

Mass Spectral Studies on Cyclic Organophosphorus Compounds

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The mass spectral studies on several structurally related series of eight, nine and ten membered cyclic phosphates with and without α -nucleophile have been studied. The fragmentation mode of cyclic phosphates under electron impact is of similar pattern and is governed by both ring size and the substituent present, thus offering a means of characterization of phosphate esters.

INTRODUCTION

Organophosphorus compounds provide not only science of organic synthesis but also play an important role for maintenance of life¹, in view of their extensive practical applications in engineering, medicine² and are of concern to the military as chemical weapons in war^{3,4}, a vigorous kinetic study of mechanism of biochemical processes⁵⁻⁷ in which individual phosphates play an important role has been carried out. However, no systematic investigation of mass spectral behaviour of cyclic phosphates has been done except in a few cases⁸.

Since there is a paucity of literature on thermal behaviour of cyclic phosphates, we have synthesized a series of cyclic phosphates varying in chain length (eight, nine and ten membered) with and without α -nucleophile, which have been subjected to a detailed mass spectral study both from the structural elucidation as well as from the analytical point of view for their detection in various biological samples. This study also further enables us to see the effect of ring size and also the substituent on their fragmentation pathways.

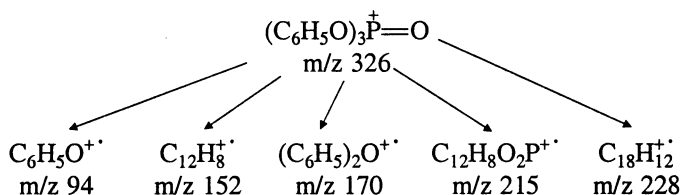
EXPERIMENTAL

Compounds (2a₁–3d₄) were prepared as per reported procedure⁹ in which cyclic phosphates were obtained from the most convenient one-step procedure by reaction of diols with substituted aryl phosphorodichloridate. All dichloridates were prepared by reaction of substituted phenols with phosphorus oxychloride at elevated temperature in presence of catalytic amount of aluminium chloride or potassium chloride¹⁰. All compounds showed analogous spectral data and microanalysis results of C, H and N were within $\pm 0.4\%$ of the theoretical values. Mass spectra were recorded on a JEOL-DS-300 double focussing mass

spectrophotometer at 70 eV using a direct insertion technique at a source temperature of about 200°C connected with a JMA online data analysis system.

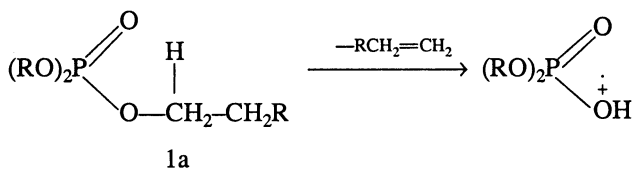
RESULTS AND DISCUSSION

The phosphate esters generally show both simple bond cleavage and rearrangement process to form complex fragmentation. Aromatic phosphates are in general more stable under electron impact giving rise to much more intense molecular ions than the alkyl esters. Triphenyl phosphate for example, besides giving molecular ion at m/z 326 ($C_{18}H_{15}PO_4$) and the ions due to the loss of C_6H_6 and C_6H_5O , exhibit a series of fairly abundant rearranged ions shown in Scheme-1.



Scheme-1

In alkyl phosphates, the degradation of alkyl group was not significant in the EI mass spectrum. The most prominent peak in the spectra appears due to the rearrangement process, which is mainly dependent on the nature of alkyl group. Loss of substituted ethylene was observed in most cases due to the well-known MacLafferty rearrangement in open chain alkyl phosphate.



