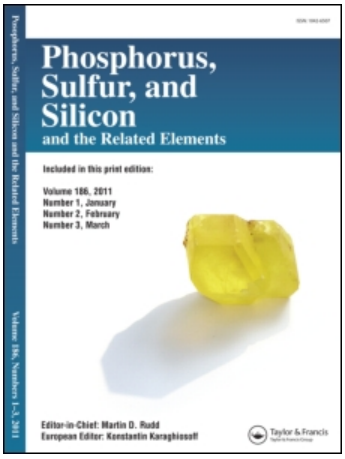

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Pathways in the Nucleophilic Substitution Reactions of Halogenocyclophosphazenes and Subtle Aspects of the Mechanism of Formation of Bicyclic Phosphazenes

P. Y. Narayana Swamy[a]; S. Ganapathiappan[a]; K. C. Kumara Swamy[a]; S. S. Krishnamurthy[a]
[a] Department of Inorganic and Physical, Chemistry Indian Institute of Science, Bangalore, INDIA

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PATHWAYS IN THE NUCLEOPHILIC SUBSTITUTION REACTIONS OF HALOGENOCYCLOPHOSPHAZENES AND SUBTLE ASPECTS OF THE MECHANISM OF FORMATION OF BICYCLIC PHOSPHAZENES

P.Y.NARAYANA SWAMY,S.GANAPATHIAPPAN,K.C.KUMARA SWAMY
AND **S.S. KRISHNAMURTHY**
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore 560012, INDIA

Abstract Both associative [$S_N2(P)$] and dissociative [$S_N1(P)$ and E_1CB] mechanisms have been established for the amination reactions of halogenocyclophosphazenes from synthetic and kinetic studies. Several intricate details concerning the formation of bicyclic phosphazenes have been unravelled.

We have developed a comprehensive mechanistic understanding of the complexities involved in the nucleophilic substitution reactions of halogenocyclophosphazenes[1] and devised a directed synthetic strategy for trans-annular bridged cyclotetraphosphazenes[2]. The results have wider implications in the context of the stereochemistry of nucleophilic displacement at a tetrahedral P^V centre.

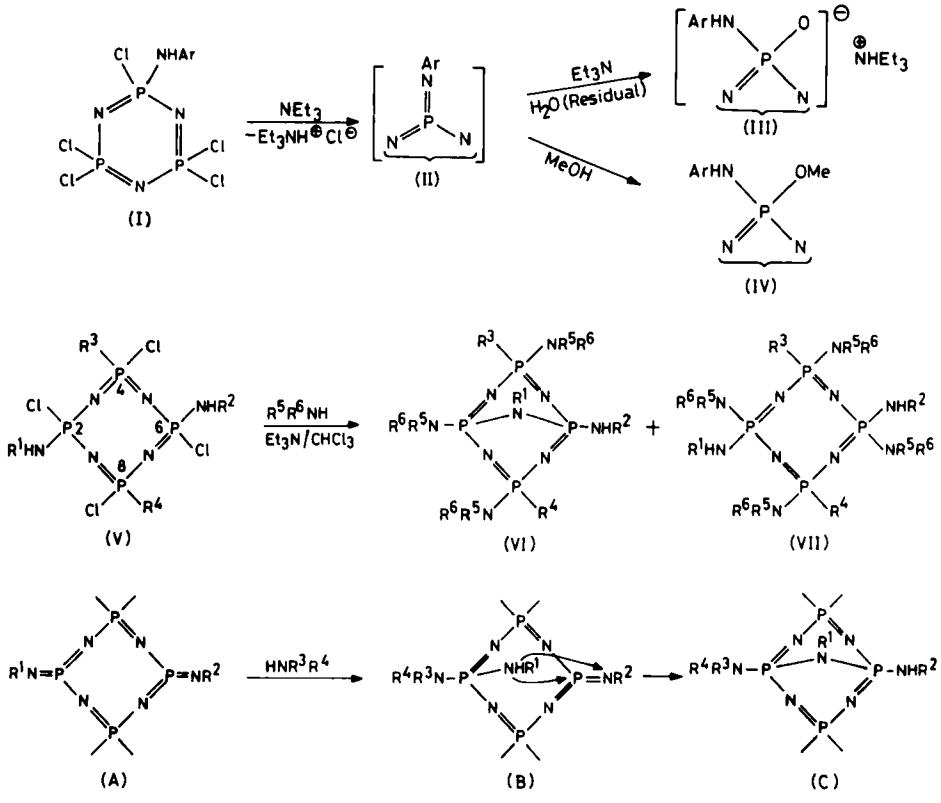
REACTIONS OF CYCLOTRIPHOSPHAZENES

We have earlier established a change-over from an associative $S_N2(P)$ to a dissociative $S_N1(P)$ mechanism in the stepwise replacement of chlorine atoms from $N_3P_3Cl_6$ by the dimethylamino group in MeCN[3]. We have now studied the kinetics of the reactions of $N_3P_3Cl_6$ with primary aromatic amines and those of gem-$N_3P_3Ph_2Cl_4$ with alkyl amines. The rate constants and activation parameters suggest that in a polar solvent such as MeCN, a one-step concerted $S_N2(P)$ mechanism operates; in less polar tetrahydrofuran, the reaction proceeds essentially via a neutral pentacoordinated phosphorus intermediate. Kinetic evidence strongly implicates an E_1CB mechanism

