Electron Impact-induced Rearrangements in Compounds having the P=S Bond

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The fragmentation processes of P=S compounds upon electron impact include the following bond-forming reactions: (i) molecular ion rearrangement of the type $-P(:S)O-R \longrightarrow -P(:O)S-R$, (ii) bond formation between substituents (especially aryl groups) on phosphorus, (iii) loss of SH· from the molecular ion where the hydrogen can be derived from an alkyl or an aryl group, and (iv) hydrogen rearrangement to give the phenol molecular ion (or an isomer) in compounds having a phenoxy-substituent.

THE propensity of organosulphur compounds to undergo rearrangement upon electron impact [1] and the fact that bond-forming reactions involving atoms other than hydrogen have been observed in phosphines,[2,3] phosphine oxides,[2,3] phosphites,[4] phosphates,[5] and phosphonates [6] led us to examine the mass spectra of compounds (I)—(XII). Methyl and aryl substituents were preferred to larger alkyl groups since hydrogen rearrangements, which are common [7] in the spectra of phosphorus compounds containing alkyl substituents, could obscure the more interesting skeletal rearrangement processes. Jörg, Houriet, and Spiteller [8] have discussed the spectra of several phosphorothioates and *S*-alkylphosphorothioates. In the present study the effects of amino-, chloro-, and alkoxyl substituents on the fragmentation of P=S compounds are considered. High-resolution measurements, deuterium labelling, and 'metastable' peaks have been used to elucidate fragmentation sequences and wherever necessary spectra have been obtained at low temperature (*ca.* 50°) to minimize the possibility of thermal rearrangements or decomposition. High resolution measurements were done on all ions

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[1] For leading references see F. Duus, S. O. Lawesson, G. Schroll, J. H. Bowie, and R. G. Cooks, *Chem. Comm.*, 1967, 697.
[2] J. M. Miller, *J. Chem. Soc.* (*A*), 1967, 828.
[3] D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 966.
[4] J. L. Occolowitz and G. L. White, *Analyt. Chem.*, 1963, **35**, 1179.
[5] A. Quale, in 'Advances in Mass Spectrometry,' ed. J. D. Waldron, Pergamon Press, London, 1959, pp. 365—383.
[6] J. L. Occolowitz and G. L. White, *Austral. J. Chem.*, 1966, **19**, 1187.
[7] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, ch. 26.
[8] J. Jörg, R. Houriet, and G. Spiteller, *Monatsh.*, 1966, **97**, 1064.

discussed in fragmentation or rearrangement sequences, employing at least one of the compounds giving rise to such sequences.

Phosphoramidothioates.—The spectra of the phosphoramidothioates (I) (Figure 1) and (II) (Table 2) show

