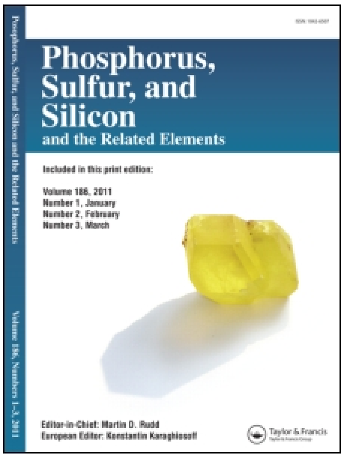


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

MASS SPECTROMETRY OF MECARBAM AND OF SOME RELATED *O,O*-DIALKYL *S*-(*N*-ETHOXYCARBONYL-*N*-METHYLCARBAMOYLMETHYL) AND *S*-METHYLCARBAMOYLMETHYL PHOSPHORODITHIOATES AND PHOSPHOROTHIOATES

J. Charalambous[a]; C. G. Herbert[a]; H. R. Hudson[a]; M. Pianka[a]; L. Powroznyk[a]; J. C. Roberts[a]; S. U. Sheikh[a]; V. P. Lynch[b]
[a] School of Chemistry, The Polytechnic of North London, London [b] Murphy Chemical Ltd., St. Albans, Hertfordshire

To cite this Article Charalambous, J. , Herbert, C. G. , Hudson, H. R. , Pianka, M. , Powroznyk, L. , Roberts, J. C. , Sheikh, S. U. and Lynch, V. P.(1984) 'MASS SPECTROMETRY OF MECARBAM AND OF SOME RELATED *O,O*-DIALKYL *S*-(*N*-ETHOXYCARBONYL-*N*-METHYLCARBAMOYLMETHYL) AND *S*-METHYLCARBAMOYLMETHYL PHOSPHORODITHIOATES AND PHOSPHOROTHIOATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 19: 3, 267 — 277

To link to this Article: DOI: 10.1080/03086648408077589

URL: http://dx.doi.org/10.1080/03086648408077589

Phosphorus and Sulfur, 1984, Vol. 19, pp. 267–277
0308-664X/84/1903-0267/$18.50/0

MASS SPECTROMETRY OF MECARBAM AND OF SOME RELATED *O,O*-DIALKYL *S*-(*N*-ETHOXYCARBONYL-*N*-METHYLCARBAMOYLMETHYL) AND *S*-METHYLCARBAMOYLMETHYL PHOSPHORODITHIOATES AND PHOSPHOROTHIOATES

J. CHARALAMBOUS, C. G. HERBERT, H. R. HUDSON, M. PIANKA,
(MRS) L. POWROZNYK, J. C. ROBERTS and S. U. SHEIKH

School of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB

V. P. LYNCH

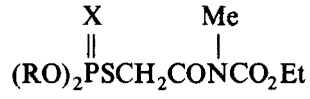
Murphy Chemical Ltd., Wheathampstead, St. Albans, Hertfordshire AL4 8QU

(*Received May 21, 1983; in final form November 14, 1983*)

The electron impact positive ion mass spectra of mecarbam and of a range of related phosphorodithioates and phosphorothioates containing substituted carbamoylmethyl groups are reported. All compounds exhibit molecular ion peaks and show fragmentation patterns which are characteristic of both the organophosphate and carbamoyl moieties. An unusual rearrangement involving phosphorus-sulphur fission and the apparent transfer of hydroxyl from the carbamoyl chain to phosphorus is discussed.

INTRODUCTION

Mecarbam (**1**) is an insecticide and acaricide containing both organophosphate and carbamate moieties.[1,2] Degradation in soil and in crops has been shown to occur with little evidence for the formation of significant levels of toxic metabolites, although the oxygen analogue (**2**) and the decarbethoxylated derivative (**5**) were detected in trace quantities in certain circumstances.[3] A further potential metabolite of mecarbam (**6**) was not detectable. We now report the electron impact mass spectra of these compounds, together with those of the corresponding *O,O*-dimethyl analogues **3** and **4**. Mass spectral data for the related pesticides dimethoate (**7**) and omethoate (**8**) have been reported previously[4] and are in agreement with our own measurements. These spectra are not repeated here but are referred to for purposes of comparison.



