REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZENE WITH N-METHYL 1,3-DIAMINOPROPANE: ISOLATION OF SPIROCYCLIC AND NOT INTERMOLECULAR BRIDGED PRODUCTS.

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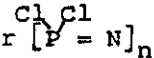
Abstract - The reactions of hexachlorocyclotriphosphazene with N-methyl-1,3-diaminopropane are discussed. The structures of the products have been established by spectroscopic methods. The products are formed exclusively via a spirocyclic pathway.

Reactivity studies on small molecules have been helpful as model systems for understanding reactions of more complex macromolecules.[2] This type of studies have been particularly successful in the case of the six-membered inorganic heterocyclic system, hexachlorocyclotriphosphazene, $N_3P_3Cl_6$(1) and the linear polymer  $[\overset{Cl\;Cl}{P}=N]_n$ derived from 1 . Several reactions of $N_3P_3Cl_6$(1) with a variety of diverse nucleophiles have been studied and these studies have helped in formulating synthetic strategies for the design of over 300 polyphosphazenes.[2] Similiarly the reactions of $N_3P_3Cl_6$(1) with difunctional reagents such as diamines have also attracted attention because these serve as model systems for condensation polymers.[3-6] Very few condensation polymers involving cyclophosphazenes are actually known. The reactions of chlorocyclophosphazenes with difunctional reagents predominantly lead to the formation of spirocyclic products where in both ends of the difunctional reagent reacts at the same phosphorus atom with the replacement of two chlorine atoms.[3]

Therefore, we were surprised at a recent report[7] where in a claim has been made about the isolation of an intermolecular bridged product between the reaction of N-methyl-1,3-diaminopropane and $N_3P_3Cl_6$(1). In pursuit of our continued interest in the reactions of $N_3P_3Cl_6$(1) with difunctional reagents in general and with non-symmetric difunctional reagents in particular, herein we report the findings of a reinvestigation on the reactions of $N_3P_3Cl_6$(1) with N-methyl-1,3-diaminopropane.

$N_3P_3Cl_6$(1) reacts with two equivalents of the diamine in ether at room temperature to afford in nearly quantitative yields, the product, $N_3P_3Cl_4[HN(CH_2)_3N(CH_3)]$(2). Use of triethylamine as a base also affords product (2) without any loss in yield. In order to characterise this product fully the tetrachloro derivative (2) has been reacted with several nucleophiles resulting in the complete substitution of the chlorine atoms.

$$(1) \xrightarrow{2H_2N(CH_2)_3NH(CH_3)} N_3P_3Cl_4[HN(CH_2)_3N(CH_3)] \ (2)$$

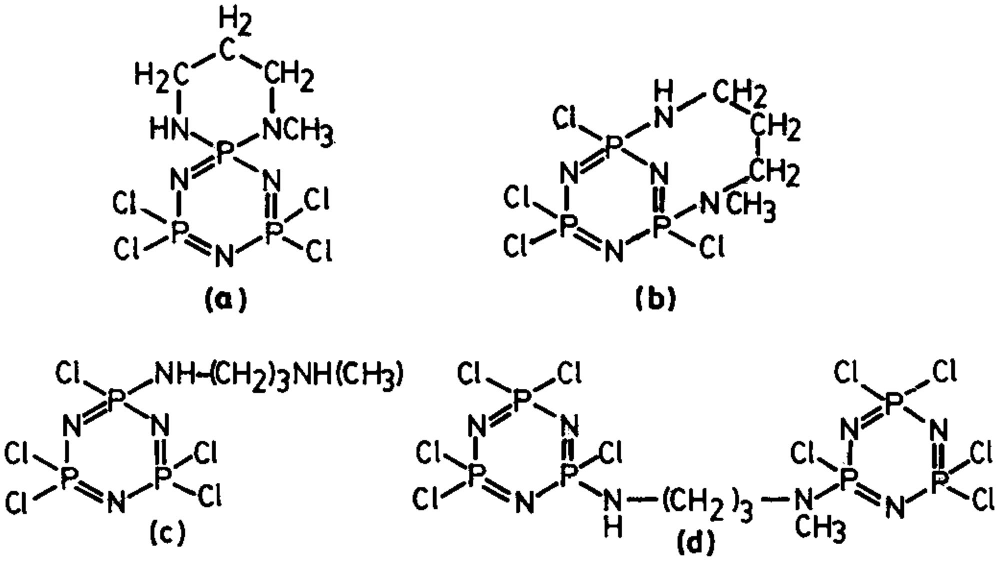
$$(2) \xrightarrow{X'SS\ C_6H_5ONa} N_3P_3(OC_6H_5)_4[HN(CH_2)_3N(CH_3)] \ (3)$$

