

The Mass Spectra of the Trimethylsilyl Derivatives of Glycerophosphoric Acids. Inter- and Intra-molecular Rearrangements of Siliconium Ions

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The trimethylsilyl derivatives of several glycerophosphoric acids are taken as model compounds for an investigation of the fragmentation mechanisms producing the characteristic ions present in the mass spectra of trimethylsilyl derivatives of organic phosphates of this type. A considerable number of rearrangement ions formed by migration of hydrogen atoms and/or trimethylsilyl groups are observed. The presence of a fully substituted phosphonium system is thought to contribute to the stability of these ions. A close similarity between the migratory properties of hydrogen atoms and trimethylsilyl groups is apparent. The spectra of the trimethylsilyl derivatives of the diphosphates exhibit ions produced by the interaction and rearrangement of intact trimethylsilyl phosphate groups. Ion-molecule reactions involving the combination of a neutral molecular species with an abundant fragment ion containing a siliconium centre are also observed. These ion-molecule reactions provide additional information regarding the structure of some of the fragment ions.

THE analysis and characterization of many compounds of biological origin has been greatly facilitated by the introduction of the combined gas chromatograph-mass spectrometer and the consequent use of volatile and stable trimethylsilyl (Tms) derivatives. The early work on the gas-phase analysis of sugar phosphates^{1,2} and nucleotides³ was conducted predominantly by g.l.c. alone. Methods for the analysis of tris(trimethylsilyl) phosphate by g.l.c.⁴ and by mass spectrometry^{5,6} have been discussed in recent papers. Further work on the g.l.c. of Tms derivatives of sugar phosphates and nucleotides has been described by Eisenberg and Bolden,⁷ and various mass spectrometric aspects of the analysis of nucleotides as their Tms derivatives have been investigated by McCloskey,^{8,9} Biemann,¹⁰ and Dolhun.¹¹ The

mass spectral fragmentation of the Tms derivatives of sugar¹² and inositol phosphates¹³ has been discussed by Sherman and his co-workers, and a recent paper discusses the mass spectrum of the Tms derivative of ethylene glycol phosphate.¹⁴

The mass spectra of these derivatives are complex and contain many rearrangement ions, some of which are formed by the intramolecular transfer of one or sometimes two hydrogen atoms, Tms groups, or phosphate groups. In a recent study the presence of a considerable number of ions produced by ion-molecule reactions was also observed.^{15,16} Most of these inter- and intramolecular rearrangements can be rationalized in terms of the localization of the charge on a silicon atom and subsequent bond formation between this silicon atom and an electronegative centre, usually an oxygen atom.¹⁷⁻²⁴ In

¹ W. W. Wells, T. Katagi, R. Bentley, and C. C. Sweeley, *Biochim. Biophys. Acta*, 1964, **82**, 408.

² T. Hashizume and Y. Sasaki, *Analyt. Biochem.*, 1966, **15**, 346.

³ T. Hashizume and Y. Sasaki, *Analyt. Biochem.*, 1966, **15**, 199.

⁴ T. Hashizume and Y. Sasaki, *Analyt. Biochem.*, 1967, **21**, 316.

⁵ M. Zinbo and W. R. Sherman, *Tetrahedron Letters*, 1969, 2811.

⁶ W. C. Butts, *Analyt. Letters*, 1970, **3**, 29; W. C. Butts and W. T. Rainey, jun., *Analyt. Chem.*, 1971, **43**, 538.

⁷ F. Eisenberg, jun., and A. H. Bolden, *Analyt. Biochem.*, 1969, **29**, 284.

⁸ J. A. McCloskey, A. M. Lawson, K. Tsuboyama, P. M. Krueger, and R. N. Stillwell, *J. Amer. Chem. Soc.*, 1968, **90**, 4182.

⁹ A. M. Lawson, R. N. Stillwell, M. M. Tacker, K. Tsuboyama, and J. A. McCloskey, *J. Amer. Chem. Soc.*, 1971, **93**, 1014.

¹⁰ D. F. Hunt, C. E. Hignite, and K. Biemann, *Biochem. Biophys. Res. Comm.*, 1968, **33**, 378.

¹¹ J. J. Dolhun and J. L. Wiebers, *J. Amer. Chem. Soc.*, 1969, **91**, 7755.

¹² M. Zinbo and W. R. Sherman, *J. Amer. Chem. Soc.*, 1970, **92**, 2105.

¹³ W. R. Sherman, M. A. Stewart, and M. Zinbo, *J. Biol. Chem.*, 1969, **244**, 5703.

¹⁴ C. B. Hirschberg, A. Kisic, and G. J. Schroepfer, jun., *J. Biol. Chem.*, 1970, **245**, 3084.

¹⁵ D. J. Harvey, M. G. Horning, and P. Vouros, *Chem. Comm.*, 1970, 898.

¹⁶ D. J. Harvey, M. G. Horning, and P. Vouros, *Analyt. Letters*, 1970, **3**, 489.

¹⁷ J. Diekmann, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, 1967, **32**, 3904.

¹⁸ J. Diekmann, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, 1968, **33**, 2271.

¹⁹ J. Diekmann, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, 1969, **34**, 3147.

²⁰ J. Å. Gustafsson, R. Ryhage, J. Sjövall, and R. M. Moriarty, *J. Amer. Chem. Soc.*, 1969, **91**, 1234.

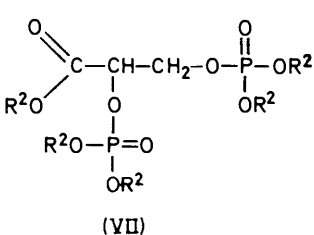
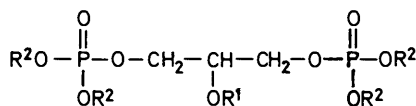
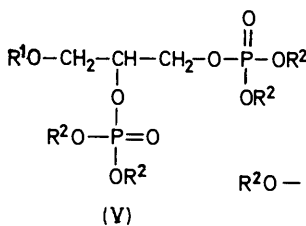
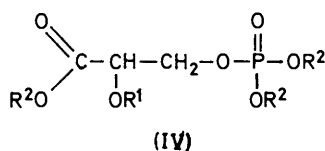
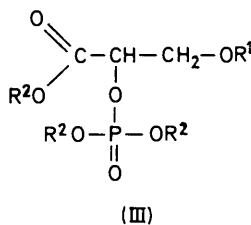
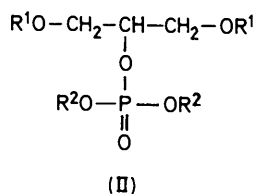
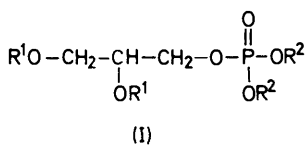
²¹ R. T. Gray, J. Diekmann, G. L. Larson, W. K. Musker, and C. Djerassi, *Org. Mass Spectrometry*, 1970, **3**, 973.

²² W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, 1969, **91**, 6544.

²³ W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, 1970, **92**, 1420.