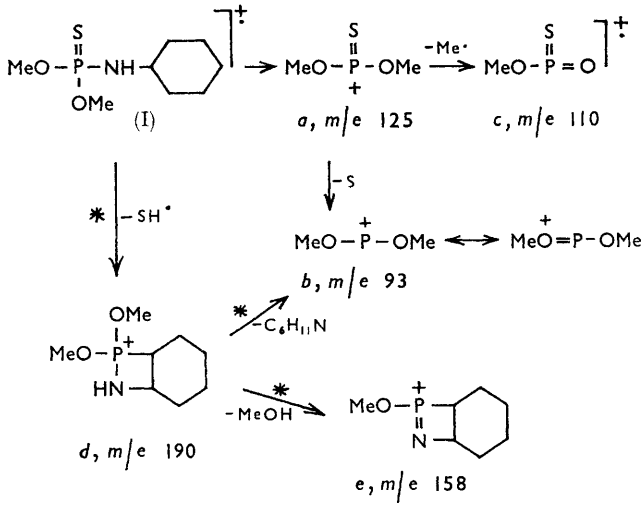
TABLE 1

$S{=}PR^1R^2R^3$

	R^1	R^2	R^3
(I)	MeO	MeO	C_6H_{11}·NH
(II)	MeO	MeO	$C_5H_{12}N$ *
(III)	MeO	*p*-NO_2·PhO	C_6H_{11}·NH
(IV)	MeO	*p*-NO_2·PhO	C_4H_9NO †
(V)	MeO	HO	C_6H_{11}·NH
(VI)	MeO	Pr^iO	C_6H_{11}·NH
(VII)	PhO	PhO	C_4H_9NO †
(VIII)	PhO	PhO	Cl
(IX)	MeO	MeO	Cl
(X)	PhO	PhO	MeO
(XI)	PhO	PhO	EtO
(XII)	MeO	C_6H_{11}·NH	Cl

* Piperidino. † Morpholino.

a number of features typical of this class of compound. In both cases the base peak is formed by loss of SH· from the molecular ion, and even at low impact energy this is an important process. The absence of an NH group in compound (II) implicates either a methyl hydrogen or a CH hydrogen from the amine substituent in this process. The spectrum of (Ia), the trideuterio-derivative ($R^1 = CD_3O$) of (I), established that hydrogen is lost from the cyclohexyl ring ,while that of (Ib), the monodeuterio-derivative ($R^3 = ND{\cdot}C_6H_{11}$) of (I), confirmed that the amino-hydrogen was not involved in the



SCHEME 1

loss of SH·. In thioureas the transfer of hydrogen from nitrogen to sulphur with subsequent loss of SH· does occur,[9] but there is no evidence for this tautomerism in phosphoramidothioates. The further loss of methanol from the M — SH ion of (I) involves specific loss of the amino-proton as shown by the spectrum of (Ib). As expected the latter process was not observed in (II). The other major ions in the spectra of (I) and (II) arise by P–N bond fission with charge retention by either fragment. Further fragmentation of ion *a* by loss of sulphur to give the stabilized bivalent phosphorus ion *b* has been noted previously [8] while an alternative process involving loss of CH_3· leads to the ionized metaphosphorothioate *c*. In Scheme 1 the structures of ions *d* and *e* are nominal.

The spectra of the *p*-nitrophenyl phosphoramidothioates (III) (Table 2) and (IV) (Figure 2) resemble

TABLE 2

Mass spectra of P=S compounds *

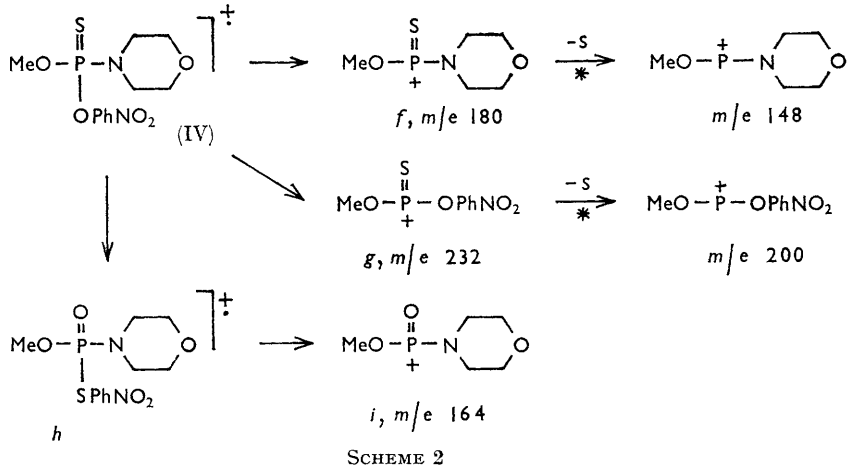
(II)	*m/e*	41	42	55	69	79	84	93	98	125
	I (%)	10	7	12	7	6	22	67	7	17
	m/e	176	177	178	209(M^+)					
	I (%)	100	10	6	48					
(III)	*m/e*	41	54	55	98	110	176	192	200	232
	I (%)	8	9	10	9	18	3	4	23	12
	m/e	265	297	298	330(M^+)					
	I (%)	4	100	17	10					
(V)	*m/e*	41	43	45	47	64	65	79	81	83
	I (%)	7	8	6	6	8	19	9	7	6
	m/e	96	98	99	111	128	166	176	209(M^+)	
	I (%)	7	100	9	7	8	12	93	54	
(VI)	*m/e*	39	41	42	43	55	56	79	81	98
	I (%)	7	18	6	10	7	20	20	6	88
	m/e	99	110	111	121	128	158	160	166	176
	I (%)	8	7	9	12	14	3	5	13	16
	m/e	192	208	218	219	251 (M^+)				
	I (%)	7	7	100	12	39				
(IX)	*m/e*	47	63	79	93	97	99	125	129	130
	I (%)	32	10	11	11	59	19	35	13	86
	m/e	131	132	160(M^+)		162(M^+)				
	I (%)	7	32	100		37				
(XI)	*m/e*	29	39	51	65	77	94	95	104	105
	I (%)	6	8	8	13	36	100	7	8	10
	m/e	109	110	141	155	157	173	184	185	186
	I (%)	21	21	12	6	13	25	4	7	3
	m/e	217	265	266	294(M^+)		295			
	I (%)	8	8	7	96		16			
(XII)	*m/e*	41	129	131	146	162	164	184	194	196
	I (%)	8	12	5	11	8	3	6	100	32
	m/e	227(M^+)		229(M^+)						
	I (%)	8		3						
(XIII)	*m/e*	39	51	65	77	91	94	123	124	140
	I (%)	6	7	10	36	7	57	6	9	9
	m/e	170	171	187	217	265	279	280(M^+)		281
	I (%)	11	7	27	5	30	14	100		17
	m/e	282								
	I (%)	6								

