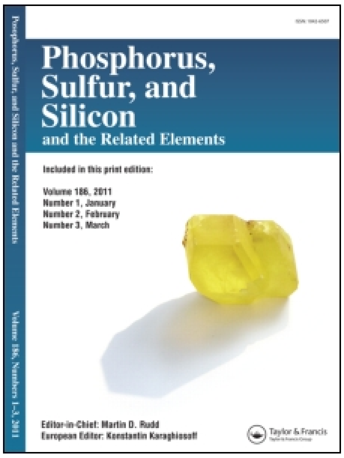

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Structures and Modes of Reactions of Some Hexachlorocyclodiphosphazane With Some Bifunctional Reagents

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STRUCTURES AND MODES OF REACTIONS OF SOME HEXACHLOROCYCLODIPHOSPHAZANE WITH SOME BIFUNCTIONAL REAGENTS

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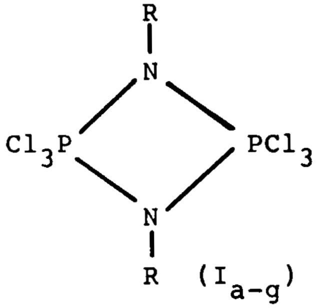
Abstract Aminocyclodiphosph(v)azanes of the type (II-V) obtained from the interaction of hexachlorocyclodiphosphazanes (I) with some bifunctional reagents (such as phenylurea, diphenylurea, thiourea and its phenyl derivatives) in acetonitrile, have been discussed.

INTRODUCTION

The reactions of hexachlorocyclodiphosph(v)azanes with monofunctional nucleophiles have been investigated in great detail (Ibrahim, 1979; Shaw, 1980). Analogous reactions with bifunctional reagents have received much less attention. In the present work, seven different hexachlorocyclodiphosphazanes of the type (I_{a-g}) have been prepared by the methods of Chapman (Chapman, 1961) and Kirsanov (Kirsanov, 1963).



(I_{a-g})

I_a; R = C_6H_5

I_b; R = C_6H_4--Cl-o

I_c; R = C_6H_4--Cl-p

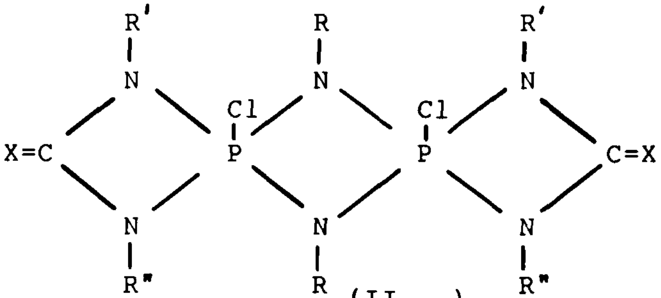
I_d; R = C_6H_4--CH_3-o

I_e; R = C_6H_4--CH_3-p

I_f; R = C_6H_4--OCH_3-o

I_g; R = C_6H_4--OCH_3-p

The reaction between halophosphazanes (I) and a bifunctional nucleophile in a non-polar solvent such as benzene or diethylether is a slow reaction, which often yields side products rather than substituted phosphorus compounds. However, when a solvent such as acetonitrile is used (Shaw et. al., 1977, 1981), the reaction is found to be rapid and the degree of substitution and the pattern of halogen replacement is sensitive to the steric characteristics of the nucleophile (Shaw, 1984). Phenylurea, diphenylurea, thiourea and its phenyl derivatives react with halophosphazanes ($I_{a-c,g}$) to give a cyclosubstitution at phosphorus. The aminosubstituted cyclodiphosphazane derivatives (II_{a-o}) have analyses compatible with the following tricyclic structure:

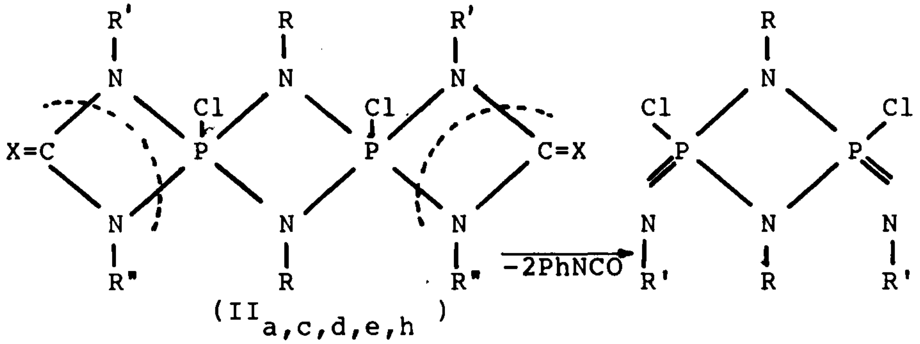


(II_{a-o})

