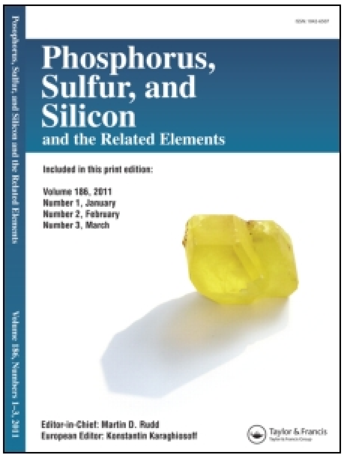

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES ON CYCLODIPHOSPHAZANES: SOME REACTIONS OF ACTIVE-METHYLENE GROUP CONTAINING COMPOUNDS

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To cite this Article Salman, A. A. , Abd-ellah, I. M. , El-khazandar, A. N. and El-Wahab, Z. H. Abd(1988) 'STUDIES ON CYCLODIPHOSPHAZANES: SOME REACTIONS OF ACTIVE-METHYLENE GROUP CONTAINING COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 40: 1, 9 — 17

To link to this Article: DOI: 10.1080/03086648808072887

URL: http://dx.doi.org/10.1080/03086648808072887

Phosphorus and Sulfur, 1988, Vol. 40, pp. 9–17
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STUDIES ON CYCLODIPHOSPHAZANES: SOME REACTIONS OF ACTIVE-METHYLENE GROUP CONTAINING COMPOUNDS

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(Received September 5, 1988)

Interaction of hexachlorocyclodiphosphazanes (**Ia–h**) with ethyl-acetoacetate, sodium ethylacetoacetate and benzyl chloride are described. The structure of the obtained cyclodipnosphazane derivatives (**II–IV**) 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.

Key words: hexachlorocyclodiphosphazanes; Cyclodiphosphazanes; Phosphonitrilic derivatives; Chlorophosphinimine dimers.

INTRODUCTION

The reaction of hexachlorocyclodiphosphazanes (**I**) with amino compounds has been investigated in great detail.[1–7] Recently, the authors showed that the reaction of hexachlorocyclodiphosphazanes (**I**) with bifunctional reagents (such as urea, thiourea and amino acids) furnished geminal and nongeminal aminocyclodiphosphazanes).[8,9,10]

RESULTS AND CONCLUSIONS

In the present investigation, ethylacetoacetate (or its sodium salt), and benzyl chloride were allowed to react with halophosph(V)azanes (**Ia–h**) in inert solvents such as benzene to give a substitution product at the phosphorus atoms. The analytical data suggest structure (**IIa–c**), (**IIIa–i**) and (**IVa–e**) for these materials.

The assignment of the proposed structures (**IIa–c**), (**IIIa–i**) and (**IVa–e**) was based on elemental analysis. Infrared spectra of these compounds showed characteristic $\nu_{P=C}$, $\nu_{P=O}$, ν_{P-N}, $\nu_{C=O}$ and ν_{P-Cl} absorption bands which are summarized in Table I, the ^{1}H n.m.r. spectra of (**IIa**, **c**), (**IIIa**, **c–f**, **i**) and (**IVa–d**) showed the characteristic proton signals, which are listed in Table II, the uv spectra showed the characteristic band at 270 nm for the phosphazane four-membered ring[11] (Figures 1 & 2).

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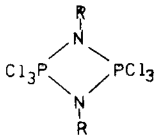
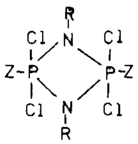
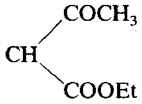


(Ia-h)

No. of compound	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_6H_4—OCH_3—p
Ig	2-pyridyl
Ih	4-pyridyl



(IIa–c)

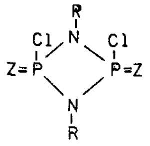
No. of compound	R	Z
IIa	C_6H_4—Cl—p	 $CH(COCH_3)(COOEt)$
IIb	2-pyridyl	”
IIc	4-pyridyl	”

Further insight concerning the structure of these products was gleaned from a consideration of their mass spectra. Thus, the mass spectrum of compound (**IIIa**), (**IIIc**) and (**IIIf**) showed the following masses at 422 m/e, 491 m/e and 482 m/e respectively as the highest mass in the spectrum corresponding to M^+—2 Cl_2.

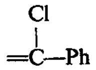
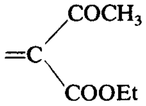
It should be noted that the parent peak of all these compounds does not appear in the spectra, presumably owing to the fact that these ions are meta stable and hence do not appear.

