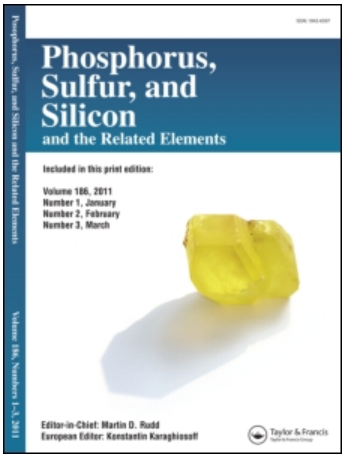

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STUDIES IN CYCLODIPHOSPHAZANES: SOME REACTIONS OF HEXACHLOROCYCLODIPHOSPHAZANES (I) WITH AMINO ACIDS

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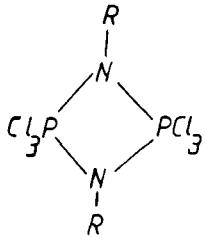
Interaction of 1,3diaryl-2,2,2-4,4,4-hexachlorocyclodiphosphazanes (I_{a-g}) with glycine, α- and β-alanine are described. The structure of the obtained aminocyclodiphosphazanes (II-V) were proposed on the basis of microanalytical data, ir, uv, ^{1}H n.m.r. and mass spectra. The mechanism of the reaction is also discussed.

The reaction of hexachlorocyclodiphosphazanes (I) with amino compounds has been investigated in great detail.[1–7] Analogous reactions with amino acids have received much less attention.

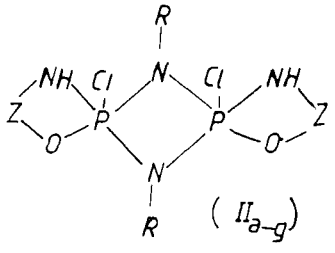
We have recently[8] shown that the reaction of hexachlorocyclodiphosphazanes (I) with bifunctional reagents (such as urea and thiourea derivatives) furnished geminal and nongeminal aminocyclodiphosphazanes.

In the present investigation, glycine, α- and β-alanine reacted with halophosph(V)azanes (I_{a-g}) in acetonitrile to give a cyclosubstitution at the phosphorus atoms. The analytical data suggest structure (II_{a-g}) and (III_{a-c}) for these materials.

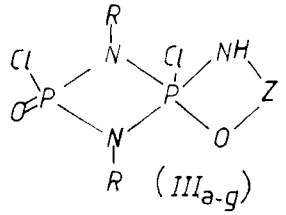


(I_{a-g})

I_1; 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



(II_{a-g})



(III_{a-g})

† To whom correspondence should be sent.

No. of Compd.	*R*	*Z*
II_a	C_6H_5	$CH_2—CO—$
II_b	C_6H_4–Cl-p	$CH_2—CO—$
II_c	$C_6H_4—OCH_3$-o	$CH_2—CO—$
II_d	$C_6H_4—OCH$-p	$CH_2—CO—$
II_e	$C_6H_4—CH_3$-p	$CH_2—CO—$
II_f	$C_6H_4—CH_3$-p	$CH(CH_3)—CO—$
II_g	C_6H_5	$CH_2—CH_2—CO—$

No. of Compd.	*R*	*Z*
III_a	$C_6H_4—CH_3$-o	$CH_3—CO—$
III_b	C_6H_5	$CH(CH_3)—CO—$
III_c	C_6H_5	$CH_2—CH_2—CO—$
III_d	$C_6H_4—CH_3$-p	$CH_2—CH_2—CO—$
III_e	$C_6H_4—OCH_3$-o	$CH_2—CH_2—CO—$

The assignment of the proposed structures (II_{a-g}) and (III_{a-e}) was based on: element analysis, the infrared spectra of these compounds showed the characteristic νNH, νC=O, νP=O, νP—N—H, νP—O—C, and νP—Cl absorption bands which are summarized in Table I, the ^{1}H n.m.r. spectra of (II_{a-g}) and (III_{a-e}) showed the characteristic proton signals, which are listed in Table II, the uv spectra showed the characteristic absorption band at 270–290 nm, characteristic for the phosphazane four-membered ring.[9]

