

STUDIES IN CYCLODIPHOSPH(V) AZANES:

Some Relations of Hexachlorocyclodiphosph(V) Azanes (I) with Ethylenediamine and *o*-Phenylenediamine

I.M. Abd-Ellah and A.N. El-Khazandar

Chemistry Department, Al-Azhar University, Nasr City, Cairo, Egypt

(Received December 11, 1986; revised June 19, 1988)

Interaction of diaryl-hexachlorocyclodiphosph(V)-azanes(Ia-g) with ethylenediamine and *o*-phenylenediamine are described. The structure of the obtained aminocyclodiphosph(V) azanes (IIa-c and IIIa-f) were proposed on the basis of microanalytical data, IR, UV, $^1\text{Hnmr}$ and mass spectra.

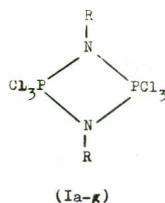
Keywords: Cyclodiphosph(V) azanes, Reactions, Hexachlorocyclodiphosph, Ethylenediamine.

INTRODUCTION

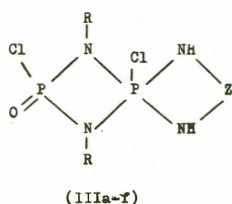
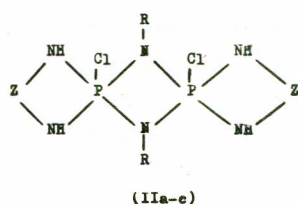
The reaction of hexachlorocyclodiphosph(V)azanes(I) with amino compounds have been investigated in great detail [1-6] analogous reactions with diamines have been received much less attention.

We have recently [7] shown that the reactions of hexachlorocyclodiphosph(V)azanes (I) with bifunctional reagents furnished geminal and nongeminal aminocyclodiphosphazanes.

In the present investigation, ethylenediamine and *o*-phenylenediamine reacted with halophosph(V)azanes (Ia-g), in acetonitrile to give a cyclosubstitution at phosphorus atoms. The analytical data suggests structure (IIa-c) and (IIIa-f) for these compounds.



Ia; R = C_6H_5
 Ib; R = *o*- ClC_6H_4
 Ic; R = *p*- ClC_6H_4
 Id; R = *o*- $\text{CH}_3\text{C}_6\text{H}_4$
 Ie; R = *p*- $\text{CH}_3\text{C}_6\text{H}_4$
 If; R = *o*- $\text{CH}_3\text{CC}_6\text{H}_4$
 Ig; R = *p*- $\text{CH}_3\text{CC}_6\text{H}_4$



No. of Compd.	R	Z
II _a	C_6H_5	$-\text{CH}_2-\text{CH}_2-$
II _b	<i>o</i> - ClC_6H_4	
II _c	<i>o</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	
III _a	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	$-\text{CH}_2-\text{CH}_2-$
III _b	C_6H_5	
III _c	<i>o</i> - ClC_6H_4	
III _d	<i>p</i> - ClC_6H_4	"
III _e	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	"
III _f	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	"

The assignment of the proposed structures (IIa-c) and (IIIa-f) was based on elemental analysis. The infrared spectra of these compounds showed the characteristic δNH , $\delta\text{P-NH}$, $\delta\text{P-Cl}$ and $\delta\text{C-H}$ bands (Table 1). The $^1\text{Hnmr}$ spectra of (IIa-c) and (IIIa-f) showed the characteristic proton signals, (Table 2) and the uv spectra showed the characteristic absorption band at 270-290 nm., for the phosphazane four-membered rings [8] (Fig. 1).

Mass spectrometric measurements for compounds (IIIb) and (IIIc) showed metastable peaks at m/z 344 and at m/z 413 respectively due to the loss of $\text{C}_6\text{H}_5\text{NH}_2$ ($M-93$) and at m/z 360 and m/z 429 corresponding to the loss of C_6H_5 radical ($M\pm 77$) as the highest masses in the spectrum. It should be noted that the precursor peak does not appear, presumably due to the fact that these being metastable ions and hence do not appear in the spectrum.

Table 1. Characteristic frequencies of cyclodiphosphazane derivatives.

No. of Compd.	Stretching frequencies in cm^{-1} (11)				
	NH	P-N-H	P=O	P-Cl	C-H
II _a	3400	2600	—	490	2880
II _b	3400	2600	—	500	2900
II _c	3200	2550	—	510	2900
III _a	3350	2650	1250	550	2900
III _b	3400	2600	1240	540	2880
III _c	3200	2600	1280	510	2900
III _d	3400	2600	1250	530	2850
III _e	3400	2600	1250	530	2870
III _f	3400	2600	1250	530	2900

Table 2. Characteristic ^1H nmr spectra of cyclodiphosphazane derivatives.

