Negative Ion Mass Spectrometry. Part III.[1] Spectra of Some Derivatives of Dibenzophosphole 5-Oxide

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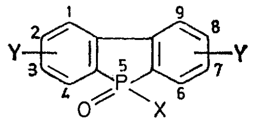
The 70 eV negative ion mass spectra of 13 compounds based on the dibenzophosphole structure have been examined and found to exhibit yields of primary ions consistent with a model based on the preferential attachment of slow electrons at positive centres. From the patterns of yields of primary and secondary ions it is concluded that only relatively low levels of excitation are involved.

At a time when new methods of ionization such as chemical ionization, field ionization, and field desorption are receiving wider application it is still the case that negative ion mass spectrometry of complex molecules is a relatively unexplored field of study. This may arise to some extent from the apparent complexity of the mechanisms by which it is stated [2] that negative ions are formed in the mass spectrometer source. It has, for example, been argued [2] that for bombardment with 70 eV electrons, no parent anions should be formed.

Recent studies on a series of aromatic nitro-compounds [3] and phosphorus ylides [4,5] have shown that at 70 eV certain types of parent ion may be stable, whilst others may not, and a set of axioms has been proposed [6] which provides a basis for rationalizing the primary fragmentation reactions involved. These are based on the postulate that a major contributing factor in anion formation in a conventional ion source is the attachment of slow secondary electrons.[7-9]

Recent evidence has shown [1] that for 2- and 3-nitrotoluenes this process can lead directly to both parent and daughter ion formation.

The possible advantages of negative ion mass spectrometry are that the spectra generally contain few peaks, and that even though the parent ion may be of low intensity, the fragmentations are so specific that structural information can be inferred from the resulting patterns. In this paper we consider the '70 eV' negative ion spectra of a series of compounds based on the dibenzophosphole system comprising phosphine oxides (I)—(III), phosphinic acids (IV)—(VII), and phosphinate esters (VIII)—(XIII).



(I)—(XIII)

RESULTS

The general types of fragmentation ions observed for the compounds studied have been divided into 'primary,' 'secondary,' and 'tertiary' products. The first category includes the parent ions, and those formed by the loss of a radical or molecule from these ions; the second covers those ions which arise from subsequent fragmentations of the primary species.

(a) *Primary Ions.*—The intensities (percentage total ionization above m/e 63) of these ions are listed in Table 1. The ions (*a*)—(*c*) are thought to result from the three possible fragmentation reactions depicted in Scheme 1. An ambiguity arises for compounds (IX) and (X) since the mass values of (*b*) and (*c*) are identical. Also listed are the yields

TABLE 1

Total ionization (% Σ_{63}) of primary ions in the 70 eV negative ion mass spectra of dibenzophosphole derivatives (I)—(XIII)

Compound (substitution type) [a]	Substitution pattern X	Y	$M^{\cdot -}$	(*a*)	(*b*)	(*c*)	$M - 1^{\urcorner -}$	Total
(I)	Et	H	1·1	76·6			8·9	86·6
(II)	Bu^n	H	1·2	67·2			14·2	82·6
(III)	Ph	H	2·0	73·3			3·2	78·5
(IV)	OH	H	1·8	0·2	93·7		*c*	95·7
(V) (*m*)	OH	3,7-$(OH)_2$	5·1	8·1	51·5		*c*	64·7
(VI) (*m*)	OH	3,7-$(OMe)_2$	1·2	6·8	55·8	2·4	*c*	65·2
(VII) (*p*)	OH	2,8-$(OMe)_2$	4·0	5·5	39·8	14·5	*c*	63·8
(VIII)	OMe	H	2·9	24·9	46·4		2·9	77·1
(IX) (*m*)	OMe	3,7-$(OMe)_2$	0·2	20·6	22·6 [b]	*b*	1·1	44·5
(X) (*p*)	OMe	2,8-$(OMe)_2$	1·0	20·7	39·9 [b]	*b*	1·8	63·4
(XI)	OEt	H	2·0	24·1	53·7		2·2	82·0
(XII) (*m*)	OEt	3,7-$(OMe)_2$	0·2	16·9	27·0	9·4	1·3	55·8
(XIII) (*p*)	OEt	2,8-$(OMe)_2$	0·3	16·6	14·2	30·6	2·1	64·6

[a] The 'substitution type' is classified according to whether the Y substituents are *meta* or *para* with respect to the phosphorus atom. [b] For (IX) and (X) the ions (*b*) and (*c*) occur at the same m/e value. [c] For (IV)—(VII) the $M - 1^{\urcorner -}$ ion corresponds to (*b*).

