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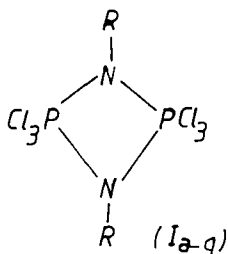
STUDIES IN CYCLODIPHOSPHAZANES. SOME REACTIONS OF HEXACHLOROCYCLO- DIPHOSPHAZANES WITH UREA AND THIOUREA DERIVATIVES

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Interaction of chlorocyclodiphosphazanes (I) with some bifunctional reagents (such as phenylurea, diphenylurea, thiourea and its phenyl derivatives) in acetonitrile furnished geminal and nongeminal aminocyclodiphosphazanes of type (II-V). The structures of the isolated products were proposed on the basis of microanalytical data, infrared, ultraviolet, ¹H n.m.r., and mass spectra. The mechanism of the nucleophilic substitution is also discussed.

The reaction of hexachlorocyclodiphosphazanes with monofunctional nucleophiles has been investigated in great detail.¹⁻⁶ Analogous reactions with bifunctional reagents have received much less attention. In the present work, seven different hexachlorocyclodiphosphazanes of type (I_{a-g}) have been prepared by the methods of Chapman⁷ and Kirsanov⁸ in which phosphorus pentachloride in cold dry benzene reacted with substituted anilines.



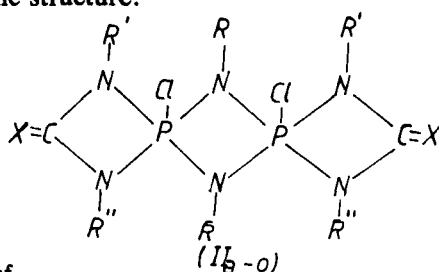
- | | |
|--|---|
| I _a ; R = C ₆ H ₅ | I _e ; R = C ₆ H ₄ -CH ₃ -p |
| I _b ; R = C ₆ H ₄ -Cl-o | I _f ; R = C ₆ H ₄ -OCH ₃ -o |
| I _c ; R = C ₆ H ₄ -Cl-p | I _g ; R = C ₆ H ₄ -OCH ₃ -p |
| I _d ; R = C ₆ H ₄ -CH ₃ -o | |

The direct reaction between halophosphazanes (I) and a bifunctional nucleophile in an inert solvent such as benzene or diethyl ether is a slow reaction, which often yields side products or decomposition species rather than substituted phosphorus. However, when a solvent such as acetonitrile is used, 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.

Thus, phenylurea, diphenylurea, thiourea and its phenyl derivatives react with

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halophosphazanes ($I_{a-e,g}$) to give a cyclosubstitution at phosphorus. The amino-substituted cyclodiphosphazane derivatives (II_{a-o}) have analyses compatible with the following tricyclic structure:



No. of Compd.	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 characteristic⁹ for electron delocalization within the four-membered ring of the dimeric structure was observed in the spectra, suggests the presence of the four-membered ring. The infrared spectra of these compounds showed characteristic absorption bands, which are summarized in Table I.

1H n.m.r. spectra of the isolated compounds (II) showed the aromatic proton signal at $\delta = 7.0$ – 7.6 ppm. The characteristic proton signals are listed in Table II.

Mass spectrometric measurements for compounds (II_a), (II_c), (II_d), (II_e) and (II_h) showed the following masses m/e 497; m/e 525; m/e 557; m/e 497 and m/e 525 respectively as the highest masses in the spectrum corresponding to $M^{+} - 2C_6H_5CNX$. These experimental findings agree with the following proposed fragmentation pathway:

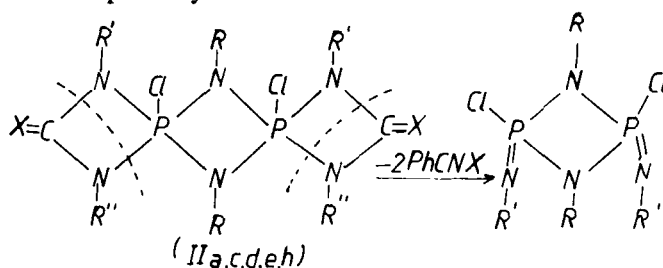


TABLE I
Infrared data of compounds (II_{a-o}) and (III_{a-c})

No. of Compound	NH	C=O	Stretching frequencies in cm ⁻¹				
			C=S	P=S	P—Cl	P—N—H	P=O
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 all these compounds does not appear in the spectra, presumably owing to the fact that these ions are metastable and hence do not appear.