No. of Compd.	Chemical shifts δ in ppm.				
	Ar	OCH_3	CH_3	CH_2	NH
II _a	7.5	—	—	2.5	8.5
II _b	7.6	—	—	3.5	8.5
II _c	7.5	3.9	—	—	8.5
III _a	7.3	3.8	—	2.8	8.3
III _b	7.2	—	—	—	8.7
III _d	7.2	—	—	—	8.4
III _e	7.3	—	2.3	—	9.0
III _f	6.9	3.8	—	—	8.9

**disappeared on the addition of H_2O .

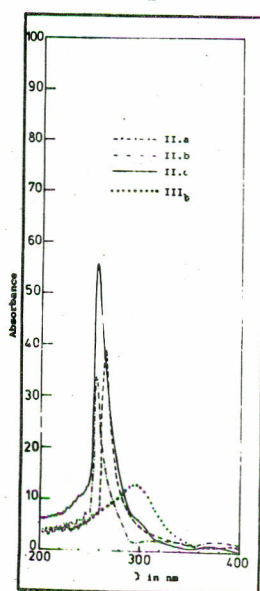


Fig. 1

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. ^1H nmr 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 direct inlet system.

Preparation of compounds. The preparation and purification of hexachlorocyclodiphosph(V)-azanes (Ia-g) are already described (9-10). All the amino compounds used were B.D.H. reagent grade products.

Synthesis of aminocyclodiphosph(V)azanes(II-III). A solution of ethylenediamine (0.026 mole) or solid *o*-phenylenediamine (0.02 mole) was added to a well stirred nylenediamine (0.02 mole) was added to a well stirred solution of the hexachlorocyclodiphosph(V)azanes (I) (0.01 mole) in 100 ml acetonitrile during $\frac{1}{2}$ hr. After the addition was complete, the reaction mixture was heated under reflux for three hours. The solid thus formed 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. The filtrate was left to cool and the solid obtained was filtered, washed several times with acetonitrile, diethylether and dried in vacuo. It gave:

IIa (0.87 g.; 20.0 % yield) as white powder m.p. 185-187°C. Anal. (Found: C, 43.6; H, 5.6; N, 20.0; P, 13.7 for $\text{C}_{16}\text{H}_{22}\text{N}_6\text{P}_2\text{Cl}_2$ req.: C, 44.5; H, 5.1; N, 9.5; P, 14.4%).

IIb (1.0 g.; 20.0% yield) as white crystals m.p. 280°C. Anal. (Found: N, 17.0; P, 11.4 for $\text{C}_{16}\text{H}_{20}\text{N}_6\text{P}_2\text{Cl}_4$ req.: N, 16.8; P, 12.4 %).

IIc (1.0 g.; 17.0 % yield) as pale violet powder m.p. 195°C. Anal. (Found: N, 15.0; P, 10.6 for $\text{C}_{26}\text{H}_{26}\text{N}_6\text{P}_2\text{O}_2\text{Cl}_2$ req.: n, 14.3; P, 10.5 %).

IIIa (1.8 g.; 39.0 % yield) as white powder m.p. 185°C. Anal. (Found: M, 13.0; P, 14.4 for $\text{C}_{16}\text{H}_{20}\text{N}_4\text{P}_2\text{O}_3\text{Cl}_2$ req.: N, 12.5; P, 13.8 %).

IIIb (0.7 g.; 16.0 % yield) as pale violet powder m.p. 150°C. Anal. (Found: N, 13.0; P, 14.1 for $\text{C}_{18}\text{H}_{16}\text{N}_4\text{P}_2\text{OCl}_2$ req.: N, 12.8; P, 14.2 %).

IIIc (2.5 g.; 49 % yield) as pale violet powder m.p. 205°C. Anal. (Found: N, 10.8; P, 11.9 for $\text{C}_{18}\text{H}_{14}\text{N}_4\text{P}_2\text{OCl}_4$ req.: N, 11.1; P, 12.3 %).

IIId (1.0 g.; 20.0 % yield) as pale violet powder m.p. 260°C. Anal. (Found: N, 11.5; P, 12.3 for $\text{C}_{18}\text{H}_{14}\text{N}_4\text{P}_2\text{OCl}_4$ req.: N, 11.1; P, 12.3%).

IIIe (0.7 g.; 16 % yield) as violet powder m.p. 195°C (decomp.) Anal. (Found: N, 11.6; P, 13.8 for $C_{20}H_{20}N_4P_2OCl_2$ req.: N, 12.1; P, 13.3 %).

IIIf (0.4 g.; 10 % yield) as pale violet powder m.p. 250°C. Anal. (Found: N, 11.0; P, 13.0 for $C_{20}H_{20}N_4P_2O_3Cl_2$ req.: N, 11.3; P, 12.5 %).

REFERENCES

1. E.H. Ibrahim and N.E. Amine, *Egypt J. Chem.*, **22**, 307 (1979).
2. R.A. Shaw, *Pure and 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.*, 840 (1980).
5. S.S. Krishnamurthy and R.A. Shaw, *Inorg. Nucl. Chem. Lett.*, **13**, 407 (1977).
6. R.A. Shaw and M. Woods, *J. Chem. Soc., Dalton Trans.*, 621 (1984).
7. I.M. Abd-Elal, E.H.M. Ibrahim and A.N. El-Khazandar, *Phosph. and Sulf.* (in press).
8. M. Becke-Coehring and B. Beppe, *Z. Anorg. Chem.*, **322**, 239 (1963).
9. I.N. Zhmurova and A.V. Kirsanov, *Zh. Obsch. Khim.*, **32**, 2576 (1963).
10. A.C. Chapman, N.L. Paddock and H.T. Searle, *J. Chem. Soc.*, 1825 (1961).
11. H.R. Allock, *Phosphorus-Nitrogen Compounds* (Academic Press, New York, 1972), p. 436.