[1] Part II, R. G. Alexander, D. B. Bigley, and J. F. J. Todd, *J.C.S. Faraday I*, 1974, **70**, 1212.

[2] C. E. Melton, 'Principles of Mass Spectrometry and Negative Ions,' Marcel Dekker, New York, 1970, p. 192.

[3] J. F. J. Todd, R. B. Turner, B. C. Webb, and C. H. J. Wells, *J.C.S. Perkin II*, 1973, 1167.

[4] R. G. Alexander, D. B. Bigley, and J. F. J. Todd, *J.C.S. Chem. Comm.*, 1972, 553.

[5] R. G. Alexander, D. B. Bigley, and J. F. J. Todd, *Org. Mass Spectrometry*, 1973, **7**, 963.

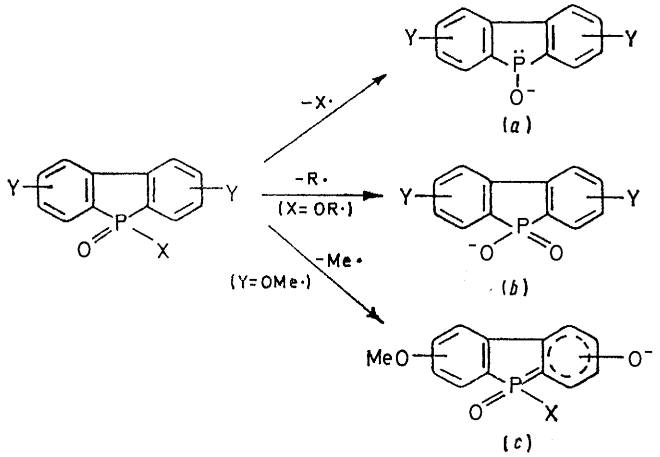
[6] R. G. Alexander, D. B. Bigley, and J. F. J. Todd, *Org. Mass Spectrometry*, 1973, **7**, 643.

[7] J. C. J. Thynne, *Chem. Comm.*, 1968, 1075.

[8] G. D. Flesch, R. M. White, and H. J. Svec, *Internat. J. Mass. Spectrometry Ion Phys.*, 1969, **3**, 339.

[9] T. McAllister, *J.C.S. Chem. Comm.*, 1972, 245.

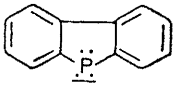
of the $M - 1\rceil^-$ ions, which for (VIII)—(XIII) are of only minor importance.



SCHEME 1

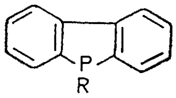
As might be expected from the idea that (*a*)—(*c*) result from the dissociation of the parent anion in a repulsive state,[6] no metastable ion peaks for these fragmentations have been observed.

(b) *Secondary and Tertiary Ions.*—From the sub-totals of the intensities listed in Table 1 it is clear that the yields of secondary and tertiary ions must generally be low, and in only a few cases do individual secondary products account for more than 10% of the total ion current. An ion common to all the mass spectra is *m/e* 63 which is thought to be mainly PO_2^-; the possibility of $C_5H_3^-$ cannot be excluded however, since the oxides (I)—(III) also fragment to form low abundances of ions with this mass. Another species common to several spectra is *m/e* 183 or its substituted analogue which is likely to be (A). This ion was observed[10] to be the base peak in the 70 eV negative ion mass spectrum of the P^{III} compounds B.