²⁴ W. P. Weber, R. A. Felix, and A. K. Willard, *Tetrahedron Letters*, 1970, 907.

order to elucidate more fully the rearrangement reactions occurring with the Tms derivatives of the sugar phosphates and, in particular, those reactions giving rise to the more characteristic phosphorus-containing ions, we chose as models a series of low molecular weight compounds of this type, namely the Tms derivatives of L- α -glycerophosphoric acid (Ia), β -glycerophosphoric acid (IIa), 2-phosphoglyceric acid (IIIa), 3-phosphoglyceric acid (IVa), glycerol 1,2-diphosphate (Va), glycerol 1,3-diphosphate (VIa), and 2,3-diphosphoglyceric acid



(VII)

- a; $\text{R}^1 = \text{R}^2 = \text{H}$
 b; $\text{R}^1 = \text{R}^2 = \text{Tms}$
 c; $\text{R}^1 = \text{R}^2 = [^2\text{H}_9]\text{Tms}$
 d; $\text{R}^1 = \text{Tms}, \text{R}^2 = [^2\text{H}_9]\text{Tms}$
 e; $\text{R}^1 = [^2\text{H}_9]\text{Tms}, \text{R}^2 = \text{Tms}$

(VIIa). Perdeuterio-Tms derivatives (Ic)—(VIIc) were prepared as described by McCloskey *et al.*,²⁵ and mixed Tms and $[^2\text{H}_9]\text{Tms}$ derivatives [(Id)—(VIId) and (Ie)—(VIIe)] were obtained by exchange reactions. The elemental compositions of all ions discussed were confirmed by high resolution measurements. Metastable transitions were observed in the low-resolution spectra and by metastable focusing²⁶ for most fragmentation reactions as indicated in the Schemes.

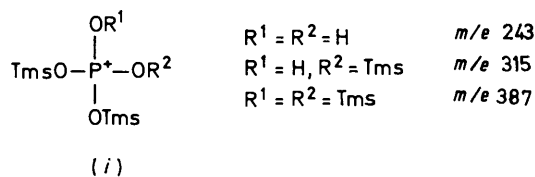
Phosphorus-containing Ions in the Mass Spectra of the

²⁵ J. A. McCloskey, R. N. Stillwell, and A. M. Lawson, *Analyt. Chem.*, 1968, **40**, 233.

Tms Derivatives (Ib) and (IIb) of L- α - and β -Glycerophosphoric Acids.—The compositions of the principal ions in the mass spectra of compounds (Ib) and (IIb) are listed in Table 1. Most of the ions are common to both compounds, but notable differences in the relative intensities of some ions are evident. The high abundance of the ions at m/e 387, 370, 357, and 256 in (Ib) and m/e 389 and 243 in (IIb) reflects the structural differences between the isomers.

Neither derivative shows a molecular ion at m/e 460. The fragment ion of highest mass is at m/e 445 ($M - 15$) (*cf.* the mass spectra of the Tms derivatives of sugar phosphates¹²). The spectra of the mixed Tms and $[^2\text{H}_9]\text{Tms}$ derivatives (Id and e) and (IIId and e) revealed that *ca.* 75% of the ions at m/e 445 were produced by loss of Me from the two ether-type Tms groups, and only 25% by loss of Me from the phosphate Tms groups.

The most characteristic phosphorus-containing fragmentation ions in the mass spectra of Tms derivatives of organic phosphates of this type occur at m/e 387 (a), 315 (b), 299 (c), 243 (d), 227 (e), and 211 (f). Suggested structures and formation pathways are shown in Schemes 1 and 2. Ions (a)—(e) are rearrangement ions formed by processes involving transfer of one or two hydrogen atoms or Tms groups to the phosphate system. Ion (f) is the fragmentation product of several of these rearrangement ions. Ions (a), (b), and (d) can be described by the general structure (i), in which each phosphate oxygen atom carries a substituent. These observations are similar to those reported previously for trialkyl phosphates.²⁷ Analogous structures can be drawn for ions (c), (e), and (f) by invoking a ring structure involving bonding between a siliconium centre and the fourth oxygen atom of the phosphate group (see Scheme 1).



The high abundance of ions of this general structure is probably due to resonance stabilization. The suggested transformations represent further examples of the similar behaviour of hydrogen atoms and Tms groups in the mass spectrometer.

The ion at m/e 387 (a) is produced from the molecular ion by the intramolecular transfer of two Tms groups to the phosphate system. Sherman¹² and McCloskey⁹ have previously reported this ion to be produced from Tms derivatives of phosphates, and it is often very abundant in the spectra of the Tms derivatives of hexose monophosphates.¹² It also occurs as an ion-molecule reaction product in the mass spectrum of tris(trimethyl)silylphosphate.²⁸

²⁶ P. Schulze and A. L. Burlingame, *J. Chem. Phys.*, 1968, **49**, 4870.

²⁷ F. W. McLafferty, *Analyt. Chem.*, 1956, **28**, 313.

²⁸ Unpublished results from this laboratory.