$(RO)_2\overset{\overset{X}{\|}}{P}SCH_2CO\overset{\overset{Me}{|}}{N}CO_2Et$

(**1**) R = Et, X = S
(**2**) R = Et, X = O
(**3**) R = Me, X = S
(**4**) R = Me, X = 0

$(RO)_2\overset{\overset{X}{\|}}{P}SCH_2CONHMe$

(**5**) R = Et, X = S
(**6**) R = Et, X = O
(**7**) R = Me, X = S
(**8**) R = Me, X = O

RESULTS AND DISCUSSION

Mass spectra, which were recorded at an electron-impact energy of 70 eV and a source temperature of 180°C, are presented in Tables I–VI. Similar results were obtained at temperatures up to 220°C and at various time intervals after insertion;

TABLE I

Mass spectral data for mecarbam, $(EtO)_2P(S)SCH_2CON(Me)CO_2Et$ (**1**)

m/z	331	330	329	298	297	296	295	228	227	226	206	199	198	186
%	5	5	35	2	2	14	2	3	8	14	10	68	11	6
m/z	185	177	171	161	160	159	157	153	148	145	144	143	132	131
%	5	8	10	9	50	49	10	31	9	11	14	9	19	100
m/z	129	128	125	121	116	104	102	97	93	87	86	79	76	75
%	31	15	51	36	36	19	9	95	28	15	39	2	17	10
m/z	74	73	65	58	57	56	55	47	46	45	44	43	42	
%	11	11	42	46	9	15	15	17	17	17	6	19	27	

TABLE II

Mass spectral data for $(EtO)_2P(O)SCH_2CON(Me)CO_2Et$ (**2**)

m/z	314	313	298	280	269	268	212	211	210	196	184	183	182	177
%	1	10	45	1	2	4	2	9	22	2	1	7	17	2
m/z	170	169	168	161	160	159	156	155	154	153	148	145	143	142
%	5	1	1	3	6	78	3	13	25	1	2	3	2	2
m/z	141	140	139	138	137	133	132	131	129	128	127	126	125	116
%	1	3	4	4	8	5	5	100	1	2	12	4	2	4
m/z	115	114	113	111	110	109	104	103	102	99	97	93	91	88
%	5	4	3	9	4	24	4	1	3	10	5	6	5	3
m/z	87	86	82	81	76	75	74	73	65	63	61	60	59	58
%	17	39	3	6	6	9	10	2	10	2	2	1	2	27
m/z	57	56	55	48	47	46	45	44	43	42	41			
%	1	1	5	1	9	10	9	5	7	16	3			

TABLE III

Mass spectral data for $(MeO)_2P(S)SCH_2CON(Me)CO_2Et$ (**3**)

m/z	303	302	301	244	230	200	199	198	174	172	171	170	160	159
%	2	2	7	6	5	4	9	11	6	45	3	6	10	15
m/z	158	157	145	144	143	132	131	126	125	121	116	115	109	102
%	5	8	6	52	9	4	38	15	69	3	9	7	12	3
m/z	97	93	86	79	77	76	75	74	73	63	58	57	50	49
%	5	85	73	32	17	8	9	10	1	20	100	6	13	19
m/z	47	46	45	43	42	40								
%	22	21	18	6	16	2								

TABLE IV

Mass spectral data for $(MeO)_2P(O)SCH_2CON(Me)CO_2Et$ (**4**)

m/z	286	285	252	185	184	183	182	168	161	160	159	157	156	155
%	1	11	1	1	3	12	44	1	3	4	65	2	7	16
m/z	154	148	144	143	142	141	133	132	131	128	127	126	125	116
%	10	2	2	4	10	2	6	7	100	1	24	3	32	4
m/z	115	113	112	111	110	109	104	102	95	93	87	86	80	79
%	4	1	5	7	21	77	3	4	6	9	13	53	6	17
m/z	76	63	58											
%	7	4	32											

TABLE V

Mass spectral data for $(EtO)_2P(S)SCH_2CONHMe$ (**5**)

m/z	259	258	257	212	187	186	184	180	172	171	156	153	144
%	6	6	34	3	6	3	6	13	3	25	3	9	3
m/z	143	142	129	125	123	121	115	110	109	106	105	104	99
%	9	3	9	19	4	19	6	3	3	6	22	6	3
m/z	97	93	89	88	87	86	81	80	73	72	65	63	58
%	41	13	6	9	100	6	3	3	34	3	22	3	19
m/z	56	55	48	47	46	45	44	43	42				
%	13	6	6	6	6	6	3	6	9				

