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THE STRUCTURES AND MODE OF FORMATION OF SOME CYCLODIPHOSPHAZANE DERIVATIVES WITH UREA AND THIOUREA

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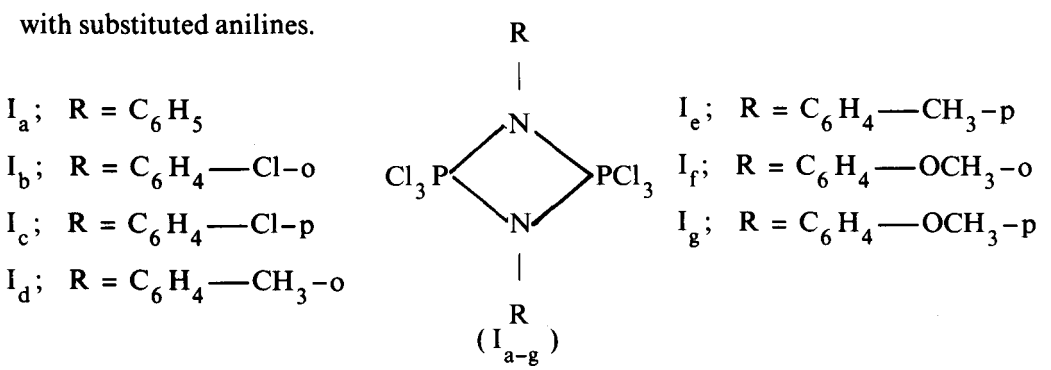
ABSTRACT

The methods of preparation and possible reaction mechanisms for the formation of some geminal and nongeminal aminocyclodiphosph (v) azanes of the type (II – V) are discussed. These cyclodiphosphazanes obtained from the interaction of chlorocyclodiphosphazanes (I) with some bifunctional reagents (such as phenylurea, diphenylurea, thiourea and its phenyl derivatives) in acetonitrile, have been investigated using infrared, ultraviolet, ^{1}H n.m.r. and mass spectrometric data.

INTRODUCTION

Interaction of hexachlorocyclodiphosph (v) azanes with monofunctional nucleophilies has 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 haxachlorocyclodiphosphazanes of type (I_{a-g}) have been prepared by the methods of Chapman, (Chapman, 1961) and Kirsanov (Kirsanov, 1963) in which phosphorus pentachloride in cold dry benzene reacted with substituted anilines.



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

(I_{a-g})

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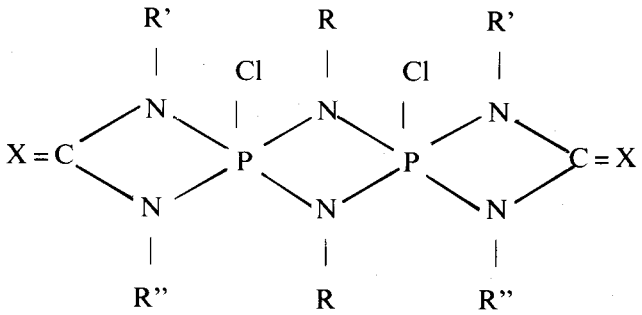
The direct reaction between halophosphazanes (I) and a bifunctional nucleophile in an inert solvent such as benzene or diethyl ether is a slow reaction, which often yields side products or decomposition species rather than substituted phosphorus. However, when a solvent such as acetonitrile is used (Shaw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

Thus, 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})