No. of compound	R	R'	R"	X
II_a	C_6H_5	C_6H_5	C_6H_5	O
II_b	C_6H_4-Cl-p	C_6H_5	C_6H_5	O
II_c	C_6H_4-CH_3-p	C_6H_5	C_6H_5	O
II_d	C_6H_4-OCH_3-p	C_6H_5	C_6H_5	O
II_e	C_6H_5	C_6H_5	C_6H_5	S
II_f	C_6H_4-Cl-o	C_6H_5	C_6H_5	S
II_g	C_6H_4-Cl-p	C_6H_5	C_6H_5	S
II_h	C_6H_4-CH_3-p	C_6H_5	C_6H_5	S
II_i	C_6H_4-OCH_3-p	C_6H_5	C_6H_5	S
II_j	C_6H_5	H	H	S
II_k	C_6H_4-CH_3-o	H	H	S
II_l	C_6H_4-Cl-p	H	H	S
II_m	C_6H_4-OCH_3-p	H	H	S
II_n	C_6H_5	H	C_6H_5	S
II_o	C_6H_4-Cl-o	H	C_6H_5	S

The structure of these compounds has been substantiated on the basis of their infrared and ultraviolet spectroscopic analysis. The fact that the expected band at 270-290 nm characteristic (Becke-Goehring, 1963) for electron delocalization within the four-membered ring of the dimeric structure,was observed in the spectra supports structure (II). The infrared spectra of these compounds showed characteristic absorption bands, which are summarized in Table 1.

Mass spectrometric measurements for compounds (II_a), (II_c), (II_d), (II_e) and (II_h) showed the following masses of the molecular ion (M^+) at m/e 734 (738), m/e 762 (766), m/e 794 (798), m/e 766 (770) and m/e 794 (798) respectively. The molecular ion peak (M^+) then loses 2 molecules of phenylisocyanate,(C_6H_5NCO) to give the positive radical at m/e 496 (500). These experimental findings agree with the following proposed fragmentation pathway:



($II_{a,c,d,e,h}$)

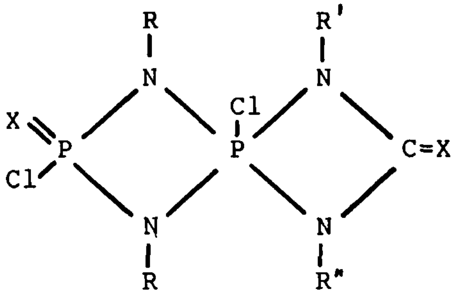
Table I

Infrared data of compounds (II_{a-o}) and (III_{a-c})

No. of Compound	NH	C=O	C=S	P=S	P-Cl	P-N-H	P=O
		Stretching frequencies in cm^{-1}					
II_a	-	1775	-	-	515	-	-
II_b	-	1775	-	-	515	-	-
II_c	-	1775	-	-	515	-	-
II_d	-	1780	-	-	515	-	-
II_e	-	-	1130	-	515	-	-
II_f	-	-	1125	-	525	-	-
II_g	-	-	1125	-	515	-	-
II_h	-	-	1125	-	515	-	-
II_i	-	-	1130	-	500	-	-
II_j	3100	-	1075	-	500	2600	-
II_k	3100	-	1110	-	500	2550	-
II_l	3100	-	1095	-	500	2600	-
II_m	3100	-	1160	-	500	2550	-
II_n	3400	-	1170	-	500	2600	-
II_o	3400	-	1170	-	530	2600	-
III_a	3200	1650	-	-	520	2600	1250
III_b	-	-	1115	610	510	-	-
III_c	3100	-	1110	635	540	2600	-

It should be noted that the parent peak of some of these compounds does not appear in the spectra, presumably owing to the fact that these ions are relatively unstable. However, these peaks were detected by the application of the link-scan technique.

The interaction of hexachlorocyclodiphosphazanes ($I_{c,d,f}$) with phenylurea, diphenylurea and thiourea gave the substituted oxyaminocyclodiphosphazanes (III_{a-c}), respectively (see Tables I-III).



