

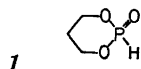
The Mass Spectrometric Fragmentation of Some 5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinanes

GEORGE W. FRANCIS, KJELL TJESSEM, ARILD DALE and THOR GRAMSTAD

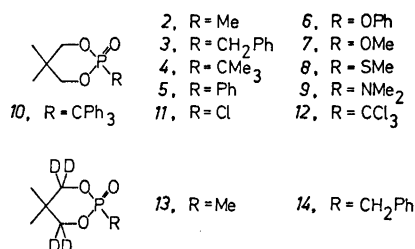
Chemistry Department, University of Bergen, N-5000 Bergen, Norway

The mass spectra of some 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanes are examined. Study of deuterated analogues and high resolution measurements allow the observed fragmentation to be rationalised. The system is typified by multiple hydrogen transfers during fragmentation. The site of charge location and the measured ionisation potentials are briefly considered.

A number of reports in the literature discuss the mass spectra of organic esters of the phosphorus oxyacids.^{1–12} 2-Oxo-1,3,2-dioxaphosphorinane (*1*) is a cyclic ester of phosphonic acid and the majority of the compounds encompassed by the present work may be regarded in this way also. The compounds here examined and whose structures (*2–14*) are given in Scheme 1 were prepared by established procedures^{13–18} or by simple modification of these to allow of deuteration. The mass spectra are presented in Fig. 1.



The fragmentation of the compounds *2–14* may be readily compartmentalised according to whether it is common to the system as a whole or depends on the presence of a particular substituent. In all cases hydrogen migration from the cyclic alkyl residue is a feature of the first type of fragmentation, while the most typical charged fragments of the second class are the result of simple bond fission.



Scheme 1. Structures of the compounds (*2–14*) studied in the present investigation.

CHARACTERISTIC FRAGMENTATION

Although the term characteristic fragmentation may be used to describe the discussion which follows, it must be borne in mind that the observation of such fragmentation depends upon the initial site of charge location and on the stability of the particular fragment under consideration. Thus, drastic changes in the electronic properties of substituents must inevitably give rise to considerable changes in the type of spectrum observed.

The identity of the various fragments in the discussion which follows in this section is based on the spectra of the deuterated compounds (*13* and *14*) and on high resolution studies carried out on the compounds *2* and *3*. The measured masses for the various fragments are given in the experimental part.

Characteristic fragments occur at *M*–15, *M*–28, *M*–30, *M*–55, *M*–67 and *M*–85 mass units in most of the accompanying spectra of the compounds *2–9*, while these fragments are largely absent from the spectra of *10–12*. This difference may be ascribed to a variation

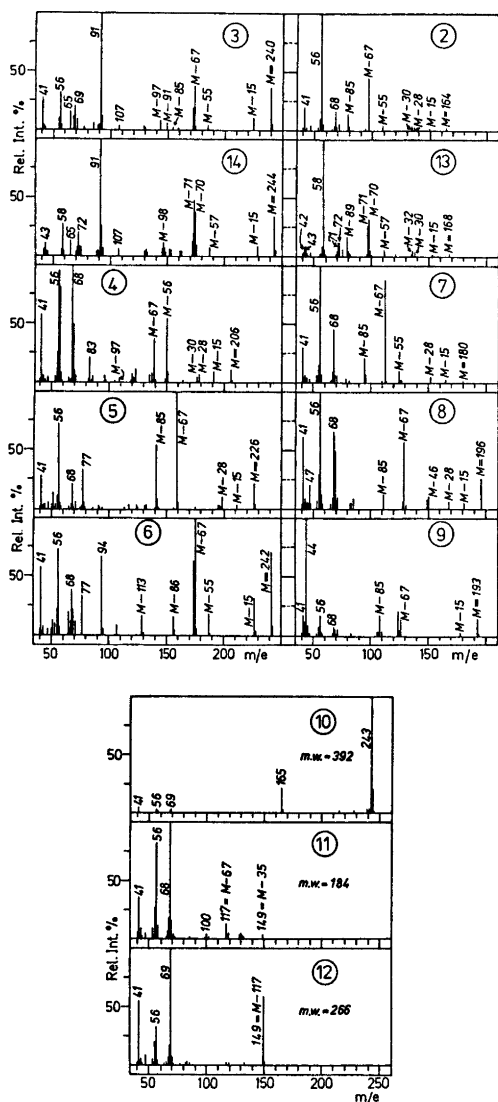
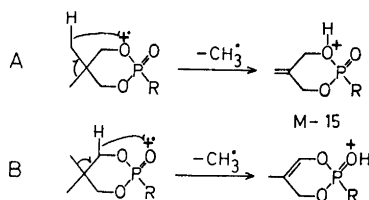