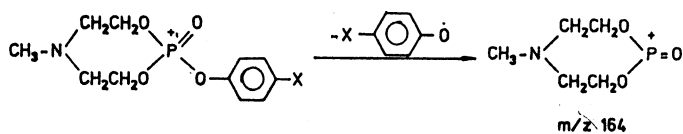
The results of mass spectral studies of the eight, nine and ten membered cyclic phosphates are given in Table-1. The mass spectrometric fragmentation pattern of the cyclic phosphates esters $2a_1$ – $3d_4$ is of similar pattern but some salient differences are however observed due to the effect of the ring size and also the substituent groups. The formation of the significant ions of different membered phosphates can be explained according to the fragmentation schemes II–VI. Besides molecular ion peaks it has been found that all the cyclic phosphates having nitrogen in the ring irrespective of ring size and the nature of substituent lose the O-aryl group to give stable ions at m/z 164 ($C_5H_{11}NPO_3^+$) in compounds $2a_1$, $2a_2$ and $2a_3$; m/z 192 ($C_7H_{15}NPO_3^+$) in $2b_1$, $2b_2$ and $2b_3$; m/z 220 ($C_9H_{19}NPO_3^+$) in $2c_1$, $2c_2$ and $2c_3$; m/z 180 ($C_5H_{11}NPO_4^+$) in $3a_1$, $3a_2$, $3a_3$ and $3a_4$; and m/z 208 ($C_7H_{15}NPO_4^+$) in $3b_1$, $3b_2$, $3b_3$ and $3b_4$ (Scheme-II).

Similar fragmentation is observed in sulphur containing cyclic phosphate also. The cyclic phosphates without nitrogen atom $3c_1$ – $3c_4$ and $3d_1$ – $3d_4$ also show the

TABLE-1
 MASS SPECTRAL DATA ON CYCLIC ORGANOPHOSPHATES

Sr. No.	Compound	X	n ₁	n ₂	R	m.f.	MS (70) eV, m/z
1.	2a ₁	N-CH ₃	0	0	H	C ₁₁ H ₁₆ NO ₄ P	258 (m + 1), 257, 256, 164, 120, 83, 70, 43
2.	2a ₂	N-CH ₃	0	0	<i>p</i> -Cl	C ₁₁ H ₁₅ NO ₄ PCl	291, 164, 83, 70, 42
3.	2a ₃	N-CH ₃	0	0	<i>m</i> -CH ₃	C ₁₂ H ₁₆ NO ₄ P	272 (m + 1), 164, 83, 70, 43
4.	2b ₁	N-C ₂ H ₅	1	0	H	C ₁₃ H ₂₀ NO ₄ P	286 (m + 1), 270, 225, 201, 192, 164, 136, 111, 98, 84
5.	2b ₂	N-C ₂ H ₅	1	0	<i>p</i> -Cl	C ₁₃ H ₁₉ NO ₄ PCl	319, 304, 249, 209, 192, 164, 111, 110, 98
6.	2b ₃	N-C ₂ H ₅	1	0	<i>m</i> -CH ₃	C ₁₄ H ₂₂ NO ₄ P	300 (m + 1), 284, 270, 229, 201, 192, 164, 136, 111, 98, 84
7.	2c ₁	N-C ₃ H ₇	1	1	H	C ₁₅ H ₂₄ NO ₄ P	313 (m+), 298, 285, 284, 270, 241, 220, 150, 98, 42
8.	2c ₂	N-C ₃ H ₇	1	1	<i>p</i> -Cl	C ₁₅ H ₂₃ NO ₄ PCl	349 (m + 2), 347 (m+), 320, 306, 220, 192, 150, 98
9.	2c ₃	N-C ₃ H ₇	1	1	<i>m</i> -CH ₃	C ₁₅ H ₂₆ NO ₄ P	327 (m+), 312, 292, 284, 220, 192, 150, 110, 96
10.	3a ₁	N-OCH ₃	0	0	<i>p</i> -NO ₂	C ₁₁ H ₁₅ N ₂ O ₇ P	318 (m+), 287, 270, 180, 159, 139, 99, 77
11.	3a ₂	N-OCH ₃	0	0	<i>p</i> -Cl	C ₁₁ H ₁₅ NO ₄ PCl	308 (m + 1), 276, 180, 150, 127, 111, 99, 68
12.	3a ₃	N-OCH ₃	0	0	H	C ₁₁ H ₁₆ NO ₅ P	274 (m + 1), 242, 197, 180, 150, 111, 99, 86, 68