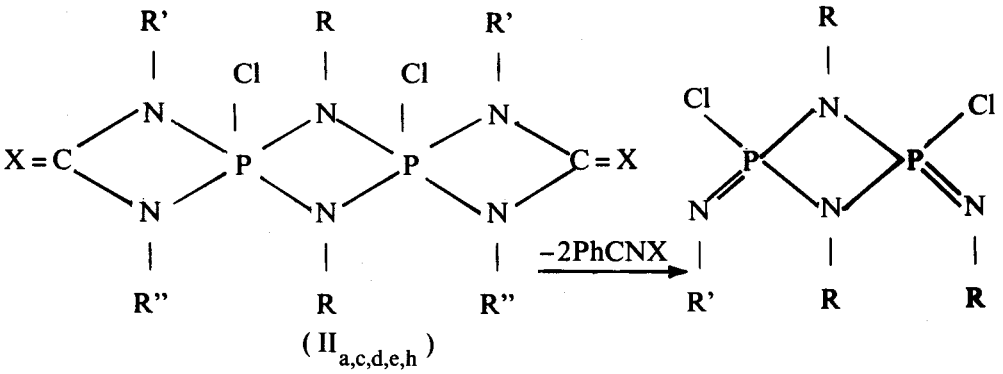
No. of compound	R	R'	R"	X
II_a	C_6H_5	C_6H_5	C_6H_5	O
II_b	C_6H_4—Cl-p	C_6H_5	C_6H_5	O
II_c	C_6H_4—CH_3-p	C_6H_5	C_6H_5	O
II_d	C_6H_4—OCH_3-p	C_6H_5	C_6H_5	O
II_e	C_6H_5	C_6H_5	C_6H_5	S
II_f	C_6H_4—Cl-o	C_6H_5	C_6H_5	S
II_g	C_6H_4—Cl-p	C_6H_5	C_6H_5	S

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-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, suggests the presence of the four – membered ring. The infrared spectra of these compounds showed characteristic absorption bands, which are summarized in Table 1.

^{1}H 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 $M^{+\cdot} - 2C_6H_5CNX$. These experimental findings agree with the following proposed fragmentation pathway :

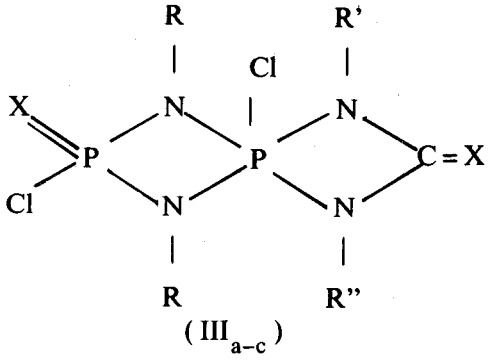


($II_{a,c,d,e,h}$)

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. This was confirmed by the use of link–field scan.

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

(III_{a-c}) respectively (see Tables 1 – 3),



(III_{a-c})

Table 1

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

No. of Compound	Stretching frequencies in cm^{-1}						
	NH	C=O	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	–

Table 2

^{1}H.n.m.r. Spectra data of 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 3

Analytical data of the Aminocyclodiphosphazane derivatives (II – V)

