HETEROCYCLES, Vol 28, No 2, 1989

REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZENE WITH 1,2-DIAMINOPROPANE

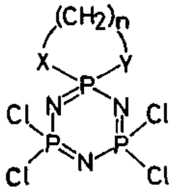
Vadapalli Chandrasekhar* and Narreddi Sivasankara Reddy[1]

Department of Chemistry
Indian Institute of Technology, Kanpur - 208016, India

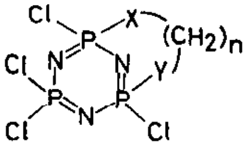
Abstract – *The reactions of hexachlorocyclotriphosphazene with 1,2-diaminopropane are discussed.*

Among the heterocyclic compounds, the cyclophosphazenes with alternating phosphorus and nitrogen atoms have been considerably well studied.[2] While the reactions of chlorocyclophosphazenes with monofunctional nucleophiles such as amines and alcohols are well understood[2], similar reactions with difunctional reagents are only recently attracting attention[3-5]. These are of considerable interest because of (a) the diversity of products possible and (b) the usefulness of these studies as models for condensation polymers of cyclophosphazenes.

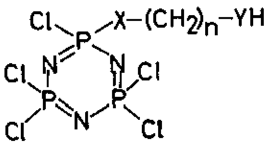
As many as four products are possible in the reaction of any difunctional reagent with chlorocyclophosphazenes. These are as follows:



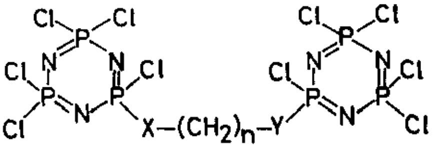
Spirocylic



Ansa



Open chain



Bridge

X=Y=NH or O, n=2-4

X=NH, Y=O

Although spirocyclic products seem to predominate when n is 2 or 3 the processes that operate in the final choice of other products are not properly understood. Another feature that needs further study is the (in)stability of products that contain five membered spirocyclic rings. With a view to gain further insight into the above we have carried out a study of the reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with 1,2-diaminopropane and the results obtained are reported here.

$N_3P_3Cl_6$ reacts with 2 equivalents of 1,2-diaminopropane in diethyl ether at about 25°C for 20 minutes to afford clearly a single product:

$$N_3P_3Cl_6 + 2\ H_2NCH(CH_3)CH_2NH_2 \xrightarrow[25^oC]{Et_2O} N_3P_3Cl_4[HNCH(CH_3)CH_2NH] \quad (\underline{1})$$
$$+\ HCl.NH_2\text{-}CH(CH_3)CH_2NH_2.HCl$$

The same product is obtained in the reaction of $N_3P_3Cl_6$ with one equivalent of the diamine in the presence of two equivalents of triethylamine. The product yield which is about 75% reduces drastically if (1) longer reaction times are employed, (2) more polar solvents such as chloroform are used and (3) higher temperatures are used for the reaction conditions. Compound (1) is extremely moisture sensitive and undergoes chemical change upon storage leading to a resinous product. Higher stoichiometric reactions between $N_3P_3Cl_6$ and the diamine in the ratio of 1:4 or 1:6 also afforded resinous materials which owing to their insolubility could not be characterised.

The spirocyclic nature of compound (1) is inferred from the ^{31}P nmr spectrum which is of the AB_2 type. The $\delta(PCl_2)$ and δ(P spiro) chemical shifts are in the same region as reported in the literature:

Table[a]

Phosphorus-31 nmr data for some spirocyclic triphosphazenes

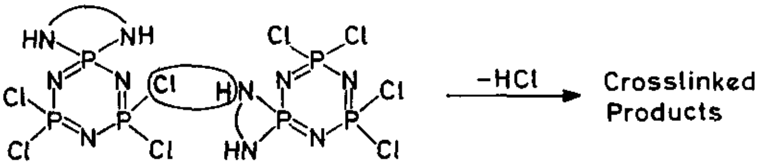
Compound	PCl_2	P spiro	$^2J(\underline{P}\text{-}N\text{-}\underline{P})$	Reference
$N_3P_3Cl_4[HN(CH_2)_2NH]$	22.0	22.00	-	3,4
$N_3P_3Cl_4[N(CH_3)(CH_2)_2O]$	25.1	22.4	53.01	3,4
$N_3P_3Cl_4[HN(CH_2)_3NH]$	21.5	7.5	45.5	3,4
$N_3P_3Cl_4[HN(CH_2)_4NH]$	21.2	12.8	46.0	3,4
$N_3P_3Cl_4[HNCH(CH_3)CH_2NH]$	22.47	21.25	46.0	This work

a: Upfield shifts are negative and the external reference (δ=0) is 85% H_3PO_4.

While the ^{31}P data does not rule out an ansa structure the formation of such a product seems improbable because the only known 'ansa' compound in literature is obtained by a two step route[6]:

$$\begin{tikzcd}
N_3P_3Cl_5(CH_3) + H_2N(CH_2)_3OH \arrow[r] & N_3P_3Cl_4(CH_3)[HN(CH_2)_3OH] \arrow[d, "NaH"] \\
 & N_3P_3Cl_3(CH_3)[HN(CH_2)_3O]
\end{tikzcd}$$

The instability of the compound (1) and the formation of crosslinked products in higher stoichiometric reactions of $N_3P_3Cl_6$ with 1,2-diaminopropane can be rationalised as proposed previously by the *intermolecular condensation* reaction[4]:



Undoubtedly presence of moisture, or use of polar solvents are conducive to the above reaction. Replacement of the labile chlorines in compound (1) by non-reactive groups such as -OMe renders the product more stable:

$$(\underline{1}) + NaOMe \xrightarrow[24\ hr,\ 25^{o}C]{MeOH} \underset{(\underline{2})}{N_3P_3(OMe)_4[HNCH(CH_3)CH_2NH]}$$

It appears that at *higher stages of* substitution the intermolecular condensation reaction leading to cross linked products is the preferred and dominant reaction pathway in the reactions of $N_3P_3Cl_6$ and 1,2-diaminopropane.

ACKNOWLEDGEMENTS

Thanks are due to the Inabata & Co. Ltd., Tokyo, Japan for their generous gift of $N_3P_3Cl_6$. One of us (VC) is extremely thankful to Prof. M.V. George, Department of Chemistry, I.I.T. Kanpur for his keen interest and encouragement.

REFERENCES

1. DMSRDE, Kanpur, India.
2. S.S. Krishnamurthy, A.C. Sau, and M. Woods, Adv. Inorg. Chem. Radiochem., 1978, 21, 41.
3. V. Chandrasekhar, S.S. Krishnamurthy, A.R. Vasudeva Murthy, R.A. Shaw, and M. Woods, Inorg. Nucl. Chem. Letts., 1981, 17, 181.
4. V. Chandrasekhar, S.S. Krishnamurthy, H. Manohar, A.R. Vasudeva Murthy, R.A. Shaw, and M. Woods, J. Chem. Soc. Dalton Trans., 1984, 621.
5. G. Guerch, M. Greffenil, J.F. Labarre, R. Enjalbert, R. Lahana, and F. Sournies, J. Mol. Struct., 1982, 85, 237.
6. P.J. Harris and K.B. Williams, Inorg. Chem., 1984, 23, 1496.

Received, 29th August, 1988