TABLE VI

Mass spectral data for $(EtO)_2P(O)SCH_2CONHMe$ (**6**)

m/z	242	241	198	196	186	185	184	183	171	170	169	168	167
%	1	4	1	3	3	3	50	1	6	4	4	6	39
m/z	166	157	156	155	152	151	149	143	142	141	140	139	138
%	9	1	21	4	3	1	1	3	3	3	47	49	61
m/z	137	132	128	127	126	125	124	123	122	121	115	114	113
%	4	3	11	4	3	3	3	20	21	4	5	3	3
m/z	112	111	110	109	105	99	97	96	95	94	93	92	91
%	50	96	60	20	14	4	4	6	40	100	29	7	6
m/z	87	83	82	81	75	73	65	61	58	57	56	55	48
%	4	17	37	31	4	16	29	3	37	3	1	4	7
m/z	47	46	45	44	43	42	41						
%	14	9	14	7	13	10	4						

thermal decomposition is not therefore considered to occur to a significant extent under these conditions. Each of the compounds under investigation gave a molecular ion, the relative abundance of which lay between 4% for *O,O*-diethyl *S*-methylcarbamoylmethyl phosphorothioate (**6**) and 35% for mecarbam (**1**). Accurate mass measurements for selected ions are given in Table VII.

TABLE VII

Accurate mass measurements

Compound	Ion (m/z)	Assignment	Measured Mass	Calculated Mass
1	329	$C_{10}H_{20}NO_5PS_2(M^{+\cdot})$	329.0519	329.0520
	296	$C_{10}H_{19}NO_5PS$	296.0742	296.0721
	226	$C_6H_{11}O_3PS_2$	225.9892	225.9887
	199	$C_5H_{12}O_2PS_2$	198.9996	199.0016
	160	$C_6H_{10}NO_2S$	160.0428	160.0432
	159	$C_6H_9NO_2S$	159.0353	159.0354
	144	$C_6H_{10}NO_3$	144.0658	144.0661
	131	$C_4H_5NO_2S$	131.0040	131.0041
	58	C_2H_4NO	58.0294	58.0293
2	313	$C_{10}H_{20}NO_6PS(M^{+\cdot})$	313.0744	313.0750
	160	$C_6H_{10}NO_2S$	160.0380	160.0432
	159	$C_6H_9NO_2S$	159.0333	159.0354
3	301	$C_8H_{16}NO_5PS_2(M^{+\cdot})$	301.0203	301.0208
	172	$C_3H_9O_2PS_2$	171.9775	171.9769
	160	$C_6H_{10}NO_2S$	160.0429	160.0432
	159	$C_6H_9NO_2S$	159.0333	159.0354
	144	$C_6H_{10}NO_3$	144.0666	144.0661
	131	$C_4H_5NO_2S$	131.0045	131.0041
	63	CH_4OP	62.9993	63.0000
	58	C_2H_4NO	58.0295	58.0293
4	285	$C_8H_{16}NO_6PS(M^{+\cdot})$	285.0436	285.0436
	182	$C_4H_7O_4PS$	181.9808	181.9802
	160	$C_6H_{10}NO_2S$	160.0386	160.0432
	159	$C_6H_9NO_2S$	159.0333	159.0354
	131	$C_4H_5NO_2S$	131.0039	131.0041
	58	C_2H_4NO	58.0293	58.0293
5	257	$C_7H_{16}NO_3PS_2(M^{+\cdot})$	257.0306	257.0310
6	241	$C_7H_{16}NO_4PS(M^{+\cdot})$	241.0538	241.0538

1. Ions resulting from phosphorus–sulphur fission.

(a) Phosphorus-containing ions

In conformity with previously reported fragmentation patterns for phosphorodithioates and phosphorothioates,[5,6] a significant proportion of the total ion current may in each case be attributed to phosphorus-containing ions (Table VIII) resulting

TABLE VIII

Ions assigned to simple cleavage of P—S

Ion	Compound					
	1	**2**	**3**	**4**	**5**	**6**
$(RO)_2PX$	153/31	137/8	125/69	109/77	153/9	137/4
$(RO)(HO)PX$	125/51	109/24	111/0	95/6	125/19	109/20
$(HO)_2PX$	97/95	81/6	97/5	81/0	97/41	81/31
$(HO)_2P$	65/42	65/10	65/0	65/0	65/22	65/29
$(RO)_2P$	121/36	121/0	93/85	93/9	121/19	121/4
$(RO)(HO)P$	93/28	93/6	79/32	79/17	93/13	93/29

Metastable ions: compound **1**, m* 61.4 [Calc. for 153 → 97: 61.5];
compound **5**, m* 75.2 [Calc. for 125 → 97: 75.3].

$$\left.(RO)_2P(X)\wr SCH_2CON(Me)Y\right]^{+\cdot} \longrightarrow \left.(RO)_2PX\right]^{+} + {}^{\cdot}SCH_2CON(Me)Y$$