No. of Compound	Reactants: Cyclodiphospha-Zane (I)	Reactants: Urea and thiourea derivatives	m.p. °C	Colour	Yield %	Formula	Microanalysis: C %	Microanalysis: H %	Found/Calcd.: N %	Found/Calcd.: P %
II_a	I_a (6.0 g.; 0.013 mole)	diphenylurea (5.57 g.; 0.026 mole)	190	white	43	$C_{38}H_{30}N_6P_2O_2Cl_2$	61.60	4.00		8.23
							62.04	4.08	–	8.43
II_b	I_c (8.0 g.; 0.015 mole)	diphenylurea (6.45 g.; 0.03 mole)	226–228	yellow	55	$C_{38}H_{28}N_6P_2O_2Cl_4$	56.00	3.40	10.08	7.59
							56.72	3.48	10.48	7.71
II_c	I_c (6.0 g.; 0.012 mole)	diphenylurea (5.24 g.; 0.02 mole)	230–231	white	30	$C_{40}H_{28}N_6P_2O_2Cl_2$	–	–	10.09	7.44
							–	–	11.01	8.13
II_d	I_g (6.0 g.; 0.01 mole)	diphenylurea (4.92 g.; 0.02 mole)	225–227	white	51	$C_{40}H_{34}N_6P_2O_2Cl_2$	–	–	10.20	7.26
							–	–	10.57	7.72
II_e	I_a (6.0 g.; 0.013 mole)	diphenylthiourea (5.98 g.; 0.026 mole)	217–218	white	8	$C_{38}H_{30}N_6P_2S_2Cl_2$	60.00	3.50	10.95	8.00
							59.54	3.91	10.95	8.08
II_f	I_b (8.0 g.; 0.015 mole)	diphenylthiourea (6.63 g.; 0.03 mole)	203		7	$C_{38}H_{28}N_6P_2S_2Cl_4$	55.00	3.50	9.90	6.56
							54.55	3.35	10.05	7.42
II_g	I_c (8.0 g.; 0.015 mole)	diphenylthiourea (6.64 g.; 0.03 mole)	237=238	white	7	$C_{38}H_{28}N_6P_2S_2Cl_4$	–	–	–	6.96
							–	–	–	7.42
II_h	I_c (6.0 g.; 0.12 mole)	diphenylthiourea (5.64 g.; 0.02 mole)	238	white	13	$C_{40}H_{34}N_6P_2S_2Cl_2$	–	–	9.86	7.20
							–	–	10.57	7.80
II_i	I_g (5.17 g.; 0.01 mole)	diphenylthiourea (4.57 g.; 0.02 mole)	217–219	white	16.5	$C_{40}H_{34}N_6P_2O_2S_2Cl_2$	–	–	9.47	7.11
									10.16	7.48
II_j	I_a (6.0 g.; 0.013 mole)	thiourea (2.0 g.; 0.026 mole)	190	yellow	17.5	$C_{14}H_{14}N_6P_2S_2Cl_2$	–	–	18.90	13.18
									18.14	13.39

Continued .....

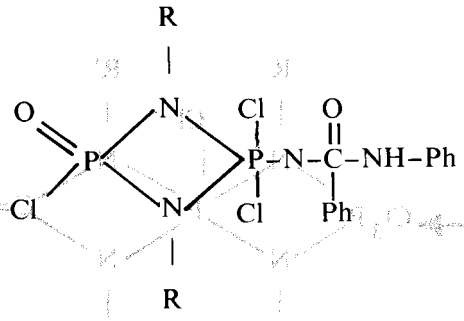
Table 3 cont.

No. of Compound	Reactants: Cyclodiphospha-zane (I)	Reactants: Urea and thiourea derivatives	m.p. °C	Colour	Yield %	Formula	Microanalysis C %	Microanalysis H %	Found/Calcd. N %	Found/Calcd. P %
II_k	I_d (5.0 g.; 0.01 mole)	thiourea (1.56 g.; 0.02 mole)	165	yellow	15	$C_{16}H_{18}N_6P_2S_2Cl_2$	38.80	3.50	–	12.12
							39.10	3.67	–	12.42
II_l	I_c (8.0 g.; 0.015 mole)	thiourea (2.31 g.; 0.03 mole)	165	pale yellow	14	$C_{14}H_{12}N_6P_2S_2Cl_4$	35.70	2.00	–	10.95
							36.44	2.60	–	11.65
II_m	I_g (6.0 g.; 0.01 mole)	thiourea (1.76 g.; 0.02 mole)	210	pale yellow	9	$C_{16}H_{18}N_6P_2O_2S_2Cl_2$	–	–	16.03	11.75
							–	–	16.06	11.85
II_n	I_a (6.0 g.; 0.013 mole)	phenylthiourea (4.0 g.; 0.026 mole)	230	white	8	$C_{26}H_{22}N_6P_2S_2Cl_2$	–	–	–	9.98
							–	–	–	10.08
II_o	I_b (8.0 g.; 0.015 mole)	phenylthiourea (4.62 g.; 0.03 mole)	170–173	white	32	$C_{26}H_{20}N_6P_2S_2Cl_2$	–	–	–	8.68
							–	–	–	9.60
III_a	I_c (8.0 g.; 0.015 mole)	phenylurea (4.13 g.; 0.03 mole)	162–164	white	2.5	$C_{19}H_{14}N_4P_2O_2Cl_4$			–	10.98
							43.00	2.80	–	11.61
III_b	I_d (8.0 g.; 0.015 mole)	diphenylthiourea (4.13 g.; 0.03 mole)	260–262	white	10	$C_{27}H_{24}N_4P_2S_2Cl_2$	42.70	2.62	10.29	11.43
							–	–	9.31	11.32
III_c	I_f (6.0 g.; 0.01 mole)	thiourea (1.76 g.; 0.02 mole)	170	pale	14	$C_{15}H_{16}N_4P_2O_2S_2Cl_2$	–	–		12.05
							–	–	–	12.88
IV	I_b (8.0 g.; 0.015 mole)	diphenylurea (6.45 g.; 0.03 mole)	183=186	yellow white	21	$C_{25}H_{19}N_4P_2O_2Cl_5$			9.00	9.48
							–	–	8.66	9.59
V	I_c (6.0 g.; 0.012 mole)	thiourea (6.78 g.; 0.222 mole)	173–175	yellow	11.5	$C_{16}H_{18}N_6P_2Cl_4$	–	–	14.90	10.68
							–	–	15.01	11.03

