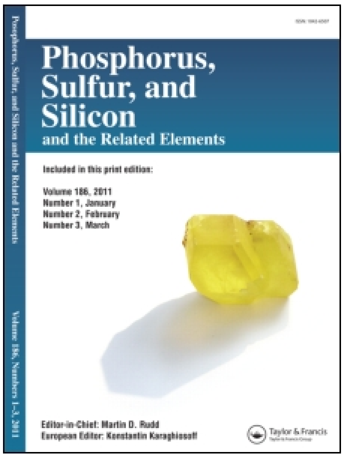

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STUDIES OF PHOSPHORUS COMPOUNDS2.[1] THE MASS SPECTRA OF SOME (TRIPHENYLPHOSPHORANYLIDENE)-SULFAMOYL DERIVATIVES

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STUDIES OF PHOSPHORUS COMPOUNDS 2.[1] THE MASS SPECTRA OF SOME (TRIPHENYLPHOSPHORANYLIDENE)-SULFAMOYL DERIVATIVES

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The mass spectra of chloro-, azido-, amino- and 2-thiophenesulfonylimino(triphenyl)phophoranes are reported. The interpretation of the spectra was based on mechanistic analogy (supported in some cases by metastable peaks) and low energy spectra. Most of the sulfonylimino(triphenyl)phosphorane derivatives do not show their parent peaks.

Published mass spectra of organophosphorus compounds[2–6] appear not to include the (trisubstituted phosphoranylidene)sulfamoyl derivatives. In the course of some studies of the chemistry of such compounds, it was found necessary to have a knowledge of their fragmentation pattern upon electron impact.

Compounds **Ia–Id** were selected as examples of (triphenylphosphoranylidene)-sulfamoyl derivatives and their mass spectra recorded.

$$\underset{\textbf{I}}{Ph_3P{=}NSO_2X}$$

$$a, X = Cl;\ b, X = N_3;\ c, X = NH_2;\ d, X = 2\text{-Th}.$$

Data for the relative intensities of the major ion fragments for the four compounds are listed in Table I. The interpretations given below (i.e., the degradation pathways) are based on mechanistic analogy and supported in some cases by metastable peaks and low energy spectra. The mass spectra of compounds **Ia–Ic** do not show their parent peaks. Cleavage of the sulfur-X ($X = Cl, N_3, NH_2$) bond is the first step, as was observed with some aryl- or heteroarylsulfonyl-X derivatives[7,8] to give the m/e 340 ion ($Ph_3P{=}NSO_2^+$) which is the base peak in the three compounds.

This is followed by loss of SO_2 ("metastable") to give a m/e 276 ion (Ph_3PN^+). This is probably followed by migration of aromatic hydrogens to N with cyclisation, in a manner similar to the hydrogen migration and cyclisation of diphenylphosphine oxide or aromatic phosphinic acids,[9] to give ion c (Scheme 1). The ion c then fragments further in two ways: (i) by loss of C_6H_6 to give ion d at m/e 198, followed by loss of C_6H_4 to give an ion at m/e 122. (ii) by loss of $PhNH_2$ to give m/e 183 ion. Unfortunately, this second route is not supported by a metastable peak. A phosphorus atom is then lost from this ion in the usual manner.[3] The ion d (m/e 198) loses PNH directly to give the m/e 152 ion (metastable between 116 and 117 and also a m/e 46 ion attributed to PNH^+). The probable fragmentation pathway of

TABLE I

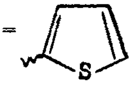
The mass spectra of (triphenylphosphoranylidene)sulfamoyl derivatives at 70 eV

	$Ph_3P{=}NSO_2X$			
m/e[a]	X = Cl	X = N_3	X = NH_2	X = Th
39	6.2	7.7	8.6	59.8
44				41.5
45				29.9
46	1.8	1.7	2.1	
51	11.5	10.1	16.4	26.4
52	3.6	3.2	2.7	
57				15.6
58				22.5
64	*	*	*	13.3
77	15.9	17.6	17.2	56.3
78	84.3	78.3	91.5	8.0
79	9.5	9.8	10.0	
84				31.3
99				11.5
107	3.2	3.9	3.0	16.1
108	4.6	5.4	4.2	23.0
122	20.1	16.5	18.4	37.2
133	10.1	10.0	10.5	
147				11.5
152	3.0	3.7	4.1	12.6
153	3.2	3.9	4.4	
170	3.8	3.9	3.6	
183	15.3	18.6	16.5	49.4
185				11.5
198	9.9	10.4	9.0	21.8
201	8.5	8.0	8.1	23.0
262				48.3
276	17.9	15.2	24.5	29.9
277	3.8	3.3	5.0	
178	5.2	4.8	7.0	
279	2.6	2.3	2.3	
324				27.6
340	100	100	100	10.3
341	24.5	26.9	26.5	
342	6.2	6.3	6.6	
359				100
423				7.6$[M]^{+\cdot}$

