

THE MASS SPECTRA OF N-PHENYLPHOSPHORAMIDATE ESTERS*

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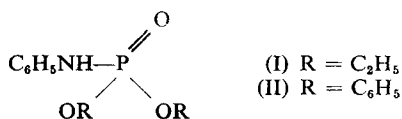
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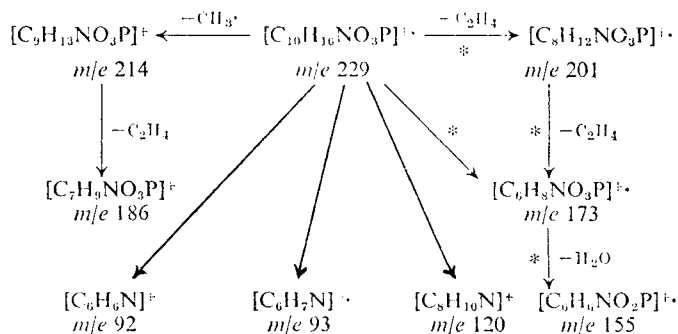
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Abstract—The mass spectra of diethyl and diphenyl N-phenylphosphoramidate are reported. Their electron-impact behavior is similar to that observed for the corresponding phosphate esters. High resolution mass measurements are used to confirm the elemental composition of all the peaks in the spectra. Some interesting rearrangement fragments are observed in the spectrum of the diphenyl N-phenylphosphoramidate ester.

WE WISH to report the electron impact behavior of the N-phenylphosphoramidates (I and II). To our knowledge, the mass spectra of these compounds have not been previously reported.



The mass spectrum of diethyl N-phenylphosphoramidate(I) is illustrated in Fig. 1 and the fragmentation pathway suggested to account for the spectrum is depicted in Scheme 1.



SCHEME 1

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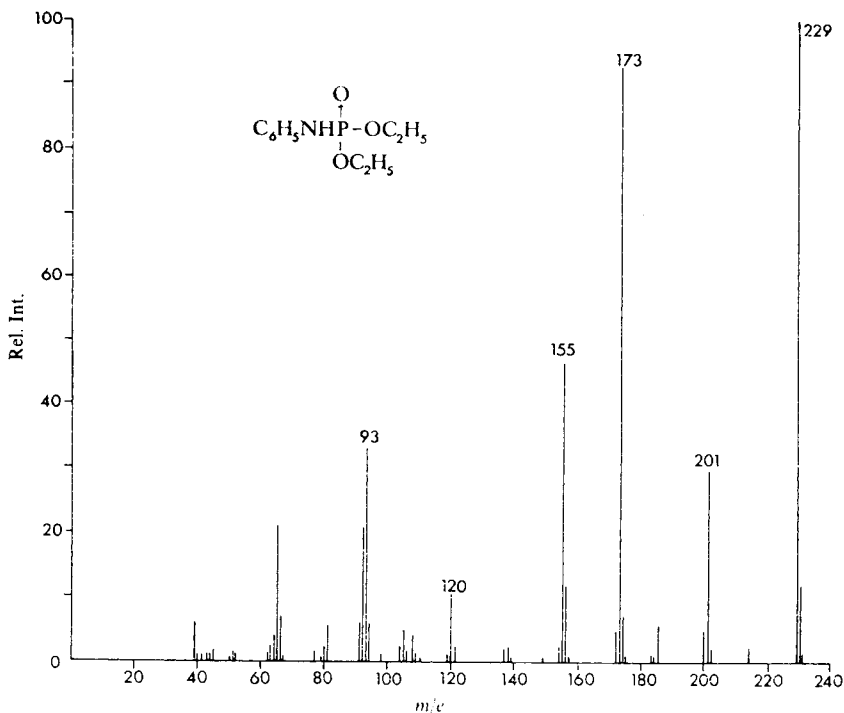


FIG. 1. The mass spectrum of Diethyl N-phenylphosphoramidate

The molecular ion, $\text{C}_{10}\text{H}_{16}\text{NO}_3\text{P}$, is the base peak in the mass spectrum of I. The fragmentation proceeds with successive losses of ethylene to yield the odd electron fragments observed at m/e 201 ($\text{C}_8\text{H}_{12}\text{NO}_3\text{P}$) and m/e 173 ($\text{C}_6\text{H}_8\text{NO}_3\text{P}$). A minor fragment derived from the loss of ethylene from the even electron $[\text{M} - 15]^+$ fragment is also observed. The fragment at m/e 173 decomposes by loss of water to yield the fragment at m/e 155. This electron-impact behavior of the phosphoramidates i.e. loss of ethylene followed by dehydration, parallels that observed for triethyl phosphate.¹ The remaining abundant fragments in the spectrum occur at m/e 120 ($\text{C}_8\text{H}_{10}\text{N}$), m/e 93 ($\text{C}_6\text{H}_7\text{N}$) and m/e 92 ($\text{C}_6\text{H}_6\text{N}$).

In appearance, the diphenyl N-phenylphosphoramidate(II) exhibits a more simplified mass spectrum (Fig. 2) than the corresponding diethyl derivative (I). The fragmentation pathway for II is summarized in scheme 2.

The mass spectrum is dominated by an intense molecular ion at m/e 325 ($\text{C}_{18}\text{H}_{16}\text{NO}_3\text{P}$). The molecular ion loses phenoxy and phenol to form the fragments at m/e 232 ($\text{C}_{12}\text{H}_{11}\text{NO}_2\text{P}$) and m/e 231 ($\text{C}_{12}\text{H}_{10}\text{NO}_2\text{P}$). The possible genesis of m/e 231 from m/e 232 by loss of hydrogen could not be confirmed. The ratio of the abundance of m/e 231 to m/e 232 at 20 eV was qualitatively the same as that at 70 eV suggesting that both were formed primarily from the molecular ion. The fragment at m/e 214 is derived by loss of water from m/e 232 and by loss of hydroxyl from the peak at m/e 231.