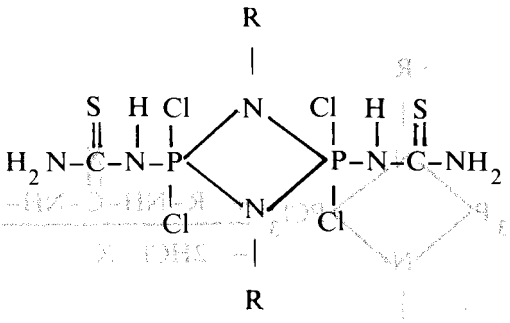
No.of Compound				
III_a	C_6H_4—Cl-p	H	C_6H_5	O
III_b	C_6H_4—CH_3-o	C_6H_5	C_6H_5	S
III_c	C_6H_4—OCH_3-o	H	H	S

The assignment of structure (III) was based on : 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_e) with thiourea led to the formation of products for which we propose structures (IV) and (V) respectively.



(IV)



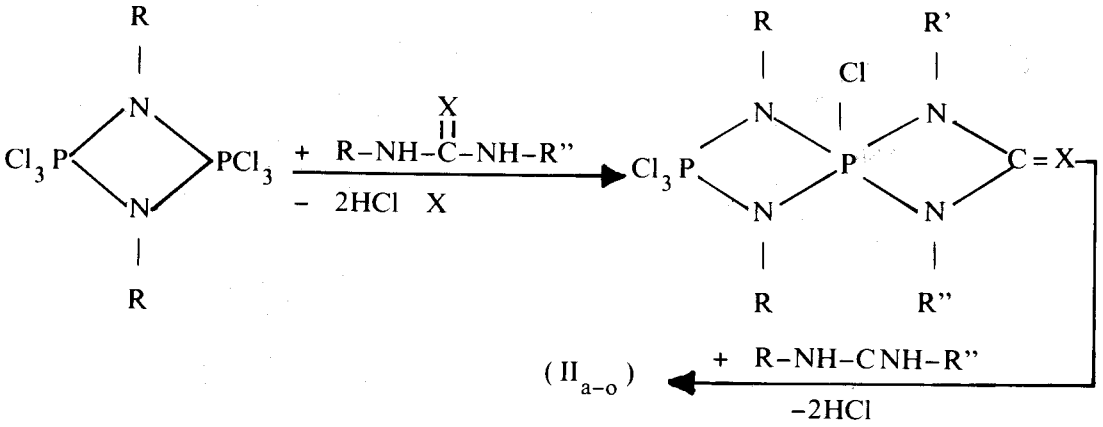
(V)

