

MASS SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS—II^{1,2}

REARRANGEMENTS IN CARBOALKOXYALKYLPHOSPHONATES

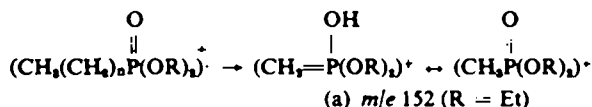
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Abstract—The mass spectra of carboalkoxyalkylphosphonates has been obtained. β -Cleavage to the phosphoryl group with a hydrogen rearrangement dominates in 3-carbethoxypropylphosphonate and 5-carbethoxyamylphosphonate, the well-known hydrogen migration to the carbonyl group being suppressed. Formation of an m/e 152 ion (a) in the spectra of carboalkoxyalkylphosphonates is interpreted in terms of skeletal rearrangement with loss of CO_2 and olefin. Scission of the C-P linkage with and without hydrogen migration is appreciable. Loss of a carboalkoxy group is noted as has been the case with amino acid esters. The $((\text{CH}_2)_n\text{P}(\text{O})(\text{OEt})_2)^+$ species is discussed.

It has been suggested^{1,3} that the McLafferty rearrangement of hydrogen under electron bombardment also operates for dialkyl alkylphosphonates probably via a 6-membered cyclic transition state, producing dialkyl methylphosphonate ion (a), which further undergoes multiple migrations of hydrogens as was the case with trialkyl phosphate⁴ and alkyl arylmethylphosphonate.⁵ As carboxylic acids and esters have been known to undergo the rearrangement of hydrogens,^{6,7} the mass spectral behaviour



of compounds in which carbonyl as well as phosphoryl functions are present e.g., carboalkoxyalkylphosphonates I, II, III, IV, and V were examined. Both functions are attached to the same carbon in the compounds I, II, and III, while they are separated via several bonds in IV and V. In addition, the mass spectra of the phosphonates VI and VII, the simplest member of this series, have been determined.

A noteworthy feature in the spectra of IV (Table 1) and V (Fig. 1) is that expected rearrangement ions (m/e 88; $(\text{CH}_2=\text{C}(\text{OH})(\text{OEt}))^+$ and m/e 60; $(\text{CH}_3\text{C}(\text{O})\text{OH})^+$) are negligible in intensity or not observed at all in favour of an m/e 152 ion which was presumed to be diethyl methylphosphonate ion (a) and amounted to over 70% in intensity to the base peak, probably reflecting the favourable charge retention on the

¹ Part I, T. Nishiwaki, *Tetrahedron* **22**, 1383 (1966).

² This is Part IV of Organophosphorus compounds. T. Nishiwaki, *Tetrahedron* **22**, 771 (1966) should be considered to be Part II of this series.

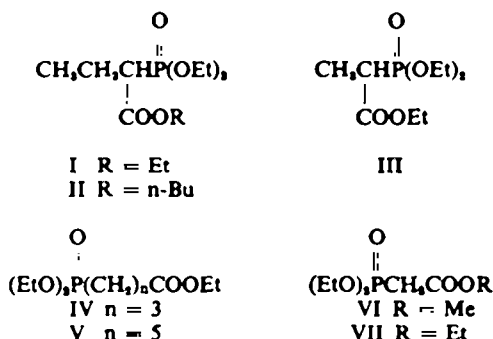
³ J. Occolowitz and J. Swan, *Austr. J. Chem.* **19**, 1187 (1966).

⁴ M. Halman, *J. Chem. Soc.* 3270 (1962).

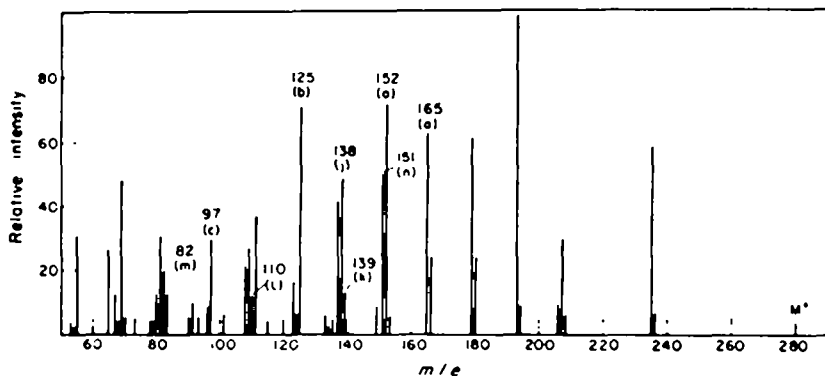
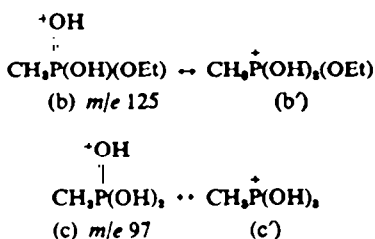
⁵ H. Budzikiewicz and Z. Pelah, *Monatsh. Chem.* **96**, 1739 (1965).