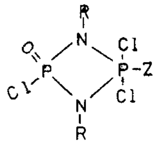
Mechanistic Proposal

We proposed that the direct interaction between a halophosphazane (**I**) and an active methylene group containing compounds or its sodium salt was found to be rapid. The degree of substitution and the pattern of halogen replacement was found to be sensitive to the steric characteristic of the reactants. Thus, the reaction between chlorocyclodiphosphazanes (**I**) and the active methylene group

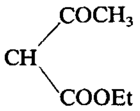


(IIIa–i)

No. of compound	R	Z
IIIa	C_6H_5	 $=C(Cl)—Ph$
IIIb	$C_6H_4—Cl—o$	"
IIIc	$C_6H_4—CL—p$	"
IIId	$C_6H_4—CH_3—p$	"
IIIe	$C_6H_4—OCH_3—o$	"
IIIf	$C_6H_4—OCH_3—p$	"
IIIg	C_6H_5	 $=C(COCH_3)(COOEt)$
IIIh	$C_6H_4—OCH_3—p$	"
IIIi	2-pyridyl	"



(IVa–e)

No. of compound	R	Z
IVa	C_6H_5	 $CH(COCH_3)(COOEt)$
IVb	$C_6H_4—CH_3—p$	"
IVc	$C_6H_4—OCH_3—o$	"
IVd	$C_6H_4—OCH_3—p$	"
IVe	4-pyridyl	"

containing compounds or its sodium salt led to the formation of cyclodiphosphazane derivatives (**II–IV**), through the elimination of HCl gas or NaCl:

The direction and rate of the reaction depend on the nature of the active methylene group compound (R′ or R″) and also on the type of substituents present (R). It is evident that direct elimination of HCL or NaCl leads eventually to the proposed cyclodiphosphazane derivatives (**II**) and (**III**) and the oxycyclic structure (**IV**). When R′ and R″ groups are electron-withdrawing groups, this makes the CH proton in compound (**II**) more acidic and facilitates the removal of the methine proton in compounds (**II**) as HCl to give eventually compounds of the type (**III**).

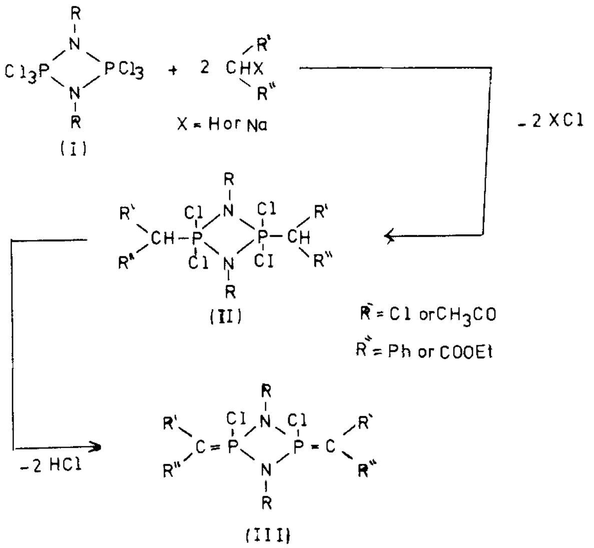


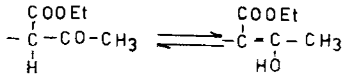
TABLE I

Characteristic infrared stretching vibrations of cyclodiphosph(v)azane derivatives (**IIa–c**), (**IIIa–i**) and (**IVa–e**)

No. of compound	Stretching frequencies cm^{-1}						
	ν_{P-N}	ν_{P-Cl}	$\nu_{C=O}$	ν_{C-H}	$\omega_{P=C}$	ν_{O-H-}[c]	$\nu_{P=O}$
IIa	1090	500	—	—	—	—	—
IIb	1010	550	1670	—	—	3420	—
IIc	(1000)[b]	(490)[b]	(1660)[b]	—	—	(3420)[b]	—
IIIa	1080	470	—	3060	930	—	—
IIIb	1090	440	—	—	1000	—	—
IIIc	1090	430	—	3100	950	—	—
IIId	1110	450	—	3020	945	—	—
IIIe	1110	465	—	—	950	—	—
IIIf	1110	490	—	—	1000	—	—
IIIg	(1050)[b]	(470)[b]	—	(2860)[b]	(940)[b]	(3440)[b]	—
IIIh	(1120)[b]	—	(1670)[b]	(2860)[b]	(940)[b]	—	—
IIIi	(1000)[b]	(500)[b]	—	—	(940)[b]	(3400)[b]	—
IVa	1020	510	—	—	—	—	1245
IVb	1010	510	—	2880	—	—	1200
	(1050)[b]	(520)[b]		(2880)[b]			(1250)[b]
IVc	1050	510	—	—	—	—	1280
	(1070)[b]	(510)[b]	—	(2840)[b]	—	(3440)[b]	(1260)[b]
IVd	1050	500	1760	2900	—	3400	1260
IVe	1120	—	1760	—	—	—	1270

