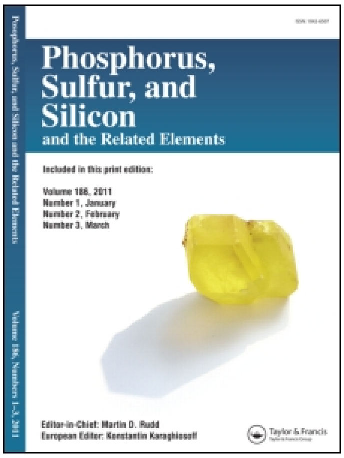

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MASS SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS II[1] UNIMOLECULAR REACTIONS OF 2-PHENYL-1,3,2-DIOXAPHOSPHOLANE 2-OXIDE DERIVATIVES IN THE GAS PHASE

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MASS SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS II[1]
UNIMOLECULAR REACTIONS OF 2-PHENYL-1,3,2-DIOXAPHOSPHOLANE 2-OXIDE DERIVATIVES IN THE GAS PHASE

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Cyclic five-membered phosphate ester ions, which are slowly fragmented in the gas phase, have been investigated by analysis of the MIKES (mass-analyzed ion-kinetic energy spectrum). An interesting unimolecular reaction leading to the migration of phenyl radical has been observed in the gas-phase decomposition of ions generated upon electron impact from some derivatives of 2-phenyl-1,3,2-dioxaphospholane 2-oxide. The spectra show that the phospholane radical cations undergo unimolecular dissociations leading to the formation of a tropylium cation (m/e 91). Spectral interpretation suggests that this ion was formed via phenyl-radical migration. The cyclic phosphate esters open by P—O or C—O bond breaking rather than P—C bond cleavage, and phenyl radical migrates to the carbon radical. The total ion current shows that the major fragmentation pathway of these phospholanes is the formation of ions induced by the phenyl-group migration.

INTRODUCTION

Over the past years, there has been an increasing amount of interest in cyclic phosphorus compounds containing oxygen in five- and six-membered rings. The mass spectra of the six-membered phosphates, the 1,3,2-dioxaphosphorinanes, have received particular attention.[2-4]

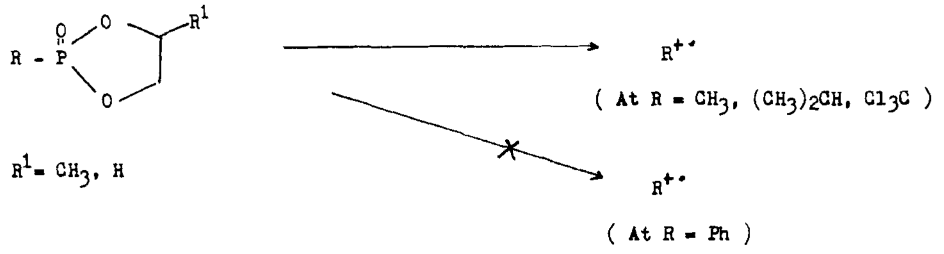
In our previous papers,[1] it was shown that the mass spectra of 2-alkyl-substituted 1,3,2-dioxaphospholane 2-oxides are characterized by cleavage of a P—C bond.[5,6]

Cleavage of the P—C bond is known to be a facile process in phosphonyl compounds.[7] However, pathways in the EI mass spectra of five-membered cyclic compounds containing a phenyl group have not been studied until now.

In this paper, we demonstrate the involvement of phenyl-radical migration by means of direct analysis by the daughter-ion technique (DADI/MIKES).[8]

RESULTS AND DISCUSSION

The cleavage of the P—C bond is a known process in the EI mass spectra of phosphoryl compounds.[7] In contrast, the mass spectra of 2-phenyl-1,3,2-dioxaphospholane 2-oxide and its derivative did not show the m/e 77 peak for the molecular ions.