* All ions of abundance greater than 5% of the base peak (100%), and skeletal rearrangement ions less than this value are recorded.

those of the dimethyl compounds (I) and (II). In the morpholino-compound (IV) P–O bond fission, leading to *f*, is competitive with P–N bond fission leading to *g*. As expected, both *f* and *g* show prominent ions owing to loss of sulphur. Another feature of (IV), of little importance in the phosphoramidothioates so far dis-

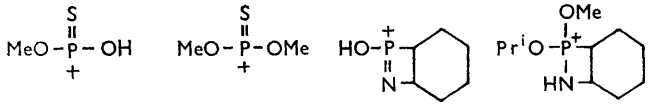
[9] M. Baldwin, A. Kirkien-Konasiewicz, A. G. Loudon, A. Maccoll, and B. Saville in 'Some Newer Physical Methods in Structural Chemistry,' ed. R. Bonnett and J. G. Davies, United Trade Press, London, 1967, p. 22.

cussed, is molecular ion rearrangement to the *S*-*p*-nitrophenylphosphoramidate ion radical *h*. Analogous isomerizations of phosphorothioates have been observed both thermally[10] and mass spectrometrically.[8] P–S cleavage in the rearranged molecular ion gives *i* with approximately half the intensity of the ion *f* which results from P–O cleavage in the 'normal' molecular ion. 'Metastable' ions show that the ion *m/e* 200 is formed by the sequence M $\xrightarrow{*}$ SH $\xrightarrow{*}$ C_4H_7NO as well as by the process M — C_4H_8NO $\xrightarrow{*}$ S which is in agreement with a structure for the M — SH ion of type *d*.



SCHEME 2

In the spectrum of (V) (Table 2) the effect of replacing a methoxyl group of (I) by a hydroxyl is seen. Loss of SH· still gives one of the most abundant ions in the spectrum. The label of the dideuterio-derivative (in which the acidic hydrogens on oxygen and nitrogen were both exchanged for deuterium) is almost completely retained in the M — SH ion, proving that the thiol tautomer is not the species undergoing loss of SH· and that the process is almost certainly analogous to that occurring in (I). Other fragmentations from the molecular ion also correspond with those in (I) except that the P–N fission goes very largely with charge retention by the nitrogen-containing fragment, indicating that ion *j* is much less stable than ion *a*. The relative instability of the HO–$\overset{+}{P}$= system may also account for the fact that loss of methanol from the M — SH ion is insignificant. The arguments already advanced suggest *k* or a similar structure for the M — SH — MeOH ion.