[R = Me or Et; X = S or O; Y = CO_2Et or H]

SCHEME 1

from simple cleavage of the bond between phosphorus and the thiolo-sulphur atom (Scheme 1), followed by stepwise loss of ethylene in the ethoxy series (**1**, **2**, **5**, and **6**), loss of CH_2O or CH_2S in the methoxy series (**3** and **4**), and/or loss of sulphur from the various ions derived from the phosphorothionates (**1**, **3**, and **5**). The strong peak at m/z 97 which occurs in a relative abundance of 95% in the mass spectrum of mecarbam (**1**) and 41% in the mass spectrum of the decarbethoxylated analogue (**5**) is assigned to $[(HO)_2PS]^+$, an ion which has previously been recognised as a major feature in the fragmentations of diethyl phosphorodithioates.[4] An additional peak at m/z 63 in the mass spectrum of **3** (Table III) may be assigned to $[MeOPH]^+$, which is known to be formed by loss of CH_2O from $[(MeO)_2P]^+$ in the case of other dimethyl phosphorodithioates.

(b) Ions derived from the carbamoyl moiety

Two of the most significant peaks in the mass spectra of mecarbam and its analogues (i.e. the *N*-ethoxycarbonyl derivatives) (**1**–**4**) occur at m/z 159 and m/z 131. The peak at m/z 131 is the base peak for compounds **1**, **2**, and **4**, and is moderately strong (relative intensity 38%) for compound **3**. Metastable ion peaks centred at m/z 108.0 in the spectra of compounds **1**, **2**, and **4** showed the ion at m/z 131 to be formed directly from that at m/z 159, the latter also giving a strong peak in the spectra of these three compounds (relative intensities 49, 78, and 65% respectively). Although present in the mass spectrum of **3**, the peak at m/z 159 is weaker (15%). Accurate mass measurements in each case showed the peak at m/z 159 to be due to an ion of elemental composition $C_6H_9NO_2S$ (Table VII), i.e. it is formed from the carbamoyl part of the molecule by fission of the bond between phosphorus and the thiolo-sulphur atom, together with the loss of one atom each of oxygen and hydrogen. The direct formation of this ion from the molecular ion is indicated by metastable ion peaks centred on m/z 80.9 and 88.7 in the mass spectra of the phosphorothiolates **2** and **4** respectively and suggests loss of a dialkyl phosphoric or thiophosphoric acid $(RO)_2P(X)OH$, as the neutral fragment (Scheme 2). An analogous process has been shown to give rise to the base peak (m/z 87) in

$$\left.(RO)_2P(X)SCH_2CON(Me)CO_2Et\right]^{+\cdot} \xrightarrow{-\ (RO)_2P(X)OH} \left.C_6H_9NO_2S\right]^{+\cdot}$$

[R = Me or Et; X = O or S] m/z 159

Metastable ions:

Compound **2** : m* 80.9 [Calc. for 313 → 159 : 80.8]

" **4** : m* 88.7 [Calc. for 285 → 159 : 88.7]

SCHEME 2

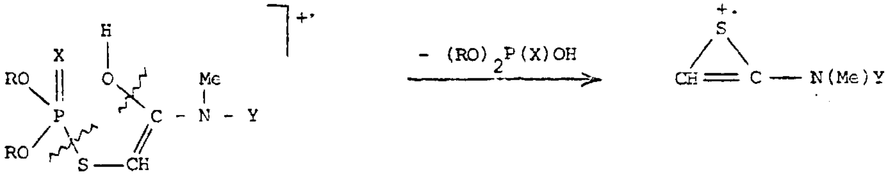
the mass spectrum of dimethoate (**7**),[4] although its mode of formation was not discussed. Our own measurements confirm that this ion gives rise to the base peak both for dimethoate (**7**) and for the diethyl analogue (**5**) and it is reasonable to assume that a similar process is involved (Scheme 3). The phosphorothiolates **6** and **8** do not, however, give rise to an ion at m/z 87. In these cases, a strong hydrogen-bonding interaction between the phosphoryl oxygen atom and the nitrogen-bonded hydrogen appears to favour an alternative fragmentation pathway (see below). The mechanism by which the rearrangement ions (m/z 159 for compounds **1**, **2**, **3**, and **4** and m/z 87 for compounds **5** and **7**) arise is not clear. Their formation from mecarbam and its analogues (**1–4**) shows, however, that loss of a nitrogen-bonded hydrogen from the carbamoyl moiety (as in dimethoate) is not a necessary part of the process. It is also clear that it is the oxygen of the carbamoyl carbonyl group which is transferred as this is the only possibility in the case of **5** and of dimethoate (**7**). This is an unusual rearrangement which may tentatively be formulated as phosphorus–sulphur fission with simultaneous transfer of hydroxyl to phosphorus in the enol form of the molecular ion (Scheme 4). The structure of the rearrangement ion is uncertain. That derived from dimethoate (**7**) has been formulated[4] as "*N*-methyl thioacetonitrile" $[S{-}CH_2{-}C{\equiv}N{-}CH_3]^+$ but an exactly analogous structure cannot be written for the ion derived from mecarbam or its derivatives which carry both methyl and CO_2Et groups on nitrogen. A cyclic sulphonium species as shown (Scheme 4) would most effectively stabilise the positive charge. Hydroxyl transfers of this type are unknown in the mass spectrometry of purely organic compounds but have been reported in the fragmentations of a number of organometallic derivatives,[7] including ferrocenyl alcohols[8] and stannyl alcohols.[8] It is likely that the rearrangement is facilitated by the ability of phos-