⁶ H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretations of mass spectra of organic compounds* Chap. 1. Holden-Day, San Francisco (1964).

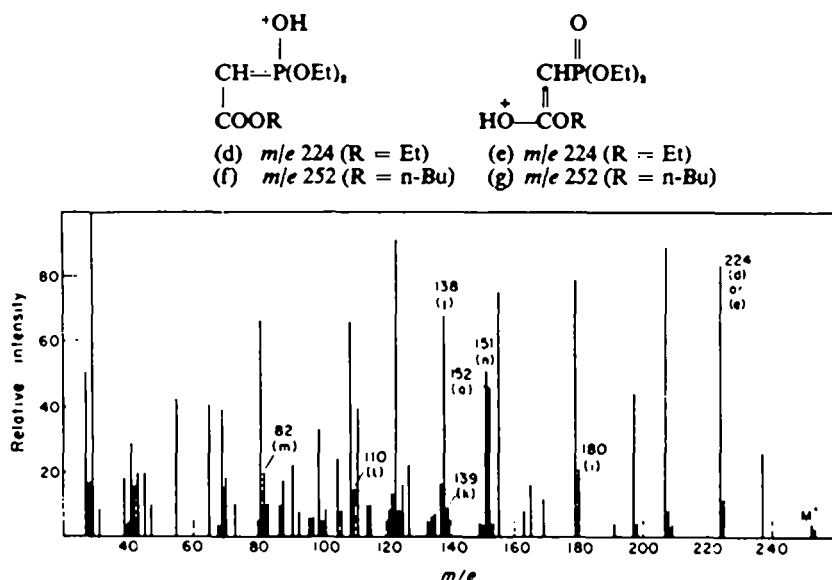
⁷ C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.* **87**, 5756 (1965).



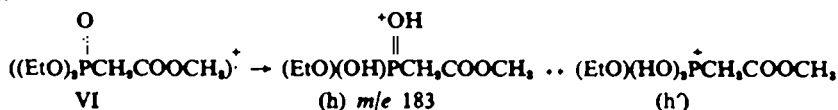
phosphoryl oxygen. Successive eliminations of mass units 28 from (a) eventually lead to an m/e 96 species. The ion (a) and the m/e 124 species lost mass units 27, respectively, in one step as evidenced by a metastable ion at m/e 103 and 76 giving rise to prominent oxonium ions (b) and (c) (or phosphonium ions (b') and (c')). The driving force for these hydrogen migrations is apparently the generation of stable onium ions. These results show that the well-known β -cleavage to carbonyl group with a hydrogen rearrangement is suppressed in favour of the transfer to the phosphoryl oxygen.



Formally the McLafferty rearrangement to the phosphoryl group can also be invoked for I and II and should produce an ion (d) or (e) for I and an ion (f) or (g) for II. The charge is retained on the phosphoryl oxygen in (d) and (f), while charge retention on the carbonyl oxygen results in the generation of (e) and (g). In fact an $(M-28)^+$ ion is very prominent for I (Fig. 2) or of moderate intensity for II (Table 1), but extent of the rearrangement to the carbonyl and the phosphoryl oxygen can not be decided. Mechanistically loss of ethylene is also possible on the $\text{P}(\text{O})(\text{OEt})_2$ and COOEt groups. For II an $(M-56)$ species which can be produced by loss of butene



is negligible. The (M-28) species further eliminates mass units 27 giving rise to an onium ion at m/e 197 for I and at m/e 225 for II in keeping with the fragmentation behaviour of VI and VII. The onium ion (h) (or (h')) is the base peak in the spectrum of VI.