[b] Infrared data of the compound which obtained from sodium ethylacetoacetate and chlorocyclodiphosphazane (**I**).

[c] The appearance of OH absorption peak in the infrared spectra and also in ^{1}H n.m.r. spectra may be due to some keto-enol toutomerism of the ethylacetoacetate radical:



$$-\underset{\displaystyle H}{\overset{\displaystyle COOEt}{C}}-CO-CH_3 \rightleftharpoons -\overset{\displaystyle COOEt}{C}=\underset{\displaystyle HO}{C}-CH_3$$

TABLE II

Characteristic ^{1}H n.m.r. spectra of cyclodiophosphazane derivatives (II, III and IV)

No. of Compound	Chemical shift (δ) in ppm.						
	CH	$COCH_3$	OCH_3	CH_2	CH_3	Aromatic	OH—[c]
IIa	—	2.2	—	3.2	1.0	7.2	13.44
IIc	—	(2.4)[b]	—	(3.2)[b]	0.9	(6.8)[b]	(14.0)[b]
IIIa	—	—	—	—	—	7.3	—
IIIc	—	—	—	—	—	7.2	—
IIId	—	—	—	—	3.2	7.2	—
IIIe	—	—	3.8	—	—	7.0	—
IIIf	—	—	3.8	—	—	7.2	—
IIIi	—	(2.7)[b]	—	2.5	1.3	(7.2)[b]	—
IVa	—	2.2	—	3.3	1.0	7.3	13.0
IVb	—	2.2	—	3.2	0.7	7.3	13.8
IVc	6.8	2.6	3.8	3.7	0.8	7.3	—
IVd	—	2.2	4.0	3.8	1.3	7.4	13.0

[b] Compounds obtained from sodium ethylacetoacetate and chlorocyclodiphosphazane (I).

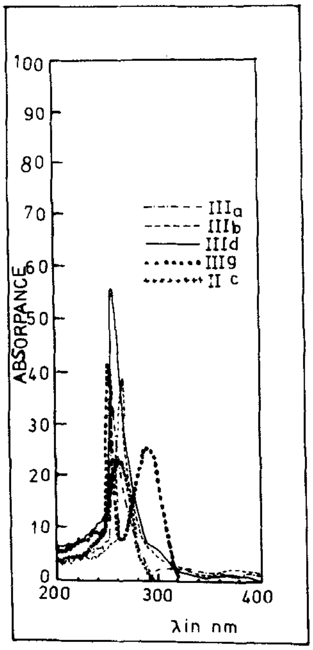


FIGURE 1 uv spectra of compds II–III.

TABLE III

Analytical Data of cyclodiphosph(V)azane Derivatives (**IIa–c**, **IIIa–i** and **IVa–e**)

