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Mass Spectra of *N*-Phosphorylated Imino Compounds

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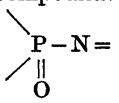
The mass spectra of diethyl phosphor(isocyanatidate) (I), diethyl phosphor(isothiocyanatidate) (II), diethyl phosphoro(thionylamidate) (III), diethyl *N*,*N*-dichlorophosphoramidate (IV), and diethyl phosphorazidate (V) have been recorded and interpreted with the aid of high resolution measurements and the metastable defocusing technique.

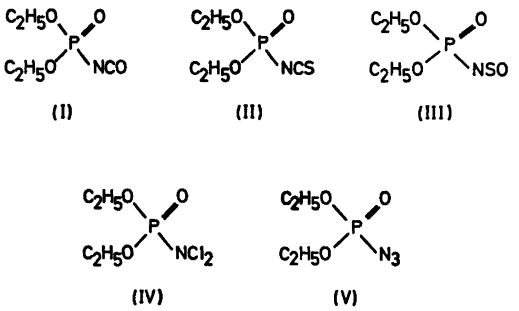
Characteristic for the fragmentations are P—N bond cleavage and degradation in the ethoxy groups. A general fragmentation scheme for the compounds is given.

Recently we have described the general fragmentation pattern of various esters of phosphoramidic acid $(RO)_2P(O)NH_2$.[1]

Continuing our mass spectrometric investigations of phosphorus compounds containing a P—N bond, we have studied some compounds in which the phosphinylimino system  is present. The purpose of this investigation is to examine to what extent mass spectrometry can be used for identification of these types of compounds, and to compare the degradation patterns of *N*-phosphorylated imino compounds with nitrogen connected to different groups.

We shall discuss here the mass spectra of the following compounds: Diethyl phosphor(isocyanatidate) (I), diethyl phosphor(isothiocyanatidate) (II), diethyl phosphoro(thionylamidate) (III), diethyl *N*,*N*-dichlorophosphoramidate (IV), and diethyl phosphorazidate (V).

The mass spectra of the *N*-phosphorylated imino compounds investigated are characterised by fragmentation in the ethoxy groups in agreement with the findings for phosphoramidic acid esters.[1] In addition to these fragmentations,



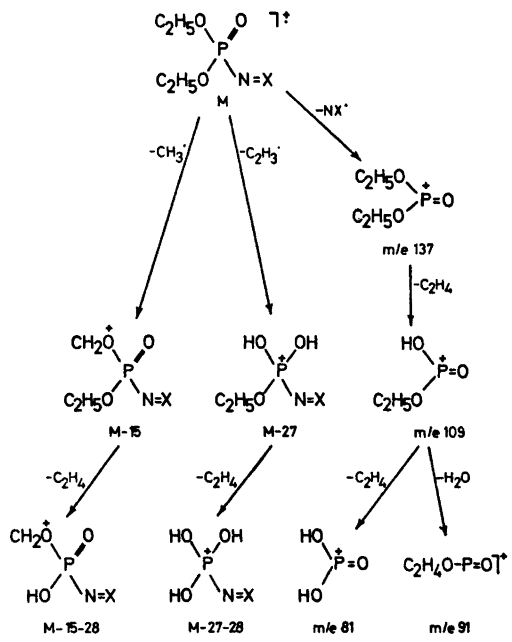
P—N bond cleavage is of importance for the degradation of the molecular ion for all the compounds investigated.

P—O bond breaking from the molecular ion is seen for all compounds except diethyl *N*,*N*-dichlorophosphoramidate, but in all cases the fragments formed are of lower intensity than for the corresponding fragments in diethyl phosphoramidic acid ester.

A generalized fragmentation scheme is given as Scheme 1 (X: C=O, C=S, S=O, Cl_2, or N_2). The P—O bond breaking (loss of C_2H_5O and C_2H_4O) is omitted from the scheme. Variations from the scheme will be mentioned in the discussion.

DISCUSSION

Diethyl phosphor(isocyanatidate) (I) fragments in accordance with the general scheme with the only exception that it splits off HNCO instead of NCO from the molecular ion. No fragmentations take place in the NCO part of the molecule which is in accordance with findings for aliphatic isocyanates.[2]



Scheme 1.