Further insight concerning the structure of these products was gleaned from a

TABLE I

Characteristic frequencies of cyclodiphosphazane derivatives

No. of compounds	Stretching frequencies in cm^{-1} [10]						
	NH	C=O	P=O	P—N—H	P—O—C	P—Cl	OH
II_a	3060	1680	—	2600	1050	530	—
II_b	3100	1680	—	2600	1030	530	—
II_c	3300	1680	—	2600	1030	500	—
II_d	3200	1680	—	2600	1030	550	—
II_e	3200	1680	—	2600	1050	530	—
II_f	3300	1680	—	2600	1030	530	—
II_g	3200	1740	—	2550	1010	530	—
III_a	3200	1680	1250	2600	1050	510	—
III_b	3200	1680	1250	2550	1040	510	—
III_c	3400	1660	1225	2600	1020	530	—
III_d	3260	1660	1215	2600	1000	530	—
III_e	3400	1640	1235	2600	1010	500	—
IV	3200	1750	—	2600	—	530	3450
V	3300	1650	1260	2600	—	500	3500

TABLE II

Characteristic ^1H n.m.r. spectra of cyclodiphosphazane derivatives (II–V)

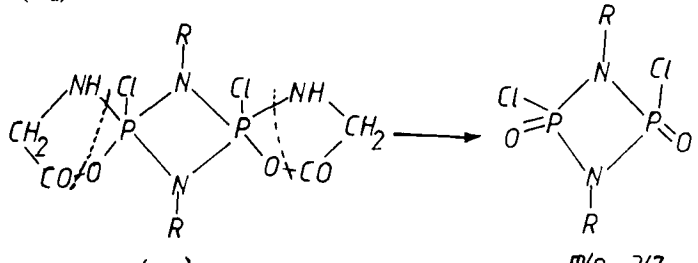
No. of compounds	Chemical shift δ in ppm. Ar.	OCH_3	CH_3	CH_2	CH	NH†	COOH†
II_a	7.0	—	—	2.3	—	8.0	—
II_b	7.2	—	—	2.3	—	7.4	—
II_c	7.0	3.8	—	2.3	—	8.6(br.)	—
II_d	6.9	3.8	—	2.5	—	7.9	—
II_e	7.0	—	2.0	2.5	—	7.9	—
II_f	7.5	—	2.0(s) & 1.1(d)	—	3.3(q)[a]	9.2(s)	—
II_g	7.5	—	—	2.4(t)	—	8.7	—
III_a	7.0	—	2.0	—	—	7.6	—
III_b	7.2	—	1.5(d)	—	3.3(q)[a]	6.5(s)	—
III_c	7.2	—	—	2.5(br.)	—	9.5	—
III_d	6.9	—	1.2	2.5(br.)	—	10.65	—
III_e	7.0	3.8	—	2.6(br.)	—	9.60	—
IV	6.9	3.8	1.4(d)	—	3.3(q)[a]	8.0	11.0
V	7.4	—	—	2.5	—	7.8	13.0

† Disappeared on addition of D_2O.

[a] q means quartlet with $J_{H-H} = 10$ Hz.

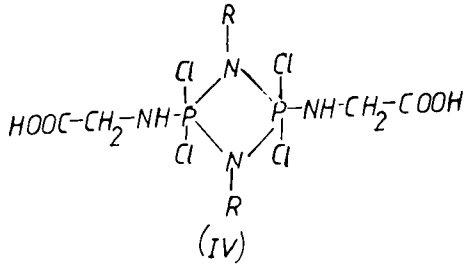
[b] The singlet at $\delta = 2.0$ ppm is characteristic for the methyl protons attached to the aromatic ring in compound (II_f), while the doublet at $\delta = 1.1$ ppm ($J_{H-H} = 7.0$ Hz) is characteristic for the methyl protons of the amino acid.

consideration of their mass spectra. Thus, the mass spectrum of compound (III_c) show the molecular peak at 418 m/e. While, the mass spectrum of (II_a) showed an intense peak at 347 m/e as the highest mass in the spectrum corresponding to $(\overset{+}{M} - 2 \times 57)$ according to the following proposed fragmentation pathway for compound (II_a).



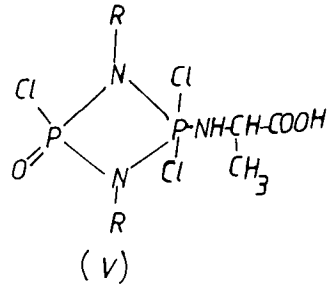
(II_a) m/e 347

The interaction of o-Chlorophenylhexachlorocyclodiphosphazane (I_b) with glycine and o-Anisidylhexachlorocyclodiphosphazane (I_d) with α-alanine led to the formation of products for which we propose structures (IV) and (V) respectively.