Fig. 1. Mass spectra of the compounds 2–14.

in the site of initial charge location and/or stability factors. The three characteristic low mass ions at m/e 41, 56 and 68 (and/or 69) are present in all cases.

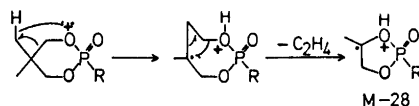
The $M-15$ ion is due to the loss of a methyl radical and as can be seen from the spectra of the deuterated compounds 13 and 14 the fragment eliminated comes entirely from the *gem*-methyl groups at position 5. Two possible fragmentation paths may be considered according to whether the charge is placed ini-

tially on the ester oxygen atoms or on the phosphoryl oxygen atom. Both paths involve hydrogen transfer and it is not possible to distinguish between them on the basis of the present evidence (Scheme 2).



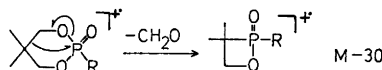
Scheme 2.

Deuteration shows that the $M-28$ ion is shifted quantitatively by two mass units and thus its formation must involve loss of the carbon atoms 4 or 6. The other carbon atom lost is most likely derived from the *gem*-methyl groups and a tentative mechanism (Scheme 3), satisfying these requirements, may be conceived based on the same hydrogen shift as in Scheme 2A.



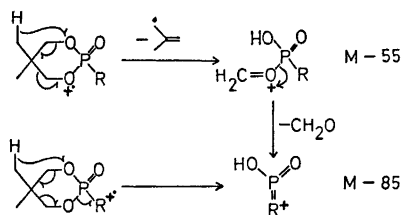
Scheme 3.

The $M-30$ ion is generally of low intensity, but like that above is shifted by two mass units on deuteration. This fact and the high resolution data accord with its origin through elimination of formaldehyde from the ring (Scheme 4).



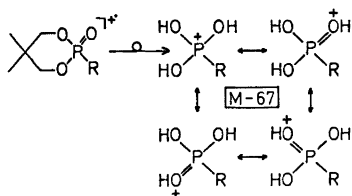
Scheme 4.

The $M-55$ and $M-85$ mass unit ions retain, respectively, two and none of the deuterium atoms from the molecule in the case of the compounds 13 and 14, and their origin may thus be formulated as in Scheme 5. The $M-85$ ion may also be formed by a concerted process where suitable charge location is available (Scheme 5).



Scheme 5.

The ion at $M-67$ is due to the loss of the hydrocarbon residue of the phosphorinane ring with prior transfer of three hydrogen atoms to the charged phosphorus-containing fragment eliminated. The occurrence of this ion in the esters of phosphonic acid has previously been commented on by McLafferty¹ and Occolowitz and White,² and its formation related to the ability of the resultant even electron ion to stabilise the charge through resonance. That this is probably the case is supported by the fact that this ion provides the base peak in the case of the phenyl derivative **5** and the phenoxy compound **6** where additional resonance structures may be written. Only the general resonance forms are shown in Scheme 6. The methoxy, thiomethoxy and dimethylamino compounds (**7-9**) show a somewhat lower intensity for this ion, but the differences between these cases may be explained in terms of variation in charge pattern in the molecular ion, and this point will not be further pursued.

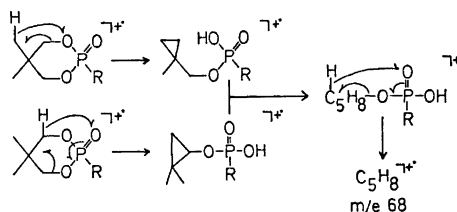


Scheme 6.