$$(2) \xrightarrow{X'SS\ HN(CH_3)_2} N_3P_3(N(CH_3)_2)_4[HN(CH_2)_3N(CH_3)] \ (4)$$

$$(2) \xrightarrow{X'SS\ CH_3ONa} N_3P_3(OCH_3)_4[HN(CH_2)_3N(CH_3)] \ (5)$$

$$(2) \xrightarrow{X'SS\ CF_3CH_2ONa} N_3P_3(OCH_2CF_3)_4[HN(CH_2)_3N(CH_3)] \ (6)$$

Labarre and coworkers have previously proposed an intermolecular bridged structure for the product isolated in a similar reaction.[7] There are at least four possible pathways by which N-methyl-1,3-diaminopropane can react with $N_3P_3Cl_6$ leading to four different structures: (a) spirocyclic



Figure

(b) ansa (c) open-chain and (d) intermolecular-bridging (Figure). Of these structures (c) and (d) can be straightaway rejected on the basis of analytical data and mass spectra.[8] By means of ^{31}P nmr it is possible to distinguish between the structures (a) and (b). Since the difunctional reagent is non symmetrical the ansa product (b) would show a three spin pattern (ABX, AMX or ABC) in the phosphorus nmr. However, a spirocyclic structure (a) would clearly show a two spin pattern (AX_2 or AB_2). Product (2) and all its other derivatives (3), (4), (5), and (6) are all of the two spin type clearly establishing a spirocyclic structure for these products. The only examples of spirocyclic compounds showing A_3 spin type in the phosphorus nmr are $N_3P_3Cl_4[HN(CH_2)_2NH]$ and $N_3P_3Cl_4[HN(CH_2)_2O]$. Even for these at higher field strengths the expected two spin type is realised.[3-4] The phosphorus chemical shifts and coupling constants are listed in the Table.

Table

Phosphorus-31 nmr data

Compound	δ PCl$_2$	δ P spiro	δPR$_2$	J(P-N-P)
$N_3P_3Cl_4[HN(CH_2)_3N(CH_3)]$ (**2**)	20.3	9.8	-	39.1
$N_3P_3(OC_6H_5)_4[HN(CH_2)_3N(CH_3)]$ (**3**)	-	19.3	8.6	58.5
$N_3P_3(N(CH_3)_2)_4[HN(CH_2)_3N(CH_3)]$ (**4**)	-	19.3	25.0	37.2
$N_3P_3(OCH_3)_4[HN(CH_2)_3N(CH_3)]$ (**5**)	-	19.8	18.8	51.0
$N_3P_3(OCH_2CF_3)_4[HN(CH_2)_3N(CH_3)]$ (**6**)	-	19.9	16.3	59.3
$N_3P_3Cl_4[HN(CH_2)_3NH]$[9]	21.5	7.5	-	45.5

Further, the values of the phosphorus chemical shifts are comparable to those observed for other six-membered spirocyclic products previously reported.[9,10] In keeping with literature trends the δ P spiro is found to be more shielded than δ PCl$_2$.

It has been observed previously that spirocyclic products such as $N_3P_3Cl_4[HN(CH_2)_2NH]$ are hydrolytically unstable and are also prone to afford crosslinked materials on storing.[9,10] This has been attributed to the presence of a sterically unfavourable 5-membered spirocyclic ring along with the presence of residual -NH's which can react intermolecularly with chlorines on another molecule. Removal of both of these factors renders the products stable. Thus in the present system presence of only one residual NH along with the six membered spirocyclic ring makes the products more stable.

In conclusion, in our hands the reaction pathway between $N_3P_3Cl_6$ and N-methyl-1,3-diaminopropane proceeds exclusively by the spirocyclic pathway.

ACKNOWLEDGEMENTS

Thanks are due to the Inabata and Co. Ltd., and Nisso Iwahi Co. Ltd., Tokyo, Japan for their generous gift of $N_3P_3Cl_6$. We are thankful to DST (India) for financial support.

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Received, 25th October, 1991