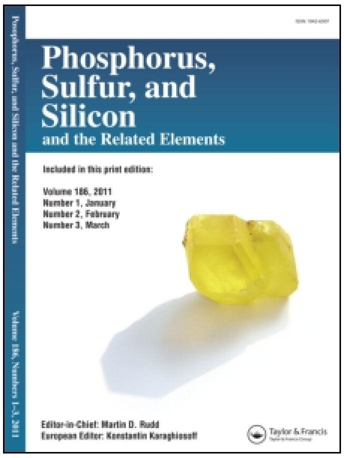

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MASS SPECTROMETRIC STUDIES ON SPIROCYCLIC DERIVATIVES OF CYCLODIPHOSPH(V)AZANES

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MASS SPECTROMETRIC STUDIES ON SPIROCYCLIC DERIVATIVES OF CYCLODIPHOSPH(V)AZANES

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The formation and subsequent fragmentation of spirocyclodiphosph(V)azanes (II-III) has been studied by mass spectrometry using the link-field scan technique and structural inferencies are drawn from these data. ^{31}P nmr measurements for compound (III) are also described.

INTRODUCTION

There is considerable current interest in compounds containing spiro and ansaorganic phosphorus rings;[1–2] Although the ammonolysis and aminolysis of some 1,3-diaryl-2,4-dithio-2,4-dichlorocyclodiphosph(V)azanes have been investigated in some detail,[3] little is known about the interaction of hexachlorocyclodiphosph(V)azanes with bifunctional reagents.[4]

The reaction of bifunctional reagents with cyclodiphosph(V)-azanes can give rise in principle to four types of structures: (i) spiro (both functional groups of reagent attached to the same phosphorus atom); (ii) ansa (the two functional groups attached to different phosphorus atoms in the same molecule); (iii) cross-linking (each functional group attached to different cyclodiphosph(V)azane rings) to give small oligomeric units or polymers; and (iv) only one functionality attached, whilst the other remains free. Spiro, ansa and cross-linking structures of phosphazenes are now well-studied synthetically, spectroscopically and crystallographically.[5–15]

In the present work, a series of dispirocyclodiphos(V)azanes (II–III) was isolated via the interaction between hexachlorocyclodiphosph(V)azanes (I) with urea and thiourea derivatives.

It was found that the interaction of hexachlorocyclodiphosph(V)azanes (I) with urea, thiourea and their phenyl derivatives furnished geminal and non-geminal aminocyclodiphosph(V)azanes (II–III)[4] (see scheme 1).

Further confirmation of the structural assignment of these products comes from mass spectrometric studies using the link-field scan technique. Thus, the mass spectrum of compound IIa showed a base peak at m/z 496 (97.3%) together, with peaks at m/z 583 (0.9%), 540 (0.1%), 498 (68.4%), 460 (0.1%), 315 (0.1%),

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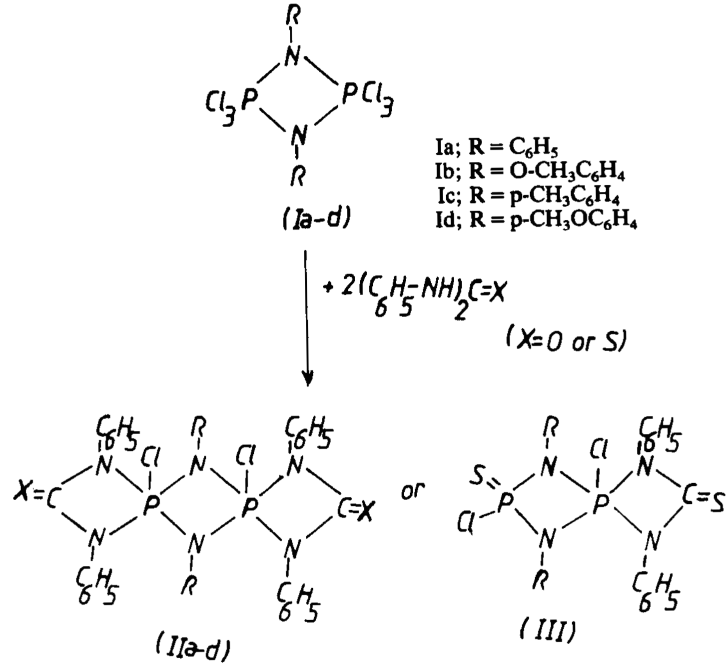
SCHEME 1 Geminal and non-geminal spirocyclodiphosph(V)azanes (II–III).



