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THE MASS SPECTRA OF PHOSPHONYL COMPOUNDS PART 3¹. DIMETHYL AND DIETHYL ALKANE- AND SUBSTITUTED-METHANE PHOSPHONATES

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THE MASS SPECTRA OF PHOSPHONYL COMPOUNDS PART 3¹. DIMETHYL AND DIETHYL ALKANE- AND SUBSTITUTED-METHANE PHOSPHONATES

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The electron impact mass spectra of 28 related phosphonates have been determined. Ethyl, iso-propyl and tert-butyl groups which are bound directly to phosphorus, fragment to the corresponding alkenes; similar iso-propyl and tert-butyl groups in the dimethyl esters also fragment to ethylene and propene respectively, i.e. the P-alkyl group rearranges with transfer of the elements of a methyl group to the phosphorus ion. The diethyl alkenephosphonates undergo double hydrogen rearrangements of an ethoxy group to give dihydroxyphosphonium ions. The di- and trihydroxyphosphonium ions have a characteristic fragmentation which involves loss of water. This characteristic has been used as evidence for the rearrangement of a phosphacylium ion to a dihydroxyphosphonium ion. Some other unusual rearrangements involving the combination of the groups bound to phosphorus and oxygen have been observed.

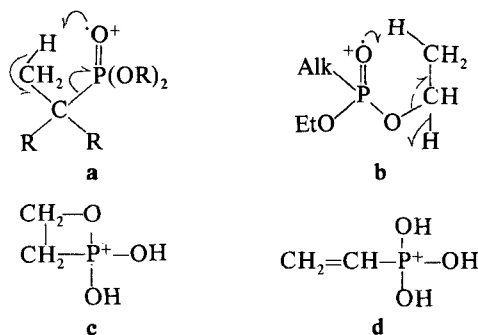
Unlike the relatively simple mass spectra of phosphonyl dichlorides¹ and phosphonic acids,² the phosphonates fragment by a wide variety of paths. Occolwitz and Swann³ have examined the widest range of phosphonates. Other workers have studied the spectra of methane- and ethanephosphonates^{4,5} substituted and higher alkane derivatives,^{6,7} norbornanephosphonates⁸ and a mixed ester of benzenephosphonic acid.⁹

Tables 1 and 2 give the common and more abundant ions that appear in the 70 eV mass spectra of the dimethyl and diethyl alkanephosphonates (1-4), the halomethanephosphonates (5-8), the O- and N-substituted methanephosphonates (9-12), the phenylmethanephosphonates (13) and the benzene-phosphonates (14). All the esters show medium to low intensity molecular ions. Notable is the common appearance of M+1 ions but very low abundance of M-1 ions (with the exception of dimethyl benzene-phosphonate where the reverse occurs).

AlkP(OR)_2	$\text{CH}_{n-3}\text{X}_n\text{P(OR)}_2$	$\text{YCH}_2\text{P(OR)}_2$
1, Alk = Me	5, n = 1 X = Cl	9, Y = OMe
2, Alk = Et	6, n = 2 X = Cl	10, Y = OAc
3, Alk = Pr ⁱ	7, n = 3 X = Cl	11, Y = PO(OMe) ₂
4, Alk = Bu ^t	8, n = 1 X = Br	12, Y = C ₆ H ₄ (CO) ₂ N
		13, Y = CH ₂ C ₆ H ₅
		14, Y = C ₆ H ₅

Ions arising from cleavage of the P-C bond are common. The resultant carbonium ions, which are

listed in the Tables under M-PO(OR)₂, are usually more abundant than the phosphacylium ions (RO)₂PO⁺ and in some spectra the carbonium ion produces the base peak. However, phosphacylium ions are the base peaks in the spectra of the halo-methanephosphonates.



The mass spectra of the alkanephosphonates (Scheme 1 and 2) show that in contrast to the corresponding acids,² ethyl and higher branched alkyl groups which are bound directly to phosphorus, fragment readily with loss of alkene to give ions listed under HPO(OR)₂. We assume that the fragmentation occurs by the process shown in (a) and that the initially formed daughter ion has the phosphite structure. This fragmentation in the spectra of the dimethyl esters (Scheme 1) gives the base peaks at m/e 110. Further fragmentation gives abundant ions at m/e 80, 79, 47 and 28 which is characteristic of the mass spectrum of dimethyl

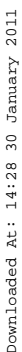
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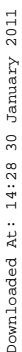
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MASS SPECTRA OF PHOSPHONYL COMPOUNDS