An interesting cluster of fragments which can only be derived from migration of an aromatic ring is noted in the spectrum of II.* The fragments are at m/e 167 ($\text{C}_{12}\text{H}_9\text{N}$),

* The mechanism of these rearrangements are now under investigation and will be the subject of a subsequent paper.

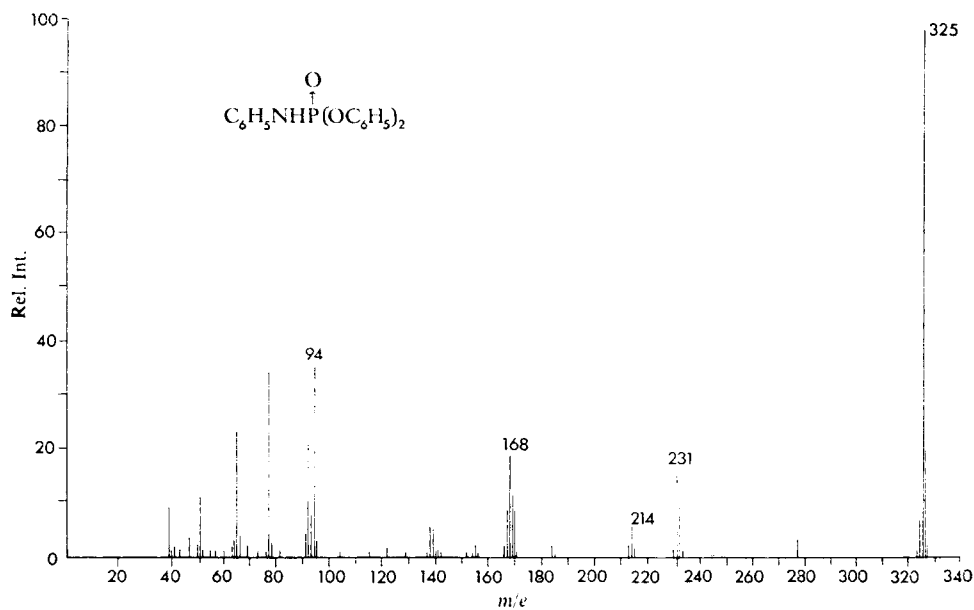
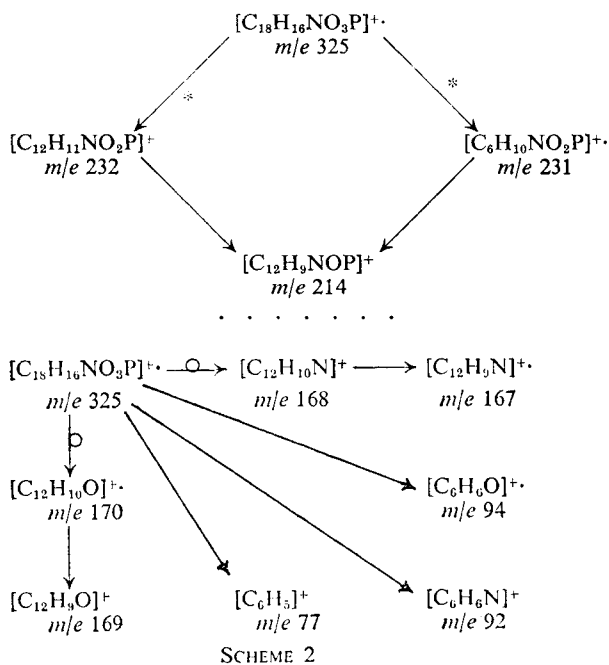


FIG. 2. The mass spectrum of Diphenyl N-phenylphosphoramidate



m/e 168 ($C_{12}H_{10}N$), m/e 169 ($C_{12}H_9O$) and m/e 170 ($C_{12}H_{10}O$). The mass spectrum of II bears a strong similarity to the mass spectrum of triphenylphosphate,² which shows a fragment at m/e 170 with the same composition ($C_{12}H_{10}O$) as well as fragments derived by loss of phenoxy (m/e 233) from the molecular ion and the subsequent loss of water from the m/e 233 fragment. The oxygen analogs corresponding to the fragments at m/e 138 (C_6H_5NPO) and m/e 139 (C_6H_6NPO) are also observed in the mass spectrum of triphenylphosphate.²

The elemental composition of the remaining intense peaks in the spectrum are m/e 77 (C_6H_5), m/e 92 (C_6H_6N) and m/e 94 (C_6H_6O).

The mass spectra of the phosphoramidates strongly resemble the mass spectra of the corresponding phosphate esters. The replacement of the alkyl substituents with aromatic groups increases the tendency of these compounds to rearrange during electron bombardment.

EXPERIMENTAL

The samples were prepared according to the general procedure of Foster *et al.*³:

Compound I: m.p. 95° to 96° (lit.⁴ 96.5°C),

Compound II: m.p. 131° to 132° (lit.³ 128 to 129°C).

The mass spectra were obtained on an AEI MS-9 mass spectrometer at 100 μ amp. ionizing current at 70 eV. The exact mass measurements were obtained at a resolution of 10,000, 500 μ amp. ionizing current at 70 eV. The accuracy of mass measurements were within 10 ppm. The samples were introduced via the direct solids probe. The source temperature was 125° to 150°C.

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