[a] Molecular ion is denoted by $[M]^{+\cdot}$

* = trace

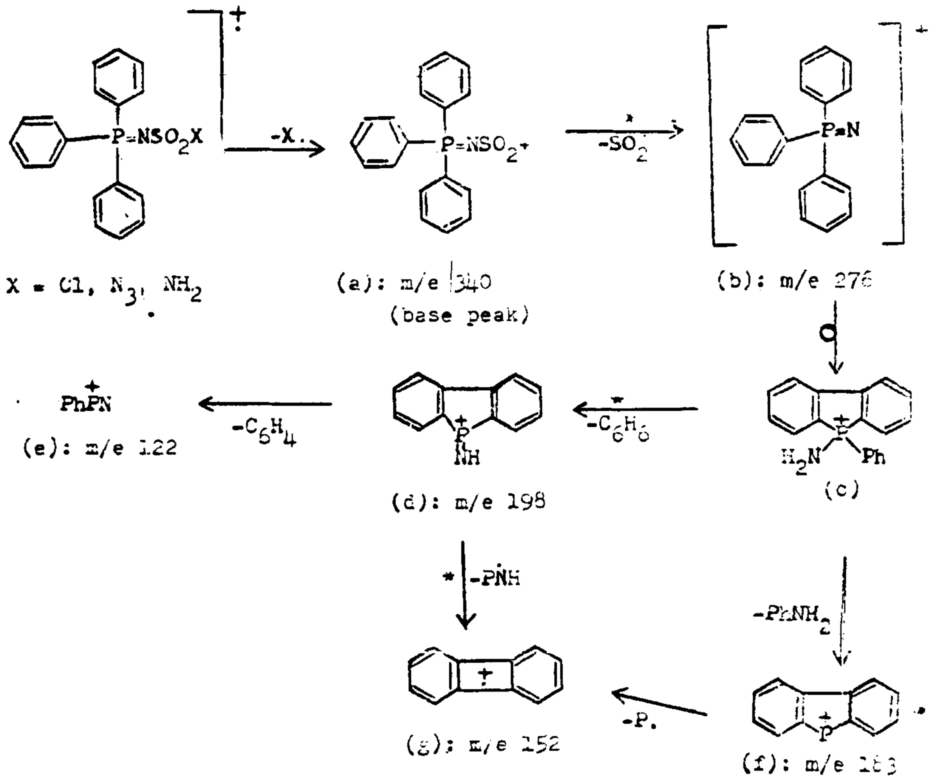
Th =



compounds **Ia–Ic** is shown in Scheme 1, while the low resolution mass spectrum of compound **Ia** is shown in Figure 1.

When the X group of structure **I** is thiophene (i.e., structure **Id**), four fragmentation pathways are observed as shown in Scheme 2:

(a) Cleavage of the sulfur–nitrogen bond giving the m/e 147 (11.5%) and m/e 276 (29.9%) ions, shown in routes (i) and (iii). Route (iii) is supported by a metastable peak lying at m/e 180.



SCHEME 1 Fragmentation route of compounds **Ia–Ic**. * indicates a process accompanied by a metastable peak.