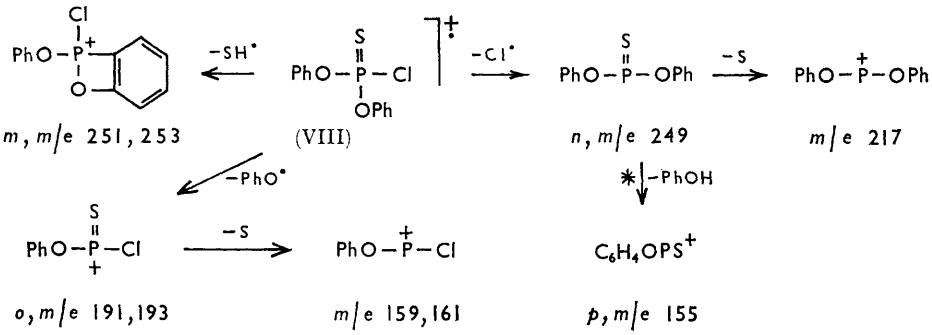
Brief comments on the spectra of the remaining phosphoramidothioates suffice. The isopropyl derivative (VI) loses SH· to give the base peak. Further loss of isopropyl alcohol from this ion is evidenced by a 'metastable' ion and is consistent with the formulation of the M — SH ion as *l*, by analogy with *d* above. Perhaps surprising is the fact that the McLafferty rearrangement leading to loss of propylene from the molecular ion is not observed. This question is taken up subsequently. In the diphenylmorpholino-derivative (VII) the molecular ion rearrangement observed in the arylmorpholino-derivative (IV) is even more pronounced. Abundant ions (Figure 3) arise by P–S cleavage of the isomerized molecular ion with charge retention by either fragment. The abundant ion *m/e* 217 was found, by use of Jennings's metastable defocusing device,[11] to arise from the ion *m/e* 302, *i.e.*, by the process M $\xrightarrow{*}$ SH — C_4H_7NO, confirming that in part at least the hydrogen lost as SH· is derived from the morpholine ring. Other major ions arise by P–O bond cleavage with subsequent phosphinium ion formation by sulphur elision, by P–N bond cleavage, and by hydrogen migration to give the phenol molecular ion or an isomer.

Phosphorochloridothioates.—The molecular ion is the base peak in the spectrum (Figure 4) of diphenyl phosphorochloridothioate (VIII). Loss of SH· from the molecular ion is reminiscent of the phosphoramidothioates although the product ion is much less abundant. An aromatic hydrogen must be lost in this process and structure *m* analogous to *d* in Scheme 1 can be written for the product ion. Also by analogy with amidothioates, P–Cl and P–O fission are expected. These processes give rise to ions *n* and *o*, of similar intensity. Loss of sulphur from *n* and *o* to give bivalent phosphorus ions is observed.

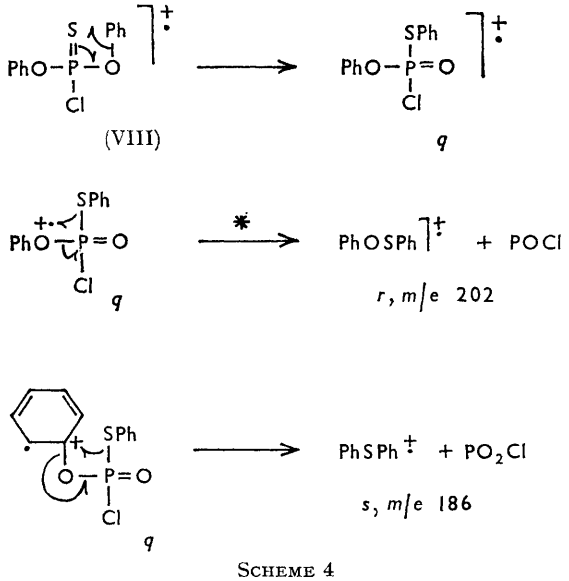
Bond formation between adjacent groups in a phosphonium ion is involved in the loss of phenol from *n* to give *p*. Two further examples of this type of bond formation involve loss of POCl and PO_2Cl from the molecular ion of (VIII). Isomerization of the molecular ion (see above) to *q* apparently precedes the rearrangement which may be written as shown in Scheme 4. The presence of an appropriate 'metastable' ion is indicative