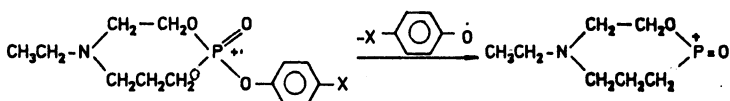
Sr. No.	Compound	X	n ₁	n ₂	R	m.f.	MS (70) eV, m/z
13.	3a ₄	N-OCH ₃	0	0	<i>m</i> -CH ₃	C ₁₂ H ₁₈ NO ₃ P	288 (m + 1), 256, 240, 180, 150, 99
14.	3b ₁	N-OCH ₃	1	1	<i>p</i> -NO ₂	C ₁₃ H ₁₉ N ₂ O ₇ P	346 (m+), 316, 288, 208, 176, 150, 139, 99
15.	3b ₂	N-OCH ₃	1	1	<i>p</i> -Cl	C ₁₃ H ₁₉ NO ₃ PCl	335 (m+), 304, 270, 208, 176, 150, 96
16.	3b ₃	N-OCH ₃	1	1	H	C ₁₃ H ₂₀ NO ₃ P	301 (m+), 271, 208, 176, 150, 96, 93
17.	3b ₄	N-OCH ₃	1	1	<i>m</i> -CH ₃	C ₁₄ H ₂₂ NO ₃ P	315 (m+), 284, 208, 176, 150, 96
18.	3c ₁	CH ₂	0	0	<i>p</i> -NO ₂	C ₁₁ H ₁₄ NO ₆ P	287 (m+), 245, 220, 203, 198, 186, 168, 149, 138
19.	3c ₂	CH ₂	0	0	<i>p</i> -Cl	C ₁₁ H ₁₄ O ₄ Cl	276, 242, 234, 186, 168, 108, 98
20.	3c ₃	CH ₂	0	0	<i>m</i> -CH ₃	C ₁₁ H ₁₅ O ₄ P	242, 200, 188, 156, 149, 129, 120, 107, 94
21.	3c ₄	CH ₂	0	0	H	C ₁₂ H ₁₇ O ₄ P	256, 214, 186, 166, 149, 107, 93
22.	3d ₁	CH ₂	1	1	<i>p</i> -NO ₂	C ₁₃ H ₁₈ NO ₆ P	315 (m+), 276, 269, 229, 200, 198, 174, 139, 93
23.	3d ₂	CH ₂	1	1	<i>p</i> -Cl	C ₁₃ H ₁₈ O ₄ PCl	305 (m + 1), 304, 215, 200, 198, 174, 139, 116, 94
24.	3d ₃	CH ₂	1	1	H	C ₁₃ H ₁₉ O ₄ P	270 (m+), 221, 200, 198, 176, 139, 116, 83
25.	3d ₄	CH ₂	1	1	<i>m</i> -CH ₃	C ₁₄ H ₂₁ O ₄ P	284 (m), 245, 216, 201, 198, 174, 138, 80



2a₁ X = H, M⁺ 257

2a₂ X = Cl, M⁺ 291/293

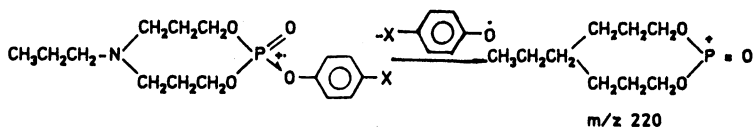
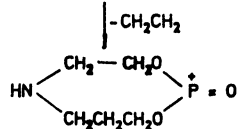
2a₃ X = CH₃, M⁺ 271



2b₁ X = H, M⁺ 285

2b₂ X = Cl, M⁺ 319/321

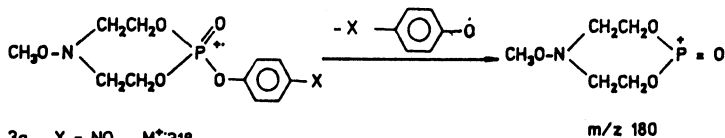
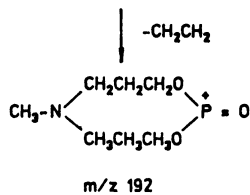
2b₃ X = CH₃, M⁺ 299