(III_{a-c})

No of Compound	R	R'	R"	X
III_a	C_6H_4-Cl-p	H	C_6H_5	O
III_b	C_6H_4-CH_3-o	C_6H_5	C_6H_5	S
III_c	C_6H_4-OCH_3-o	H	H	S

The assignment of structure (III) was based on: elemental analyses, uv spectra(which demonstrated the presence of the four- membered ring),ir and ^1H nmr spectra (see Tables I-II).

TABLE II

^{1}H.n.m.r. Spectra compounds (II_{a-o}) and (III_{a-c})

No. of Compound	Chemical shifts in ppm. CH$_3$	OCH$_3$	Aromatic	NH**
II_a	-	-	7.3	-
II_b	-	-	7.6	-
II_c	2.2	-	7.7	-
II_d	-	3.5	6.9	-
II_e	-	-	7.2	-
II_f	-	-	7.4	-
II_g	-	-	7.3	-
II_h	2.5	-	7.5	-
II_i	-	3.6	7.0	-
II_j	-	-	7.2	9.5
II_k	2.0 -	-	7.2	8.0
II_l	-	-	7.2	9.3
II_m	-	3.7	7.0	7.8
II_n	-	-	7.2	6.8
II_o	-	-	7.3	8.6
III_a	-	-	7.2	7.6
III_b	2.2	-	7.3	-
III_c	-	3,85	7.1	9.90

** Disappeared on the addition of D_2O.

TABLE III

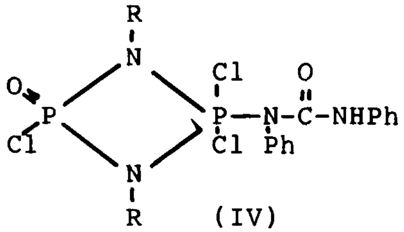
Analytical data of the Aminocyclodiphosphazane derivatives (II-V)

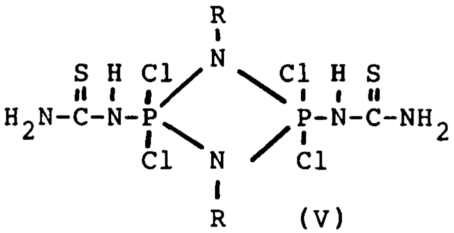
of nd	Reactants		m.p. °C	Colour	Yield %	Formula	Microanalysis Found/Cal			
	Cyclodiphospha-zane (I)	Urea and thiourea derivatives					C%	H%	N%	P
	I_a	diphenylurea	190	white	43	$C_{38}H_{30}N_6P_2O_2Cl_2$	61.60	4.00		8
	(6.0 g.; 0.013 mole)	(5.57 g.; 0.026 mole)					62.04	4.08	-	8
	I_c	diphenylurea	226-228	yelow	55	$C_{38}H_{28}N_6P_2O_2Cl_4$	56.00	3.40	10.08	7
	(8.0 g.; 0.015 mole)	(6.45 g.; 0.03 mole)					56.72	3.48	10.48	7
	I_c	diphenylurea	230-231	white	30	$C_{40}H_{28}N_6P_2O_2Cl_2$	-	-	10.09	7
	(6.0 g.; 0.012 mole)	(5.24 g.; 0.02 mole)					-	-	11.01	8
	I_g	diphenylurea	225-227	white	51	$C_{40}H_{34}N_6P_2O_2Cl_2$	-	-	10.20	7.
	(6.0 g.; 0.01 mole)	(4.92 g.; 0.02 mole)					-	-	10.57	7.
	I_a	diphenylthiourea	217-218	white	8	$C_{38}H_{30}N_6P_2S_2Cl_2$	60.00	3.50	10.95	8.
	(6.0 g.; 0.013 mole)	(5.98 g.; 0.026 mole)					59.54	3.91	10.95	8
	I_b	diphenylthiourea	203		7	$C_{38}H_{28}N_6P_2S_2Cl_4$	55.00	3.50	9.90	6.
	(8.0 g.; 0.015 mole)	(6.63 g.; 0.03 mole)					54.55	3.35	10.05	7.
	I_c	diphenylthiourea	237=238	white	7	$C_{38}H_{28}N_6P_2S_2Cl_4$	-	-	-	6.
	(8.0 g.; 0.015 mole)	(6.64 g.; 0.03 mole)					-	-	-	7.
	I_c	diphenylthiourea	238	white	13	$C_{40}H_{34}N_6P_2S_2Cl_2$	-	-	9.86	7.
	(6.0 g.; 0.012 mole)	(5.64 g.; 0.02 mole)					-	-	10.57	7.
	I_g	diphenylthiourea	217-219	white	16.5	$C_{40}H_{34}N_6P_2O_2S_2Cl_2$	-	-	9.47	7.
	(5.17 g.; 0.01 mole)	(4.57 g.; 0.02 mole)							10.16	7.
	I_a	thiourea	190	yellow	17.5	$C_{14}H_{14}N_6P_2S_2Cl_2$	-	-	18.90	13.
	(6.0 g.; 0.013 mole)	(2.0 g.; 0.026 mole)							18.14	13.