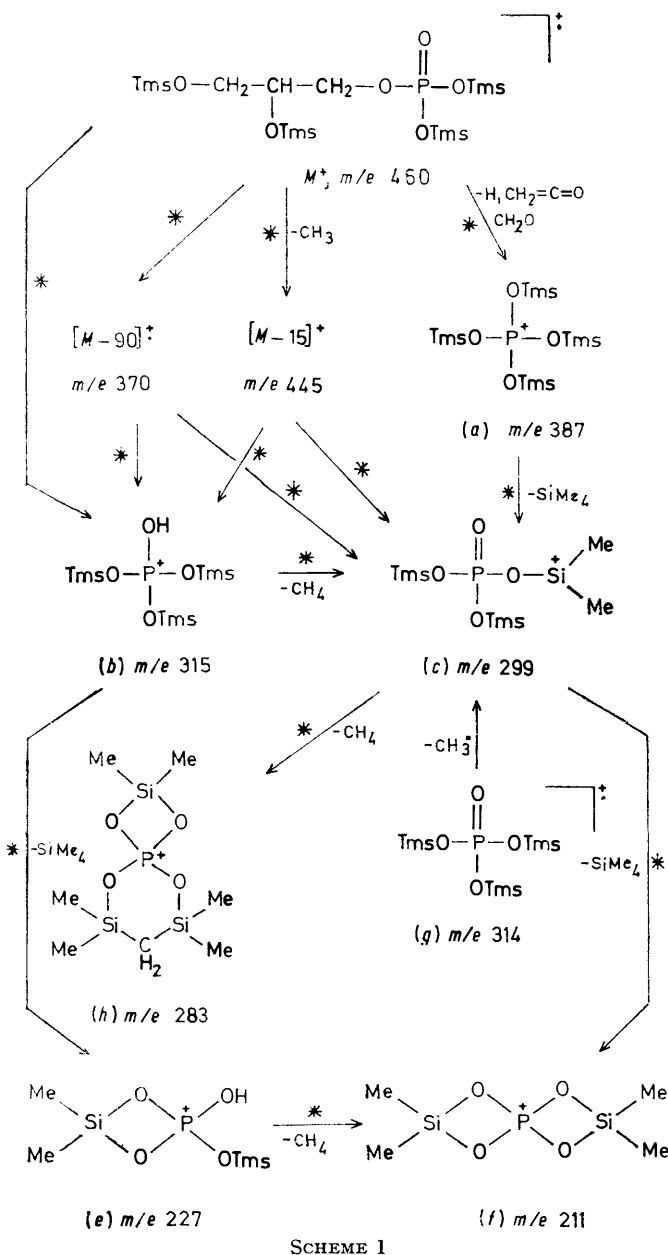
TABLE 1

Compositions of the principal ions

<i>m/e</i>	Composition	Ion ^a	[² H ₉]Tms		Relative intensity (%)														
			<i>m/e</i>	Shift	(Ib)	(IIb)	(IIIb)	(IVb)	(Vb)	(VIb)	(VIIb)								
626	C ₁₅ H ₁₆ O ₁₀ P ₂ Si ₅		671	45															
611	C ₁₇ H ₄₅ O ₁₀ P ₂ Si ₅		653	42															
597	C ₁₇ H ₄₇ O ₉ P ₂ Si ₅	(<i>dd</i>)	639	42															
541	C ₁₄ H ₄₃ O ₈ P ₂ Si ₅	(<i>ee</i>), (<i>ff</i>)	583	42															
539	C ₁₅ H ₄₅ O ₇ P ₂ Si ₅	(<i>ii</i>)	584	45															
523	C ₁₃ H ₃₃ O ₁₀ P ₂ Si ₄		553	30															
522	C ₁₅ H ₄₀ O ₉ P ₂ Si ₄		558	36															
509	C ₁₄ H ₃₉ O ₈ P ₂ Si ₄		545	36															
474	C ₁₅ H ₃₉ O ₇ P ₂ Si ₄		510	36															
467	C ₁₅ H ₃₇ O ₇ P ₂ Si ₄	(<i>hh</i>)	503	36															
466	C ₁₂ H ₃₆ O ₇ P ₂ Si ₄	(<i>bb</i>)	502	36															
459	C ₁₄ H ₃₆ O ₇ P ₂ Si ₄		492	33															
451	C ₁₁ H ₃₃ O ₇ P ₂ Si ₄	(<i>cc</i>)	484	33															
445	C ₁₇ H ₃₆ O ₅ P ₂ Si ₄	(<i>n</i>)	478	33															
444	C ₁₄ H ₃₇ O ₆ P ₂ Si ₄	(<i>z</i>)	480	36															
431	C ₁₅ H ₃₆ O ₆ P ₂ Si ₄		464	33															
429	C ₁₄ H ₃₆ O ₅ P ₂ Si ₄		465	36															
	C ₁₅ H ₃₄ O ₆ P ₂ Si ₄		462	33															
415	C ₁₃ H ₃₆ O ₅ P ₂ Si ₄		448	33															
389	C ₁₁ H ₃₄ O ₅ P ₂ Si ₄	(<i>o</i>), (<i>p</i>)	422	33															
387	C ₁₂ H ₃₆ O ₄ P ₂ Si ₄	(<i>a</i>)	423 ^b	36															
385	C ₁₂ H ₃₀ O ₆ P ₂ Si ₃		412	27															
384	C ₁₅ H ₂₆ O ₆ P ₂ Si ₃		411	27															
373	C ₁₀ H ₃₀ O ₅ P ₂ Si ₄	(<i>q</i>)	403	30															
370	C ₁₅ H ₃₁ O ₅ P ₂ Si ₃		397	27															
369	C ₁₁ H ₂₆ O ₆ P ₂ Si ₃	(<i>y</i>)	393	24															
357	C ₁₁ H ₃₀ O ₅ P ₂ Si ₃	(<i>k</i>)	384	27															
355	C ₁₁ H ₂₆ O ₅ P ₂ Si ₃		379	24															
341	C ₁₆ H ₂₆ O ₅ P ₂ Si ₃	(<i>l</i>), (<i>m</i>)	365	24															
328	C ₁₆ H ₂₉ O ₄ P ₂ Si ₃	(<i>v</i>), (<i>w</i>)	355	27															
315	C ₉ H ₂₈ O ₄ P ₂ Si ₃	(<i>b</i>)	342	27															
314	C ₉ H ₂₇ O ₄ P ₂ Si ₃	(<i>g</i>)	341	27															
299	C ₈ H ₂₄ O ₄ P ₂ Si ₃	(<i>c</i>), (<i>oo</i>)	323	24															
297	C ₈ H ₁₈ O ₆ P ₂ Si ₂		312	15															
285	C ₆ H ₁₈ O ₅ P ₂ Si ₃	(<i>r</i>)	303	18															
283	C ₇ H ₂₀ O ₄ P ₂ Si ₃	(<i>h</i>)	303	20															
	C ₈ H ₂₀ O ₅ P ₂ Si ₂	(<i>gg</i>)	298	15															
269	C ₆ H ₁₈ O ₄ P ₂ Si ₃		287	18															
268	C ₈ H ₂₁ O ₄ P ₂ Si ₂		286	18															
256	C ₇ H ₂₁ O ₄ P ₂ Si ₂	(<i>s</i>)	274	18															
253	C ₇ H ₁₈ O ₄ P ₂ Si ₂		268	15															
243	C ₈ H ₂₀ O ₄ P ₂ Si ₂	(<i>d</i>)	261	18															
241	C ₆ H ₁₈ O ₄ P ₂ Si ₂	(<i>u</i>)	256	15															
227	C ₅ H ₁₆ O ₄ P ₂ Si ₂	(<i>e</i>)	242	15															
225	C ₆ H ₁₈ O ₃ P ₂ Si ₂	(<i>x</i>)	243	18															
218	C ₉ H ₂₂ O ₂ Si ₂		236	18															
217	C ₉ H ₂₁ O ₂ Si ₂		235	18															
	C ₈ H ₁₇ O ₃ Si ₂		232	15															
211	C ₄ H ₁₂ O ₄ P ₂ Si ₂	(<i>f</i>)	223	12															
207	C ₅ H ₁₅ O ₃ Si ₃		222	15															
205	C ₈ H ₂₁ O ₂ Si ₂		223	18															
203	C ₈ H ₁₉ O ₂ Si ₂		218	15															
195	C ₂ H ₇ O ₅ Si ₃		201	6															
193	C ₄ H ₁₃ O ₃ Si ₃		205	12															
149	C ₄ H ₁₃ O ₂ Si ₂		161	12															
147	C ₃ H ₁₅ O ₂ Si ₂	(<i>jj</i>), (<i>nn</i>)	162	15															
135	C ₂ H ₇ O ₃ Si ₂		141	6															
133	C ₃ H ₉ O ₂ Si ₂		142	9															
129	C ₅ H ₁₃ O ₂ Si	(<i>kk</i>)	138	9															
	C ₅ H ₉ O ₂ Si	(<i>ll</i>)	135	6															
116	C ₅ H ₁₂ O ₂ Si		125	9															
103	C ₄ H ₁₁ O ₂ Si		112	9															
101	C ₁ H ₅ O ₂ Si		107	6															
89	C ₃ H ₇ O ₂ Si		95	6															
75	C ₂ H ₅ O ₂ Si		81	6															
73	C ₃ H ₉ Si		82	9															
59	C ₂ H ₇ Si		65	6															
45	CH ₃ Si		48	3															

^a This refers to the structure given in the text. ^b Shift to 422 in (IIIb) (see text).

The peak at m/e 299 is the base peak in the spectrum of the derivative (Ib) and has been observed in all the spectra of compounds of this type.^{8,9,12} Structure (c) (Scheme 1) has been suggested¹² for this ion. Metastable focusing indicated various fragmentation pathways leading to its formation. The ions observed to fragment to give (c) were m/e 315 (loss of CH_4), 387 (loss of SiMe_4), 445 (probably by a process analogous to the formation of m/e 147 in the fragmentation of Tms derivatives of diols^{29,30}), 328, 341, 357, and 370.

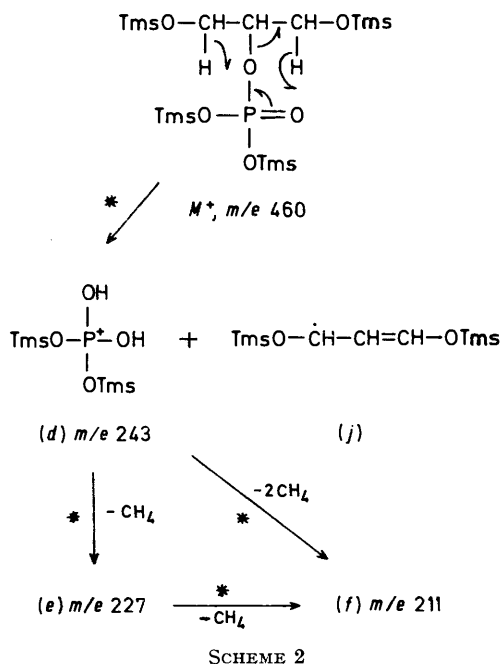


SCHEME 1

One of the ions produced from the fragmentation of m/e 299 is the ion at m/e 283, for which structure (h) is

²⁹ G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrometry*, 1968, **1**, 669.

suggested on the basis of deuterium labelling experiments. This ion has apparently lost a hydrogen atom from a Tms group and therefore most probably has the bicyclic structure shown in Scheme 1.



