Mass Spectra of $N$-Phosphorylated Imino Compounds

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The mass spectra of diethyl phosphor(isocyanatidate) (I), diethyl phosphor(isothiocyanatidate) (II), diethyl phosphor(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 $(RO)_{4}P(O)NH_{2}$.1

Continuing our mass spectrometric investigations of phosphorus compounds containing a $P-N$ bond, we have studied some compounds in which the phosphinylimino system $\text{P=N=O}$ 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 phosphor(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 phosphoramic acid ester.

A generalized fragmentation scheme is given as Scheme 1 ($X: C=O, C=S, S=O, Cl$, or $N_{3}$). The $P-O$ bond breaking (loss of $C_{2}H_{4}O$ and $C_{2}H_{2}O$) 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
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⁺ (m/e 59) which is general for aliphatic isothiocyanates 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 [C₆H₅OP(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 or loss of SO or HSO as reported for the aliphatic thionylamines is observed. Another degradation involving complex rearrangements results in the formation of the base peak m/e 73 with the composition C₆H₅NS.

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.

Diethyl phosphorazidate (V) fragments according to the general scheme following all the three routes. No loss of N₂ from the molecular ion like the "normal" azide degradation is observed. This is in accordance with results found for sulphonylazides where loss of N₂ is shown to be of minor importance.

Loss of N₂ is observed from m/e 124 and m/e 106.

Table 1. Exact mass measurements.

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<th>Compound</th>
<th>m/e</th>
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Fig. 1. Mass spectrum of diethyl phosphor(isocyanatidate) (I).

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

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

Fig. 4. Mass spectrum of diethyl N,N-dichlorophosphoramidate (IV).
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 $\text{C}_2\text{H}_4$, $\text{C}_3\text{H}_7$ and $\text{CH}_3$. In addition $\text{P} - \text{N}$ 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, $n_\text{D}^{20}$ 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, $n_\text{D}^{20}$ 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, $n_\text{D}^{20}$ 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, $n_\text{D}^{20}$ 1.4622, yield 83%.

Diethyl phosphazidate (V) was prepared from diethyl phosphorochloridate and sodium azide in acetone solution according to Scott et al.$^{12}$ B.p. 78 °C/4 mmHg, $n_\text{D}^{20}$ 1.4268, yield 85%.

Acknowledgement. The authors acknowledge the help of Dr. Jørgen Møller, Physical Laboratory II, University of Copenhagen, the H. C. Ørsted Institute, in obtaining the mass spectral data.

The assistance of Mrs. E. Wolff-Jensen in recording the spectra and performing the measurements is also acknowledged.

REFERENCES


Received February 6, 1974.