Continued...

. of ound	Reactants						Microanalysis Found/Ca		
	Cyclodiphosphazane (I)	Urea and thiourea derivatives	m.p. °C	Colour	Yield %	Formula	C%	H%	N%
I_k	I_d	thiourea	165	yellow	15	$C_{16}H_{18}N_6P_2S_2Cl_2$	38.80	3.50	-
	(5.0 g.; 0.01 mole)	(1.56 g.; 0.02 mole)					39.10	3.67	-
I_l	I_c	thiourea	165	pale	14	$C_{14}H_{12}N_6P_2S_2Cl_4$	35.70	2.00	-
	(8.0 g.; 0.015 mole)	(2.31 g.; 0.03 mole)		yellow			36.44	2.60	-
I_m	I_g	thiourea	210	pale	9	$C_{16}H_{18}N_6P_2O_2S_2Cl_2$	-	-	16.03
	(6.0 g.; 0.01 mole)	(1.76 g.; 0.02 mole)		yellow			-	-	16.06
I_n	I_a	phenylthiourea	230	white	8	$C_{26}H_{22}N_6P_2S_2Cl_2$	-	-	-
	(6.0 g.; 0.013 mole)	(4.0 g.; 0.026 mole)					-	-	-
I_o	I_b	phenylthiourea	170-173	white	32	$C_{26}H_{20}N_6P_2S_2Cl_2$	-	-	-
	(8.0 g.; 0.015 mole)	(4.62 g.; 0.03 mole)					-	-	-
II_a	I_c	phenylurea	162-164	white	2.5	$C_{19}H_{14}N_4P_2O_2Cl_4$			-
	(8.0 g.; 0.015 mole)	(4.13 g.; 0.03 mole)					43.00	2.80	-
II_b	I_d	diphenylthiourea	260-262	white	10	$C_{27}H_{24}N_4P_2S_2Cl_2$	42.70	2.62	10.29
	(8.0 g.; 0.015 mole)	(4.13 g.; 0.03 mole)					-	-	9.31
II_c	I_f	thiourea	170	pale	14	$C_{15}H_{16}N_4P_2O_2S_2Cl_2$	-	-	
	(6.0 g.; 0.01 mole)	(1.76 g.; 0.02 mole)					-	-	-
V	I_b	diphenylurea	183=186	yellow	21	$C_{25}H_{19}N_4P_2O_2Cl_5$			9.00
	(8.0 g.; 0.015 mole)	(6.45 g.; 0.03 mole)		white			-	-	8.66
	I_c	thiourea	173-175	yellow	11.5	$C_{16}H_{18}N_6P_2Cl_4$	-	-	14.90
	(6.0 g.; 0.012 mole)	(6.78 g.; 0.222 mole)					-	-	15.01

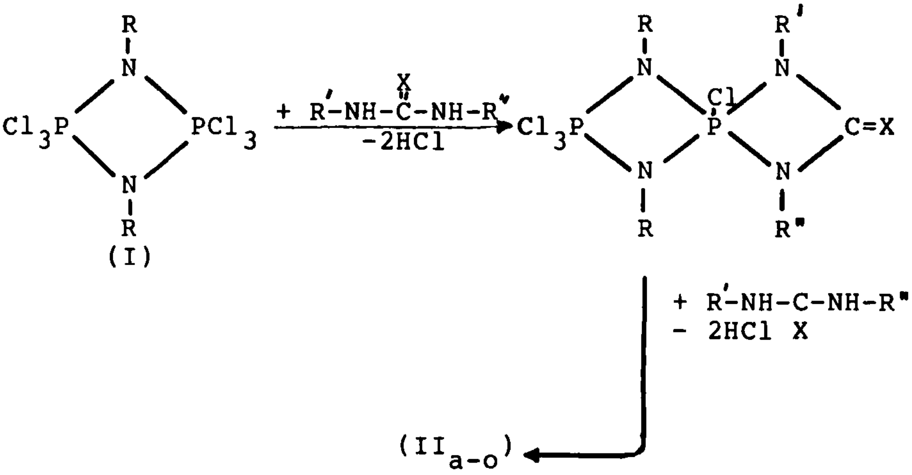
The reaction of (I_b) with diphenylurea and (I_e) with thiourea led to the formation of products for which structures (IV) and (V) were proposed respectively.