No. of Compd.	Reactants		M.P. °C	Colour	Solvent of crystallization	Yield %	Formula	Microanalysis Found/Calcd.	
	Cyclodiphos-phazene (I)	CH_2- group Compd.						%N	%P
IIa	Ic (5.3 g; 0.01 mole)	Ethylacetoacetate (2.5 ml; 0.02 mole)	184	White	Benzene/ diethyl ether	(2.9 g, 21%)	$C_{24}H_{26}N_2P_2O_6Cl_4$	—	8.1/8.7
IIb	Ig (4.3 g, 0.01 mole)	Ethylacetoacetate (2.5 ml, 0.02 mole)	164	Buff	Benzene/ diethyl ether	(2.7 g, 42%)	$C_{22}H_{26}N_4P_2O_6Cl_4$	—	9.6/9.6
IIc	Ih (4.3 g, 0.01 mole)	Sodium ethyl-acetoacetate[a]	152	Buff	Benzene/ diethyl ether	(2.6 g, 40%)	$C_{22}H_{26}N_4P_2O_6Cl_4$	—	9.2/9.6
IIIa	Ia 9.1 g, 0.02 mole)	Benzyl chloride 50 ml in excess	148	Pale Yellow	Benzyl chloride/ diethyl ether	(3.1 g, 28%)	$C_{26}H_{20}N_2P_2Cl_4$	5.7/5.0	12.1/11.0
IIIb	Ib (5.3 g, 0.01 mole)	Benzyl chloride 50 ml in excess	215	Yellow	Benzyl chlroide/ diethyl ether	(1.0 g, 13.7%)	$C_{26}H_{18}N_2P_2Cl_6$	5.0/4.4	8.8/9.8
IIIc	Ic (10.6 g, 0.02 mole)	Benzyl chloride 50 ml in excess	153	Pale Yellow	Benzyl chloride/ diethyl ether	(1.7 g, 12%)	$C_{26}H_{18}N_2P_2Cl_6$	4.6/4.4	9.8/9.8
IIId	Id (9.7 g, 0.02 mole)	Benzyl chloride 50 ml in excess	179	Pale Yellow	Benzyl chloride/ diethyl ether	(1.8 g, 18.4%)	$C_{28}H_{24}N_2P_2Cl_4$	4.7/4.7	11.4/10.5
IIIe	Ie (10.4 g, 0.02 mole)	Benzyl chloride 50 ml in excess	175	Pale Yellow	Benzyl chloride/ diethyl ether	(2.0 g, 21%)	$C_{28}H_{24}N_2P_2O_2CL_4$	—	9.6/9.9
IIIf	If (10.4 g, 0.02 mole)	Benzyl chlroide 50 ml in excess	198	Pale Yellow	Benzyl chloride/ diethyl ether	(4.0 g, 42%)	$C_{28}H_{24}N_2P_2O_2Cl_4$	4.1/4.5	10.4/9.9

IIIg	Ia (4.6 g, 0.01 mole)	Sodium ethylaceto-acetate[a] (0.02 mole)	176	Pale Yellow	Benzene/ diethyl ether	(0.63 g, 10%)	$0_{24}H_{26}N_2P_2O_6Cl_5$	5.5/4.9	10.8/10.9
IIIh	If (5.2 g, 0.01 mole)	Sodium ethyl-acetoacetate[a]	194	Buff	Benzene/ diethyl ether	(0.3 g, 4%)	$C_{26}H_{30}N_2P_2O_8Cl_2$	3.7/4.4	9.8/9.8
IIIi	Ig (4.6 g, 0.01 mole)	Sodium ethyl-acetoacetate[a]	216	Buff	Benzene/ diethyl ether	(3.3 g, 56%)	$C_{22}H_{24}N_4P_2O_6Cl_2$	—	10.9/10.8
IVa	Ia (9.1 g, 0.02 mole)	Ethylacetoacetate (5 ml, 0.04 mole)	182–184	White	Benzene/ diethyl ether	(2.17 g, 21%)	$C_{18}H_{19}N_2P_2O_4Cl_3$	6.1/5.7	12.7/12.5
IVb	Id (4.9 g, 0.01 mole)	Ethylacetoacetate (2.5 ml, 0.02 mole)	191–194	Yellow	Benzene/ deithyl ether	(1.7 g, 32%)	$C_{20}H_{23}N_2P_2O_4Cl_3$	5.8/5.4	12.2/11.8
IVc	Ie (5.2 g, 0.01 mole)	Ethylacetoacetate (2.5 ml, 0.02 mole)	178	Yellow	Benzene/ diethyl ether	(1.3 g, 22%)	$C_{20}H_{23}N_2P_2O_6Cl_3$	4.6/5.0	11.3/11.2
IVd	If (5.2 g, 0.01 mole)	Ethylacetoacetate (2.5 ml, 0.02 mole)	215	Yellow	Benzene/ diethyl ether	(1.2 g, 7%)	$C_{20}H_{23}N_2P_2O_6Cl_3$	5.4/5.0	11.2/11.2
IVe	Ih (4.3 g, 0.01 mole)	Ethylacetoacetate (2.5 ml, 0.02 mole)	150	Yellow	Benzene/ diethyl ether	(3.8 g, 20%)	$C_{16}H_{17}N_4P_2O_4Cl_3$	—	12.9/12.5
IVb	Id (4.9 g, 0.01 mole)	Sodium ethyl-acetoacetate[a]	194	Yellow	Ethanol	(1.6 g, 14%)	$C_{20}H_{23}N_2P_2O_4Cl_3$	—	11.5/11.8
IVc	Ie (5.2 g, 0.01 mole)	Sodium ethyl-acetoacetate	177	Yellow	Ethanol	(1.2 g, 21%)	$C_{20}H_{23}N_2P_2O_6Cl_3$	—	10.5/10.2
IVd	If (5.2 g, 0.01 mole)	Sodium ethyl-acetoacetate	215	Yellow	Ethanol	(0.3 g, 2%)	$C_{20}H_{23}N_2P_2O_6Cl_3$	5.5/5.0	—

[a] Sodium ethylacetoacetate was prepared from ethylacetoacetate (2.5 ml, 0.02 mole) and 0.46 g sodiummetal in 30 ml benzene. The solution was heated under reflux for half hour.