2c₁, X = H, M⁺ 313

2c₂, X = Cl, M⁺ 347/349

2c₃, X = CH₃, M⁺ 327

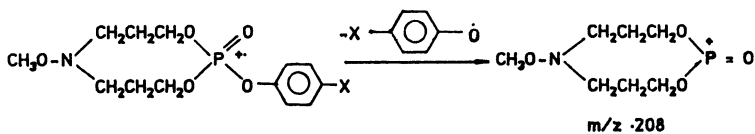


3a₁, X = NO₂, M⁺ 318

3a₂, X = Cl, M⁺ 307

3a₃, X = H, M⁺ 273

3a₄, X = CH₃, M⁺ 287



3b₁, X = NO₂, M⁺ 346

3b₂, X = Cl, M⁺ 335

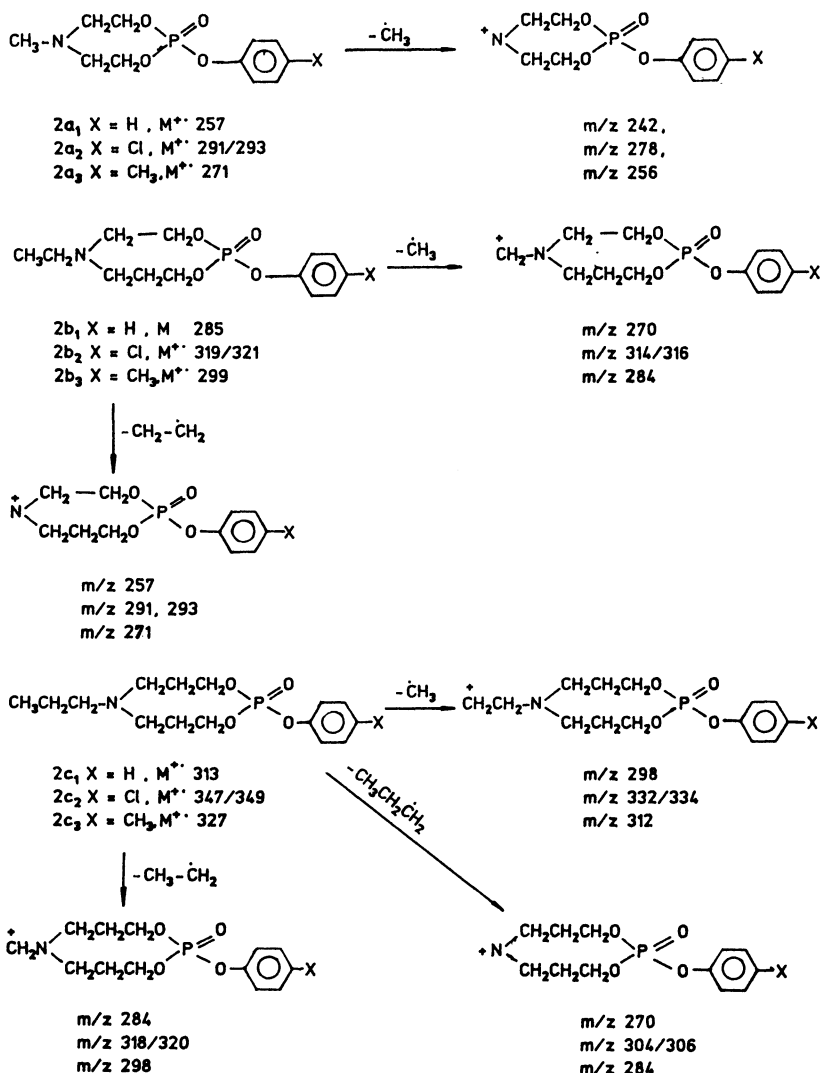
3b₃, X = H, M⁺ 301

3b₄, X = CH₃, M⁺ 315

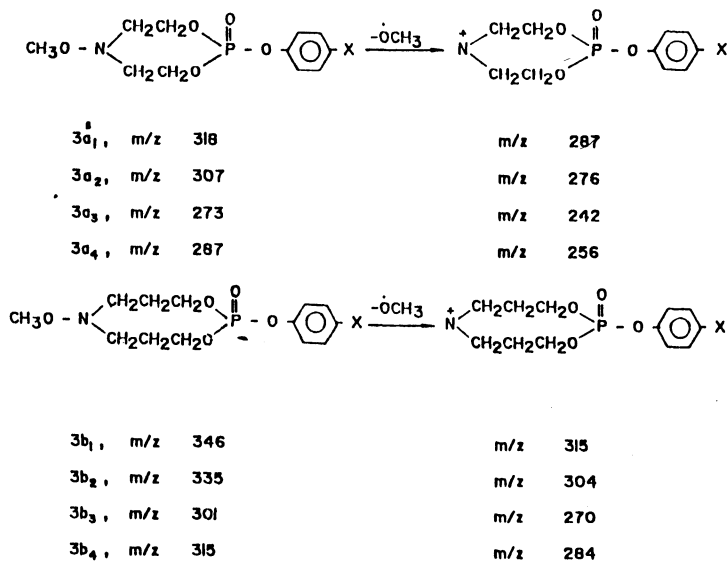
Scheme-II

loss of O-aryl group from the molecular ions at m/z 149 and at m/z 176 respectively.