$$\left.(RO)_2P(S)SCH_2CONHMe\right]^{+\cdot} \xrightarrow{-\ (RO)_2P(S)OH} \left.C_3H_5NS\right]^{+\cdot}$$

[R = Me or Et]

m/z 87

SCHEME 3

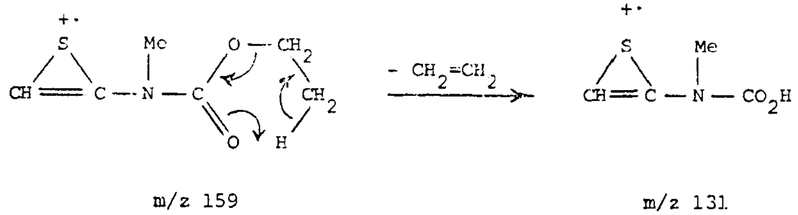


m/z 159 (Y = CO_2Et)

m/z 87 (Y = H)

[R = Me or Et, X = S, Y = CO_2Et or H; R = Me or Et, X = O, Y = CO_2Et]

SCHEME 4



Metastable ions m* 108.0 [Calc. for 159 → 131 : 107.9]

(Compounds **1**, **2**, **4**)

SCHEME 5

phorus to use d-orbitals in the formation of the transition state and by its tendency to retain the oxidation state +5. The transfers of O, OH, or Ph_2P to phosphorus have similarly been reported in the electron-impact mass spectrometry of acylphosphines, the phosphorus atom in these instances being said to act as an excellent electron acceptor.[10] In these examples the positive charge remains with phosphorus, whereas in our present examples the phosphorus-containing moiety is lost as the neutral fragment.

Conversion of the ion at m/z 159 to that at m/e 131 (metastable supported—see above) presumably occurs *via* loss of ethylene from the *N*-ethoxycarbonyl group (Scheme 5), a process that cannot occur for the analogous ion (m/z 87) derived from **5** or **7**.

In addition to the peak at m/z 159, an accompanying peak at m/z 160 appears in the mass spectra of the *N*-ethoxycarbonyl compounds. Although relatively weak for compounds **2**, **3** and **4**, it is of comparable relative intensity (*ca.* 50%) to the peak at m/z 159 in the mass spectrum of mecarbam (**1**). In each case, accurate mass measurements showed the elemental composition of the ion to be $C_6H_{10}NO_2S$, i.e. it differs by one hydrogen atom only from that at m/z 159. Whether it is formed directly, e.g. by phosphorus–sulphur fission together with oxygen transfer to the phosphorus in the keto-form of the parent ion, or by other process, is not known.

2. *Ions resulting from primary fission of bonds in the carbamoyl chain.*

Ions derived directly by simple fission of bonds in the carbamoyl chain are in general of minor significance in all compounds (Table IX). Exceptions are the phosphorus-containing ion (m/z 199, relative intensity 68%) (Table I) which is obtained by fission of the CH_2—CO bond of mecarbam (**1**) (Scheme 6), and the carbamate fragment (m/z 144) which results from S—CH_2 bond fission. This ion, which occurs in the mass spectra of mecarbam (**1**) and of its methyl analogue (**3**) with relative intensities of 14% and 52% respectively, may possibly be stabilized by ring-closure involving the neighbouring nitrogen atom (Scheme 7). Its further fragmentation by loss of ethylene is indicated by a metastable peak, m* 93.5, in the mass spectrum of mecarbam.