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 (Allcock, 1972). Finally,

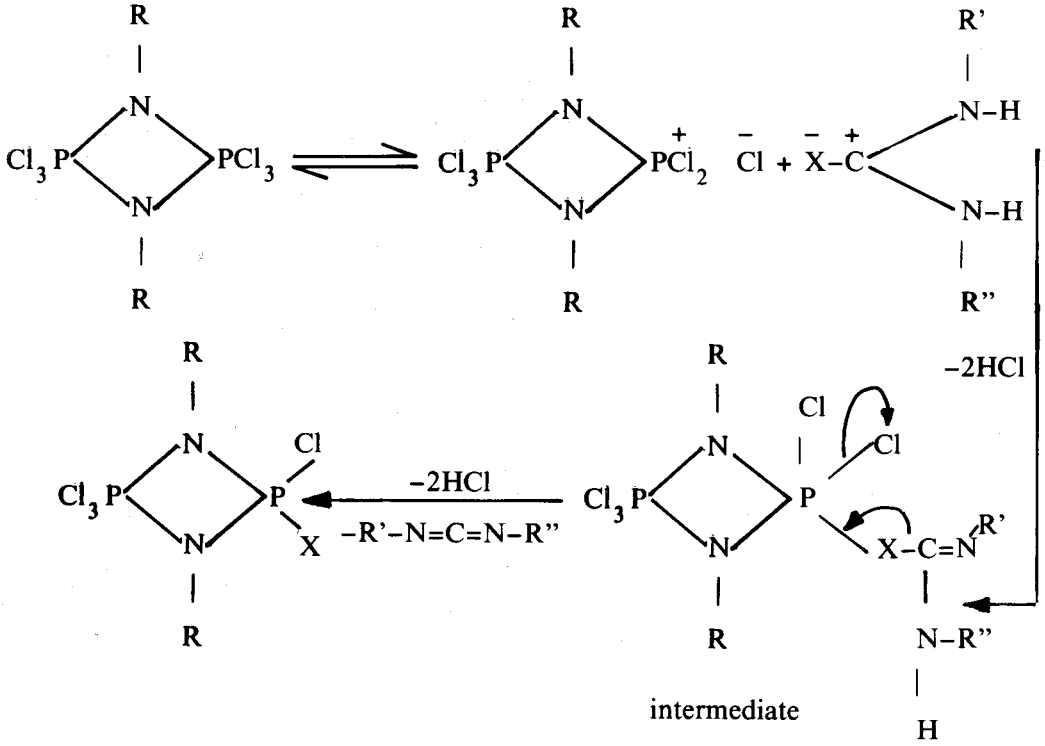
the ^{1}H n.m.r. spectra : the spectrum of compound (IV) showed a signal at δ= 7.25 ppm. characteristic for the aromatic protons, and a signal at = 8.36 ppm. due to the NH, which disappeared on the addition of D_2O. The ^{1}H.n.m.r. spectrum of compound (V) show a signal at δ = 2.1 ppm. due to the methyl 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 NH_2 proton signal appeared at δ= 2.3 ppm. The last two signals disappeared upon the addition of D_2O owing to proton exchange.

MECHANISTIC PROPOSAL

It is proposed that the interaction of the nucleophilic reagent with hexachlorocyclodiphosphanzane (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 :