The interaction of hexachlorocyclodiphosphazanes (I_{c,d,f}) with phenylurea, diphenylurea and thiourea gave the substituted oxyaminocyclodiphosphazanes

TABLE II
¹H n.m.r. spectra of compounds (II_{a-o}) and (III_{a-c})

No. of Compound	CH ₃	Chemical shifts δ in ppm.		
		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

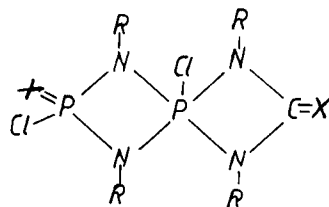
** Disappeared on the addition of D₂O.

TABLE III
Analytical data of the Aminocyclodiphosphazane derivatives (II–V)

No. of Compound	Reactants		Urea and thiourea derivatives	m.p. °C	Color	Yield %	Formula	Microanalysis Found/Calcd.		
	Cyclodiphosphazane (I)							C%	H%	N% P%
II _a	I _a (6.0 g.; 0.013 mole)	diphenylurea (5.57 g.; 0.026 mole)	190	white	43	C ₃₈ H ₃₀ N ₆ P ₂ O ₂ Cl ₂	61.60	4.00	—	8.23
II _b	I _c (8.0 g.; 0.015 mole)	diphenylurea (6.45 g.; 0.03 mole)	226–228	yellow	55	C ₃₈ H ₂₈ N ₆ P ₂ O ₂ Cl ₄	62.04	4.08	—	8.43
II _c	I _c (6.0 g.; 0.012 mole)	diphenylurea (5.24 g.; 0.02 mole)	230–231	white	30	C ₄₀ H ₂₈ N ₆ P ₂ O ₂ Cl ₂	56.00	3.40	10.08	7.59
II _d	I _k (6.0 g.; 0.01 mole)	diphenylurea (4.92 g.; 0.02 mole)	225–227	white	51	C ₄₀ H ₃₄ N ₆ P ₂ O ₂ Cl ₂	56.72	3.48	10.48	7.71
II _e	I _a (6.0 g.; 0.013 mole)	diphenylthiourea (5.98 g.; 0.026 mole)	217–218	white	8	C ₃₈ H ₃₀ N ₆ P ₂ S ₂ Cl ₂	—	—	10.09	7.44
II _f	I _b (8.0 g.; 0.015 mole)	diphenylthiourea (6.63 g.; 0.03 mole)	203	—	7	C ₃₈ H ₂₈ N ₆ P ₂ S ₂ Cl ₄	60.00	3.50	10.20	8.13
II _g	I _c (8.0 g.; 0.015 mole)	diphenylthiourea (6.64 g.; 0.03 mole)	237 = 238	white	7	C ₃₈ H ₂₈ N ₆ P ₂ S ₂ Cl ₄	59.54	3.91	10.57	7.26
II _h	I _c (6.0 g.; 0.012 mole)	diphenylthiourea (5.64 g.; 0.02 mole)	238	white	13	C ₄₀ H ₃₄ N ₆ P ₂ S ₂ Cl ₂	55.00	3.50	10.95	8.00
II _i	I _k (5.17 g.; 0.01 mole)	diphenylthiourea (4.57 g.; 0.02 mole)	217–219	white	16.5	C ₄₀ H ₃₄ N ₆ P ₂ O ₂ S ₂ Cl ₂	54.55	3.35	10.95	8.08
II _j	I _a (6.0 g.; 0.013 mole)	thiourea (2.0 g.; 0.026 mole)	190	yellow	17.5	C ₁₄ H ₁₄ N ₆ P ₂ S ₂ Cl ₂	—	—	10.05	6.56
							—	—	—	7.42
							—	—	—	6.96
							—	—	—	7.20
							—	—	—	9.86
							—	—	—	10.57
							—	—	—	7.80
							—	—	—	9.47
							—	—	—	7.11
							—	—	—	10.16
							—	—	—	18.90
							—	—	—	13.18
							—	—	—	18.14
							—	—	—	13.39