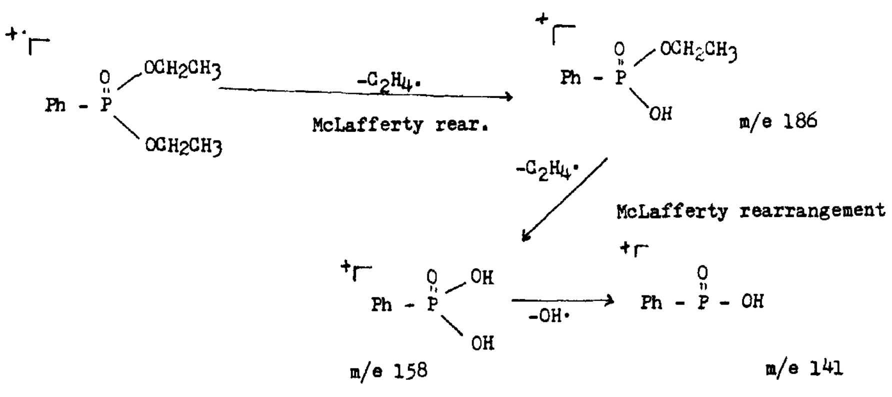


1. Decomposition of 2-phenyl-1,3,2-dioxaphospholane 2-oxide.

In the unimolecular decomposition of 2-phenyl-1,3,2-dioxaphospholane 2-oxide, the major reaction pathway involves initial cleavage of a P—O or C—O bond with successive phenyl-radical migration leading to production of peaks at m/e 120, 104, and 91, whose relative intensities are 30%, 12%, and 19%, respectively, of the base peak (m/e 141).

For the phenylphosphate diethyl ester, the migration of a phenyl radical is not observed, (Scheme 1) and the m/e 186 and 158 peaks are produced directly from the molecular ion (m/e 214). These ions are formed by a McLafferty rearrangement.

The m/e 141 peak is also observed in the mass spectra of 2-phenyl-1,3,2-dioxaphospholane 2-oxide; it is generated by P—O bond cleavage and subsequent loss of $C_2H_3O^{\cdot}$. The MIKE spectrum of the unimolecular dissociation of the molecular ion m/e 184 is shown in Figure 1. Seven metastable transitions are associated with formation of product ions m/e 183, 154, 141, 124, 120, 104, and 91, whose relative intensities are 17.8%, 6.3%, 6.7%, 7.0%, 20.4%, 38.6%, and 2.2%, respectively, of the total metastable-ion current. The MIKE spectrum of m/e 104



SCHEME 1

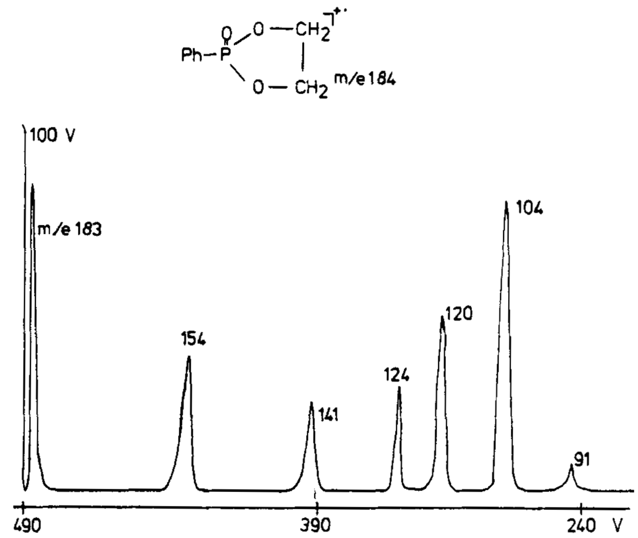
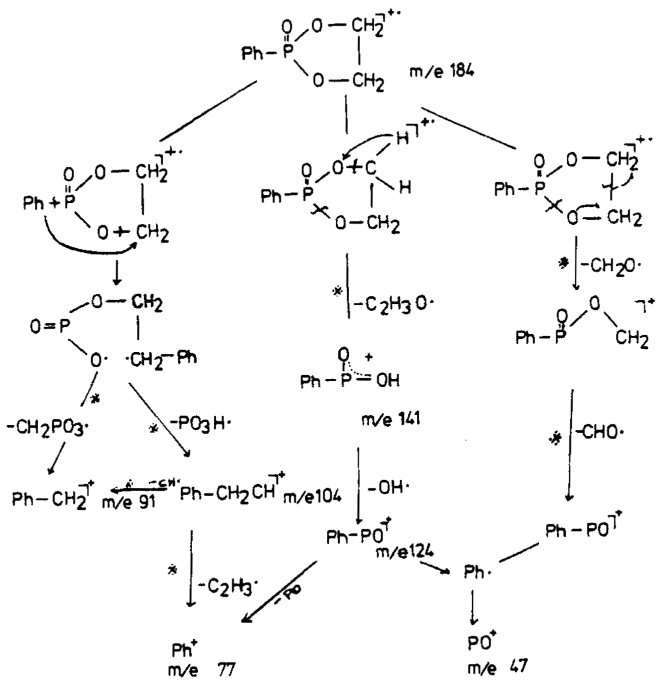