(IV)

R = C_6H_4—Cl-o



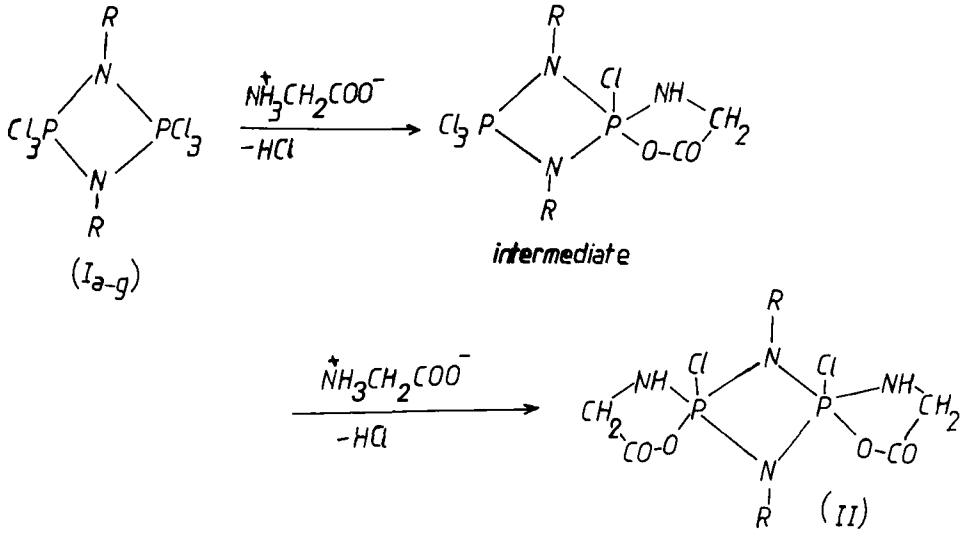
(V)

R = C_6H_4—OCH_3-o

The assignment of structure (IV) and (V) for the above compounds was based on: element analysis, uv spectra which demonstrated the presence of an absorption at 270–290 cm^{-1} corresponding to the phosphazane four-membered ring,[9] ir spectra which showed the characteristic νNH, νC=O, νP=O, νP—N—H and νP—Cl stretching vibrations (see Table I), the appearance of the terminal P=O group in (V) and its elemental analysis demonstrates that only one chlorine atom of the cyclodiphosphazane (I) has been replaced by an organic radical, the ^1H n.m.r. spectra of (IV) and (V) are in good agreement with the proposed structures (see Table II).

MECHANISTIC PROPOSAL

We propose that the interaction between the amino acid and the hexachlorocyclodiphosphazane (I) is a nucleophilic reaction, involving direct substitution of halogen atoms by a nucleophilic attack on phosphorus, according to the following reaction scheme;



The direction of the course of the reaction depends on the nature of the amino acid and the type of substituents present (R). It is expected, however, that if (R) group attached to nitrogen is bulky and the amino acid contain a bulky group such an interaction will not be facile due to steric factors and led to the formation of an intermediate such as compound (IV) and (V).

The formation of the terminal P=O group in some products may be due to decomposition of (II) or air oxidation of the intermediate products.

The possibility, also exists that the nongeminal replacement pattern observed with compound (IV) and (V) 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 also due to steric factors in which little difficulty is encountered in effecting complete replacement of halogens in spite of

TABLE III

Analytical data of the Aminocyclodiphosphazane derivatives (II–V)

