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STUDIES ON CYCLODIPHOSPHAZANES: SOME REACTIONS OF CYCLODIPHOSPHAZANES WITH MALONIC ACID AND ITS DERIVATIVES

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Interaction of chlorocyclodiphosphazanes (I) with bifunctional reagents containing active methylene groups such as malonic acid, diethylmalonate and disodium malonate furnished geminal, non-geminal and ansa-cyclodiphosphazane derivatives of type (II-V). The structure of the isolated products were proposed on the basis of microanalytical data, infrared, ultraviolet and H nmr spectroscopic analysis.

Key words: Cyclodiphosphazanes, Malonic acid.

Introduction

The reaction of hexachlorocyclodiphosphazanes with mono-functional nucleophiles has been investigated in great detail [1-6]. Analogous reactions with bifunctional reagents have received much less attention.

Recently, Abd-Ellah *et. al.* [7-9] reported that the reaction of hexachlorocyclodiphosphazanes with bifunctional re-agents (such as urea, thiourea and amino acids) furnished geminal and non-germinal aminocyclodiphosphazanes.

The aim of the present investigation is to extend the scope of reaction of the prepared halophosphazanes to cover reactions with other bifunctional reagents such as malonic acid, diethyl malonate and disodium malonate.

Experimental

Microanalytical data 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 recording spectrophotometer and ^{1}H nmr. spectra were measured on a Varian EM-360L, 60 MHz spectrometer.

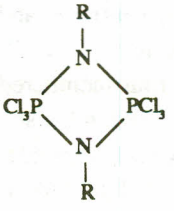
Preparation of compounds. The preparation and purification of hexachlorocyclodiphosphazanes (Ia-h) has been described elsewhere [10,11]. All compounds used were B.D.H. reagent grade products.

Synthesis of malonic acid and diethyl malonate cyclodiphosphazane derivatives (IIa-c) and (IIIa-e). The solid malonic acid or the liquid diethyl malonate (0.02 mole) was added in small protions to a well-stirred solution of the hexachlorocyclodiphosphazanes (I) (0.01 mole) in 70 ml benzene during 1/2 hour. After complete addition, the reaction mixture was heated under reflux for three hours. After completion of the reaction (HCl gas ceased to evolve), the reaction mixture was filtered hot. The solid obtained after cooling was filtered, washed several times with benzene, diethyl ether and dried in vacuo to gave the corresponding cyclodiphosphazane derivatives (IIa-c) and (IIIa-e). The data obtained are listed in Table 5.

Synthesis of malonatocyclodiphosphazane derivatives (IV and V). The solid disodium malonate (0.02 or 0.03 mole) was added in small portions to a well-stirred solution of hexachlorocyclodiphosphazanes (I) (0.01 mole in 70 ml benzene during 1/2 hour. After the complete addition, the reaction mixture was filtered while hot and the obtained solid was washed with ethanol, diethylether and dried in vacuo gave the corresponding dichlorobismalonatocyclodiphosphazanes (IIIac) and tris-malonatocyclodiphosphazane (Va-c). The data obtained are summarized in Table 5.

Results and Discussions

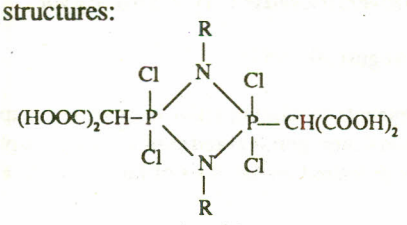
Various hexachlorocyclodiphosphazanes of type (Ia-g) have been prepared essentially by the methods of Champan [10] and Kirsanov[11] in which phosphorus pentachloride in cold dry benzene reacted with substituted anilines and o-, p-pyridines.



(Ia-g)

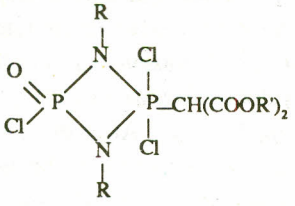
Compound No.	R
Ia	$-C_6H_5$
Ib	$-C_6H_4$-Cl-o
Ic	$-C_6H_4$-Cl-p
Id	$-C_6H_4-CH_3$-p
Ie	$-C_6H_4-OCH_3$-o
If	$-C_5H_4N$-0
Ig	$-C_5H_4N$-p