for the reaction of $N_3P_3Cl_5(NHAr)$ (I) [Ar = C_6H_4Me-p or $C_6H_4(OMe)$-p] with $ArNH_2$ in the presence of an excess of tri-n-butylamine to yield the geminal bis(amino) derivative. The intermediacy of a three-coordinated P^V species (II) is unambiguously established by trapping it with methanol and also by the isolation of the unusual products, [gem-$N_3P_3Cl_4$ $(NHAr)(O)^-$ $[NHEt_3]^+$(III) when I is treated with triethylamine in MeCN in the absence of $ArNH_2$.[3] The results lead to the formulation of a unified mechanistic framework which can readily explain the "regioselectivity" observed in the nucleophilic displacement reactions of halogenocyclophosphazenes. The "stereoselectivity" cannot be rationalized completely although several plausible hypotheses have been proposed.[1,3,4]

REACTIONS OF CYCLOTETRAPHOSPHAZENES : FORMATION OF BICYCLIC PHOSPHAZENES

Amination reactions of (primary amino)chlorocyclotetraphosphazenes can yield novel bicyclic phosphazenes which must arise by a trans-annular intramolecular attack.[2] We now demonstrate that a tetrakis(amino) intermediate of type V is involved in the formation of bicyclic phosphazenes (VI). The relative yields of the two types of products (VI, VII) depend on the solvent and the amino substituents on the ring (Table). The reaction of 2-trans-4-$N_4P_4Cl_6(NMePh)_2$ (structure known from X-ray analysis) with an excess of $EtNH_2$ in $CHCl_3$ in the presence of Et_3N affords only the octakis(amino)cyclotetraphosphazene, $N_4P_4(NMePh)_2(NHEt)_6$ and there is no evidence for any other product. One may conclude that the trans-annular bridge is formed only when both the antipodal phosphorus centres carry a PCl(NHR) group and one or both of the R groups is capable of being accommodated at the bridgehead nitrogen.Bridging of adjacent phosphorus atoms does not occur. A base-catalysed proton abstraction step generates a three coordinated P^V intermediate (A); intramolecular addition of a -NHR group from the antipodal phosphorus to the exocyclic P-N double bond leads to the bicyclic phosphazene(C).



CONCLUSIONS

All the possible mechanisms for nucleophilic displacement at a tetrahedral P^V centre have been realized in cyclophosphazene chemistry. The formation of reactive three coordinated P^V intermediates (II) has been established conclusively. Such an intermediate plays a key role in the formation of bicyclic phosphazenes from (amino)cyclotetraphosphazenes. The results unfold several subtle aspects concerning the effect of substituents and the solvent on the formation of bicyclic phosphazenes.

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Table : Effect of solvent and substituents on the formation of bicyclic phosphazenes

R^1,R^2	Phosphazene (V) R^3	Phosphazene (V) R^4	Reacting amine (R^5R^6NH)	Solvent[a]	Relative yields(%)[b] VI	Relative yields(%)[b] VII
Et	NMe_2	NMe_2	Me_2NH	$CHCl_3$	70	30
Et	NMe_2	NMe_2	Me_2NH	Et_2O	0	100
Et	NHEt	NHEt	Me_2NH	$CHCl_3$	70[c]	30
Et	NHEt	NHEt	Me_2NH	Et_2O	< 5	> 95[c]
Et	NMe_2	NMe_2	$EtNH_2$	$CHCl_3$	70[c]	30[c]
Et	NMe_2	NMe_2	$EtNH_2$	Et_2O	0	100[c]
Et	$NHBu^t$	$NHBu^t$	$EtNH_2$	$CHCl_3$	33	67
Et	$NHBu^t$	$NHBu^t$	$EtNH_2$	CH_3CN	40	60[c]
Et	$NHBu^t$	$NHBu^t$	$EtNH_2$	Et_2O	0	100[c]
Et	$NHCH_2Bu^t$	$NHCH_2Bu^t$	$EtNH_2$	$CHCl_3$	20	80
Et	NMePh	NMePh	$EtNH_2$	$CHCl_3$	33	67
Et	NMePh	NMePh	$EtNH_2$	Et_2O	0	100[c]
Et	$N(CH_2Ph)_2$	$N(CH_2Ph)_2$	$EtNH_2$	$CHCl_3$	45	55[c]
Et	$N(CH_2Ph)_2$	$N(CH_2Ph)_2$	$EtNH_2$	Et_2O	< 5	> 95[c]
Et,Bu^t	NHEt	$NHBu^t$	$EtNH_2$	$CHCl_3$	60	40
Et,Bu^t	NHEt	$NHBu^t$	$EtNH_2$	CH_3CN	55	45

a Reaction carried out at the boiling point of the solvent; for reactions in $CHCl_3$, Et_3N was also used. b Determined by phosphorus-31 NMR spectroscopy

c Pure product isolated.

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