[10] G. Hilgetag and H. Teichmann, *Angew. Chem. Internat. Edn.*, 1965, **4**, 914.
[11] K. R. Jennings, *J. Chem. Phys.*, 1965, **43**, 4176.

of a one-step process from *q*. It should be noted that the mechanisms of formation of *r* and *s* suggested here are merely examples of a general mass-spectrometric rearrangement mechanism [12] involving nucleophilic migration to a positive centre with concomitant elimination of a neutral species. Other examples of this process in the field of phosphorus chemistry include the formation of intense $C_7H_7R^+$ ions from benzylphosphonates [6] and an intense ion corresponding to $PhOPh^{+\cdot}$ in the spectrum of triphenyl phosphite.[4] Yet another ion which must involve rearrangement and which is common to the spectra of triphenyl phosphite and (VIII) is the phenol molecular ion (or an isomer). Further evidence for the molecular ion rearrangement process in (VIII) is the presence of an intense PhS^+ ion.



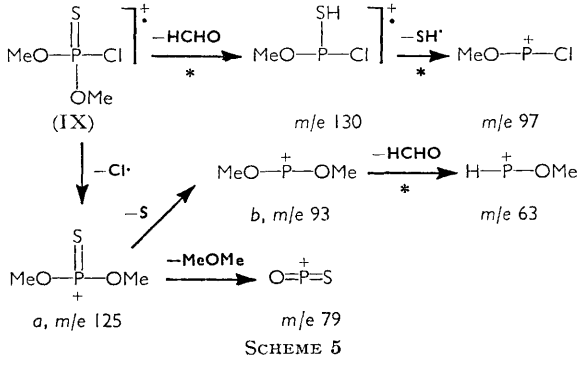
SCHEME 3



SCHEME 4

In view of the fact that (VIII) and (VII) differ only in that the chloro-group of the former is replaced by a morpholino-group it must be asked why rearrangements such as those leading to $PhSPh^{+\cdot}$ were not observed in the spectrum of (VII). Two reasons may contribute to this result; first rearrangement apparently occur best when small stable species are ejected and, secondly, sufficient low-energy paths of normal fragmentation are open to the morpholinothioate to preclude bond forming processes. The latter statement is not true of the chloridate where normal fragment ions are very much less intense, perhaps in part because the P–Cl bond is stronger than the P–N bond.

The spectrum of dimethyl phosphorochloridothioate (IX) is much simpler than that of the diphenyl analogue and because of the absence of aromatic groups it contains fewer rearrangement ions.[13] Loss of SH· from the molecular ion was not expected on the basis of foregoing arguments and indeed it was not observed. The compound shows as its main fragmentation process the sequence $M \xrightarrow{*} M - HCHO \xrightarrow{*} M - HCHO - SH$, which was not observed in the corresponding amidothioates (I) and (II). Molecular ion rearrangement to the *S*-alkylphosphate was insignificant, and this was also the cae in the dimethyl phosphoramidothiates. The bond-formation reaction $M - Cl \longrightarrow M - Cl$–MeOMe as well as the other fragmentations of *a* indicated, were also observed in the amidothioate (II).