m/e 183

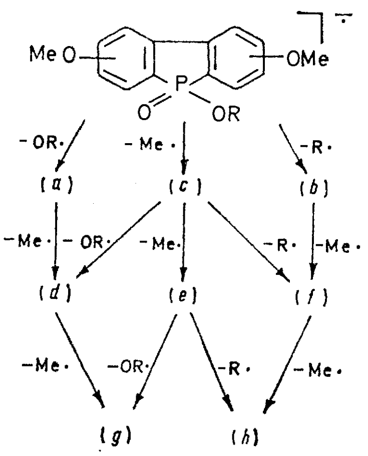
(A)



R = Et or Bu^n

(B)

The pattern of decomposition established for the molecular ion can be used to rationalize the formation of secondary and later ions, assuming that the cyclic phosphole system is retained. For example ion (*c*) may lose X· or, when X = OMe, eliminate Me. It thus follows that only when Y = OMe will sequential product ions be of any significance. This can be seen from Table 1 where only for the substituted compounds (V)—(VII), (IX), (X), (XII), and (XIII) do the yields of primary ions fall below 77%. A possible comprehensive scheme for the dimethoxy-acids and -esters is shown in Scheme 2 with the corresponding ion intensities listed in Table 2. Unfortunately the absence of metastable ion data makes it impossible to differentiate between alternative routes leading to the same ion. As with the primary ion data ambiguities arise for products from the methyl esters (IX) and (X) since $(M - Me\cdot) - Me\cdot\rceil^-$ is indistinguishable from $(M - R\cdot) - Me\cdot\rceil^-$ and $(M - Me\cdot) - R\cdot\rceil^-$. A further difficulty arises because the overall ion intensities are insufficient to afford the resolution necessary to distinguish between $(M - Me\cdot) - Me\cdot\rceil^-$ and the rearrangement ion $M - CH_2O\rceil^{-\cdot}$. However we elect to discount the possibility of elimination of a formaldehyde molecule since (i) as this involves a rearrangement it would be expected to be a slow process, yet no appropriate metastable ion peaks were observed, (ii) the yields of the parent anions were extremely low suggesting a high degree of instability, and (iii) it has been observed[6,11] that quite generally in negative ion mass spectra the preferred primary fragmentation corresponds to expulsion of a radical with the formation of an even-electron ion.



SCHEME 2

TABLE 2

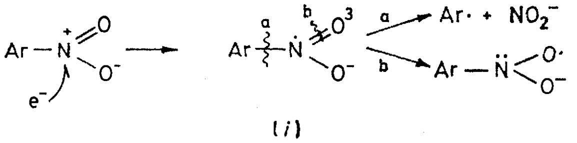
Total ionization (% Σ_{63}) of secondary and tertiary ions from dimethoxy acids and esters

Compound (substitution type)[a]	(*d*)	(*e*)	(*f*)	(*g*)	(*h*)	Total
(VI) (*m*)	0	7·2	9·2	4·8	2·4	23·6
(VII) (*p*)	4·0	5·9	14·1	3·8	1·4	29·2
(IX) (*m*)	4·5	37·3	*b*	11·4	0·7	53·9
(X) (*p*)	11·2	8·3	*b*	0	2·6	22·1
(XII) (*m*)	2·3	20·7	2·9	6·8	0·6	33·3
(XIII) (*p*)	7·2	2·7	7·6	0·9	1·5	19·9

[a] See note *a* to Table 1. [b] For (IX) and (X) ions (*e*) and (*f*) occur at the same *m/e* value.

DISCUSSION

We consider first the rationalized approach[6] to negative ion fragmentation reactions, as exemplified by an aromatic nitro-compound. The initial postulate is that the attachment of slow electrons occurs at positive centres within the molecule, to give species (*i*), and that this is followed by homolytic cleavage of an adjacent bond and electron coupling to form (relatively) stable products (Scheme 3).



