaction was greatly reduced and the methods of isolation considerably simplified by using 18-Crown-6 in catalytic quantities.[7,8]

Hexabromocyclotriphosphazene, (III), has been previously prepared by allowing ammonium bromide, phosphorous tribromide and bromine to react in a high boiling solvent.[9] In low boiling solvents, less than 130 °C, the major products were found to be NP_2Br_7 and NP_2Br_9.



III

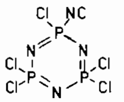
The reaction between potassium bromide, I, and 18-Crown-6 at either 81 °C or 138 °C results in only the formation of NP_2Br_9. Attempts to polymerize this material at 100 °C and 140 °C in a vacuum oven or in sealed tubes did not yield III but only NP_2Br_7 and a small quantity of $(NPBr_2)_n$ polymer.

Previous attempts to get bromine substitution using either AgBr, NH_4Br, $(CH_3)_4NBr$, KBr, or NaBr in a variety of solvents and at a wide range of refluxing solvents resulted in no detectable chlorine displacement.

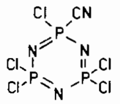
These observations would indicate that if bromine substitution occurs the phosphazene ring will degrade to the more stable linear form of NP_2Br_9. This would also mean that III is formed in solution by a competing mechanism with NP_2Br_9 and not as a combination of NP_2Br_9 molecules as previously assumed.

When potassium cyanide, I, and 18-Crown-6 are allowed to react in refluxing THF, displacement of chlorine can be detected.

The initial product which can only be isolated at low temperatures on a vacuum line has an I.R. peak at 2130 cm^{-1} characteristic of an isocyanide group.[10] When allowed to warm to room temperature over a period of an hour this peak moves to 2250 cm^{-1} indicating a change to a cyanide group. When heated to 60 °C in either a solvent or on a vacuum line this new compound loses the peak in the cyanide region and gains a set of 3 peaks at 1610, 1522, and 1489 cm^{-1}. The most plausible explanation is that the first compound is $N_3P_3Cl_5$ (iso CN), (IV), the next is $N_3P_3Cl_5$ (CN), (V);



IV



V

and that the final compound is a polymeric imine. The P=N region remains unchanged throughout thus indicating that polymerization does not occur by displacement of another chlorine to give –P–C=N–P– bonds.

These observations would account for the fact that all previous attempts to prepare cyanide derivatives of phosphazenes have been unsuccessful to date. Normal techniques of polymerization require refluxing solvents thus only polymerized material would be isolated.

Experimental

The Preparation of Hexafluorocyclotriphosphazene

A solution of 8.33 g (0.1437 mol) of KF and 2.64 g (0.01 mol) of 18-Crown-6 in 75 ml of either THF, benzene, or acetonitrile was stirred at reflux for 20 minutes. To this solution was added dropwise a solution of 5.0 g (0.01436 mol) $N_3P_3Cl_6$ in 50 ml of the same solvent. Reflux was continued for one hour then the reaction vessel fitted with a distillation head and a fractionating column. The fraction distilling to 59 °C was collected then redistilled to yield from 75–90% $N_3P_3F_6$. B.p. 50–51 °C, m.p. 27 °C.[8] The solvent of choice would be either benzene or acetonitrile because the boiling point of THF is low enough to make the separation of product and solvent difficult.

The Preparation of Hexaisothiocyanatocyclotriphosphazene

The quantities for this reaction were in the same ratio as for the preparation of the hexafluoro derivative. The yield was 5.55 g to 6.01 g (80–87%) of $N_3P_3(SCN)_6$. The use of the crown ether allows a greatly simplified workup by allowing removal of the solvent in a rotary evaporator followed by recrystallization from heptane. M.p. 40 °C.[7]

The Preparation of NP_2Br_9 and NP_2Br_7

17.1 g (0.1437 mol) of KBr and 2.64 g (0.01 mol) of 18-Crown-6 were stirred at room temperature in 100 ml acetonitrile. This solution was then brought to reflux and a solution of 5.0 g (0.01437 mol) of $N_3P_3Cl_6$ in 50 ml acetonitrile added dropwise. Reflux was continued overnight for 18 hours to yield a dark orange solution with KBr and KCl solids. Filtration followed by vacuum evaporation of the acetonitrile yielded 7.86 g of an orange solid which was found to be 90.56% Br and 7.92% P (calculated for NP_2Br_9, 90.45% Br and 7.79% P). Heating of this compound in a vacuum oven at 75 °C for 24 hours evolved Br_2 gas, with concurrent formation of NP_2Br_7. Found 88.0% Br and 9.82% P (calculated 88.04% Br and 9.75% P). Heating above 125 °C decomposes this compound. Similar reactions carried out in THF, benzene or xylene yielded the same products.

The Reaction of KCN with $N_3P_3Cl_6$

9.33 g (0.1436 mol) of KCN and 2.64 g (0.01 mol) of 18-Crown-6 were allowed to react at reflux temperature in 100 ml THF for 20 minutes. This solution was then allowed to cool to −78 °C and 5.0 g (0.01436 mol) $N_3P_3Cl_6$ was added with vigorous stirring. An immediate evolution of an acid gas occurred with the formation of a brown oil. The oil was less dense than THF and was insoluble in THF. After three hours decantation of the cool oil followed by transference on a vacuum line (0.01 mmHg) to a section at −196 °C yielded 2.4 g of a clear oil. The infrared spectrum of this oil (neat) had a very sharp peak at 2130 cm^{-1} (iso cyanide) and a strong P=N peak at 1235 cm^{-1}. The P–Cl peak at 620 cm^{-1} present in $N_3P_3Cl_6$ disappears. Calculated for $N_3P_3Cl_5(NC)$: % P 27.47, % Cl 52.44. Found: 27.40% P, 53.04% Cl.

Allowing this oil to come to room temperature over a period of one hour yields an opaque oil which is very hygroscopic and which has an infrared spectrum similar to the above product but which has a peak shift to 2258 cm^{-1} (cyanide). This oil is also thermally unstable and rearranges on setting overnight at room temperature or upon heating to give a compound without the cyanide peak but one which has new infrared peaks at 1610, 1522 and 1486 cm^{-1}. No change is noted in the P=N region, thus a polyimine is indicated.

If the reaction is carried out in a refluxing solvent, acetonitrile, THF, or benzene, the only product obtained is the polyimine type.

Acknowledgments

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References

1. For a complete review of synthetic techniques of phosphazenes chemistry see H. R. Allcock, "Phosphorous–Nitrogen Compounds", Academic Press, New York, 1972.
2. G. W. Gokel and H. D. Durst, "Principles and Synthetic Application in Crown Ether Chemistry". In Press.
3. C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, *96*, 2250 (1974).
4. D. J. Sam and H. E. Summons, *ibid.*, *96*, 2252 (1974).
5. H. D. Durst, J. W. Zubruk and G. R. Kieczykowski, *Tetrahedron Letters*, 1777 (1974).
6. (a) J. W. Zubruk, B. I. Dunbar and H. D. Durst, *ibid.*, *71* (1975); (b) F. L. Cook, C. W. Bowers and D. L. Liotta, *J. Org. Chem.*, *39*, 3416 (1974).
7. G. Tecti, R. J. A. Otto, F. G. Sherif and L. F. Audrieth, *J. Am. Chem. Soc.*, *82*, 528 (1960).
8. T. Moeller and F. Tsang, *Inorg. Syn.*, *9*, 78 (1967).
9. K. John and T. Moeller, *J. Inorg. Nucl. Chem.*, *22*, 199 (1961).
10. L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London, 1966.