The m/e 152 species is prominent in the spectra of I and VII but is less abundant for II. Formation of this species can be rationalized by invoking a skeletal rearrangement, namely a concerted loss of CO_2 and ethylene in the case of VII. A metastable ion can characterize this process. But the presence of an (M-44)⁺ ion with metastable ions at m/e 145 (calc. $224 \rightarrow 180, 144.6$) and at m/e 128 (calc. $180 \rightarrow 152, 128.4$) might not exclude the stepwise process. Similar skeletal rearrangement can explain the genesis of an m/e 166 ion in the spectrum of III, which is the molecular ion of diethyl ethylphosphonate⁸ (i; R = Me). A metastable ion at m/e 116 can support this process. This proposal is supported by the negligible abundance of the m/e 152 ion in the spectrum of the methyl ester VI. For the compound VI skeletal rearrangement brought about by loss of CO_2 operates and gives rise to the m/e 166 ion with a metastable ion at m/e 131. This will be produced by a Me rearrangement to the carbon atom (i; R = Me) or to the phosphoryl oxygen (i').* Such an elimination of a section of an open-chain of atoms as a neutral fragment from the linear portion of the ion is not unprecedented.⁹⁻¹²

* One of the referees kindly drew the author's attention to this point, to whom thanks are due.

⁸ J. Occolowitz and G. White, *Analyt. Chem.* **35**, 1179 (1963).

⁹ M. Fisher and C. Djerassi, *Chem. Ber.* **99**, 750 (1966).

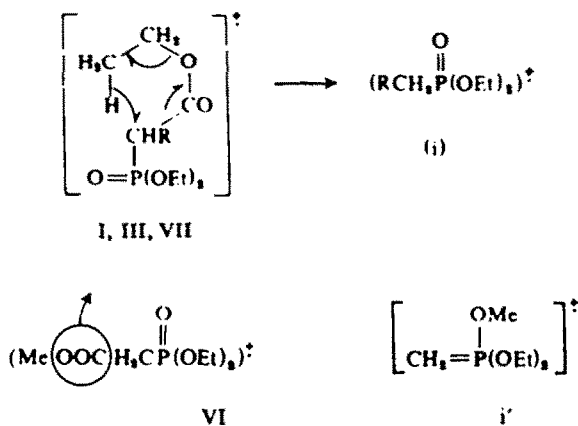
¹⁰ J. Bowie, R. Griggs, S.-O. Lawesson, P. Madsen, G. Schroll and D. H. Williams, *J. Am. Chem. Soc.* **88**, 1699 (1966).

¹¹ H. Bowie, D. H. Williams, S.-O. Lawesson and G. Schroll, *J. Org. Chem.* **31**, 1792 (1966).

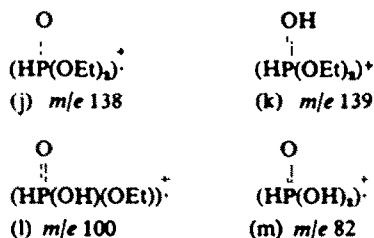
¹² J. Bowie, S.-O. Lawesson, G. Schroll and D. H. Williams, *J. Am. Chem. Soc.* **87**, 5742 (1965).