II _k	I _d (5.0 g.; 0.01 mole)	thiourea (1.56 g.; 0.02 mole)	165	yellow	15	C ₁₆ H ₁₈ N ₆ P ₂ S ₂ Cl ₂	38.80	3.50	—	12.12
II _l	I _c (8.0 g.; 0.015 mole)	thiourea (2.31 g.; 0.03 mole)	165	pale	14	C ₁₄ H ₁₂ N ₆ P ₂ S ₂ Cl ₄	39.10	3.67	—	12.42
II _m	I _g (6.0 g.; 0.01 mole)	thiourea (1.76 g.; 0.02 mole)	210	pale	9	C ₁₆ H ₁₈ N ₆ P ₂ O ₂ S ₂ Cl ₂	35.70	2.00	—	10.95
II _n	I _a (6.0 g.; 0.013 mole)	phenylthiourea (4.0 g.; 0.026 mole)	230	yellow			36.44	2.60	16.03	11.65
II _o	I _b (8.0 g.; 0.015 mole)	phenylthiourea (4.62 g.; 0.03 mole)	170–173	white	8	C ₂₆ H ₂₂ N ₆ P ₂ S ₂ Cl ₂	—	—	16.06	11.85
III _a	I _c (8.0 g.; 0.015 mole)	phenylurea (4.13 g.; 0.03 mole)	162–164	white	32	C ₂₆ H ₂₀ N ₆ P ₂ S ₂ Cl ₂	—	—	—	9.98
III _b	I _d (6.0 g.; 0.01 mole)	diphenylthiourea (5.64 g.; 0.02 mole)	260–262	white	2.5	C ₁₉ H ₁₄ N ₄ P ₂ O ₂ Cl ₄	43.00	2.80	—	10.98
III _c	I _f (6.0 g.; 0.01 mole)	thiourea (1.76 g.; 0.02 mole)	170	white	10	C ₂₇ H ₂₄ N ₄ P ₂ S ₂ Cl ₂	42.70	2.62	10.29	11.61
IV	I _b (8.0 g.; 0.015 mole)	diphenylurea (6.45 g.; 0.03 mole)	183 = 186	pale yellow	14	C ₁₅ H ₁₆ N ₄ P ₂ O ₂ S ₂ Cl ₂	—	—	9.31	11.32
V	I _c (6.0 g.; 0.012 mole)	thiourea (1.78 g.; 0.022 mole)	173–175	white yellow	21	C ₂₅ H ₁₉ N ₄ P ₂ O ₂ Cl ₅	—	—	—	12.05
				yellow	11.5	C ₁₆ H ₁₈ N ₆ P ₂ S ₂ Cl ₄	—	—	9.00	12.88
							—	—	8.66	9.48
							—	—	14.90	9.59
							—	—	15.01	10.68
							—	—	—	11.03

(III_{a-c}) respectively (see Tables I–III),

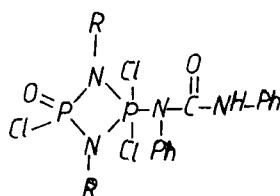


(III_{a-c})

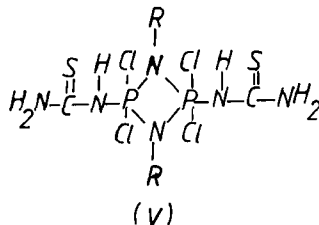
No. of Compd.	R	R'	R''	X
III _a	C ₆ H ₄ —Cl—p	H	C ₆ H ₅	O
III _b	C ₆ H ₄ —CH ₃ —o	C ₆ H ₅	C ₆ H ₅	S
III _c	C ₆ H ₄ —OCH ₃ —o	H	H	S

The assignment of structure (III) was based on: element analysis, uv spectra, which demonstrated the presence of the four-membered ring, ir and ¹H n.m.r. spectra (see Tables I–II).

The interaction of *o*-chlorophenylhexachlorocyclodiphosphazane (I_b) with diphenylurea and *p*-tolylhexachlorocyclodiphosphazane (I_c) with thiourea led to the formation of products for which we propose structures (IV) and (V) respectively.



(IV)

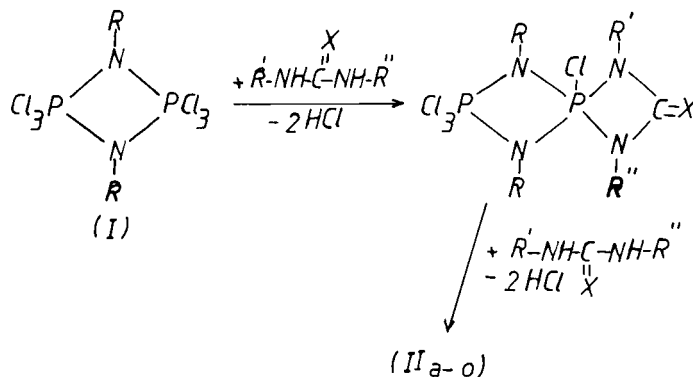


(V)