SCHEME 2

The third characteristic phosphorus-containing ion occurs at m/e 315 (b). Metastable focusing indicated that several ions fragment to give (b); notably the ions at m/e 370 ($M-90$), 445 ($M-15$), and 460 (M^+).

Ion (d) (m/e 243) is common to the mass spectra of all Tms derivatives of sugar phosphates and nucleotides.⁹ A structure for this ion is suggested in Scheme 2, and metastable focusing indicated that fragmentation of the ions at m/e 357, 370 ($M-90$), 445 ($M-15$), and 460 (M^+) contributes to its abundance. The higher abundance of ion (d) in the mass spectrum of the Tms derivative of β -glycerophosphoric acid (100%) than in that of the α -isomer (8%) is probably best explained by a mechanism of the type depicted in Scheme 2. The greater stability of the expelled neutral radical (j) over the corresponding radical produced from the L- α -isomer (Ib) presumably contributes to the formation of ion (d) in the spectrum of the β -isomer (IIb). When the spectrum of compound (IIb) was recorded at 15 eV, ion (d) was found to carry 41% of the total ion current as against 13.5% at 70 eV, a further indication that it is predominantly formed as a primary fragment of the molecular ion.

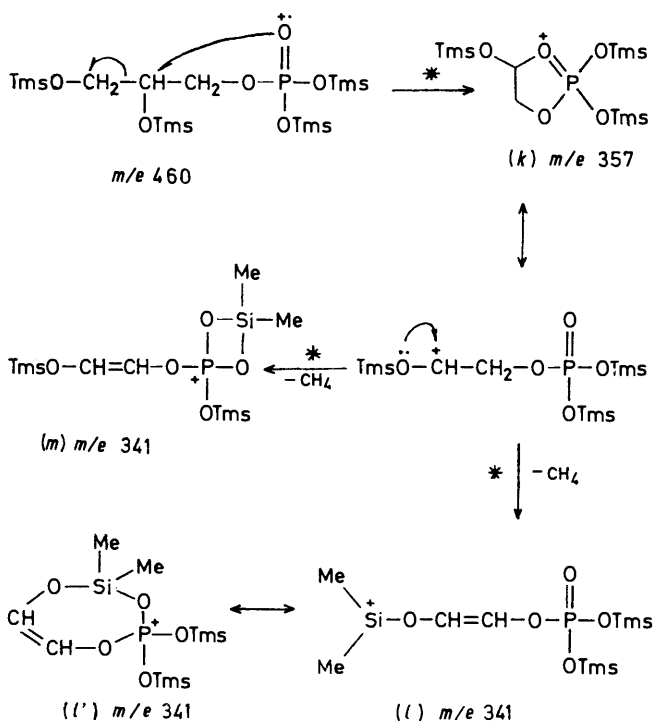
Ion (d) (m/e 243) yields the ion at m/e 227 (e) by the loss of methane, as supported by evidence from metastable transitions. Subsequent elimination of a molecule of methane from (e) (m/e 227) is observed in the spectra of both derivatives (Ib) and (IIb) and leads to m/e 211 (f). A prominent metastable transition in the low resolution spectrum of (IIb) and a smaller one in the spectrum of

³⁰ S. Sloan, D. J. Harvey, and P. Vouros, *Org. Mass Spectrometry*, 1971, **5**, 789.

(Ib) indicates formation of ion (*f*) directly from *m/e* 243 by the elimination of the elements of two molecules of methane in an apparently concerted manner.

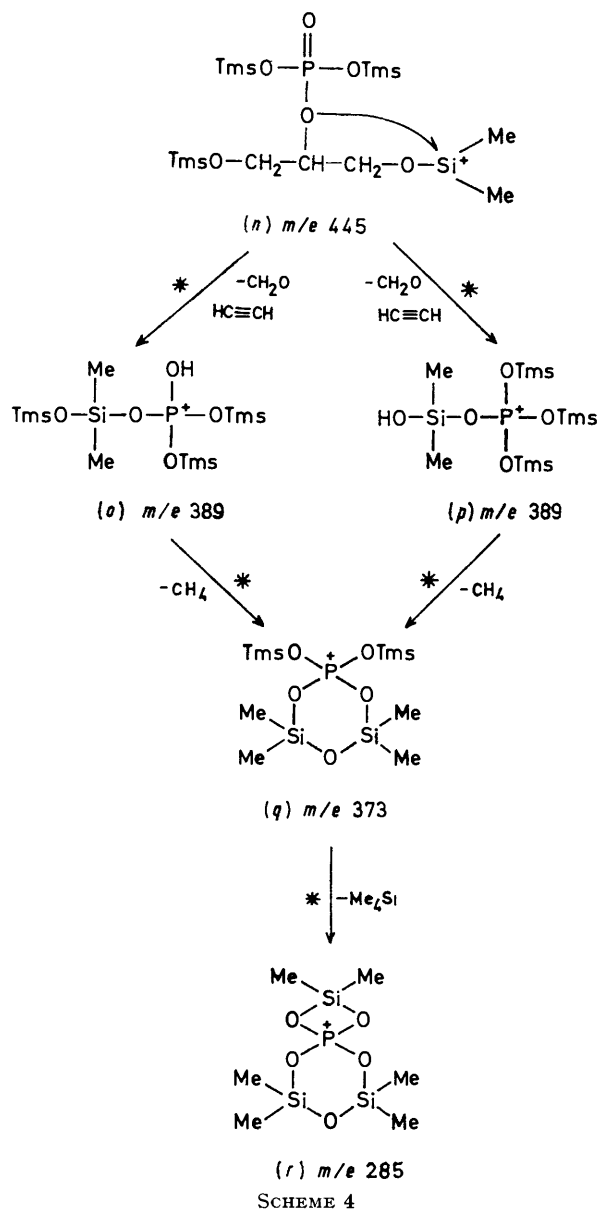
Metastable focusing supported these transitions and also indicated alternative sources of both ions (*e*) and (*f*). One of these fragmentations involves the elimination of the elements of tetramethylsilane from *m/e* 315 and *m/e* 299 to give (*e*) and (*f*), respectively. The elimination of Me_4Si from *m/e* 299 to form *m/e* 211 is apparently more favourable than the corresponding elimination from *m/e* 387 to form *m/e* 299. This is evident from the spectra of the partially labelled Tms analogues (Id and e) and (II d and e).

The characteristic ion at *m/e* 357 differs from the previously discussed ions (*a*)–(*f*) in that in addition to the phosphate system it contains a C_2 side chain. It is highly abundant in the mass spectrum of the α -isomer (Ib) (98%), but is only a minor peak in that of the β -isomer (IIb) (3.5%). Deuterium labelling and the consequent shift of this peak by 27 a.m.u. to *m/e* 384 in the spectra of compounds (Ic) and (IIc) is consistent with the expected loss of a $\text{TmsO}\cdot\text{CH}_2\cdot$ radical, characteristic of compounds of this type.³¹ The higher abundance of ion (*k*) (*m/e* 357) in the spectrum of (Ib) than in that of the β -isomer (IIb) can be accounted for by the occurrence of the process depicted in Scheme 3, a



the cyclic structure (*k*) is not as favourable as with the α -isomer (Ib).