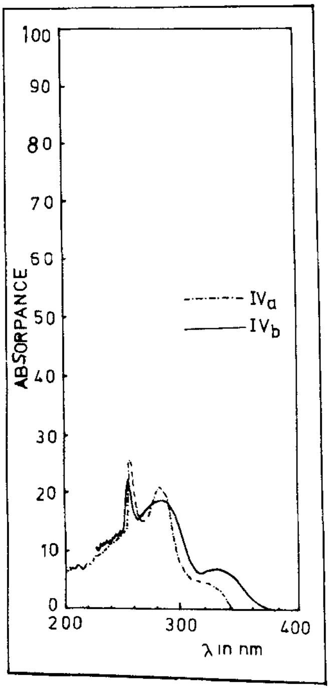
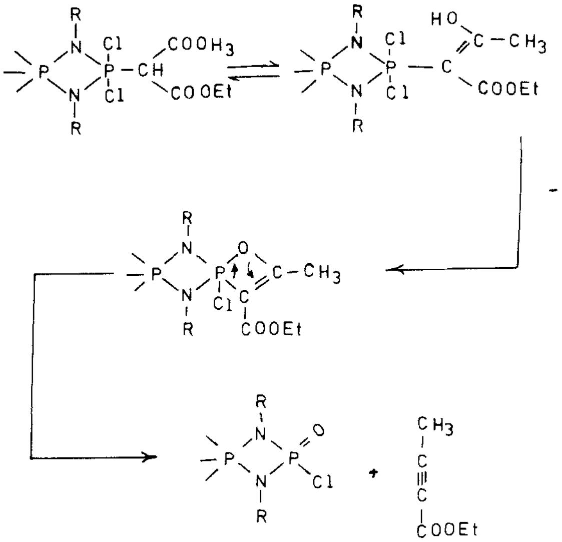


FIGURE 2 uv spectra of compds IV.

The formation of the terminal P═O group in some products demonstrates that the reaction in these products go according to the following reaction scheme to give the partially substituted products as follows:



The possibility, also exists that the nongeminal replacement pattern observed with compound (**IV**) may results from electron supply from substituent to phosphorus, which lowers the reactivity of Cl—P—C-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 the steric retardation which must be involved and only a so called intermediate as the above compounds would be possible.

EXPERIMENTAL

Micoranalytical 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 MH$_z$ 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 (**Ia–h**) has been described previously.[12,13] All compounds used were B.D.H. reagent grade products.

Synthesis of cyclodiphosphazane derivatives (II–IV):

preparation of ethylacetoacetate derivatives:

A solution of ethylacetoacetate (or a suspension of sodium ethylacetoacetate) (0.02 mole) was added dropwise to a cold well-stirred solution of hexachlorocyclodiphosphazane (**I**) (0.01 mole) in 100 ml benzene during 1/2 hour. After the addition was completed, the reaction mixture was heated under reflux for three hours. After the completetion of the reaction (HCl gas ceased to evolve or NaCl precipitated), the reaction mixture was filtered while hot. The solid obtained after cooling was filtered, washed several times with benzene, diethylether and dried in vacuo to give the corresponding cyclodiphosphazane derivatives (**IIa–c**, **IIIg–i** and **IVa–e**) (Table III).

Preparation of benzyl chloride derivatives

The hexachlorocyclodiphosphazane (**I**) (0.02 mole) was added to excess benzyl chloride (50 ml) in a round-bottom flask fitted with a condenser. The reaction mixture was heated under reflux for ten hours. During this time, the hexachlorocyclodiphosphazane (**I**) was dissolved with the evolution of HCl gas. After completion of the reaction (HCl gas ceased to evolve), the reaction mixture was cooled to room temperature and the formed solid was filtered, washed several times with diethyl ether, then dried in vacuo to give the corresponding cyclodiphosphazane derivatives (**IIIa–f**) (Table III).

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