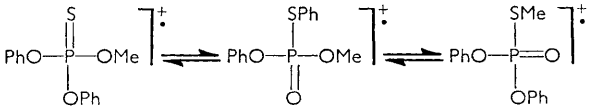
SCHEME 5

Phosphorothioates.—Although Spiteller and his coworkers have discussed the spectra of several phosphorothioates,[8] it was decided to examine the diaryl phosphorothioates (X) and (XI) (Figure 5 and Table 2) because of the extensive bond formation reactions involving phenyl rings observed in the corresponding

[12] R. G. Cooks, J. Ronayne, and D. H. Williams, *J. Chem. Soc.* (*C*), 1967, 2601.

[13] For the general observation that aryl compounds have a greater tendency to undergo skeletal rearrangement processes than have alkyl, see P. Brown and C. Djerassi, *Angew. Chem. Internat. Edn.*, 1967, **6**, 477.

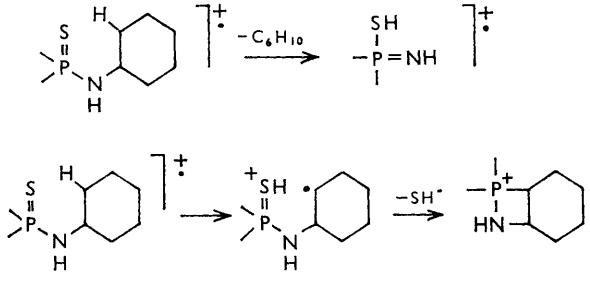
phosphorochloridate (VIII). The P=S ⟶ P=O isomerization previously observed [8] in this class of compound was confirmed and spectra run at low temperature (*ca.* 60°) support the view that this is a mass spectrometric and not a thermal rearrangement. Both aryl and alkyl migration to sulphur can occur as evidenced by the presence of PhS^+, MeS^+, M — PhS, and M — MeS ions. However, aryl migration results in far more intense ions, as was also observed in the phosphoramidothioates and phosphorochloridothioates. A sample of (XIII), the expected product of methyl migration to sulphur in (X), was available and its mass spectrum (Table 2) showed many ions in common with (X). The PhS^+ and M — PhS ions were, however, considerably less intense and the M — CH_3 ion considerably more intense than in (X), indicating that equilibration of the various isomeric molecular ions before fragmentation is incomplete.



(X) (XIII)

Bond formation between substituents in a phosphonium ion is implicated in the formation of abundant phenol molecular ions, or their isomers, in the spectra of both (X) and (XI). The thiophenol molecular ion is also present in the spectrum of (XI) suggesting molecular ion isomerization and hydrogen abstraction from the ethyl group. Ions corresponding to $PhSPh^{+\cdot}$ and $C_7H_7^+$, observed in the spectrum of (X), are presumably generated by the type of mechanism already suggested in Scheme 4. The occurrence of $PhSMe^{+\cdot}$ rather than $PhSPh^{+\cdot}$ in (XIII) further serves to distinguish it from (X) although analogous rearrangements give rise to both ions.

Loss of methoxyl occurred to a very small extent only from (X) and comparison of this spectrum with those of (VIII) and (VII) suggests that the P–OMe bond is



considerably more stable than the P–Cl or P–N bonds. Loss of SH· from the molecular ions of (X) and (XI) was virtually absent. Compound (XI) did however show a McLafferty rearrangement in which hydrogen migration to sulphur (or to oxygen in the rearranged form of the molecular ion) is accompanied by elision of ethylene. The loss of SH· and the McLafferty rearrangement are seen to be competitive processes in this case and in those of the primary amino-derivatives (I), (III), (V), (VI), and (XII), and may be mechanistically similar. If so, the fact that almost exclusive elimination of SH· occurs in the cyclohexylamino-derivatives suggests steric or other impediments to the complete McLafferty rearrangement. The ease with which McLafferty rearrangements normally take place serves only to emphasize how favoured is the loss of SH·. This is seen particularly clearly in the isopropyl derivative (VI) where in spite of the fact that hydrogens on both the propyl and the cyclohexyl ring should be capable at taking part in McLafferty rearrangements, the M — SH process is dominant.