TABLE 1. MASS SPECTRA OF THE PHOSPHONATES II, III, IV, VI AND VII

II	<i>m/e</i>	27	28	29	31	39	40	41	42	43	45	47	55	56	57	65
	I (%)	19	7	45	3	3	2	38	11	9	6	4	22	8	12	19
	<i>m/e</i>	69	70	73	81	82	83	87	88	91	93	99	105	106	107	108
	I (%)	12	9	4	31	8	6	12	6	10	6	12	12	3	3	2
	<i>m/e</i>	109	110	111	121	122	123	124	125	127	133	134	135	137	138	139
	I (%)	30	7	20	3	6	55	4	7	10	3	2	3	9	40	8
	<i>m/e</i>	141	143	149	150	151	152	153	155	163	165	169	179	180	181	196
	I (%)	3	4	3	5	35	18	4	20	4	14	9	78	19	3	4
III	<i>m/e</i>	197	198	207	208	209	224	225	252	253	265	280	281			
	I (%)	12	3	100	9	3	3	28	23	4	12	4	2			
	<i>m/e</i>	27	28	29	31	41	42	43	45	47	55	56	57	59	65	73
	I (%)	36	34	66	6	3	3	9	24	11	29	31	4	4	32	8
	<i>m/e</i>	74	81	82	83	91	92	93	94	99	102	109	110	111	119	120
	I (%)	18	65	18	6	25	18	9	5	45	33	100	17	35	6	6
	<i>m/e</i>	121	122	123	127	136	137	138	139	149	155	164	165	166	183	192
	I (%)	6	6	4	34	15	73	40	16	4	50	15	82	35	14	10
IV	<i>m/e</i>	193	194	209	210	211	238	239								
	I (%)	94	8	13	4	24	10	1								
	<i>m/e</i>	27	28	29	31	32	39	41	42	43	45	47	55	57	60	61
	I (%)	49	64	92	11	9	15	56	48	24	24	11	11	3	4	4
	<i>m/e</i>	65	68	69	70	78	79	80	81	82	83	88	91	93	96	97
	I (%)	39	5	7	5	11	6	12	15	21	13	4	12	20	12	30
	<i>m/e</i>	105	106	107	108	109	110	111	121	122	123	124	125	127	133	134
	I (%)	21	7	4	18	51	11	46	6	10	71	9	60	4	4	6
VI	<i>m/e</i>	137	138	139	149	150	151	152	153	155	165	166	178	179	180	207
	I (%)	24	37	11	5	5	82	88	5	4	100	10	15	57	11	53
	<i>m/e</i>	208	252													
	I (%)	5	2													
	<i>m/e</i>	27	28	29	31	42	43	45	47	59	65	74	78	79	80	81
	I (%)	18	8	30	20	28	24	17	11	9	21	48	8	4	3	29
	<i>m/e</i>	91	93	95	96	97	99	105	106	109	110	111	113	122	123	124
	I (%)	8	13	34	8	7	4	14	5	33	4	7	3	11	73	6
VII	<i>m/e</i>	125	127	137	138	139	151	152	155	165	166	179	183	184	210	211
	I (%)	4	4	40	5	4	28	3	46	22	16	27	100	6	17	2
	<i>m/e</i>	27	28	29	31	41	42	43	44	45	47	48	49	59	60	61
	I (%)	36	15	63	19	3	41	4	3	22	13	5	3	4	10	9
	<i>m/e</i>	65	70	78	79	80	81	82	88	89	91	93	95	96	97	99
	I (%)	26	6	13	5	8	47	3	41	3	10	7	5	12	19	12
	<i>m/e</i>	105	106	107	108	109	110	111	122	123	124	125	127	137	138	139
	I (%)	24	10	3	6	52	2	2	13	100	7	22	7	15	2	3
	<i>m/e</i>	141	149	150	151	152	154	169	179	180	197	198	224	225		
	I (%)	8	3	3	63	48	5	29	71	13	72	5	10	3		



A feature common with these compounds is the cleavage of the C-P linkage with and without one or two hydrogen rearrangements resulting in the formation of m/e 137, 138, and 139 species. Appropriate metastable ions indicated in Table 2 suggest the molecular ion to be at least in part the immediate precursor for these ions. The m/e 138 ion is the molecular ion of diethyl hydrogen phosphite (j),¹³ while the m/e 139 species will be an onium ion (k). The exact origin of these rearranged hydrogens has not yet been unequivocally established, but negligible abundance of the m/e 138 and 139 ions in the spectra of VI and VII suggests that a hydrogen remote than α to phosphorus may be involved for these rearrangements. As is expected, the ion (j) further undergoes the McLafferty rearrangement of hydrogens to produce ions (l), (m), and their onium ions, which are abundant in the spectra of I, II, III, IV, and V.

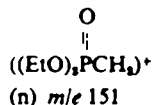
TABLE 2. METASTABLE IONS FOR THE PROCESSES: $M \rightarrow 137$, $M \rightarrow 138$, $M \rightarrow 139$

	$M \rightarrow 137$		$M \rightarrow 138$		$M \rightarrow 139$	
	Calc.	Observed	Calc.	Observed	Calc.	Observed
I	74.5	74	75.6	76	76.7	77
II	67.0	67	68.0	68	69.0	—†
III	78.9	79	80.0	80	81.2	—†
IV	74.5	74	75.6	76	76.7	77
V	67.0	—†	68.0	—†	69.0	—†
VI	89.4	89				
VII	83.8	84				

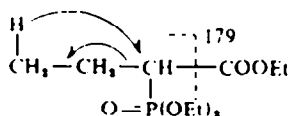
† A diffuse peak was obscure due to an intense fragment peak.

¹³ R. Harless, *Analyt. Chem.* 33, 1387 (1961).