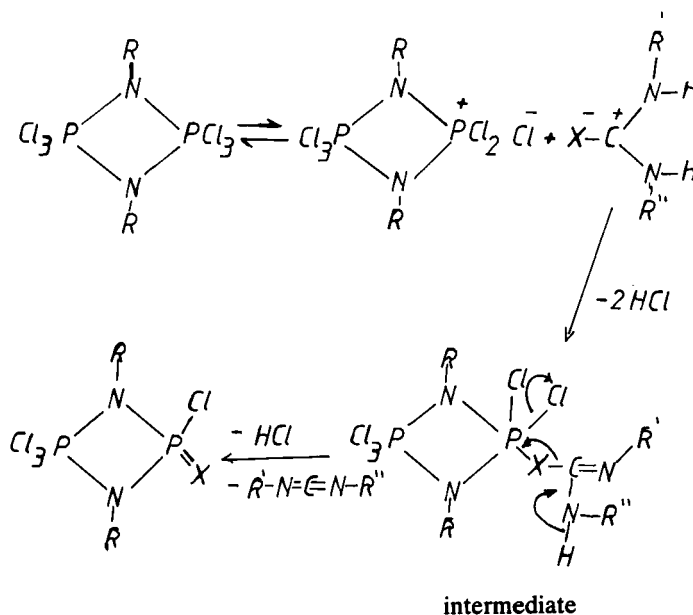
The assignment of structures (IV) and (V) for the above compounds was based on: element analysis, uv spectra which demonstrated the presence of the four-membered ring, ir spectra which showed the characteristic NH stretching vibration at 3400 cm⁻¹, P=O stretching mode at 1250 cm⁻¹, C=O stretching vibration at 1650 cm⁻¹ (for compound IV), P—Cl stretching mode at 515 cm⁻¹, C=S stretching vibration at 1115 cm⁻¹ (for compound V) and a band at 2600 cm⁻¹ characteristic for the P—N—H stretching vibration.¹⁰ Finally, the ¹H n.m.r. spectra: the spectrum of compound (IV) showed a signal at δ = 7.25 ppm. characteristic for the aromatic protons, and a signal at δ = 8.36 ppm. due to the NH, which disappeared on the addition of D₂O. The ¹H n.m.r. spectrum of compound (V) show a signal at δ = 2.1 ppm due to the methyl protons, a signal at δ = 7.1 ppm characteristic of the aromatic protons and at δ = 7.5 ppm due to the NH protons, and the NH₂ proton signal appeared at δ = 2.3 ppm. The last two signals disappeared upon the addition of D₂O owing to proton exchange.

Mechanistic Proposal

It is proposed that the 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:



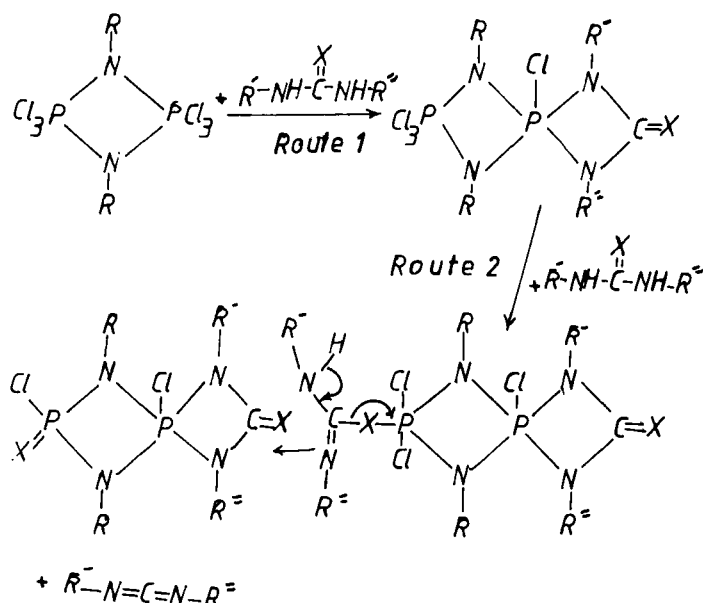
The second mechanism involves a chloride ion which ionizes from phosphorus, followed by nucleophilic attack as follows:



The direction of 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 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.

The formation of the terminal P=O group in some products demonstrates that the reaction in these cases follows the second mechanism to give the partially substituted products as follows



The formation of compounds like (IV) and (V) can be explained as follows:

The possibility also exists that the nongeminal replacement pattern observed with compound (IV) may result from electron supply from the substituent to phosphorus, which lowers the reactivity of a $Cl-P-N$ unit below that of a $Cl-P-Cl$ unit, or to steric factors in which little difficulty is encountered in effecting complete replacement of halogens in spite of the steric retardation which must be involved. In the latter only a so-called intermediate in the form of the above compounds (IV) and (V) would be possible.

EXPERIMENTAL

Microanalytical determinations were carried out by the microanalytical laboratory, Cairo University. Infrared spectra were recorded on a Unicomp Sp 1200 spectrophotometer (KBr technique). Ultraviolet spectra were recorded on a Unicomp 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 1125 mass spectrometer by the direct inlet system.

PREPARATION OF COMPOUNDS

The preparation and purification of hexachlorocyclodiphosphazanes (I_{a-g}) has been described previously.⁷⁻⁸ All the amino compounds used were B.D.H. reagent grade products.

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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