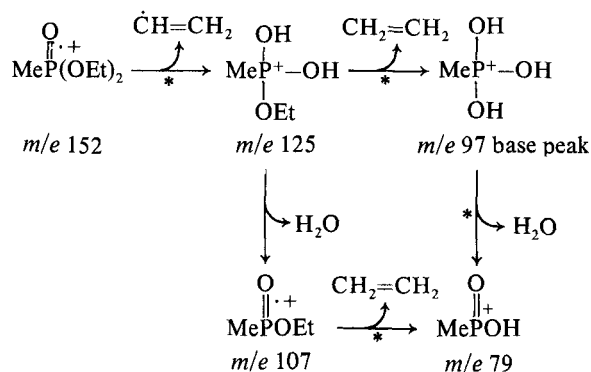
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TABLE 2
Normalized abundancies of some common cations in the mass spectra of diethyl phosphonates (1-14, R = Et)

Compound	M	M + 1	M - OEt	M - PO(OEt) ₂	HPO(OEt) ₂	PO(OEt) ₂	m/e 125	HP(OH) ₂ OEt	m/e 109	m/e 93	m/e 91	m/e 83	m/e 81	m/e	%	m/e	%
1	7 ^f	4	36	20	1	10	90 ^{ef}	5	15	12	9	2	32	107 ^b 97 ^{de} 139 ^a 100	36 100 63 65 ^g	80 ^{ac} 79 ^{bd} 82 63	63 88 63 72
2	40 ^j	11 ^k	53 ^h	69	79 ^u	21	5	100 ^j	70	73 ^{ab}	36	60	60	94 153 ^m 110 110 ^o 82 ^o 159 st	64 30 40 24 54 71	82 65 65 41 ⁿ 131 ^s	96 93 21 50 45
3	27	7	20	100	90 ^j	10	73 ^m	73 ⁱ	60 ^j	53	27 ⁱ	57	70	95 152 ^u 97 ^u 110 153 ^u 96 95 ^v 171 ^y 65 ^z 186 ^p 158 ^{cd}	28 74 61 23 26 23 61 18 26 8	95 80 61 82 82 80 161 25 60 36 52	51 61 62 62 17 28 25 60 34
4	5 ^a	1	2	100 ⁿ	65 ^{iq}	3	1	64 ^{io}	6	10	3	33 ^v	16				
5	14 ^s	2	20	16	5	48 ^r	0	5	100 ^u	2	34 ⁱ	14	80				
6	1	1	1	18	4	77 ^r	0	7	100 ^u	6	21 ⁱ	18	58				
7	1	0	1	10	11	71 ^r	0	11	100 ^u	15	38 ⁱ	27	77				
8	4	0	8	84	0	16	4	0	44 ⁱ	84	36 ⁱ	16	100				
9	3	2	22	61	9	22	100 ^{uu}	27	60	18	34	11	62				
10	3	1	14	8	100 ^j	40	10 ^u	78 ⁱ	28 ⁱ	11	11 ⁱ	31	37				
11 ^{wx}	2	3	5	18	10	7	100 ^{uv}	37	31 ⁱ	15	12 ⁱ	10	61				
12	22 ^y	4	1	100	2	1	0	0	1	1	8	6	6				
13	12	2	1	100	0	1	1	0	21 ⁱ	4	100 ^u	3	17				
14	20 ^z	4	4	100 ^{ab}	0	0	2	0	4	6	4	4	10				

Meta-stable ions in the mass spectra of diethyl phosphonates (1-14, R = Et)

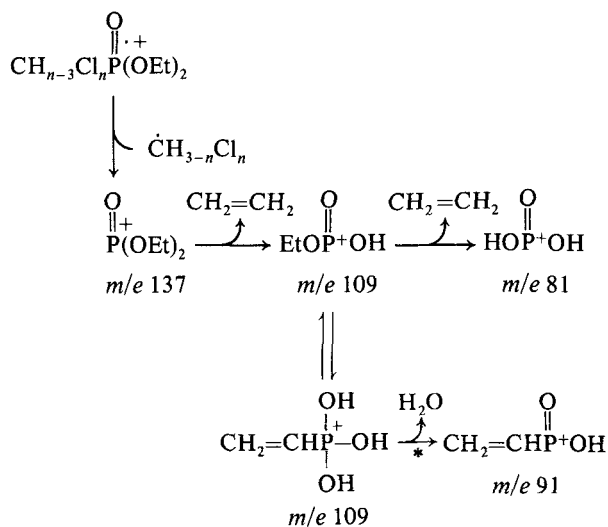
a	52.8	(80 → 65)	q	98.2	(194 → 138)
b	58.3	(107 → 79)	r	86.7	(137 → 109)
c	59.2	(108 → 80)	s	108.0	(159 → 131)
d	64.3	(97 → 79)	t	136	(186 → 159)
e	75.3	(125 → 97)	u	102.8	(152 → 125)
f	102.8	(152 → 125)	v	129.3	(181 → 153)
g	45.4	(93 → 65)	w	164.6	(212 → 189)
h	71.5	(121 → 93)	x	192.2	(245 → 217)
i	89.3	(138 → 111)	y	98.5	(297 → 171)
j	114.7	(166 → 138)	z	46.4	(91 → 65)
k	115.6	(167 → 139)	A	33.8	(77 → 51)
l	76.0	(109 → 91)	B	42.1	(141 → 77)
m	102.1	(153 → 125)	C	55.9	(158 → 94)
n	29.5	(57 → 41)	D	134.2	(186 → 158)
o	61.1	(110 → 82)	E	161.2	(214 → 186)
p	62.1	(111 → 83)			