The direct reaction between halophosphazanes (I) and a bifunctional reagent such as malonic acid and diethyl malonate leads to cyclosubstitution at the phosphorus atom, by the elimination of HCl which involves the methylene proton and the chlorine atom on phosphorus. The cyclodiphosphazane derivatives (IIa-c) and (IIIa-e) have analyses compatible with the following structures:



(IIa-c)

Compound No.	R
IIa	$-C_6H_4$-Cl-p
IIb	$-C_6H_4-CH_3$-p
IIc	$-C_6H_4-OCH_3$-o



(IIIa-c)

Compd. No.	R	R'
IIIa	$-C_6H_4-CH_3$-p	$-C_2H_5$
IIIb	$-C_6H_4-OCH_3$-p	$-C_2H_5$
IIIc	$-C_5H_4N$-o	$-C_2H_5$
IIId	$-C_6H_5$	H
IIIe	$-C_6H_4-OCH_3$-o	

The structure of these compounds has been substantiated on the basis of their infrared and ultraviolet spectroscopic analysis. The expected band at 270-290 nm characteristic for the phosphazane four-membered ring [12] of the dimeric structure was observed in the spectra (Fig. 1). The infrared spectra of these products showed the characteristic absorption bands which are listed in Table 1.

^{1}H nmr spectra of the isolated compounds (II) and (III) showed the characteristic proton signals which are listed in Table 2.

On the other hand, the interaction of hexachlorocyclodiphosphazanes (I) with disodium malonate leads to the formation of products for which the tricyclic structure (IVa-c) and the ansa-type structure (Va-c) are proposed.

The assignment of structures (IV) and (V) for the above compounds was based on element analysis (Table 5), uv spectra (which demonstrated the presence of the four-

Table 1. Characteristic Infrared Stretching Vibrations of Cyclodiphosphazane Derivatives (IIa-c) and (IIIa-e).

Compound No.	Stretching frequencies (cm)				
	P-N	P-Cl	P=O	C=O	OH
IIa	1100	490	—	—	3500
IIb	1030	490	—	1740	—
IIc	1100	510	—	1760	3400
IIIa	1010	—	—	1760	—
IIIb	1060	510	1200	1760	—
IIIc	1135	520	1260	—	—
IIId	1060	520	1230	—	3460
IIIe	1020	470	1260	1640	—

Table 2. Characteristic ^{1}HNMR Spectra of Cyclodiphosphazane Derivatives (II) and (III).

Compound No.	Chemical shift (δ) in ppm				
	Aromatic	CH	OCH_3	CH_3	COOH
IIa	7.3	6.8	—	—	11.0
IIb	7.4	6.8	—	—	11.0
IIc	7.3	6.8	3.7	—	11.5
IIIa	7.2	—	—	0.7	—
IIIc	7.2	6.9	—	—	—
IIId	7.5	6.6	—	—	11.0

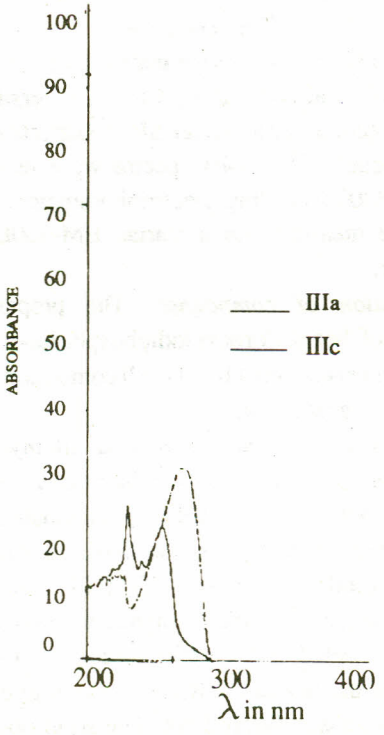
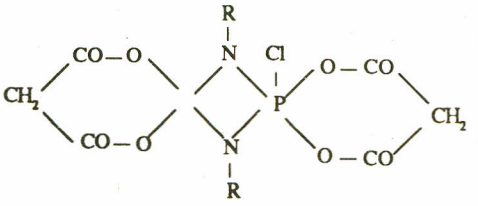
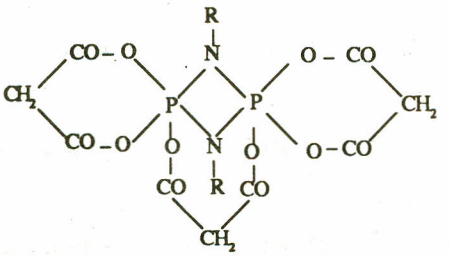