Peaks which may be attributed to ions resulting from fission of the CO–N bond are fairly weak but an accompanying hydrogen transfer from the phosphorus-con-

TABLE IX

Ions assigned to simple fissions of the carbamoyl chain

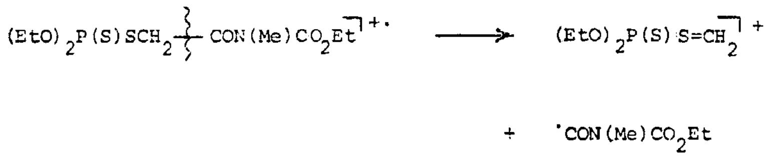
Phosphorus-containing ions	Compound 1	2	3	4	5	6
$(RO)_2P(X)S$	185/5	169/1	157/8	141/2	—	169/4
$(RO)_2P(X)SCH_2$	199/68	183/7	171/3[c]	155/16	—	183/1
$(RO)_2P(X)SCH_2CO$	227/8	211/9	199/9	183/12	—	—
$(RO)_2P(X)SCH_2CONMe$	—	—	—	—	—	—
Non-phosphorus containing ions[a]						
$CH_2CON(Me)Y$	144/14	—	144/52	—	72/3	—
CON(Me)Y[b]	—	—	—	—	58/19	58/37
N(Me)Y	102/9	102/3	102/3	102/4	—	—
Y	73/11	73/2	73/1	—	—	—

---

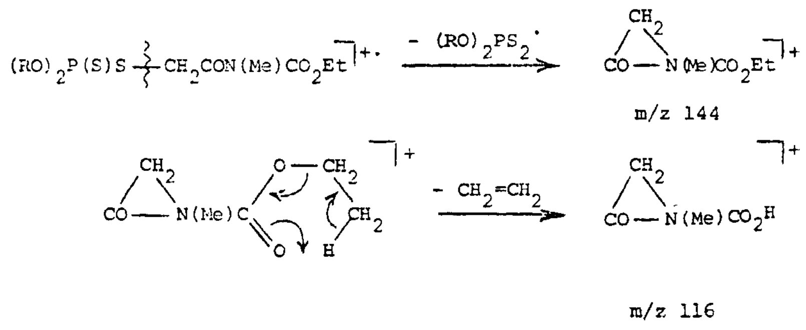
[a] Y = CO_2Et in cpds **1**–**4**; Y = H in cpds. **6**–**8**.

[b] Although this ion, m/e 130, is absent from the spectra of compounds **1**–**4**, it is a possible precursor of the relatively strong ion which these compounds give at m/z 53 (Scheme 12).

[c] In addition, the dimethyl phosphorodithioate (**3**) gives a peak of medium intensity at m/z 172, assigned to $[(MeO)_2P(S)SMe]^+$ on the basis of its elemental composition (Table VII). This ion is presumably formed by CH_2—CO fission, with transfer of a hydrogen from the carbamate moiety to the CH_2 group.



SCHEME 6



[R = Me or Et]

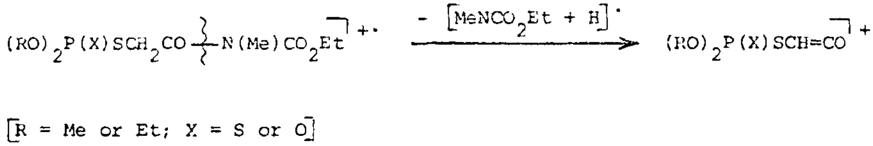
Metastable ion: m* 93.5 [Calc. for 144 ⟶ 116 : 93.4]

(Compound **1**)

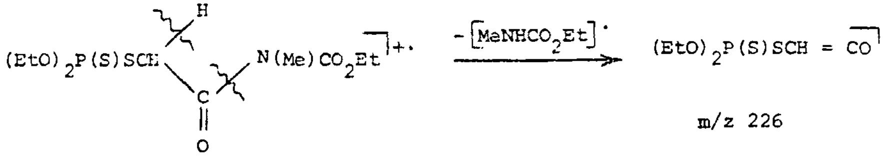
SCHEME 7

taining fragment in the case of the *N*-ethoxycarbonyl derivatives gives rise to ions at m/z 226 (14%), 210 (22%), 198 (11%) and 182 (44%) in the mass spectra of compounds **1**, **2**, **3** and **4** respectively (Scheme 8). For mecarbam (**1**) and for **4**, the elemental composition was confirmed by accurate mass measurement (Table VII), a likely structure being that shown (Scheme 8). Accelerating voltage scanning showed the ion at m/z 226 in the mass spectrum of mecarbam to be formed from the parent ion (m/z 329), probably in a concerted rearrangement (e.g. Scheme 9), and also from an unidentified ion at m/z 327. The latter indicates initial loss of H_2 although the ion itself was not detectable and its structure is unknown.