Diethyl phosphor(isothiocyanatidate) (II) fragments similarly to the isocyanate (I), but the ion M − HNCS is of low intensity whereas M − NCS is abundant. The formation of $HNCS^{+\cdot}$ (*m/e* 59) which is general for aliphatic isothiocyanates [8] is also of importance for this phosphor(isothiocyanatidate).

Diethyl phosphoro(thionylamidate) (III) shows no peak at *m/e* 137 corresponding to loss of NSO from the molecular ion, but a metastable peak at *m/e* 94.3 indicates that the P − N bond is cleaved. Furthermore *m/e* 137 is shown by the defocusing technique to be precursor for *m/e* 109 [$C_2H_5OP(O)OH$], so the fragmentation of this thionyl compound is in accordance with the general scheme. No cleavage in the NSO group like loss of SO, as reported for the aromatic thionylamines [4] or loss of SO or HSO as reported for the aliphatic thionylamines [5] is observed. Another degradation involving complex rearrangements results in the formation of the base peak *m/e* 73 with the composition C_2H_3NS.

Diethyl *N,N*-dichlorophosphoramidate (IV) follows only one of the three degradation routes given in scheme 1, namely P − N bond cleavage followed by degradation in the ethoxy groups. It is remarkable that no fragmentation in the ethoxy groups is observed from the molecular ion as this degradation is of importance for both the imino compounds investigated and for diethyl phosphoramidate.[1]

Diethyl phosphorazidate (V) fragments according to the general scheme following all the three routes. No loss of N_3 from the molecular ion like the "normal" azide degradation [6] is observed. This is in accordance with results found for sulphonylazides [7] where loss of N_3 is shown to be of minor importance.

Loss of N_3 is observed from *m/e* 124 and *m/e* 106.

Table 1. Exact mass measurements.

Compound	*m/e*	Composition	Compound	*m/e*	Composition
I	124	CH_3NO_4P	III	73	C_2H_3NS
	136	$C_2H_3NO_4P$		81	H_2O_3P
	124	CH_3NO_4P		99	H_4O_4P
				109	$C_2H_6O_3P$
				126	HNO_3PS
II	59	CHNS	V	81	H_2O_3P
	81	H_2O_3P		91	$C_2H_4O_2P$
	91	$C_2H_4O_2P$		106	$C_2H_3O_3P$
	109	$C_2H_6O_3P$		109	$C_2H_6O_3P$
	122	$CHNO_3PS$		124	$H_3N_3O_3P$
	137	$C_4H_{10}O_3P$		137	$C_4H_{10}O_3P$
	151	$C_3H_6NO_2PS$			

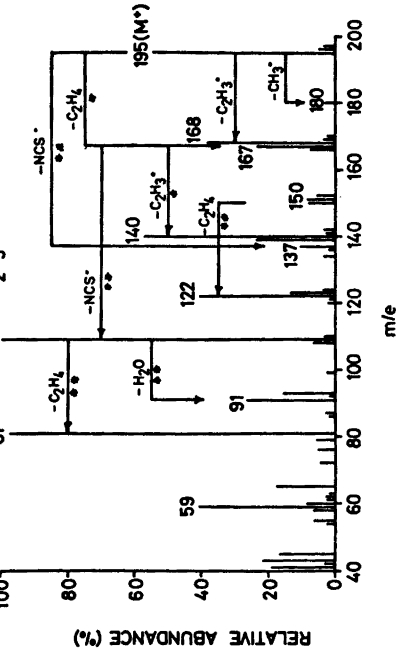


Fig. 2. Mass spectrum of diethyl phosphor(isothiocyanatidate) (II).

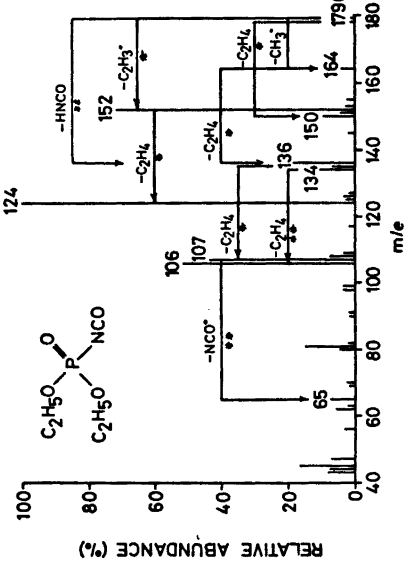


Fig. 1. Mass spectrum of diethyl phosphor(isocyanatidate) (I).