SCHEME 3

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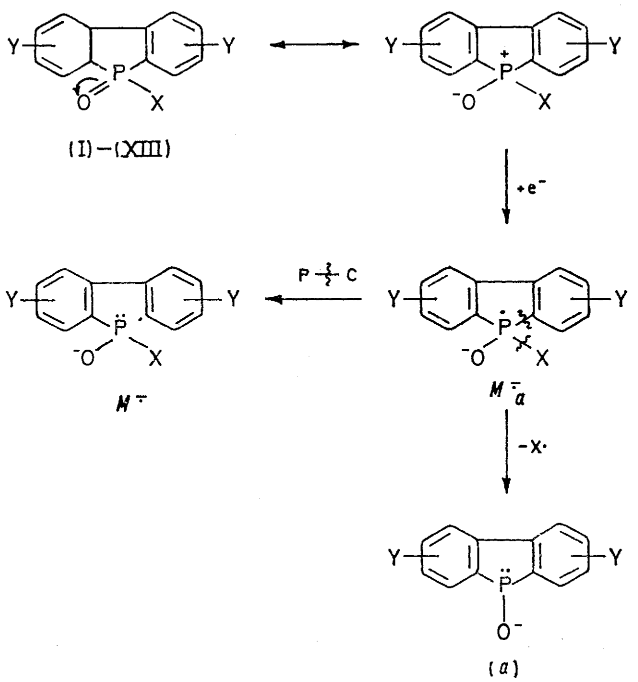
[10] R. G. Alexander, D. B. Bigley, and J. F. J. Todd, unpublished results.

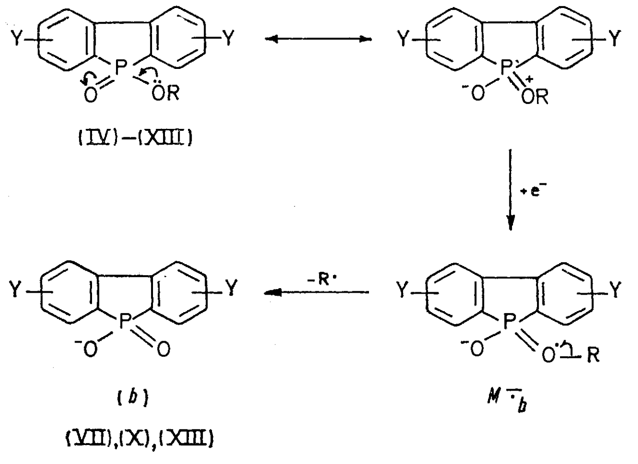
[11] J. H. Bowie, *Austral. J. Chem.*, 1971, **24**, 989.

For the compounds under consideration application of this idea would lead to electron attachment at phosphorus (Scheme 4) but there is the additional possibility that conjugative effects may offer alternative sites of initial electron attachment, resulting in additional primary fragmentation routes (Schemes 5—7).

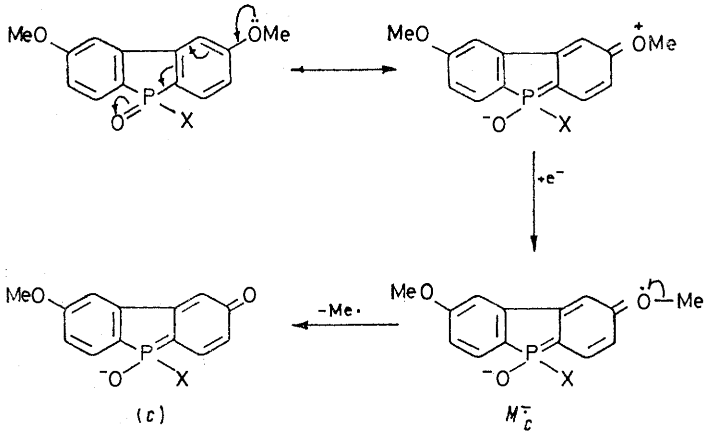


SCHEME 4

The apparent success of the predictions of the primary cleavage reactions is seen from the high percentage total ionization attributable to the ions (*a*)—(*c*). Evidently production of these species is more favourable than the scission of a P–C bond which leads to formation of stable parent ion but partially breaks the cyclic structure. The observation that the dibenzophosphole oxide system can exist as a stable anion (*a*) offers an interesting comparison with positive ion studies where the same system is found as a stable cation.[12-14] However, the negative ion spectra of β-ketophosphoranes [5] indicate that actual formation of this ion is preferred in the positive ion mode.