Fig. 1. Ultraviolat spectra of compounds IIIa,c



(IVa-c)

Compound No	R
IVa	$-C_6H_5$
IVb	$-C_6H_4-CH_3$-p
IVc	$-C_6H_4-OCH_3$-o



(Va-c)

Compound No	R
Va	$-C_6H_5$
Vb	$-C_6H_4-CH_3$-p
Vc	$-C_6H_4-OCH_3$-p

membered ring) (Fig. 2), ir spectra (which showed the characteristic υ C=O stretching vibration at 1650 cm^{-1}, υ P-Cl stretching vibration at 510 cm^{-1}) for compound (IV), and υ P-O-C stretching vibration at 1050 cm^{-1}. These data are listed in Table 3. Finally, the ^1H nmr spectra showed the characteristic proton signals which are summarized in Table 4.

TABLE 3. CHARACTERISTIC INFRARED STRETCHING VIBRATION OF CYCLODIPHOSPHAZANE DERIVATIVES (IV) AND (V).

Compound No.	Stretching frequencies (cm^{-1})			
	υP-N	υP-Cl	υP-O-C	υC=O
IVa	1120	510	1030	1660
IVa	1110	530	1050	1650
IVc	1120	520	1010	1650
Vb	1020	—	1050	1700
Vc	1120	—	1020	1760

TABLE 4. CHARACTERISTIC ^1H NMR SPECTRAOFCYCLODIPHOSPHAZANE DERIVATIVES (IV) AND (V).

Compound No.	Chemical shift (δ) in ppm				
	Aromatic	CH	OCH_3	CH_3	CH_2
IVb	7.1	6.4	—	1.0	3.1
IVc	7.1	6.7	4.0	—	3.1
Va	7.1	6.6	—	—	3.1
Vb	7.4	6.9	—	1.7	3.3

TABLE 5. ANALYTICAL DATA OF CYCLODIPHOSPHAZANE DERIVATIVES (II-V).

Compd. No.	Reactants		MP °C	Colour	Yield	Formula	Microanalysis Found/Calcd	
	Cyclodiphos-phazane (I)	Malonic acid or its derivatives					%N	%P
IIa	Ic 5.3g 0.01 mole	Malonic acid 2.1g, 0.02 mole	decom. at 80	Brownish orange	2.7g, 40%	$C_{18}H_{14}N_2P_2O_8Cl_6$	4.0/4.2	9.5/9.4
IIb	Id 4.9g, 0.01 mole	Malonic acid 2.1g, 0.02 mole	decomp. at 140	dark orange	2.3g, 37%	$C_{20}H_{20}H_2P_2O_8Cl_4$	4.8/4.5	10.2/10.0
IIc	Ic 5.2g, 0.01 mole	Malonic acid 2.1g, 0.02 mole	200	Pale orange	1.7g, 27%	$C_{20}H_{20}N_2P_2O_{10}Cl_4$	3.5/4.3	9.3/9.5
IIIa	Id 4.85g, 0.01 mole	Diethylmalonate 3 ml, 0.02 mole	196	White	1.2g, 22%	$C_{21}H_{25}N_2P_2O_5Cl_3$	6.2/5.1	10.7/11.2
IIIb	If 5.2g, 0.01 mole	Diethylmalonate 3 ml, 0.02 mole	217	Yellow	0.15g, 9%	$C_{21}H_{25}N_2P_2O_7Cl_3$	5.6/4.8	10.5/10.6
IIIc	Ig 4.59g, 0.01 mole	Diethylmalonate 3 ml, 0.02 mole	204	Yellow	3.0g, 57%	$C_{17}H_{19}N_4P_2O_5Cl_3$	-------	11.1/11.8

(Continued.....)

(Table 5 continued...)