No. of compounds	Reactants: Cyclodiphosphazane	Reactants: Amino acid	m.p.°C	Color	Yield %	Formula	Microanalysis found/calc: C%	H%	N%	P%	
II_a	I_a	glycine	260	brown	54	$C_{16}H_{16}N_4P_2O_4Cl_2$	41.65	3.47	12.15	13.52	
	(4.57 g; 0.01 mole)	(1.50 g; 0.02 mole)	210				41.60	3.50	12.20	13.45	
II_b	I_c	glycine	160	brown	35	$C_{16}H_{14}N_4P_2O_4Cl_4$	36.80	3.00	10.80	11.69	
	(5.26 g; 0.01 mole)	(1.50 g; 0.02 mole)	210				36.23	2.64	10.57	11.70	
II_c	I_c	glycine	215	yellow	35	$C_{18}H_{20}N_4P_2O_6Cl_2$	—	—	10.00	12.27	
	(4.85 g; 0.01 mole)	(1.50 g; 0.02 mole)	225						10.75	11.92	
II_d	I_g	glycine	220	brown	80	$C_{18}H_{20}N_4P_2O_6Cl_2$	—	—	10.50	11.68	
	(5.17 g;60.01 mole)	(1.5 g; 0.02 mole)							10.75	11.92	
II_e	I_e	glycine		brown	61	$C_{18}H_{20}N_4P_2O_4Cl_2$	—	—	11.00	12.63	
	(4.85 g; 0.01 mole)	(1.50 g; 0.02 mole)							11.45	12.68	
II_f	I_c	α-alanine		pale	39	$C_{20}H_{24}N_4P_2O_4Cl_2$	—	—	10.50	12.29	
	(4.85 g; 0.01 mole)	(1.78 g; 0.02 mole)		brown					10.83	11.99	
II_g	I_e	β-alanine		yellow	63	$C_{18}H_{20}N_4P_2O_4Cl_2$	—	—	11.00	12.63	
	(4.85 g; 0.01 mole)	(1.78 g; 0.02 mole)							10.75	12.68	
III_a	I_d	glycine	205	brown	32	$C_{16}H_{17}N_3P_2O_3CL_2$	45.20	4.00	10.00	15.17	—
	(4.85 g; 0.01 mole)	(1.50 g; 0.02 mole)					44.44	3.94	9.72	14.35	
III_b	I_a	α-alanine	220	pale	64	$C_{15}H_{15}N_3P_2O_3Cl_2$	43.80	3.70	10.45	14.19	—
	(4.57 g; 0.01 mole)	(1.78 g; 0.02 mole)		brown			43.06	3.59	10.05	14.83	
III_c	I_a	β-alanine	225	yellow	14	$C_{15}H_{15}N_3P_2O_3Cl_2$	—	—	—	14.78	—
	(4.57 g; 0.01 mole)	(1.78 g; 0.02 mole)								14.83	
III_d	I_e	β-alanine	220	yellow	7	$C_{17}H_{19}N_3P_2O_3Cl_2$				14.30	16.2
	(4.85 g; 0.01 mole)	(1.78 g; 0.02 mole)								13.90	15.9
III_e	I_f	β-alanine	225	yellow	16	$C_{17}H_{19}N_3P_2O_5Cl_2$	—	—	8.20	13.26	—
	(5.17g; 0.01 mole)	(1.78 g; 0.02 mole)							8.79	12.97	
IV	I_b	glycine	225	gray	11	$C_{16}H_{16}N_4P_2O_4Cl_6$	—	—	10.10	10.66	36.2
	(5.26 g; 0.01 mole)	(1.50 g; 0.02 mole)						—	9.28	10.28	35.3
V	I_f	α-alanine	190	pale	15	$C_{17}H_{20}N_3P_2O_5Cl_3$	—		7.50	12.32	21.3
	(5.17 g; 0.01 mole)	(1.78 g; 0.02 mole)		brown					8.16	12.05	20.7

the steric retardation which must be involved and only a so called intermediate as the above compounds would be possible.

EXPERIMENTAL

Microanalytical determinations were carried out by the microanalytical laboratory, Cairo University. Infrared spectra were recorded on a Unicam Sp 1200 spectrophotometer (KBr technique). Ultraviolet spectra were recorded on a Unicam Sp 8000 ultraviolet recording spectrophotometer. ^{1}H 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.[11-12] All the amino compounds used were B. D. H. reagentgrade products.

SYNTHESIS OF AMINOCYCLODIPHOSPHAZANE DERIVATIVES (II–V): GENERAL PROCEDURE

The solid amino acid (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 $\frac{1}{2}$ 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.

REFERENCES

1. E. H. M. Ibrahim and N. E. Amine, *Egypt J. Chem.*, **22,** No. 4, 307–312 (1979).
2. R. A. Shaw, *Pure Appl. Chem.*, **52,** 1083 (1980).
3. R. A. Shaw and M. Woods, *Inorg. Nucl. Chem. Lett.*, **17,** 181 (1981).
4. R. A. Shaw and M. Woods, *J. Chem. Soc., Dalton, Trans.*, 1980 (1977).
5. R. A. Shaw and M. Woods, *J. Chem. Soc. Dalton. Trans.*, 840 (1980).
6. S. S. Krishnamurthy and R. A. Shaw, *Inorg. Nucl. Chem. Lett.*, **13,** 407 (1977).
7. R. A. Shaw and M. Woods, *J. Chem. Soc. Dalton. Trans.*, 621 (1984).
8. I. M. Abd-Ellah, E. H. M. Ibrahim and A. N. El-Khazandar, accepted for publication in *Phosphorus and Sulfur J.* (1986).
9. M. Becke-Goehring and B. Bopple, *Z. Anorg. Chem.*, **322,** 239 (1963).
10. H. R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, New York, p. 436 (1972).
11. A. C. Chapman, N. L. Paddock and H. T. Searle, *J. Chem. Soc.*, 1825 (1961).
12. I. N. Zhmurova and A. V. Kirsanov, *Zh. Obsch. Khim.*, **32,** 2576 (1963).