The origin of the hydrogen atoms transferred to the charged fragment in the formation of the $M-67$ ion is somewhat surprising, in that the hydrogens involved, as evidenced by the deuterated compounds, are largely derived from the *gem*-methyl groups. This provides some circumstantial evidence for the siting of the charge in the molecular ion at the ester

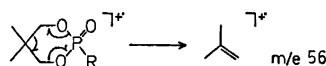
oxygen atoms since the required hydrogen shifts seem more probable under these conditions. While a detailed mechanism cannot be suggested at the present time, the comments made below on the formation of the m/e 68 ion also apply to this ion in a general way.

The ion at m/e 68 is shifted in the deuterated analogues to masses 71 and 72, thus showing that hydrogens of different origin may be transferred. Scheme 7 suggests possible origins for this ion.



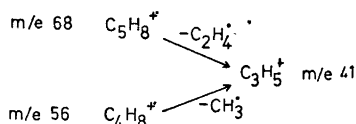
Scheme 7.

The m/e 56 ion is shifted quantitatively to m/e 58 in the compounds **13** and **14**, and may be readily rationalised as resulting from bond rearrangement in the phosphorinane ring (Scheme 8). That this ion is normally the strongest in the lower end of the mass spectrum fits well with such a mechanism which involves a simpler process than that described immediately above or that giving rise to the m/e 41 ion below.



Scheme 8.

The ion at m/e 41 (C_3H_5) can be formed only as a result of considerable prior rearrangement and seems likely to go *via* either the m/e 68 or m/e 56 species. Such an explanation requires the loss of an ethenyl or a methyl radical, respectively, as the final stage of the process, Scheme 9.

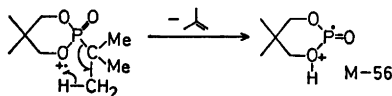


Scheme 9.

SPECIFIC FRAGMENTATION ATTRIBUTABLE TO SUBSTITUENTS AT PHOSPHORUS

While the presence of substituents alters, sometimes drastically, the intensities of the characteristic ions described above, a number of specific fragments attributable to particular substituents normally occur. That the former normally dominate in the spectrum is largely explicable in terms of the highly directive effects of the dioxaphosphorinane ring system. That this is the case is seen in the fact that specific fragmentation is most marked in the presence of those substituents expected to have the largest effects on the electronic distribution.

The compound **2** having a *P*-methyl group provides no fragment ion specific for the presence of the methyl group. However, when the bulkier *tert*-butyl group is present, compound **4**, a change occurs in the characteristic fragmentation in that the *M*-55 ion is apparently largely replaced by an *M*-56 ion. This may be rationalised in terms of the loss of isobutene (Scheme 10), a process involving H-transfer to one of the ring oxygen atoms and hence in direct competition with that envisaged by Scheme 2A.

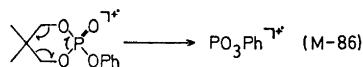


Scheme 10.

As expected, the presence of the *P*-benzyl and *P*-phenyl groups in the compounds **3** and **5** leads to the observation of *m/e* 91 and 77 ions, respectively, with charge retention on the aromatic moiety. A relatively low intensity *M*-91 ion with charge retention on the phosphorinane ring is also observed in the former case.

The ability of aromatic moieties to stabilise the charge is further seen in the spectrum of the compound **6** which has a phenoxy substituent. Ions at *m/e* 77 and 94 are readily explicable as phenyl and phenol species, respectively. However, the *M*-86 ion is apparently specifically favoured in this case over the normal

M-85 ion, and represents the most unique feature of the spectrum (see Scheme 11).



Scheme 11.

While the methoxy function in compound **7** is not revealed by specific fragmentation, ions of low intensity at *m/e* 47 and *M*-46 mass units in compound **8** can be readily associated with the presence of the *S*-methyl group. These observations are in contrast with the finding in the spectrum of the dimethyl-amino compound (**9**) that the low mass *m/e* 44 ion is by far the strongest ion in the whole mass range. This probably reflects initial charge siting at nitrogen in agreement with the known data for the relative abundances of similar ions in amino-alcohols.