FIGURE 1 DADI/MIKE spectrum of ions m/e 184, from 2-phenyl-1,3,2-dioxaphospholane 2-oxide.

ion shows two peaks at m/e 91 and 77 resulting from the loss of CH$^•$ and $C_2H_3^•$, respectively. We propose the fragmentation pathway outlined in Scheme 2, in which these ions arise directly from the molecular ion. It is conceivable that formation of these ions (m/e 104, 91) results from a migration of phenyl radical to a methylene



SCHEME 2

radical. A search of the MIKE spectrum of 2-alkyl-1,3,2-dioxaphospholane 2-oxides showed no alkyl-radical migration.

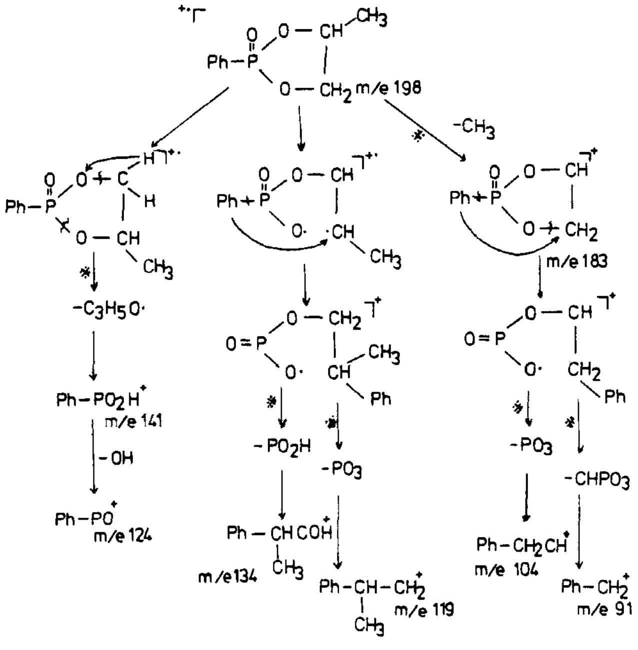
The m/e 141 ion is formed directly from the molecular ion and is the base peak for this compound in the EI spectrum. The m/e 154 (M—$CH_2O^{\cdot}$) and 124 ions are important because these ions are formed when the P—C bond is retained.

2. *Decomposition of 4-Methyl-2-phenyl-1,3,2-dioxaphospholane 2-oxide*

A similar observation on the dissociation of 4-methyl-2-phenyl-1,3,2-dioxaphospholane 2-oxide can be made from the MIKE spectrum of the molecular ion. The fragmentation pathways are proposed as shown in Scheme 3 from the MIKE spectrum and EI mass spectral data.