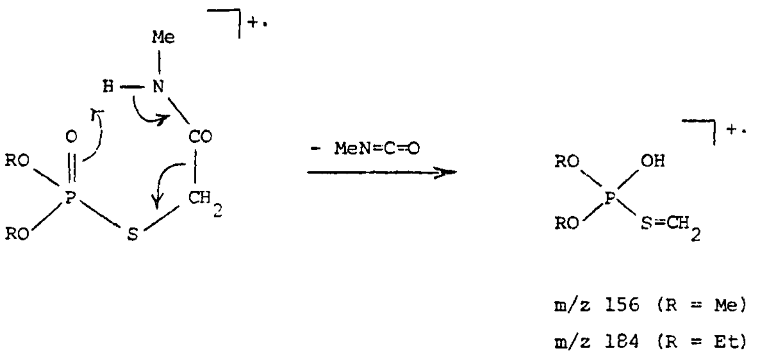
Analogous rearrangements are not observed in the case of dimethoate and its analogues (**5**, **6**, **7** and **8**). An important process in the fragmentation of the phosphorothioates (**6**, **8**) appears to occur as the result of a hydrogen-bonding interaction between the NH group of the carbamoyl moiety and the phosphoryl oxygen atom, leading to the elimination of the elements of methyl isocyanate with cleavage of the CH_2—CO bond (Scheme 10). The phosphorus-containing ions produced by this process occur with relative intensities of > 95% in dimethoate (**8**),[4] and of 50% in the diethyl ester (**6**). Corresponding ions are not detectable in the



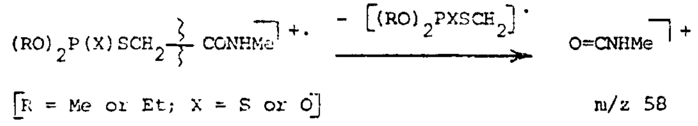
SCHEME 8



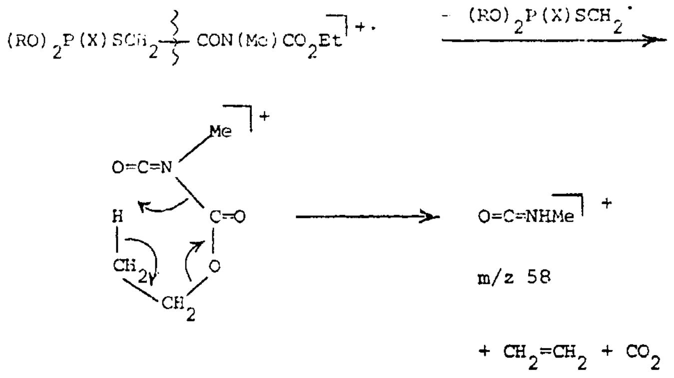
SCHEME 9



SCHEME 10



SCHEME 11



SCHEME 12

mass spectra of the dithioates (**5**, **7**) and are precluded in the case of the *N*-ethoxycarbonyl derivatives which show little evidence of the cleavages and rearrangements typical of carbamates.[11-14] A significant peak at m/z 58 in the mass spectra of **5** and **6** indicates that CH_2—CO cleavage in these compounds may alternatively give rise to the ion $[CH_3NHCO]^+$ (Scheme 11). This peak is also relatively strong in the mass spectrum of omethoate (8) (relative intensity *ca.* 30%), although it is weak in dimethoate (7).[4]

The presence of this same ion as a relatively abundant species in the mass spectra of the *N*-ethoxycarbonyl compounds (**1**–**4**) (for **3** it is the base peak) may possibly be accounted for by the loss of ethylene and of carbon dioxide from the ion produced initially by cleavage of the CH_2—CO bond (Scheme 12). The intermediate ion is not, however, detectable.

Loss of methyl from the *N*-ethoxycarbonyl-*N*-methylcarbamoyl group of **2** is suggested by the presence of a peak of relative intensity 45% at m/z 298, although analogous peaks were completely absent in the spectra of all other compounds studied.