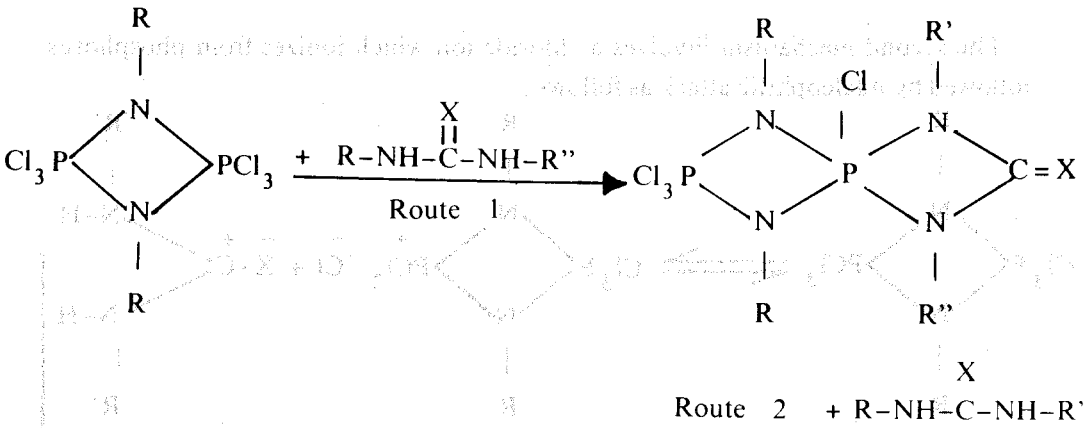
The second mechanism involves a chloride ion which ionizes from phosphorus, followed by nucleophilic attack as follows ;

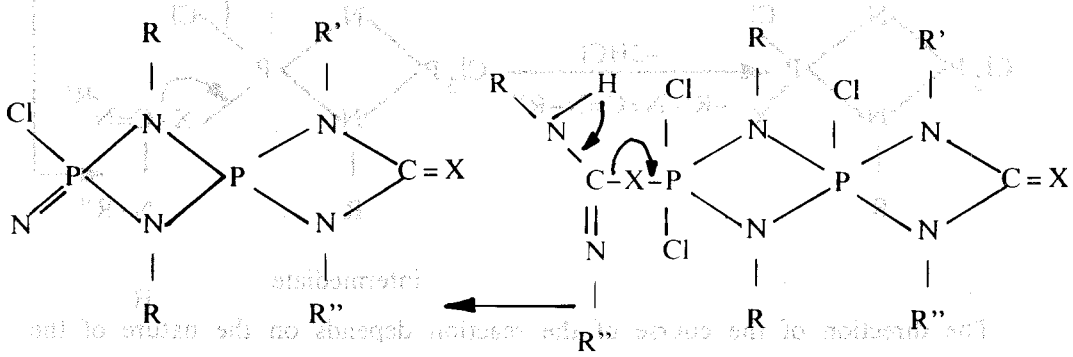


The direction of the course of the reaction depends on the nature of the nucleophilic reagent, the type of substituents present (R) and also on the relative rate of both reactions. It is feasible that direct attack of the nucleophile is possible by both mechanisms. Both routes will lead eventually to 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 mechanisms to give the partially substituted products as follows ;





+ R–N=C=N–R"

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 Unicom SP 1200 spectrophotometer (KBr technique). Ultraviolet spectra were recorded on a Unicom Sp 8000 ultraviolet recording spectrophotometers. ^{1}H n.m.r. spectra were measured on a Varian EM-3 60L, 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}) have been described previously (Chapman, 1961; Kirsanov, 1963). All the aminocompounds used were B.D.H. reagent grade products.

Synthesis of aminocyclodiphosphazane derivatives (II – V) is as follows :

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 3.

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دراسات عن تكوين وتركيب بعض مشتقات ثنائي الفوسفازانات الحلقية مع اليوريا والثيويوريا

عز الدين حرب محمد إبراهيم و إبراهيم عبد اللاه

و

عوني الخازندار

إشتملت هذه الدراسة على تحضير بعض مشتقات ثنائي الفوسفازانات الحلقية مع اليوريا والثيويوريا حيث تم فصل بعض أمينو ثنائي الفوسفازانات الحلقية الجيمينيلية وغير الجيمينيلية ذات النشاط البيولوجي كمضادات للخلايا السرطانية ، كما تمت دراسة التراكيب الجزيئية لهذه المشتقات بدراسة أطياف الأشعة فوق البنفسجية والأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي وأطياف الكتلة لهذه المركبات ، وقد أمكن التحقق من التراكيب الجزيئية لبعض هذه المشتقات باستخدام طريقة الإرتباط المجالي في طيف الكتلة حيث أمكن التأكد من وجود الأيونات غير الثابتة .