(IV)

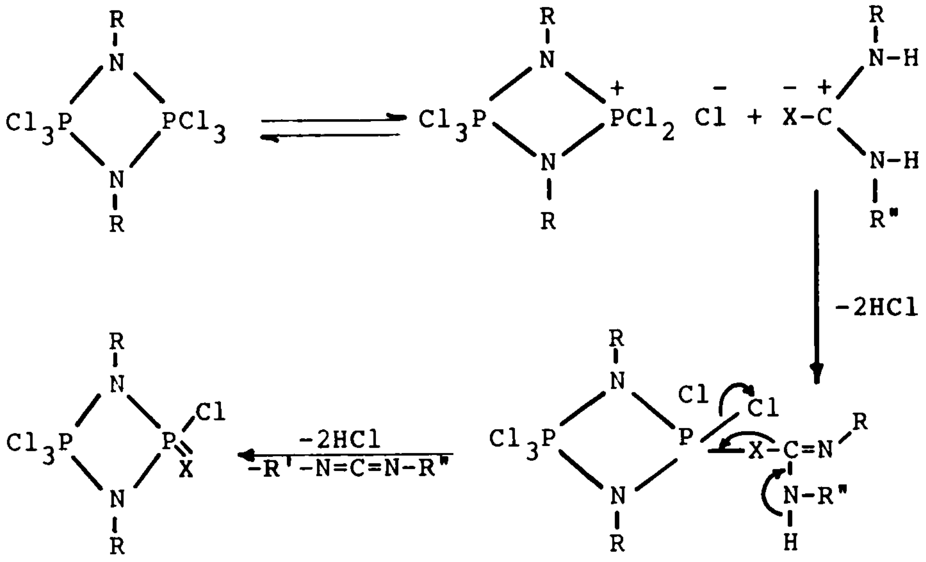

(V)

MECHANISTIC PROPOSAL:

Interaction of the nucleophilic reagent with hexachlorocyclodiphosphazane (I) may take one of the following courses, or even both. The first mechanism is one involving direct substitution of halogen atoms by a nucleophilic attack on phosphorus according to the following reaction scheme.



The second mechanism involves a chloride ion which ionizes from phosphorus, followed by nucleophilic attack.



intermediate

The course of the reaction depends on the nature of the nucleophilic reagent, the type of substituents present (R),and also on the relative rate of both reactions. It is feasible that direct attack of the nucleophile is possible by both mechanisms. Both routes will lead eventually to the proposed tricyclic and oxycyclic structures.

It is expected, however, that if the R group attached to the cyclodiphosphazane nitrogen is bulky and the R' or R" group derived from the nucleophilic reagent is an aromatic group, such an interaction will not be facile owing to steric factors and would lead to the formation of intermediate products.

EXPERIMENTAL

Microanalytical determinations were carried out by the microanalytical laboratory, Cairo University. Infrared spectra were recorded on a Unicom SP 1200 spectrophotometer (KBr technique). Ultraviolet spectra were recorded on a Unicom Sp 8000 ultraviolet recording spectrophotometer. ^1H n.m.r. spectra were measured on a Varian EM-360L, 60 MHz spectrometer and mass spectrometric measurements were carried out using a Finnigan MAT 112S mass spectrometer by the direct inlet system.

Synthesis of aminocyclodiphosphazane derivatives (II-V):

GENERAL PROCEDURE

The solid bifunctional reagent (0.02 mole) was added in small portions to a well stirred solution of the hexachlorocyclodiphosphazane (I) (0.01 mole) in 100 ml acetonitrile during 1/2 hour. After the addition was complete, the reaction mixture was heated under reflux for three hours. The solid formed subsequently dissolved with the evolution of HCl gas. After the completion of the reaction (HCl gas ceased to evolve), the reaction mixture was filtered while hot and the solid obtained was washed several times with acetonitrile, diethyl ether and dried in vacuo to give the corresponding aminocyclodiphosphazane derivatives (II-V); the data obtained are listed in Table III.

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