IIId	Ia 4.6g, 0.01 mole	Malonic acid 2.1g, 0.02 mole	172	dark buff	0.2g, 3%	$C_{15}H_{13}N_2P_2O_5Cl_3$	6.2/6.0	12.7/13.2
IIIe	Ie 5.2g, 0.01 mole	Molanic acid 2.1g, 0.02 mole	179	pale brown	0.2g, 3%	$C_{17}H_{17}N_2P_2O_7Cl_3$	6.2/5.3	10.7/11.7
IVa	Ia 4.0g, 0.01 mole	Disodium malonate 3.0g, 0.02 mole	199	yellow	0.2g, 4%	$C_{18}H_{14}N_2P_2O_8Cl_2$	5.8/5.4	10.5/11.9
IVb	Ig 4.9g, 0.01 mole	Disodium malonate 3.0g, 0.02 mole	222	pale yellow	0.3g, 6%	$C_{20}H_{18}N_2P_2O_8Cl_2$	5.8/5.1	10.3/11.3
IVc	If 5.2g, 0.01 mole	Disodium malonate 3.0g, 0.02 mole	154	yellow	0.12g, 2%	$C_{20}H_{18}N_2P_2O_{10}Cl_2$	6.5/4.8	10.2/10.7
Va	Ia 4.4g, 0.01 mole	Disodium malonate 4.4g, 0.03 mole	197	yellow	0.2g, 4%	$C_{21}H_{16}N_2P_2O_{12}$	5.8/5.1	11.0/11.3
Vb	Id 4.9g, 0.01 mole	Disodium malonate 4.4g, 0.03 mole	202	yellow	0.3g, 5%	$C_{23}H_{20}N_2P_2O_{12}$	5.5/4.8	10.3/10.7
Vc	If 5.2g, 0.01 mole	Disodium malonate 4.4g, 0.03 mole	212	yellow	1.7g, 27%	$C_{23}H_{20}N_2P_2O_{14}$	5.3/4.6	9.8/10.2

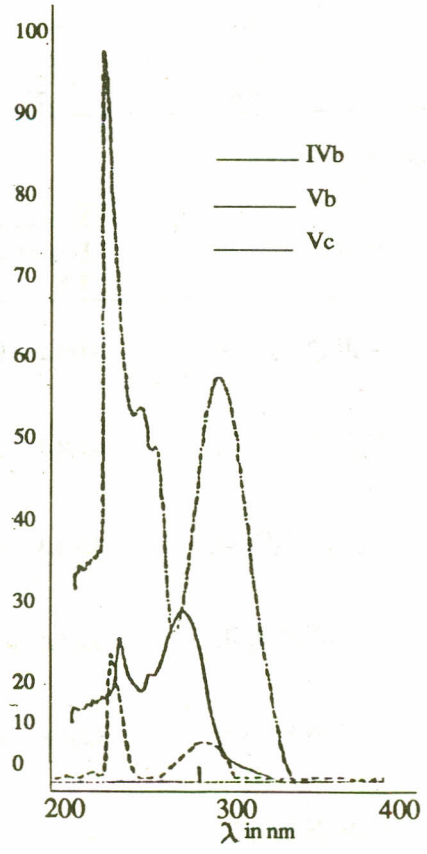
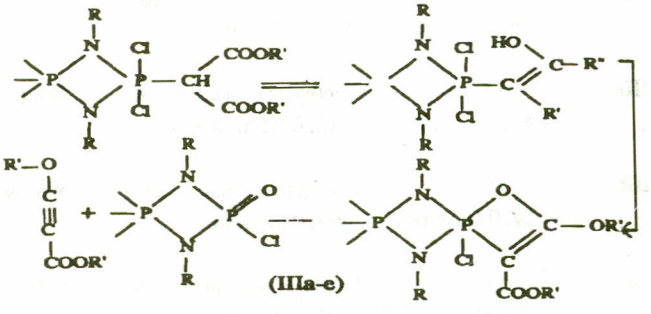


Fig. 2. Ultraviolet spectra of compounds IVb and Vb,c

The formation of cyclodiphosphazane derivatives of the type (II and III) by the reaction of halocyclodiphosphazane (I) and a methylene-containing compound (malonic acid and diethyl malonate) in an inert solvent (benzene) was proposed through the elimination of HCl gas from the methylene proton and the chlorine atom attached to phosphorus.

The presence of the carboxyl groups in compounds (IIa-c) and (IIId) was demonstrated by ^1H n.m.r. measurements which showed a signal at = 11.0 - 11.5 ppm. The stability of the $-CH(COOH)_2$ group was proofed also by the absence pf any CO_2 evolution during the reaction.

The formation of the terminal P=O groups in products (IIIa-e) demonstrates that the reaction in these products may proceed according to the following scheme:



R' = H or - C_2H_5

On the other hand, halocyclodiphosphazanes (I) react with disodium malonate to give a geminal cyclization leading to the formation of ansa-type cyclodiphosphazane derivatives (IVc) and (Va-c) through the elimination of NaCl.

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