None of the remaining compounds (**10**–**12**) provide molecular ions and the high mass part of the characteristic fragmentation of the system is inhibited. It should also be noted that in both **10** and **12** the *m/e* 68 ion is replaced by an *m/e* 69 ion, presumably of similar origin but reflecting the drastic changes in electron distribution and charge stabilisation caused by the substituents here present. In the case of the trityl compound (**10**) it is apparent that the charge is preferentially located on the trityl moiety as evidenced by the intense trityl and diphenylmethenyl ions which completely dominate the spectrum. The chloro substituent in compound **11** and the trichloromethyl group in compound **12** each make available an energetically favourable radical loss to yield *M*-35 and *M*-117 ions, respectively.

GENERAL CONSIDERATIONS

The compounds studied here are unusual in having present so many hetero-atoms in such proximity. This, and the wide variation expected in the electronic distribution within the molecule as highly divergent substituents are attached to the phosphorus atom make intuitive consideration of charge siting in the molecular ion more difficult than in most organic molecules.

Previous work by Bafus *et al.*³ has shown that in the case of trimethyl and triethyl phosphates (15 and 16) initial charge siting in the molecular ion was at one of the ester oxygen atoms. Consideration of the mass spectrometric ionisation potentials of the sulfur analogues, 17–19, of 15, where one of the oxygen atoms had been replaced by a sulfur atom led Santoro¹⁸ to the conclusion that in the latter cases the first electron removed was a sulfur non-bonding electron.

Molecular orbital calculations (CNDO/2) by one of the present authors showed¹³ that the atom making the greatest electronic contribution to the highest bonding molecular orbital, *i.e.* having the largest coefficient in the

HOMO, varies according to the substituent present on phosphorus. However, in all cases where such calculations were carried out the highest electronic contribution to the HOMO was made by one of the cyclic ester oxygen atoms or by the substituent at the phosphorus atom. These calculations were in general accord with the experimentally measured ionisation potentials (for the latter see Table 1).

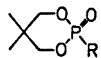
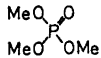
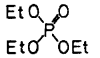
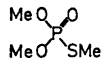
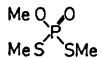
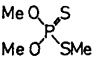
Among the compounds whose ionisation potentials were measured (2–6, 8 and 9) the lowest values were obtained for 3, 5 and 6 where the substituent was, respectively, benzyl, phenyl and phenoxy. These I.P.'s (8.25–8.81 eV) we feel able to associate with the removal of an electron from the benzene nucleus: CNDO/2 calculations show that in 5 and 6 the highest electronic contribution to the HOMO is made by the atoms of the aromatic nucleus.¹³

The I.P. values for the thiomethoxy and dimethylamino compounds, 8 and 9, lie close together at 9.21 and 9.07 eV, respectively, and compare well with the values found for the compounds 17–19 (9.5, 9.2 and 9.0 eV) by Santoro.¹⁸ Further, the MO calculations¹³ indicate that the highest HOMO contribution is made by the sulfur atom in 8 and by the nitrogen in 9. It thus seems likely that in 8 and 9, as in 17–19,¹⁴ the electron removed on formation of the molecular ion originates as a non-bonding electron on the hetero-substituent.

The somewhat higher I.P. values found for the compounds 2 and 4 (10.55 and 9.74 eV) which have *P*-alkyl substituents compare well with those reported for triethyl phosphate (10.1 eV) and trimethyl phosphate (10.7 eV).^{3,12} The conclusion^{3,12} that in the latter compounds the electron removed was from an ester oxygen atom may thus be extended to the present case. This is further supported by the MO calculations which show that the highest electronic contribution to the HOMO is made by an ester oxygen atom in each case.

While extension of the above results to 70 eV spectra is fraught with difficulties,²⁰ the general conclusion that the charge in the molecular ion is carried by either an ester oxygen atom or the substituent at phosphorus seems valid. Examination of the characteristic fragmentation modes shows that when they give rise to high mass ions they are usually ex-

Table 1. Ionisation potentials (I.P., eV) in electron volts as determined for the compounds 2–9 in the present investigation and from the literature^{3,14} for the compounds 15–19. The atom(s) whose electrons make the greatest contribution(s) to the highest occupied molecular orbital are indicated (XS) for the compounds 2–9.¹³

			
2–9			
			
15			
			
16			
			
17			
			
18			
			
19			
Compound No.	R	IP eV	XS
2	Me	10.55	ring O
3	CH ₂ Ph	8.25	Ph
4	CMe ₃	9.74	ring O
5	Ph	8.81	Ph
6	OPh	8.43	Ph
7	OMe	—	ring O
8	SMe	9.21	S
9	NMe ₂	9.07	N
15 ^a		10.77	
15 ^b		10.7	
16 ^a		10.06	
17 ^b		9.5	
18 ^b		9.2	
19 ^b		9.0	

^a Ref. 3. ^b Ref. 14.

plicable in terms of charge location on an ester oxygen atom.