The m/e 183 ion arises from loss of $CH_3^{\cdot}$ followed by a ring cleavage reaction of the cyclic ion. A facile process is the C—O bond breaking and phenyl-radical migration to the methylene radical, which was also observed in the unimolecular reaction of 2-phenyl-1,3,2-dioxaphospholane 2-oxide in the gas phase. It was observed that the unimolecular reaction of molecular ion m/e 198 showed eight metastable transitions in the MIKE spectrum. Also, the MIKE spectrum of m/e 198 ion showed that 80% of the total metastable ion current is induced by phenyl-group migration and loss of $CH_3^{\cdot}$.

The m/e 134 and 119 ions, shown in Scheme 3, were formed directly from the molecular ion. The former could occur via a phenyl-radical migration involving a C—O bond cleavage and P—O bond breaking.



SCHEME 3

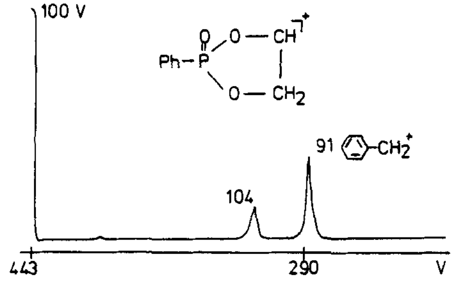


FIGURE 2 DADI/MIKE spectrum of ions m/e 183, from 4-Methyl-2-phenyl-1,3,2-dioxaphospholane 2-oxide.

The practical procedure for stepwise detection of ion generation by MIKE spectrometry is shown in Figure 2. After electron-impact ionization, the species m/e 183 ($M-CH_3^{\cdot}$) is set by means of the magnetic field. The MIKE spectrum is recorded by automatic variation of the electrostatic analyzer voltage with the valve (443 V) downwards.

We should like to stress the following points: (1) the methyl-group loss is particularly favored in the mass spectra: (2) in spite of the substituent effect, the migration of the phenyl radical remains the prominent pathway. Therefore, we have assumed that the 2-phenyl-1,3,2-dioxaphospholane 2-oxides fragment by phenyl-group migration in the gas-phase upon electron impact.

EXPERIMENTAL

Mass spectra have been determined using a double-focusing mass spectrometer of the reversed Nier-Johnson geometry by automatic variation of the electrostatic analyzer (ESA) voltage from the initial value (E_0) downward. Each metastable peak arises from unimolecular decomposition in the field-free drift region; the parent (m_1) and daughter (m_2) mass numbers are determined using the relationship $m_2 = m_1 E/E_0$.

All the mass spectra were recorded on a Varian MAT 212 mass spectrometer connected on-line with a SS MAT 188 computer. Samples were introduced through the direct inlet system at room temperature; the ion-source temperature was 250°C; the constant acceleration voltage was 3 kV; and a 70 eV ionization potential was employed.

2-Phenyl-1,3,2-dioxaphospholane 2-oxide and its derivatives were prepared in the usual manner[9, 10] by reaction of the diols with phenylphosphonic dichloride in the presence of triethylamine in benzene or ether. Compounds were purified by thin-layer chromatography.

Detailed mass-spectral data:

2-Phenyl-1,3,2-dioxaphospholane 2-oxide: 184 (M, relat. abund. 61.5%), 158 (2.3%), 142 (8.5%), 141 (100%, base peak), 125 (6.2%), 124 (72.3%), 104 (12.7%), 91 (21.6%), 77 (75.3%), 47 (13.2%).

4-Methyl-2-phenyl-1,3,2-dioxaphospholane 2-oxide: 198 (M, 42.5%), 183 (7.3%), 159 (25.7%), 142 (37.3%), 124 (100%, base peak), 119 (2.1%), 117 (43.1%), 104 (12.7%), 77 (72.6%), 51 (45.8%), 47 (13.1%).

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