Ion (*k*) fragments by the elimination of methane to give the ion of *m/e* 341. Deuterium labelling experiments indicate the loss of Me from a Tms group accompanied by a hydrogen atom from the C_2 chain. In the



spectra of the partially labelled analogues (Id and e) and (II d and e) two peaks were observed for the *m/e* 341 ion, indicating that methyl loss occurs from all three Tms groups to give ions formulated here as (*l*) and (*m*). An alternative cyclic structure (*l'*) involving bonding between the siliconium centre and the free phosphate oxygen atom may also be suggested for *m/e* 341. Loss

³¹ D. C. DeJongh, T. Radford, J. D. Hribar, S. Hanessian, M. Bieber, G. Dawson, and C. C. Sweeley, *J. Amer. Chem. Soc.*, 1969, **91**, 1728.

of Me from the phosphate Tms groups to give ion (*m*) accounted for only about 30% of *m/e* 341.

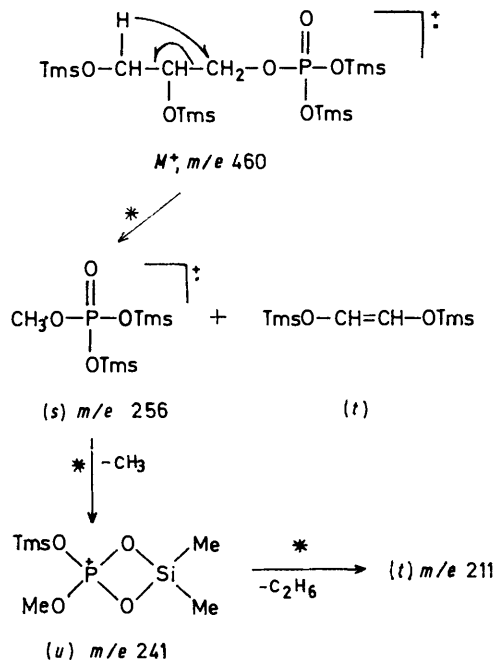
A rearrangement ion, much more abundant in the spectrum of the Tms derivative (IIb) of β -glycerophosphoric acid than in its α -isomer (Ib), is seen at *m/e* 389. It is related to the *M* - 15 ion (*m/e* 445) by the appropriate metastable transition. Deuterium labelling results and high resolution data suggest the structure (*o*) or (*p*) for this ion (Scheme 4). The spectra of the partially labelled analogues (Id and e) and (IIId and e) indicate that *m/e* 389 has been formed exclusively from the *M* - 15 ion that was produced by the elimination of Me from the ether-type Tms group. The first stage of the fragmentation of (*n*) to form *m/e* 389 is postulated as involving the transfer of the trimethylsilyl phosphate group to the siliconium centre of (*n*) as shown in Scheme 4. This is followed by hydrogen (from the C_3 chain) and Tms migrations to give (*o*) or (*p*) depending on the site of attachment of the migrating groups. The elimination of the elements of acetylene and formaldehyde as neutral species probably provides the driving force for this reaction.

The ion at *m/e* 389 eliminates CH_4 to give (*q*) (*m/e* 373), as supported by evidence from metastable transitions. Deuterium labelling experiments show that only three deuterium atoms are lost during this fragmentation and therefore the fourth hydrogen atom must be the one attached to the phosphate oxygen atom of (*o*) [or the silicon oxygen of (*p*)]. The ion of *m/e* 373 is thus visualized as having the cyclic structure (*q*). The latter ion fragments to give an ion at *m/e* 285 of molecular composition $C_8H_{18}O_5PSi_3$ formulated as the bicyclic structure (*r*). The observed 18 a.m.u. shift of *m/e* 285 in the spectra of the perdeuterio-analogues (Ic) and (IIc) supports the structure suggested for (*r*) which involves the loss of Me_4Si from (*q*). In addition to the fragmentation route *m/e* 373 \rightarrow *m/e* 285, metastable focusing provided evidence for the occurrence of two more decomposition pathways to give ion (*r*), namely the fragmentations of *m/e* 445 and *m/e* 357.

The mass spectrum of the Tms derivative of L- α -glycerophosphoric acid (Ib) shows a moderately abundant (17%) phosphorus-containing ion at *m/e* 256 related by a metastable transition to the molecular ion. This ion is absent in the spectrum of the β -isomer (IIb). An accurate mass measurement gives the composition $C_7H_{21}O_4PSi_2$ for this ion and deuterium labelling of the Tms groups (Ic—e) reveals that eighteen of these hydrogen atoms originate from the phosphate Tms groups. The structure of *m/e* 256 may thus be written as (*s*), and Scheme 5 shows a mechanism for its formation from the molecular ion. The absence of (*s*) from the spectrum of the β -isomer (IIb) may be explained by the fact that in the latter compound formation of (*s*) would involve a double hydrogen atom transfer in addition to a rearrangement to produce the proposed stable neutral species (*t*) of Scheme 5.

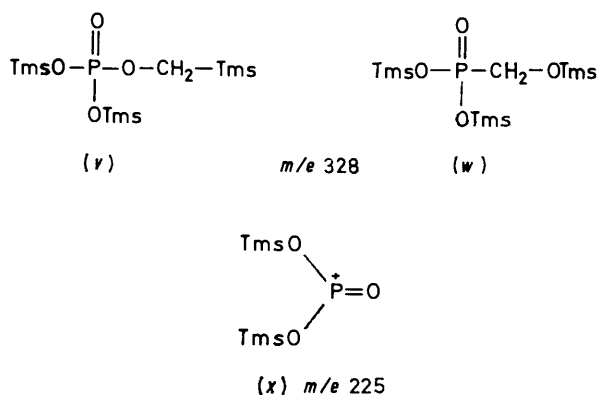
A metastable transition in the low resolution spectrum of (Ib) indicates that ion (*u*) (*m/e* 241) is formed by

loss of Me from ion (*s*) (Scheme 5). The shift of ion (*u*) by 15 a.m.u. to *m/e* 256 in the spectrum of (Ic) shows that the methyl radical is expelled exclusively from a Tms group. An interesting fragmentation of (*u*) is the elimination of C_2H_6 to give ion (*f*) (*m/e* 211).



SCHEME 5

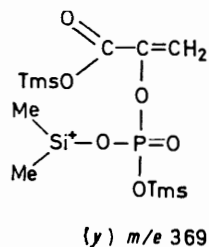
Several other phosphorus-containing ions of lower relative abundance are also present in the mass spectra of (Ib) and (IIb) (*m/e* 225, 269, 328, 415, 417, and 429). Their elemental compositions are given in Table 1. On the basis of their a.m.u. shifts upon deuterium labelling, structures (*v*) and (*w*) can be written for *m/e* 328 and (*x*) for *m/e* 225.



Phosphorus-containing Ions in the Mass Spectra of the Tms Derivatives (IIIb) and (IVb) of 2- and 3-Phosphoglyceric Acids.—The mass spectra of (IIIb) and (IVb) and the mechanisms producing the major ions are generally similar to those of the glycerophosphoric acids (Ib) and (IIb). Unlike the spectra of (Ib) and (IIb), those of (IIIb) and (IVb) contain molecular ions of low

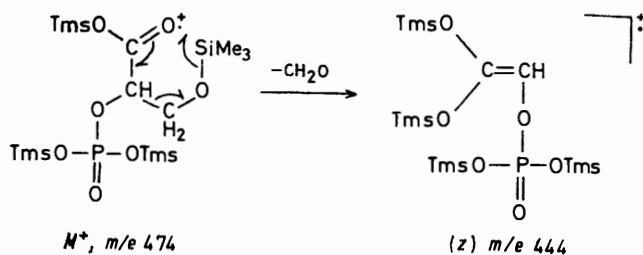
abundance at m/e 474. The $M - 15$ (m/e 459) ions are again produced predominantly by elimination of Me from Tms groups not attached to a phosphate system.