SCHEME 5



SCHEME 6

The rapid cleavage reactions suggested by Schemes 5—7 proceed *via* the unstable parent ions $M^{-\cdot}{}_b$ and $M^{-\cdot}{}_c$ with a resulting absence of metastable ions. For (I)—(III) where these alternative fragmentations are inapplicable there are low intensity (3—4% Σ_{63}) peaks at *m*/*e* 183 which may result from a rearrangement analogous to that described for the positive ion studies (Scheme 8). In the absence of metastable ion evidence this scheme cannot be defined but it is perhaps significant that for compound (III; X = Ph) the ion *m*/*e* 93 corresponding to PhO^- is observed (5·3% Σ_{63}).

The relative intensities of the individual primary ions for (IV)—(XIII) appear to illustrate a competition for stability either through reduction, $P^{V} \longrightarrow P^{III}$, to form (*a*) or a retention of phosphorus in the pentavalent state

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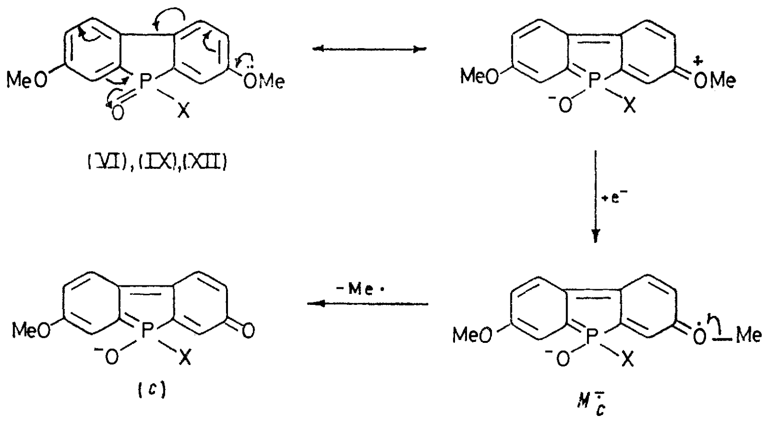
[12] R. G. Cooks, R. S. Ward, D. H. Williams, N. A. Shaw, and J. C. Tebby, *Tetrahedron*, 1968, **24**, 3289.

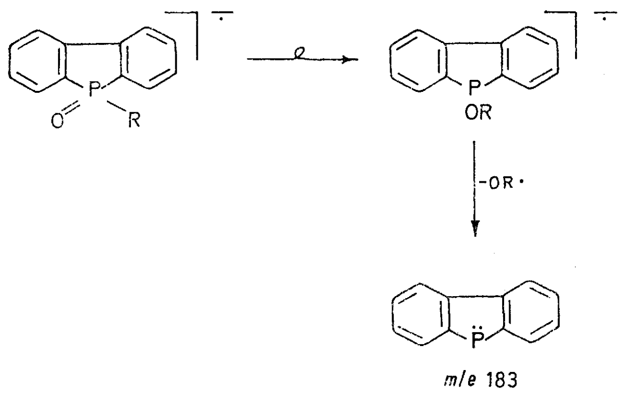
[13] A. P. Gara, R. A. Massy-Westropp, and J. H. Bowie, *Austral. J. Chem.*, 1970, **23**, 307.

[14] R. T. Aplin, A. R. Hands, and A. J. H. Mercer, *Org. Mass Spectrometry*, 1969, **2**, 1017.

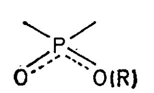
and extended conjugation involving system (C) present in (*b*) and (*c*). From Table 1 it would appear that this latter effect is the more important. This is particularly clear for the product ions of type (*c*) formed from (VII) and (XIII) where conjugation involving the *para*-semiquinone (Scheme 6) does not suggest an unfavourable canonical form involving the bridgehead C–C bond as in the case of the *meta*-semiquinones. Thus for (IX) and (XII) ions (*c*) appear to favour secondary and tertiary fragmentation to give (*e*) and (*g*) respectively. Such a prominent secondary loss of a radical seems to be quite rare in negative ion mass spectrometry.