The spectrum of compound (XII), which contains chloro-, methoxyl, and cyclohexylamino-substituents on the basic P=S unit was of considerable interest in indicating the relative ease of fission of the various phosphorus–heteroatom bonds. Loss of MeO· was not observed, while loss of Cl· gave rise to a peak of 3% relative abundance and loss of the cyclohexylamino-radical to a peak of 17% abundance. The most striking feature of the spectrum of (XII) is the fact that the M — SH ion carries 47% of the total ion current ($\sum_{40}$), while no other ion has relative abundance of more than 12%. It seems that the electronegative substituents play some part in promoting loss of SH·.

EXPERIMENTAL

Mass spectra were determined at 70 ev on an AEI MS9 instrument with source temperature either 60° or *ca.* 200°. Samples were introduced by the direct insertion technique. Introduction through the heated inlet system caused only minor changes in spectra and this method was used for high-resolution measurements which were made relative to heptacosafluorotributylamine at resolution 10,000 (10% valley definition).

The purity of all compounds was established by n.m.r. and elemental analysis. Compounds (I),[14] (III),[15] (IV),[15] (V),[14] (VIII),[16] (IX),[17] (X),[18] (XI),[18] (XII),[19] and (XIII) [20] were prepared by reported procedures.

Dimethyl Phosphoropiperidinothioate (II).—This was prepared by the same method [14] as (I), from (IX) (16 g.) and piperidine (20 g.), and was obtained by fractional distillation as a clear *liquid*, b.p. 80°/0·3 mm. (Found: C, 40·1; H, 7·7; N, 6·4. $C_7H_{16}NO_2PS$ requires C, 40·2; H, 7·7; N, 6·7%).

Methyl Isopropyl N-Cyclohexylphosphoramidothioate (VI).—To a mixture of isopropyl alcohol (3 ml.) and 0·5N-sodium hydroxide (2 ml.) was added a solution of (XII) (30 mg.)

[14] N. K. Hamer, *J. Chem. Soc.*, 1965, 2731.
[15] A. F. Gerrard and N. K. Hamer, *J. Chem. Soc.* (*B*), 1967, 1122.
[16] J. Lecoq and A. R. Todd, *J. Chem. Soc.*, 1954, 2381.
[17] V. A. Mandelbaum, V. M. Lomakina, and N. N. Melinka, *Doklady Akad. Nauk S.S.S.R.*, 1954, **96**, 1173.
[18] Belg. Pat. 659,073; *Chem. Abs.*, 1963, **63**, 17,772.
[19] A. F. Gerrard and N. K. Hamer, *J. Chem. Soc.* (*B*), 1968, 539.
[20] G. Hilgetag, G. Lehmann, A. Martini, G. Schramm, and H. Teichmann, *J. prakt. Chem.*, 1959, **8**, 207.

FIGURE 1—5. The mass spectra of compounds (I), (IV), (VII), (VIII), and (X)