The most significant differences between the mass spectra of the derivatives (IIIb) and (IVb) are the relatively high abundances of the ions (k) (m/e 357) in (IVb) and (y) (m/e 369) in (IIIb). The mechanism of formation of m/e 357 is similar to that described in



Scheme 3. The ion at m/e 369 in the spectrum of (IIIb) is derived from the $M - 15$ ion (m/e 459) by the loss of trimethylsilanol, as indicated by the metastable ion at m/e 296.6. The spectra of the [$^2\text{H}_9$]Tms and partially labelled analogues (IIIId) and (IIIe) show that the methyl loss from the molecular ion is from a phosphate Tms group and that the eliminated trimethylsilanol contains the ether-type and not an ester Tms group. Structure (y) is therefore suggested for this ion.

A further difference between the spectra of (IIIb) and (IVb) is the presence of a moderately abundant ion at m/e 444 (z) in the spectrum of (IIIb), probably produced by a McLafferty-type rearrangement, involving a Tms transfer (Scheme 6). No ion at m/e 444 was observed in the spectrum of (IVb). Loss of Me from ion (z) produces the low intensity peak at m/e 429.



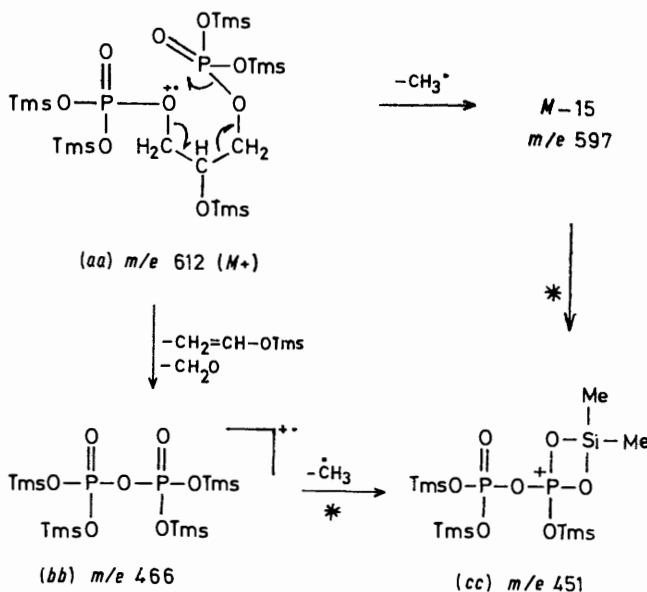
SCHEME 6

The ion at m/e 387, as previously discussed, is thought to have the structure (a) and to contain all four Tms groups attached to the phosphate system. In the spectra of the [$^2\text{H}_9$]Tms analogues of (Ib), (IIb), and (IVb) this ion was observed to shift by 36 a.m.u. In the case of (IIIb), however, a shift of only 35 a.m.u. was observed, indicating an exchange between the carboxylic Tms hydrogen atoms and those of the C_3 chain.

Phosphorus-containing Ions in the Mass Spectra of the Tms Derivatives (Vb) and (VIb) of Glycerol 1,2- and 1,3-Diphosphates.—Most of the prominent fragment ions are identical with those in the spectra of the monophosphates. The ion compositions are given in Table 1.

Notable are the characteristic phosphorus-containing rearrangement ions (a)—(f).

Ions of m/e 541, 526, 466, and 451 produced by the migration of an intact trimethylsilyl phosphate group are present. The elemental composition of the ion at m/e 451 is $\text{C}_{11}\text{H}_{33}\text{O}_7\text{P}_2\text{Si}_4$, and the shift by 33 a.m.u. in the spectra of the labelled analogues shows that both phosphate systems are present; structure (cc) is suggested for this ion. In compounds (Vb) and (VIb) metastable focusing showed that (cc) was related to both the $M - 15$ ion (m/e 597) and to the ion of low abundance at m/e 466 (bb) as shown in Scheme 7.

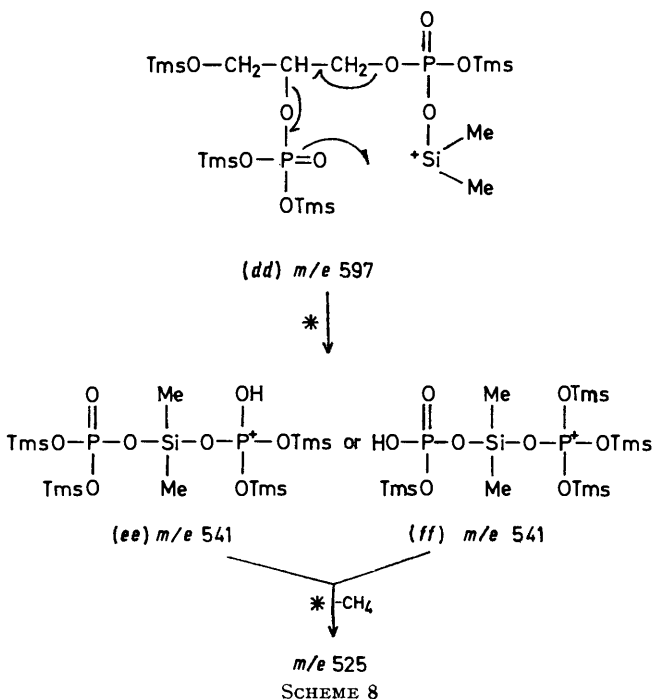


SCHEME 7

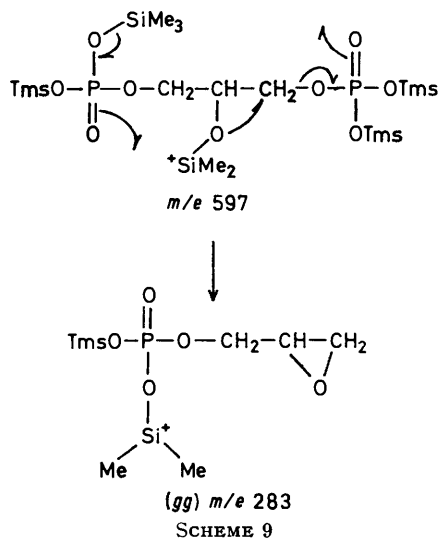
A rearrangement ion, more abundant in the spectrum of the Tms derivative of glycerol 1,2-diphosphate (Vb) than in that of the 1,3-isomer (VIb) is observed at m/e 541. The mass spectra of the labelled analogues (Vc—e) show that a methyl group is lost exclusively from a trimethylsilyl phosphate system during the formation of this ion. A very prominent metastable ion at m/e 490.2 relates m/e 541 to the $M - 15$ ion at m/e 597. Two probable structures [(ee) and (ff)] for this ion are shown in Scheme 8, and these may be considered as the phosphate analogues of the rearrangement ion m/e 389. The ion of m/e 541 fragments further by loss of methane to give a low abundance ion at m/e 525.

Elimination of the trimethylsilyl phosphate system from the molecular ion is a more favourable process in these compounds than in the monophosphate derivatives. It results in the ions at m/e 371, 370, 355, and 283. Formation of the ion at m/e 370 has involved the elimination of bistrimethylsilyl hydrogen phosphate, a process analogous to the elimination of trimethylsilanol from trimethylsilyl ethers. This is followed by the loss of Me to give m/e 355, as supported by a metastable transition.