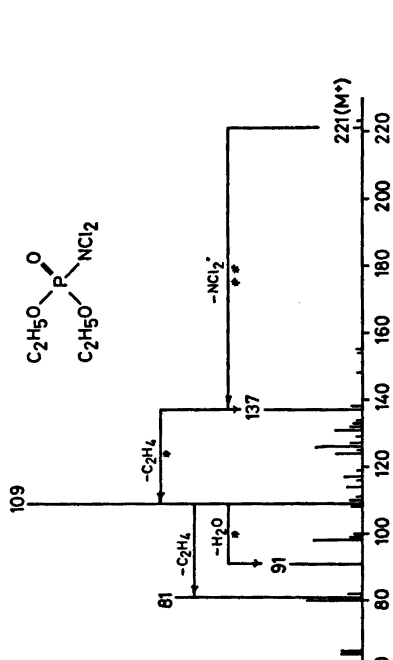


Fig. 4. Mass spectrum of diethyl *N,N*-dichlorophosphoramidate (IV).

Fig. 3. Mass Spectrum of diethyl phosphoro(thionylamidate) (III).

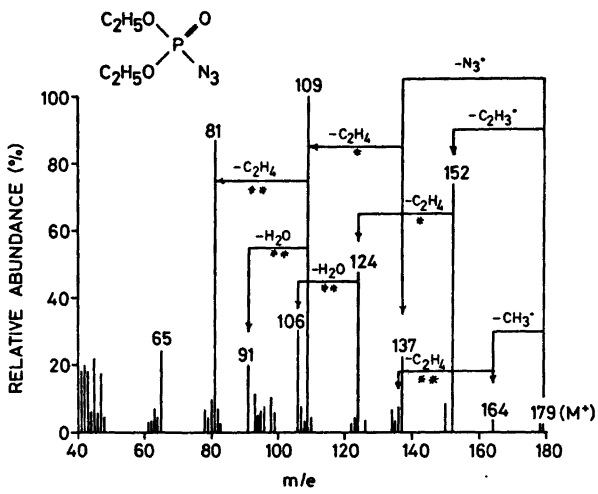


Fig. 5. Mass spectrum of diethyl phosphorazidate (V).

CONCLUSION

As is evident from the discussion above electron impact induced fragmentations of the phosphinylimines investigated are dominated by degradations in the ethoxy groups, namely loss of C_2H_4, C_2H_3· and CH_3·. In addition P – N bond cleavage in the molecular ion is of importance. The phosphinylimines follow, with minor exceptions, three main degradation routes (Scheme 1), a fact which might be useful for characterisation of similar compounds.

EXPERIMENTAL

The mass spectra were recorded on an AEI MS-902 mass spectrometer. The samples were introduced through the heated glass inlet system below 100 °C. All the decompositions given are, unless otherwise noted, supported by accompanying metastable peaks or verified by metastable defocusing (indicated by two asterisks in the figures). The elemental compositions of all characteristic ions have, when necessary, been determined by high resolution mass measurements (Table 1).

The measurements were performed on analytically pure compounds.

Diethyl phosphor(isocyanatidate) (I) was prepared by the action of oxalyl chloride on diethyl phosphoramidate.[8] B.p. 95 °C/15 mmHg, n_D^{20} 1.4170, yield 62 %.

Diethyl phosphor(isothiocyanatidate) (II) was synthesized from the corresponding phosphorochloridate and potassium thiocyanate in acetone solution.[9] B.p. 58 °C/0.12 mmHg, n_D^{20} 1.4795, yield 60 %.

Diethyl phosphoro(thionylamidate) (III) was obtained by the action of thionyl chloride on diethyl phosphoramidate.[10] B.p. 76 °C/0.1 mmHg, n_D^{20} 1.4578, yield 72 %.

Diethyl *N,N*-dichlorophosphoramidate (IV) was prepared by chlorination of the acetate-buffered aqueous solution of diethyl phosphoramidate.[11] B.p. 59 °C/0.03 mmHg, n_D^{20} 1.4622, yield 83 %.

Diethyl phosphorazidate (V) was prepared from diethyl phosphorochloridate and sodium azide in acetone solution according to Scott *et al.*[12] B.p. 70 °C/4 mmHg, n_D^{20} 1.4268, yield 85 %.

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