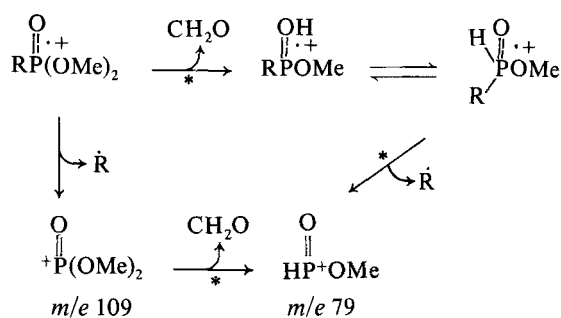
Scheme 3

acids¹¹ show that di- and trihydroxyphosphonium ions fragment with loss of water to give phosphacylium ions. A similar transition was confirmed in the spectrum of diethyl methanephosphonate and the regular appearance, in the mass spectra of diethyl alkanephosphonates, of abundant ions 18 m.u. below all ions which have di- or trihydroxyphosphonium structures lead us to conclude that this transition is a general characteristic of these structures.

The dimethyl esters of the branched-alkane-phosphonic acids (3, R = Me) and (4, R = Me) exhibit an unusual fragmentation $M^+ \rightarrow 124$ which corresponds to the elimination of ethylene and propylene respectively. Thus rearrangements of the P-alkyl groups occur which involve transfer of the elements of a methyl group to the phosphorus fragment. This type of rearrangement has been observed in the mass spectrum of di(1-methyl-



Scheme 4

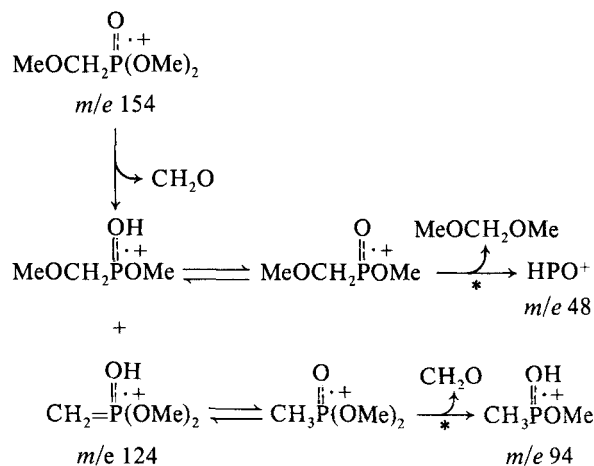


Scheme 5

ethane)phosphonic acid.¹¹ The ester (4, R = Me) gives a meta-stable ion 72.8 (124/95) for a subsequent fragmentation which corresponds to the loss of an ethyl radical. The corresponding ethyl esters also show similar transformations although they are less abundant and not supported by meta-stable ions. Further work is required before a meaningful rationalisation can be suggested.

A common transition for the diethyl halo-methane- and phenylmethane-phosphonates is $m/e\ 109 \rightarrow 91$ (Scheme 4). The loss of water is characteristic of di- and trihydroxyphosphonium ions. Thus it appears that the phosphacylium ion has a pathway available by which it can rearrange to a more stable phosphonium structure such as the cyclic ion (c) or the trihydroxyvinylphosphonium ion (d).