Turning to the specific fragmentation, it is apparent that here too the results just discussed can be usefully applied. The compounds with *P*-alkyl substituents (2 and 4), where we would expect the initial charge site to be on an ester oxygen atom, show no characteristic fragmentation. However, while this is true of the methoxy compound (7) with a similar charge siting, the *S*-methyl compound (8) where some charge siting on the sulfur atom might be expected does indeed show an ion, albeit of only moderate intensity, at *m/e* 47.

The expected charge siting in the dimethyl-amino compound (9) is reflected in the spectrum by the dominance of the *m/e* 44 ion: no other ion has a relative intensity of more than 20 %. Further, in all compounds containing phenyl groups (3, 5, 6, and 10), that at least part of the charge siting is on these groups is seen in the observation of appropriate ions.

It is interesting to compare the spectra of the compounds 10 and 12 since both triphenyl-methyl and trichloromethyl radicals are known to be energetically favourable species. The difference between these spectra must thus be the result of variation in initial charge siting and an extension of the theoretical calculations to these compounds seems desirable.

In conclusion, it seems that the system here examined provides a case where mass spectral data and theoretical calculations may be usefully compared and yield mutual support.

EXPERIMENTAL

The syntheses of the compounds used in this study have been described elsewhere¹³ and follow general literature procedures.¹⁴⁻¹⁸ The mass spectra were obtained on two AEI MS9 instruments with the kind cooperation of the Universities of Oslo and Trondheim. The spectra reproduced were recorded at 70 eV and at the lowest temperature of the ion source allowing of volatilisation. Accurate mass measurements and ionisation potentials were determined using suitable standards.

2,5,5-Trimethyl-2-oxo-1,3,2-dioxaphosphorinane (2). *M*, measured *m/e* 164.061, calc. 164.060 for $C_8H_{13}O_3P$. *M*-15, measured *m/e* 149.037, calc. 149.037 for $C_8H_{10}O_3P$ (*M*-CH₃). *M*-28, measured *m/e* 136.031, calc. 136.029 for $C_8H_9O_3P$ (*M*-C₂H₅). *M*-30, measured *m/e* 134.052, calc. 134.050 for $C_8H_{11}O_2P$ (*M*-CH₂O). *M*-55, measured *m/e* 109.006, calc. 109.005

for $C_8H_9O_3P$ (*M*-C₂H₅). *M*-67, measures *m/e* 97.005, calc. 97.006 for CH_3O_3P (*M*-C₅H₇). *m/e* 68, measured *m/e* 68.063, calc. 68.063 for C_5H_8 . *m/e* 56, measured *m/e* 56.066, calc. 56.063 for C_4H_8 .

2-Benzyl-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (3). *M*, measured *m/e* 240.086, calc. 240.087 for $C_{12}H_{17}O_3P$. *M*-15, measured *m/e* 225.066, calc. 225.068 for $C_{11}H_{14}O_3P$ (*M*-CH₃). *M*-28, measured *m/e* 212.060, calc. 212.060 for $C_{10}H_{13}O_3P$ (*M*-C₂H₅). *M*-30, measured *m/e* 210.081, calc. 210.081 for $C_{11}H_{15}O_2P$ (*M*-CH₂O). *M*-55, measured *m/e* 185.037, calc. 185.037 for $C_9H_{10}O_3P$ (*M*-C₄H₉). *M*-67, measured *m/e* 173.034, calc. 173.037 for $C_9H_{10}O_3P$ (*M*-C₅H₉). *m/e* 68, measured *m/e* 68.062, calc. 68.063 for C_5H_8 . *m/e* 56, measured *m/e* 56.065, calc. 56.063 for C_4H_8 .

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