The ion at m/e 283 is produced by the elimination of tris(trimethylsilyl) phosphate from the $M - 15$ ion. The spectra of the labelled analogues indicate the presence of the intact C_3H_5 chain. Selective labelling with $[^2H_9]Tms$ groups on the phosphate system [(Vd) and



(VIId)] produced a shift of only 9 a.m.u. in m/e 283. This indicates that three phosphate Tms groups have been eliminated in this rearrangement and that the initial loss of Me occurred from the ether-type Tms groups. A reasonable structure for m/e 283 (gg) and a mechanism for its formation are depicted in Scheme 9.



Elimination of one trimethylsilyl phosphate group, along with a methylene group from the C_3 chain (the phosphate analogue of the $TmsO\cdot CH_2\cdot$ radical frequently

eliminated from the Tms derivatives of primary alcohols³²) is seen in the spectrum of (VIb), yielding the ion at m/e 357. This ion probably has a structure similar to that of the ion observed at the same mass in the spectra of the monophosphate derivatives. The corresponding elimination of a $TmsO\cdot CH_2\cdot$ radical from (Vb) occurs to only a limited extent to give a minor peak at m/e 509.

From the mass spectra of the partially labelled analogues (Vd and e) and (VIId and e) information can be obtained regarding the identity of the Tms groups which migrate to produce the characteristic phosphorus-containing ions at m/e 387 (a), 315 (b), and 299 (c). Approximately half of the abundance of ion (a) is due to the ion in which both Tms groups from one trimethylsilyl phosphate system have migrated to the other charged phosphate species. The remainder of the ion at m/e 387 contains three phosphate and one ether-type Tms groups. A similar situation is seen for the peak at m/e 299, the predominant component of this ion having been produced by migration of a phosphate Tms group. A different situation is apparent with ion (b) (m/e 315); here the major contribution is due to the ion produced by the migration of the ether-type Tms group, this ion being nearly twice as abundant as the ion containing three phosphate Tms groups.

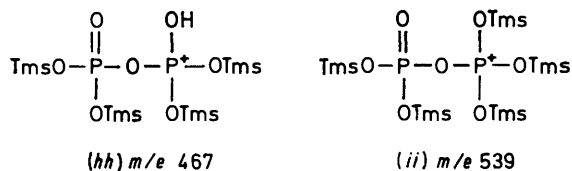
Phosphorus-containing Ions in the Spectrum of the Tms Derivative (VIIb) of 2,3-Diphosphoglyceric Acid.—A feature of this spectrum is the appearance of several ions produced by the elimination of tris(trimethylsilyl) phosphate. This seems to reflect a greater tendency for the carboxylic Tms ester group to migrate to the phosphate system as compared with the Tms ether groups in (Vb) and (VIb). Unfortunately, it was not possible to prepare selectively labelled analogues of this compound as all the Tms groups were replaceable under the labelling conditions employed.

The elimination of tris(trimethylsilyl) phosphate initiates the production of three moderately intense peaks at m/e 297, 268, and 253. Evidence from metastable ions and from the labelled analogues shows that the first ion is formed from m/e 312 by loss of a methyl group. The second ion (m/e 268) probably arises from m/e 312 by the loss of CO_2 , and subsequent loss of $CH_3\cdot$ from m/e 268 produces m/e 253.

As an alternative to the migration of a Tms group to a trimethylsilyl phosphate system and the subsequent elimination of tris(trimethylsilyl) phosphate, a hydrogen atom may migrate, resulting in the elimination of bis(trimethylsilyl) hydrogen phosphate. Loss of this species from the molecular ion of (VIIb) produces an ion at m/e 384. The ion at m/e 385 represents a similar loss but without concomitant hydrogen transfer. The ion at m/e 384 further fragments by loss of Me to give the ion at m/e 369, as supported by the presence of a metastable ion at m/e 354.6.

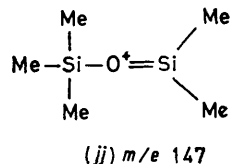
³² H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, pp. 471—477.

The migration and interaction of intact Tms phosphate groups is reflected by the presence in low abundance of the two related ions at m/e 467 and m/e 539. Formation of these has involved the migration of a hydrogen atom and a Tms group, respectively, to a rearranged phosphate system containing the pyrophosphate group. The structures suggested are (*hh*) and (*ii*) and they may be regarded as the pyrophosphate analogues of the ions



observed at m/e 315 (*b*) and 387 (*a*) in the orthophosphate series. The loss of methane from (*hh*) probably gives rise to the ion at m/e 451 (*cc*).

Other Characteristic Silicon-containing Ions.—The mass spectra of the acid derivatives (IIIb) and (IVb) contained an ion of mass 217 with an empirical formula of $\text{C}_8\text{H}_{17}\text{O}_3\text{Si}_2$, apparently produced by elimination of the trimethylsilyl phosphate group accompanied by the loss of a methyl radical. The remaining ions appearing in the low mass region of these spectra are mainly silicon-containing fragments, many of which have been reported previously as fragment ions of most Tms derivatives.³²

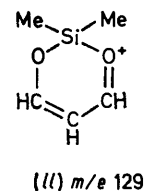
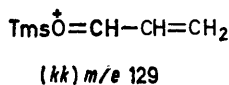


The frequently reported rearrangement ion, m/e 147 (*jj*), has multiple sources, the major one being the $M - 15$ ion as shown by the presence of the appropriate metastable ion. The spectra of the partially labelled analogues (Id)—(VIId) and (Ie)—(VIE) show that all the Tms groups can be involved in the formation of (*jj*) and that the initial methyl loss to form a siliconium ion centre can take place from any of the Tms groups. In these spectra peaks due to ions of structure (*jj*) are observed at m/e 147, 153, 156, and 162 and contain 0, 2, 3, and 5 perdeuteriomethyl groups, respectively. In compounds (Ib) and (IIb) approximately 60% of the ions of structure (*jj*) originate from the ether-type Tms groups and about 20% are formed from the Tms phosphate groups. The remaining 20% contain Tms groups from both sources.

Two ions are seen at m/e 129, the most abundant having the structure (*kk*) as indicated by a shift of 9 rather than 6 a.m.u. in the spectra of the $[\text{}^2\text{H}_9]$ Tms analogues. About 10% of the intensity of the peak at m/e 129 is due to ion (*ll*), a structure reported previously.^{9,12}

Ion-Molecule Reactions.—An outstanding feature of the spectra of these compounds is the presence of a large number of relatively abundant ions produced by ion-molecule reactions.^{15,16} These were first observed

at $M + 1$ and $M + 73$ when the spectra were recorded under normal electron-impact conditions. A shift of $M + 1$ by 36 rather than by 37 a.m.u. in the spectra of the $[\text{}^2\text{H}_9]$ Tms derivatives indicates that the additional hydrogen atom comes from the C_3 chain and not from a Tms group.



At higher pressures, several other ions resulting from ion-molecule reaction were observed.¹⁶ All of the ions appearing at masses higher than that of the molecular ion were apparently the result of the combination of the neutral molecular species with one of its abundant fragment ions containing a positively charged silicon centre. Table 2 lists the ions which have been observed

TABLE 2
Relative intensities ^a of the ion-molecule reaction products in the spectra of (Ib)—(IVb) ^b

Fragment ion m/e	(Ib)		(IIb)		(IIIb)		(IVb)	
	m/e	%	m/e	%	m/e	%	m/e	%
1	461	2.8	461	0.27	475	0.8	475	0.6
73	533	4.1	533	0.11	547	1.15	547	0.92
		(313) ^c		(124)		(280)		(258)
147	607	0.13	607	0.003	621	0.075	621	0.065
		(55)		(28)		(57)		(96)
227	687	0.03	687		701		701	0.05
		(8)		(9.5)		(13)		(87)
299	759	0.27	759	0.004	773	0.01	773	0.025
		(100)		(48)		(100)		(100)
369					843	0.01	843	0.005
						(67)		(4)
459					933	0.005	933	
						(90)		(43)

^a Percentage of the base peak, excluding the m/e 73 ion.