Dimethyl methane- and substituted-methane-phosphonates fragment by the pathways shown in Scheme 5. The spectra of both esters of methoxymethanephosphonate (9) show abundant (74%) $M-\text{CH}_2\text{O}$ ions showing that formaldehyde is eliminated from the methoxymethane group as well as the



Scheme 6

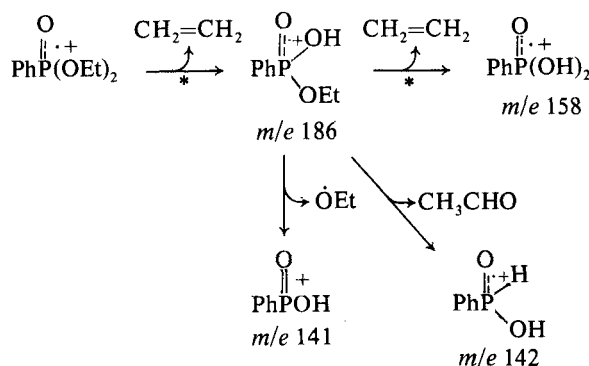
POMe group. The spectrum of the dimethyl ester (**9**, R = Me) resembles that of the diphosphonate (**11**, R = Me). Very intense peaks occur at m/e 124 and both spectra exhibit m/e 124 \rightarrow 48 and m/e 124 \rightarrow 94 transitions which correspond to loss of dimethoxymethane and formaldehyde respectively. We suggest that this is due to the formation of isomeric ions at m/e 124 as shown in Scheme 6.

The mass spectra of the corresponding ethyl esters (**9**, R = Et) and (**11**, R = Et) and diethyl acetoxymethanephosphonate (**10**, R = Et) are dominated by intense peaks corresponding to $(\text{EtO})_2\text{PO}^+$ and $\text{CH}_2=\text{P}(\text{OH})(\text{OEt})$ and their daughter ions. The spectrum of the acetate (**10**, R = Et) also exhibits a m/e 138 \rightarrow 111 transition reminiscent of the double hydrogen rearrangement shown in Scheme 2. Fragmentation of the acetoxymethyl group to formaldehyde and ketone readily accounts for the formation of the ion at m/e 138.

The spectra of the phthalimidomethanephosphonates (**12**) contain abundant ions at m/e 161, 160, 104, and 50 which also appear in the spectrum of phthalimide. Phosphorus containing ions were of low abundance.

The spectra of the phenylmethanephosphonates (**13**) contain the expected ions due to the benzyl (tropylium) cation and loss of a benzyl radical by the molecular ion. However the methyl ester also gave abundant ions at m/e 105 and 104 which are attributed to the methyltropylium and methylene-tropylium ions respectively. Migration of a hydrocarbon fragment from the ester group to the hydrocarbon moiety attached to phosphorus has been observed previously.³

The methyl and ethyl esters of benzene-phosphonic acid (**14**, R = Me) and (**14**, R = Et) respectively show quite different fragmentation patterns apart from the common base peak at m/e 77 (C_6H_5^+). The methoxy group is again a source of



Scheme 8

methylene producing tropylium cations whilst the ethyl group of (**10**, R = Et) leads to the formation of methyltropylium ions at m/e 105. Schemes 7 and 8 rationalize the other abundant ions observed in the spectra. Both esters appear to exhibit migration of the phenyl group from phosphorus to oxygen but whereas the methyl ester gives an ion at m/e 93 corresponding to PhO^+ and/or $[\text{M}-\text{PhO}]^+$, the ethyl ester gives an ion at m/e 94 corresponding to PhOH^+ . It appears that loss of ethylene from the ethyl ester gives an acidic group which presumably acts as a proton source for the formation of phenol.

Although the mass spectra of the phosphonates are relatively complicated some general fragmentation patterns have emerged. This broad investigation has also shown the occurrence of some very interesting rearrangements which deserve more detailed study using a high resolution spectrometer.

We thank Keele University for providing mass spectrometry facilities and the Science Research Council for a studentship to W. R. Griffiths.

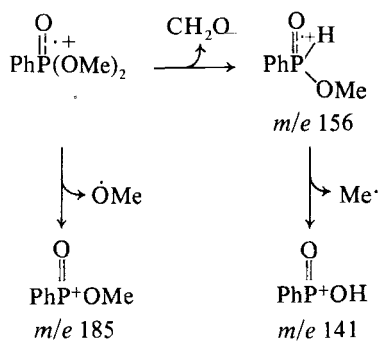
EXPERIMENTAL

The mass spectra were determined on a Perkin-Elmer Hitachi RMU 6 instrument at 70 eV by the direct insertion method.

The esters were prepared mainly by addition of the appropriate alcohol to the phosphonyl dichloride in the presence of a base. Some were prepared by the Arbuzov rearrangement and treatment of tetrachlorophosphoranes with the appropriate alcohol. The esters were purified by vacuum distillation except the phthalimidomethyl compounds which were solids. The identity and purity of the esters were established by boiling point or melting point, infra-red, ^1H and ^{31}P nmr spectroscopy.

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Scheme 7

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