Ia; R = C_6H_5
Ib; R = O-$CH_3C_6H_4$
Ic; R = p-$CH_3C_6H_4$
Id; R = p-$CH_3OC_6H_4$

IIa; R = C_6H_5 ; X = 0
IIb; R = p-$CH_3C_6H_4$; X = S
IIc; R = p-$CH_3C_6H_4$; X = 0
IId; R = p-$CH_3OC_6H_4$; X = 0

194 (100%), 119 (76.2%) and 77 (53.2%) representing the various fragmentation patterns.

Application of the link-field scan on the mass number m/z 460 fragment showed two metastable transitions at m/z 498 and 518, indicating that the peaks at m/z 540 and 583 are precursor peaks of that product as given by the equation

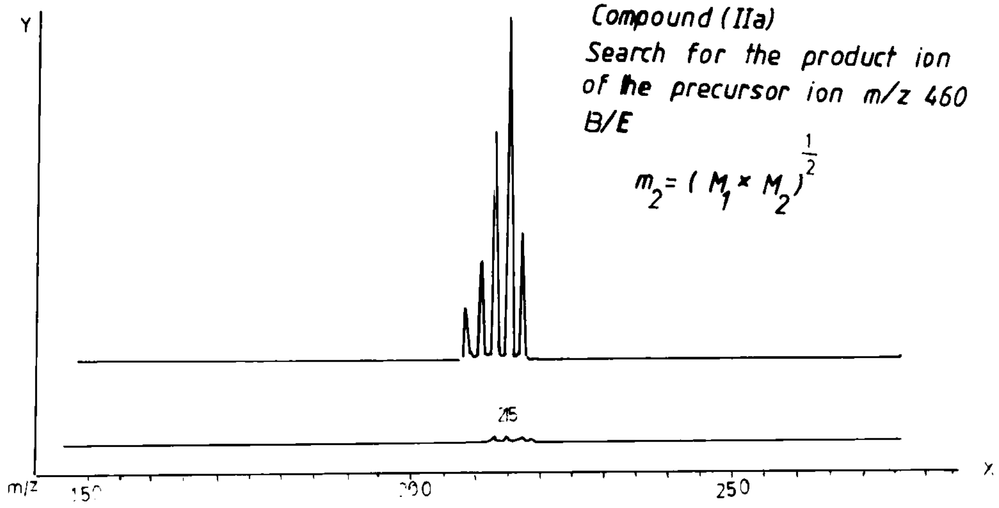
$$\begin{aligned} m_1 &= m_2 \times M_2/M_1 \\ &= 518 \times 518/460 = 583 \end{aligned}$$

Also, by using the link-field scan measurements on the mass number m/z 460 as the precursor ion, it was indicated that the product ion must appear as a metastable peak at m/z 215 (Figure 1), suggesting that the peak at 315 is a product of that ion as determined by the relation;[16]

$$\begin{aligned} m_2 &= (M_1 \times M_2)^{1/2} \\ &= (460 \times 215)^{1/2} \\ &= 314.5 \text{ m/z} \end{aligned}$$

m/z at 215 is a metastable peak for the product at 314.5 m/z

$$m^* = \frac{(314.5)^2}{460} = 215 \text{ m/z}$$



(Fig.1)

Also, compound IId showed the following fragments: at m/z 675 (1.0%); 556 (57.4%); 406 (1.9%) with *m** at m/z 207.6, 481 (22.2%); and at m/z 194 (93.3%). It should be noted that these fragments are consistent with the mode of fragmentation pattern represented in Scheme 2 (Table I).

On the other hand, compounds IIb and IId both showed a base peak at m/z 406 (4.1% for IIb) and 406 (1.9% for IId) corresponding to the ions $[(p\text{-}CH_3C_6H_4)NP(S)Cl]_2$ and $[(p\text{-}CH_3OC_6H_4)NP(O)Cl]_2$, respectively, data that add further substantial evidence to the structure of the dispirocyclodiphosph(V)azanes(II).