SCHEME 7



SCHEME 8



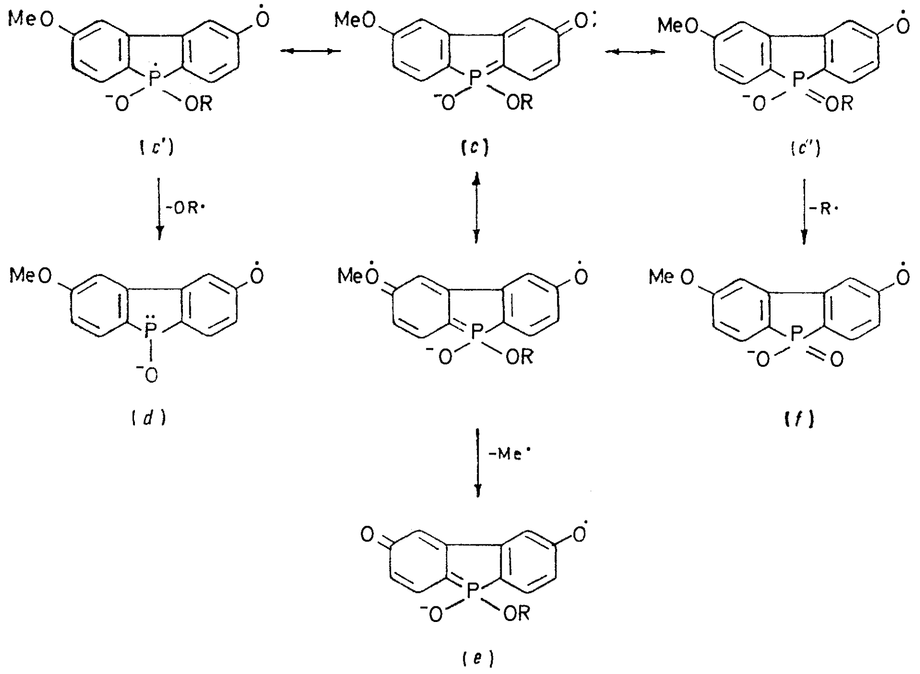
(C)

A more detailed comparison of the primary ion intensities reveals some remarkable consistences in the fragmentations of similar compounds. Thus the total percentage parent ion and primary cleavage products exhibit correlations: oxides (I)—(III) (78·5—86·6%); acids (V)—(VII) (63·8—65·2%); unsubstituted esters (VIII) and (XI) (77·1—82%); *m,m'*-dimethoxy-esters (IX), (XII) (44·5—55·8%) *p,p'*-dimethoxy-esters (X), (XIII) (63·4—64·4%). This indicates that for similar compounds the total number of ions involved in forming the primary species remains fairly constant. Considering individual species, we note that for esters (VIII)—(XIII) the yields of ion (*a*), formed by loss of OMe• or OEt•, are virtually identical for the respective pairs (VIII)/(XI), (IX)/(X), and (XII)/(XIII). It would thus appear that the orientation of the methoxy-substituents has little influence on the probability expulsion of an alkoxyl radical with reduction of the phosphorus atom. For (XIII) we note that the ratio of intensities for (*b*) : (*c*) is *ca.* 1 : 2, and since (*c*) can arise by either of two equivalent routes it appears that for the *para*-substituted compounds the probability of loss of OR· is independent of the siting of the alkoxy-groups. If it is assumed that this situation also obtains for the methyl ester (X) then the ambiguity in the relative yields of (*b*) and (*c*) from this compound (*cf.* note *b* of Table 1) can be resolved, and these should be *ca.* 13 and *ca.* 27% respectively.