3. *Loss of SH from the molecular ion*

The initial loss of SH from the molecular ion was observed in the case of mecarbam (**1**) only. A peak was thus observed at m/z 296 (14%), corresponding to an ion of elemental composition $C_{10}H_{19}NO_5PS$ (Table VII). This is an unusual fragmentation, not previously reported for organophosphates and which may involve the loss of the thiono-sulphur atom together with a hydrogen atom from the carbamoylmethyl chain, possibly in the enol form (cf. Scheme 4 for an alternative fragmentation which may also involve the enol structure).

EXPERIMENTAL

Mass spectra (Tables I–VI) were recorded on an AEI MS9 instrument operating with an electron-impact energy of 70 eV and at a source temperature of 180–220°C. Samples were introduced using the direct insertion probe; first field-free metastable ions were detected by the accelerating voltage scanning technique.[15] Accurate mass measurements were obtained either on the MS9 at a resolution of 10,000 or by PCMU, Harwell, using a VG ZAB 1F instrument with a resolution of 10,000 or 15,000.

Materials. Mecarbam (**1**) was supplied by Murphy Chemical Ltd., with a purity (g.l.c.) of not less than 97%. Compounds **2**, **5** and **6** were prepared as described.[3] Compounds **3** and **4** were prepared by analogous procedures by the reaction of ethyl *N*-chloroacetyl-*N*-methylcarbamate[16] with potassium *O*,*O*-dimethyl phosphorodithioate and with potassium *O*,*O*,-dimethyl phosphorothioate respectively.[17] The products were finally purified by passing solutions in light petroleum (b.p. 30–40°C) through a short column of Florisil. Removal of the solvent under reduced pressure then yielded almost colourless liquid residues of *S-(N-ethoxycarbonyl-N-methylcarbamoylmethyl) O,O,-dimethyl phosphorodithioate* (**3**) (Found: C, 32.5; H, 5.4; N, 4.5; M^+ 301.0203. $C_8H_{16}NO_5PS_2$ requires C, 31.9; H, 5.3; N, 4.7%; M^+ 301.0208), δ_P ($CDCl_3$) + 98.2 ppm (ref. 85% H_3PO_4), and of *S(N-ethoxycarbonyl-N-methylcarbamoylmethyl)O,O-dimethyl phosphorothioate* (**4**) (Found: C, 33.3; H, 5.7; N, 4.8; M^+ 285.0436. $C_8H_{16}NO_6PS$ requires C, 33.7; H, 5.6; N, 4.9%; M^+ 285.0436), δ_P ($CDCl_3$) + 30.0 ppm.

ACKNOWLEDGMENT

We thank the Physico-Chemical Measurements Unit (PCMU), Harwell, for carrying out a number of accurate mass measurements.

REFERENCES

1. M. Pianka, *Chem and Ind.*, 1961, 324.
2. M. Pianka, and D. J. Polton, (Murphy Chemical Ltd.) British Patent, 867, 780 (1961).
3. V. P. Lynch, H. R. Hudson, and M. Pianka, *Pesticide Sci.*, **12**, 65 (1981).
4. J. N. Damico, *J. Assoc. Offic. Anal. Chem.*, **49**, 1027 (1966).
5. J. M. Desmarchelier, D. A. Wustner, and T. R. Fukuto, *Residue Reviews*, **63**, 77 (1976).
6. S. Safe, and O. Hutzinger, "Mass Spectrometry of Pesticides and Pollutants," CRC Press, Cleveland, Ohio (1973).
7. "Fragmentation of Metal-containing ions," J. Charalambous, in "Mass Spectrometry of Metal Compounds," ed. J. Charalambous, Butterworths, London (1975), ch. 3, p. 45.
8. H. Egger, *Monatsch. Chem.*, **97** 602 (1966).
9. D. G. I. Kingston, H. P. Tannenbaum, and H. G. Kuivila, *Org. Mass Spectrom.*, **9**, 31 (1974).
10. J. Martens, K. Praefcke, H. Schwarz, and H. Simon, *Phosphorus*, **6**, 247 (1976).
11. B. Blessington, *Org. Mass Spectrom.*, **2**, 929 (1969).
12. C. P. Lewis, *Anal. Chem.*, **36**, 1582 (1964).
13. C. P. Lewis, *Anal. Chem.*, **36**, 176 (1964).
14. J. B. Thomson, P. Brown, and C. Djerassi, *J. Amer. Chem. Soc.*, **88**, 4049 (1966).
15. M. Barber, and R. M. Elliott, ASTM Committee E-14, 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964.
16. M. Pianka, and D. J. Polton, *J. Chem. Soc.*, 1960, 983.
17. M. Pianka, *J. Sci. Food Agric.*, **18**, 63 (1967).