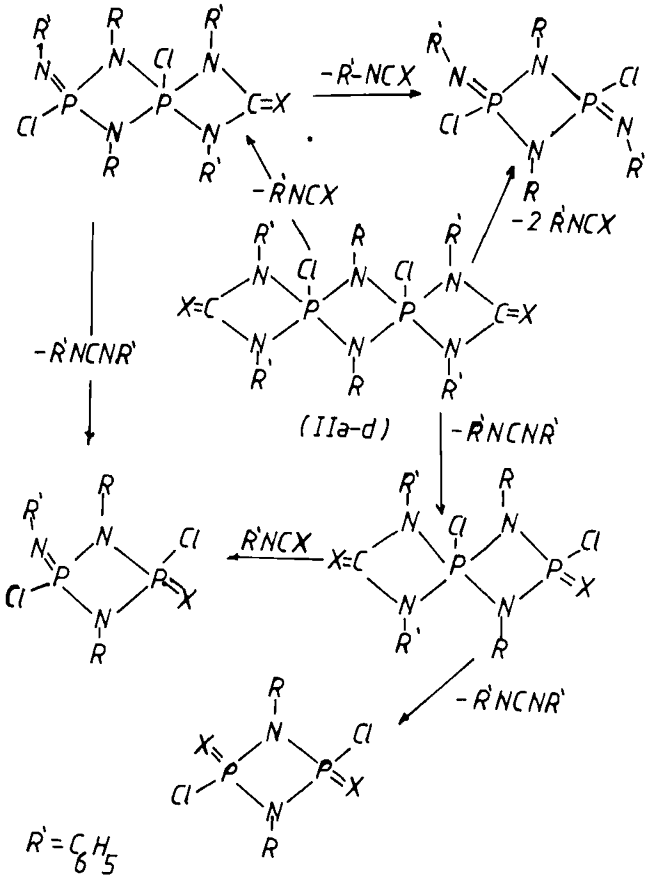
Also, the mass spectrum of the analogous urea derivative (IIc) which showed the following fragments at m/z 524 (13.1%) corresponding to the loss of a fragment having a mass of m/z to two C_6H_5-NCO moieties. Further fragmentation of the ion at m/z 643, again by the loss of $C_6H_5NCNC_6H_5$, yields the base peak at m/z 449 (1.2%). It should be noted that the link-field scan measurements on the precursor peak at m/z 449 clearly indicate that the following fragments are the products of that precursor ion:

m/z	% RA	Fragment
194	100.0	$C_6H_5NCNC_6H_5$
157	5.1	C_6H_5NPCL
122	57.1	C_6H_5NP
119	76.2	C_6H_5NCO
91	52.2	C_6H_5P
77	53.2	C_6H_5

The mode of fragmentation could be visualized as shown in Scheme 2 (Table II).

Similarly, the mass spectrum of compound (III) showed the following m/z values: a peak at 407 (5.0%) due to the loss of $C_6H_5NCNC_6H_5$ moiety.

SCHEME 2 Proposed Fragmentation pathway of Aminocyclodiphosph(V)-azanes (IIa–d).



The spectrum also showed the following fragments:

m/z	% RA	Fragment
91	11.3	C_7H_7
106	100.0	C_7H_7N
135	36.9	C_6H_5NCS
136	41.1	C_7H_7NP
168	34.3	C_7H_7NPS
194	0.3	$C_6H_5NCNC_6H_5$
203	53.1	C_7H_7NPSCl

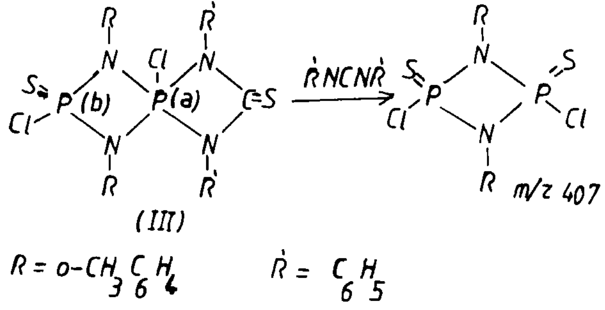


TABLE I

Relative intensity of major ions in the mass spectra of Aminocyclodiphosph(V)azanes (IIa–d)

Compd.	Mol. peak M m/z %RA	$\overset{+}{M}-C_6H_5NCX$ m/z %RA	$\overset{+}{M}-2C_6H_5NCX$ m/z %RA	$\overset{+}{M}-C_6H_5NCNC_6H_5$ m/z %RA	$\overset{+}{M}-2C_6H_5NCNC_6H_5$ m/z %RA	$\overset{+}{M}-C_6H_5NCX\text{-}C_6H_5NCNC_6H_5$ m/z %RA
IIa	734 (n.o.)	615 (0.3)	496 (97.3)	540 (0.1)	356 (n.o.)	421 (55.6)
IIb	794 (n.o.)	659 (n.o.)	524 (0.4)	600 (n.o.)	406 (4.1)	465 (0.5)
IIc	762 (n.o.)	643 (n.o.)	524 (13.1)	568 (n.o.)	374 (0.5)	449 (9.2)
IId	794 (n.o.)	675 (n.o.)	556 (57.3)	600 (n.o.)	406 (1.9)	481 (22.2)

X = 0 or S
n.o. means not observed
RA = relative intensity

The ^{31}P nmr spectrum of compound (III) adds further substantial evidence supporting the proposed structure since the the ^{31}P nmr spectrum showed two signals at $\delta = 46.2$ and at $\delta = 44.07$ ppm, corresponding to the two phosphorus environments (a) and (b) designated in the above structure.

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