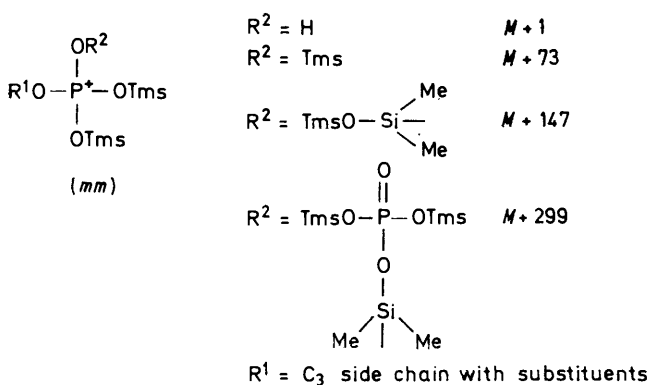
^b The values given for any one particular compound are those obtained with the highest ion source pressure used. Because of their dependence on the operating conditions of the instrument, they cannot be used for comparisons between individual compounds. ^c The figures in parentheses are the relative intensities of the reacting fragment ions.

to combine with the neutral molecular species for four of the compounds under discussion. In later experiments³³ it was shown that bond formation probably took place between the silicon centre and an electro-negative site, usually an oxygen atom, in the neutral molecule [*e.g.* structure (*mm*)]. The ease with which these phosphates form ion-molecule addition complexes, undoubtedly reflects, as discussed earlier, the increased stability of the resulting substituted phosphonium cation compared with that of the free phosphate ion.

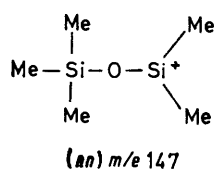
From these observations, it is possible to draw tentative conclusions about the structures of both the siliconium fragment ions and the ion-molecule reaction

³³ D. J. Harvey, M. G. Horning, and P. Vouros, *Org. Mass Spectrometry*, 1971, 5, 599.

products. Since the latter are most probably produced by bond formation between a silicon atom and an electro-negative site in the neutral molecular species,³³ ions such



as m/e 147 are thought to exhibit charge localization on the silicon atom (mn) rather than on the oxygen atom (jj).

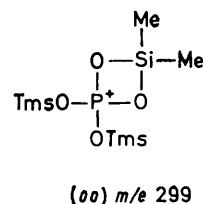


This accords fully with previous observations on the reluctance of silicon to form double bonds³⁴ in the solid phase, but it is possible that some double-bond character of the linkage between the oxygen atom and the silicon centre contributes to the stability and high abundance of this and similar ions.

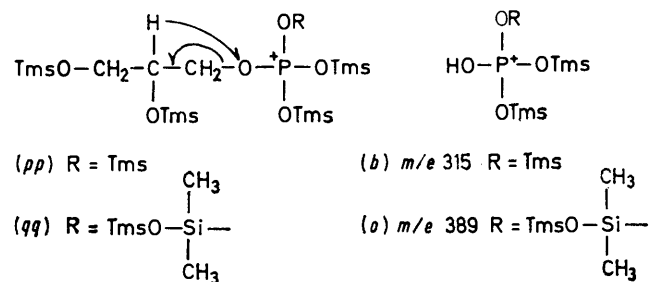
The ions at m/e 299, 227, and 211 can be written as fully substituted phosphonium cations by invoking bond formation between the silicon from which a methyl group was eliminated and the phosphonyl oxygen atom [e.g. (oo) for m/e 299]. The cyclic form is considerably stabilized by resonance. Valency considerations necessitate the adoption of a cyclic structure for m/e 211 (f). In addition, no ion-molecule reaction products corresponding to the addition of this ion have been detected. Hence, in this case, charge localization on the silicon atom is unlikely, and the existence of the resonance-stabilized structure (f) containing two four-membered rings is assumed.

Although these four-membered rings are thought to contribute to the overall structure of several other ions, most of the fragments for which this type of structure can be written are observed to take part in ion-molecule additions (e.g. m/e 299). As these cyclic structures require charge delocalization, it is apparent that the open structure must also have a real existence, as the requirement for an ion of this type to take part in an ion-molecule reaction is thought to be charge localization on silicon.³³ Both open [e.g. (c)] and cyclic [e.g. (oo)] forms, therefore, most probably represent extreme struc-

tures contributing to the overall composition of these ions.



Two fragmentations (Scheme 10) of these ion-molecule reaction products were observed by metastable focusing; both involved a hydrogen atom transfer to give a fully substituted phosphonium cation and were not simple



SCHEME 10

cleavage reactions. The $M + 73$ ion (pp) was observed to fragment by the transfer of a hydrogen atom to give m/e 315 (b). The source of the migrating hydrogen atom has not been determined, but it is most likely that this is a non-specific migration analogous to those observed for Tms groups.³² The second fragmentation is analogous and involves the $M + 147$ ion. Formation of the fragment ion m/e 389 has been discussed previously as having involved three migrations from the $M - 15$ ion. Of the two structures (o) and (p) suggested for this ion the fragmentation from the $M + 147$ ion (qq) provides the only evidence that structure (o) contributes to the abundance of m/e 389.

EXPERIMENTAL

Compounds (Ia) and (IVa)—(VIIa) (as their cyclohexylammonium salts) and compounds (IIa) and (IIIa) (as their sodium salts) were obtained from commercial suppliers. Samples (1 mg) of these were converted into their Tms derivatives by heating with trifluorobis(trimethylsilyl)acetamide (BSTFA) (0.1 ml) and chlorotrimethylsilane (TMCS) (0.05 ml) in acetonitrile (0.1 ml) at 80° for 30 min in a sealed tube. [²H₉]Tms derivatives were prepared by heating the sample (0.01 mg) with [²H₁₈]bistrimethylsilylacetamide [²H₁₈]BSA and [²H₉]TMCS.

The derivatives containing [²H₉]Tms groups on the phosphate system (Id)—(VIId) were prepared as follows. The g.l.c. column of an LKB 9000 mass spectrometer was saturated with a 20:1 mixture of [²H₁₈]BSA and [²H₉]TMCS. The sample (1 ml) of the Tms derivative was injected on to the column, followed after about 30 s by 10 μl of the [²H₁₈]BSA—[²H₉]TMCS mixture. Spectra were recorded as usual. The labelled analogues (Ie)—(VIe) were obtained from the perdeuterio-Tms derivatives by injecting

³⁴ C. Eaborn, 'Organosilicon Compounds,' Butterworth, London, 1960, pp. 113—114.

them on to a column saturated with BSA-TMCS and then injecting 10 μ l of a BSA-TMCS mixture.

Low resolution spectra were recorded with an LKB 9000 mass spectrometer; the samples (1 μ l) were introduced *via* the g.l.c. inlet (9 ft 1% SE30 column at 160°). Spectra were recorded at 70, 20, and 15 eV with an accelerating voltage of 3.5 kV and an ion-source temperature of 270°. Ion-molecule reaction products were observed by injecting large samples (up to 4 μ l, 16 μ g).

High resolution and metastable focusing data were

obtained with a CEC 21-110B mass spectrometer. Samples were introduced *via* the g.l.c. inlet.

The complete spectra have been submitted to Archives of Mass Spectral Data.

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[1/547 Received, 14th April, 1971]