FIGURE 1

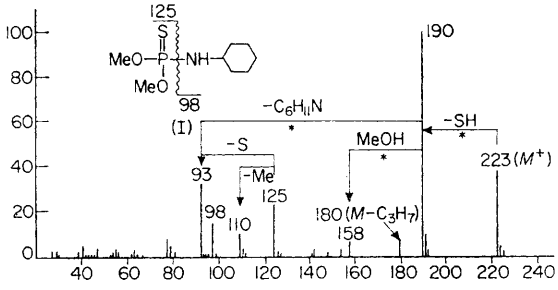


FIGURE 2

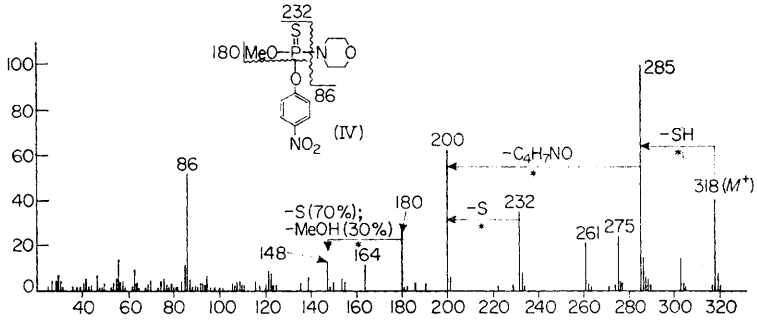


FIGURE 3

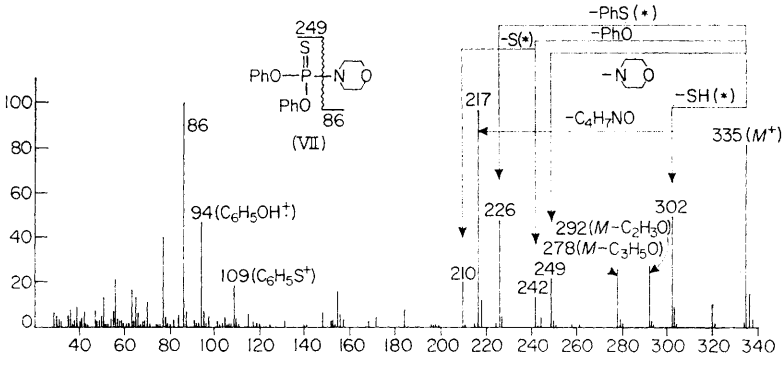


FIGURE 4

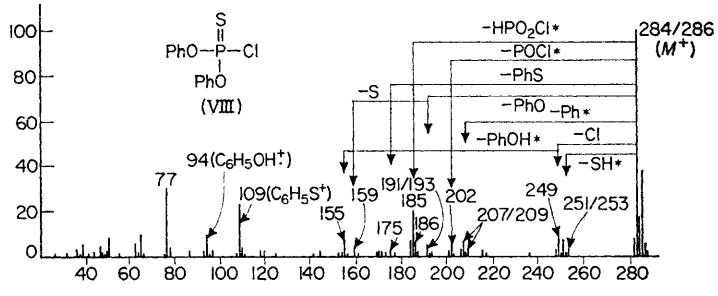
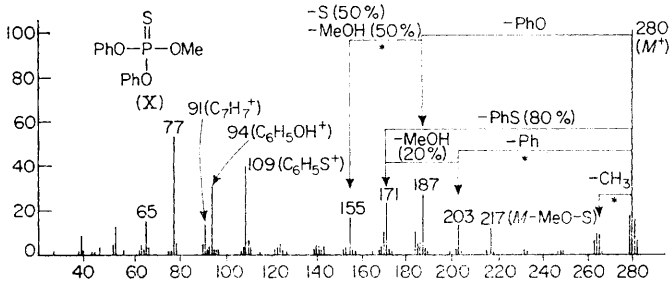


FIGURE 5



in dimethoxyethane (1 ml.). Addition of water precipitated the ester as *needles* (8 mg.), m.p. 69—71° (Found: C, 48·1; H, 8·4. $C_{10}H_{22}NO_2PS$ requires C, 47·8; H, 8·8%).

Diphenyl Phosphoromorpholidothioate (VII).—Morpholine (2·0 g.) was added to a solution of (VIII) (2·5 g.) in chloroform (25 ml.). The solution was maintained at room temperature for 1 hr., water was added, and the chloroform solution removed, washed with dil. HCl, and dried ($MgSO_4$). Evaporation of the solvent left the product which was recrystallized from methanol to give *needles* (0·8 g.), m.p. 97—98° (Found: C, 57·4; H, 5·1. $C_{16}H_{18}NO_3PS$ requires C, 57·3; H, 5·4%). Deuteriated compounds were prepared by direct exchange with D_2O in the source except the trideuterio-derivative of (I; $R^1 = CD_3O$) which was prepared by the normal method [20] in [$^2H_4$]methanol–water.

We thank Dr. D. H. Williams for discussion and the S.R.C. for a maintenance award (to A. F. G.).

[8/165 *Received, February 5th,* 1968]