The compounds, $2a_1$ – $2a_3$ show the loss of methyl radical from the molecular ions to give ions at m/z 242, 276/278 and 256 respectively. Similar loss of ethyl group from compound $2b_1$ – $2b_3$ and propyl group from compounds $2c_1$ – $2c_3$ is also observed to give their respective ions (Scheme-III). In case of compounds $3a_1$ – $3a_4$ and $3b_1$ – $3b_4$ loss of methoxy radical is observed (Scheme-IV).

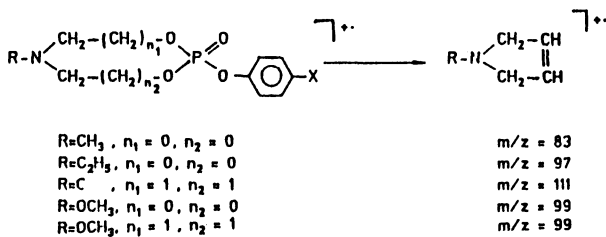


Scheme-III



Scheme-IV

Another type of fragmentation observed in nitrogen containing heterocycles is the formation of pyrroline type of fragment ion (Scheme-V). These ions are formed at m/z 83 ($C_5H_9N^+$), m/z 97 ($C_6H_{11}N^+$) and 111 ($C_7H_{13}N^+$) in N—CH₃ (2a) N—C₂H₅ (2b) and N—C₃H₇ (2c) series respectively.

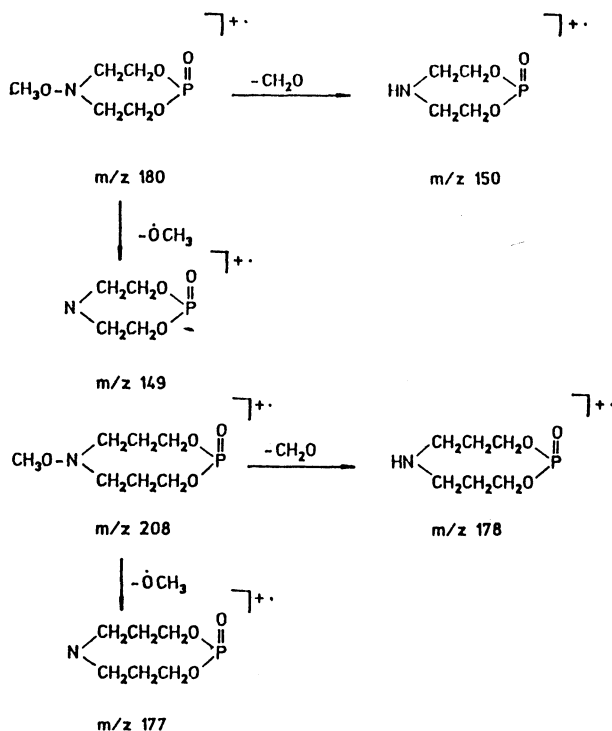


Scheme-V

The N-methoxy compounds (3a) and (3b) series give the corresponding ion at m/z 99 ($C_5H_9NO^+$).

The N-methoxy cyclic phosphates 3a and 3b series show loss of both CH₂O and CH₃O (Scheme-VI) from the ions formed at m/z 180 and m/z 208 in eight and ten-membered cyclic phosphates. Besides these, certain fragmentation modes common to phosphates¹¹ are also observed almost in all these compounds.

Thus on the basis of foregoing discussion, we can easily infer that the fragmentation mode of cyclic phosphates under electron impact is governed by both the ring size and the substituent present. It is mainly dependent on the presence or absence of hetero atom in the cyclic phosphates. The EI mass spectra of cyclic phosphates thus give valuable informations regarding the structure of these compounds.



Scheme-VI

ACKNOWLEDGEMENT

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