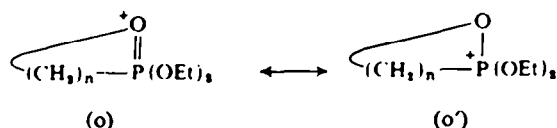
Among the remaining peaks a (M-59) species in the spectrum of VI and a (M-73) ion in VII corresponds with elimination of a carboalkoxy group. They can be represented as (n). The (M—COOR) species is also appreciable for the α -carboalkoxyalkylphosphonates I, II, III and is analogous to the behaviour of α -amino acid esters under electron bombardment.^{6,14} Migration of a hydrogen with concurrent elimination of ethylene via a four-membered cyclic transition state from the



(M—COOR) ion leads to the m/e 151 species (n), which is illustrated by I as an example. Alternatively, elimination of ethylene with subsequent loss of carboalkoxy group can also furnish the ion (n). In matter of fact metastable ions corresponding to the processes: (M—COOR) \rightarrow 151 and (M-28) \rightarrow 151 were observed in the spectra of I and II. The ion (n) loses mass units 28 to give rise to an m/e 123 species with a metastable ion at m/e 100, which is the base peak in VII and very prominent in I, II, IV and VI but less abundant in V. For III the m/e 123 ion was negligible.



Finally it should be noted that the $((\text{CH}_2)_n\text{P}(\text{O})(\text{OEt})_2)^+$ ions which may be formally produced by simple fission of the chain of IV and V (without any implications on rearrangement⁶) are abundant in contrast to negligible abundances of the $((\text{CH}_2)_n\text{COOEt})^+$ ions. Relatively high abundances of the $((\text{CH}_2)_n\text{P}(\text{O})(\text{OEt})_2)^+$ ions may associate with their existence in more stabilized onium ions (o) and (o'). For com-



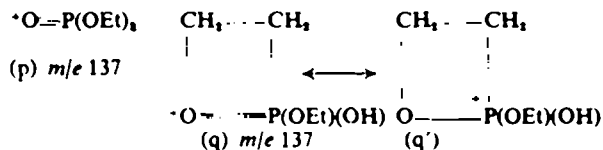
parison the partial spectra of diethyl n-butyl (VIII) and diethyl n-octylphosphonates (IX) are reproduced in Table 3. High abundances of the ions (o) and (o') where n

TABLE 3. INTENSITIES OF THE $((\text{CH}_2)_n\text{P}(\text{O})(\text{OEt})_2)^+$ IONS IN THE SPECTRA OF IV, V, VIII AND IX

		Σ''							
		n = 1	n = 2	n = 3	n = 4	n = 5	n = 6	n = 7	n = 8
	<i>m/e</i>	151	165	179	193	207	221	235	249
IV		5.4	6.6	3.8	—	—	—	—	—
V		3.6	4.9	4.4	7.3	2.0	—	—	—
VIII		0.4	2.9	0.6	0.3	—	—	—	—
IX		1.2	4.4	1.9	1.0	0.8	0.5	0.3	0.1

¹⁴ H. Budzikiewicz, C. Djerassi and D. H. Williams, *Structure elucidation of natural products by mass spectrometry* Vol. II; p. 183. Holden-Day, San Francisco (1964).

is 2 ~ 4 may support this proposal. It is interesting that the $((\text{CH}_2)_2\text{COOCH}_3)^+$ ion is also of medium intensity in long-chain fatty acid methyl esters.⁶ A metastable ion at m/e 114 was observed in the spectra of IV and V, which corresponds to the process: m/e 165 \rightarrow m/e 137. In the absence of deuterium labeling, the determination of the ion structure of the m/e 137 species thus formed is not possible although (p) and (q) or (q') are likely structures for this species.



The compounds examined were prepared by the Michaelis-Arbuzov reaction¹⁵ with an appropriate haloester and triethyl phosphite.

EXPERIMENTAL

The spectra were obtained with a Hitachi RMU 6D mass spectrometer fitted with an all glass inlet system at an ionization energy of 80 eV and an ionizing current at 80 μA . Ion source and inlet system are heated at about 200°. Compounds I, II, III, IV, VI and VII are known and were compared with the published physical constants.

Diethyl 5-carbethoxyamylphosphonate (V)—Ethyl ω -bromocaproate (6.7 g) and triethyl phosphite (7.5 g) were heated at 180° until all EtBr was removed. The reaction mixture was fractionally distilled using a Widmer column to give the compound (5.4 g), b.p. 114–118°/0.03 mm, n_D^{25} 1.4348. (Found: C, 51.03; H, 9.41. $\text{C}_{13}\text{H}_{26}\text{O}_5\text{P}$ requires: C, 51.42; H, 8.99%.)

¹⁵ K. Sasse, *Organische Phosphor Verbindung*. Teil 1; p. 433. George Thieme Verlag, Stuttgart (1963).