The additional primary route of hydrogen loss leading to $M - 1]^{-}$ is observed in the spectra of all 13 compounds, and for the series of acids (IV)—(VII) the major component of the $M - 1]^{-}$ species is apparently ion (*b*), as the esters (VIII)—(XIII) only exhibit minor contributions for this process.

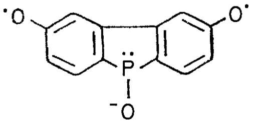
The prediction of secondary decomposition processes is outside the scope of the rationale proposed for the primary fragmentation reactions. However examination of the data in Table 2 suggests that for the dimethoxy-acids and -esters the major balance of ionization not accounted for in Table 1 arises in secondary and tertiary processes which are analogous to the three major primary steps. Thus it may be supposed that electron decoupling in (*c*) from (X) or (XIII) may result in formation of (*d*), (*e*), or (*f*) by loss of OR·, Me·, or R· respectively (Scheme 9). The unusual nature of these sequential radical losses has already been noted.

From Scheme 2 it is seen that (*d*)—(*f*) may decompose further to forms (*g*) or (*h*). It is evident from drawing plausible structures for these ions that (*g*) contains a tervalent phosphorus atom whilst in (*h*) the P^V state is maintained. Comparing the relative yields in Table 2 suggests that except for (X) and (XIII) (*g*) is the more

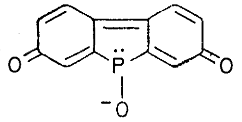


Scheme 9

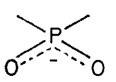
stable species. A further significant point is that for the *para*-substituted compounds the tertiary losses must result in the formation of diradicals, *e.g.* (*g'*) whereas for the *meta*-dimethoxy-derivatives the tertiary products are fully conjugated, *e.g.* (*g''*). This enhanced stability in the latter case is clearly reflected in the higher total yields of (*g*) and (*h*) from (VI), (IX), and (XII) compared to (VII), (X), and (XIII). A similar situation obtains for the relative intensities of the secondary ions (*e*) formed from the above compounds. By contrast the relative yields of ions of type (*d*) are reduced for the *meta*-substituted, a trend which may be a consequence of the relative ratios of the precursor ions (*c*). Thus for (XII) and (XIII) we have $(c)_m/(c)_p = 0{\cdot}31$ and $(d)_m/(d)_p = 0{\cdot}32$. Arguments based on ratios of yields may possibly be used to distinguish further between competing pathways in Scheme 2. Thus for (XII) and (XIII) we have $(b)_m/(b)_p = 1{\cdot}9$ and $(f)_m/(f)_p = 0{\cdot}38$ which suggests that for this pair of compounds (*f*) is formed predominantly from (*c*) rather than from (*b*). This may reflect the stability of the delocalized grouping (D) present in (*b*).



(*g'*)



(*g''*)



(D)

Conclusions.—For the family of compounds studied we have observed that the '70 eV' negative ion mass spectra are simple, and, furthermore, that in most cases the application of our rationalized approach to primary fragmentation accounts for upwards of 60% of the total ion current. Indeed, for the less complex compounds this is as high as 80—95%.

For the substituted acids and esters it has been possible to infer probable secondary and later fragmentation processes and to use ratios of intensities to provide a guide to the likelihood of certain reaction paths. The fact that both the primary and secondary product yields appear to follow a fairly specific pattern is consistent with the notion that little excitation energy is imparted to the internal modes when a negative ion is formed, and as a consequence relative product stability is extremely important in determining ion abundancies. We consider that organic negative ion mass spectrometry deserves wider consideration as a possible analytical technique alongside the other 'gentler' methods of ionization.

EXPERIMENTAL

All the mass spectra, which are average values taken from at least three reproducible scans, were run on an A.E.I. MS902 instrument fitted with a 'Massmaster' modified for use with negative ions (the G.T. modification).[15] The electron energy was 70 eV (nominal) and the source was operated at 100—150° and *ca.* 5 × 10^{-6} Torr. The samples were admitted by means of a heated direct insertion probe.

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[15] D. A. Gallagher and J. F. J. Todd, *Internat. J. Mass Spectrometry Ion Phys.*, 1971, **7**, 336.