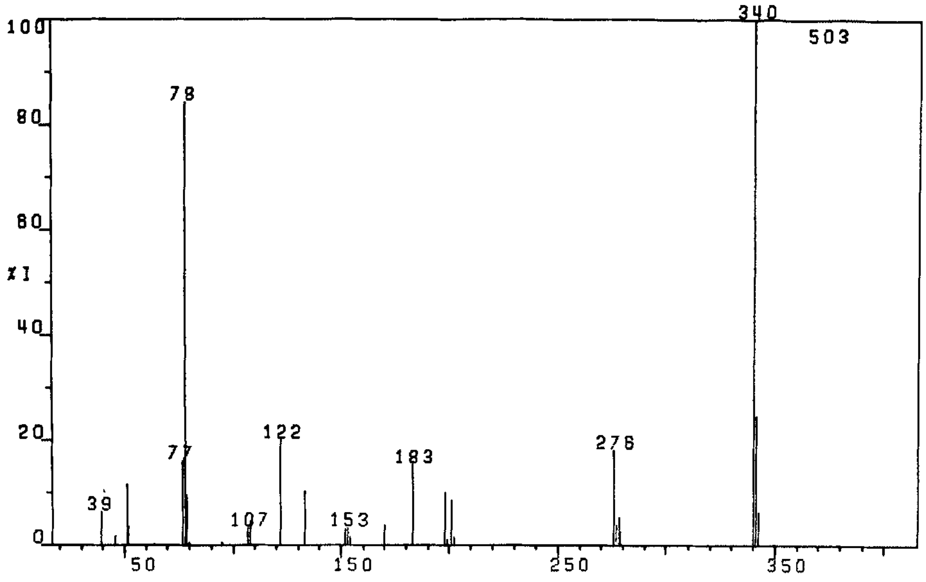
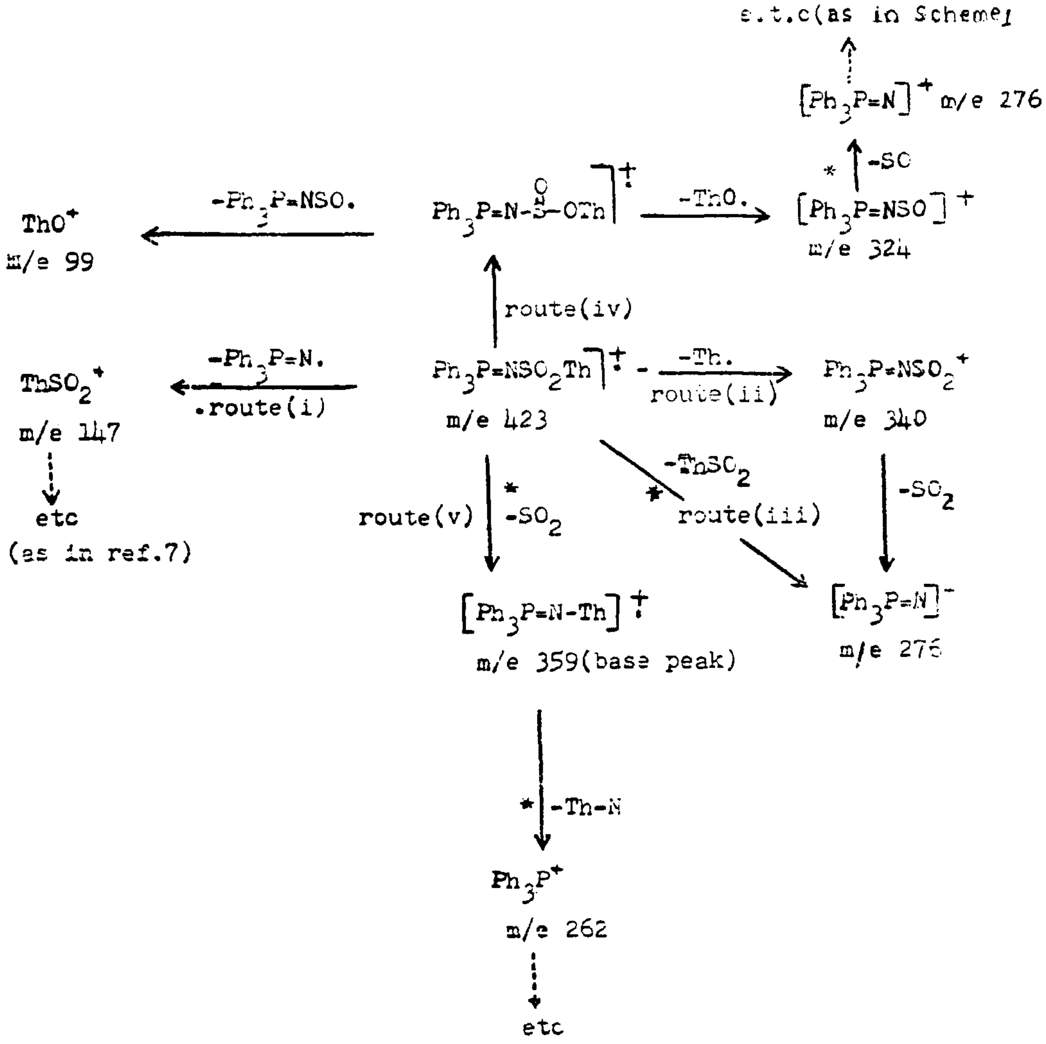


FIGURE 1 Mass spectrum of compound **Ia**.



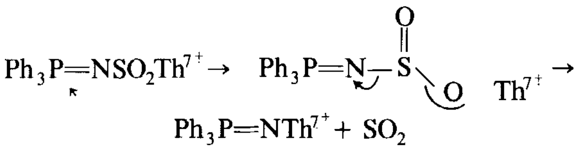
SCHEME 2 Fragmentation routes of triphenyl(2-thiophenesulfonylimino)phosphorane.

(b) Cleavage of the thiophene–sulfur bond (route (ii) giving rise to the m/e 340 ion ($Ph_3P{=}NSO_2^+$, 10.3%). It is worth noting that this ion is the base peak in the other three compounds, **Ia–Ic**.

(c) A thiophene-S → thiophene-O rearrangement (route iv) followed by a sulfur–oxygen cleavage affording the 2-thiophene oxide ion at m/e 99 and an ion at m/e 324, corresponding to $Ph_3P{=}NSO^+$, which then loses SO (metastable peak support) to give the m/e 276 ion $(Ph_3P{=}N)^+$.

This type of thiophene-sulfur → thiophene-oxygen rearrangement has been observed previously[10] during the fragmentation of some 2-thiophenesulfonyl derivatives. Similar rearrangements have also been observed during electron-impact fragmentations of aryl sulfones[11] and α-mesylsulfonyl chlorides.[12]

(d) Direct loss of SO_2 from the molecular ion (route v) affording the m/e 359 ion, $Ph_3P{=}NTh^7$, which is the base peak. That this is a one-step process is supported by a metastable peak lying between m/e 304 and 305. The loss of a molecule of sulfur dioxide from the molecular ions of organosulfonyl compounds is common. For example, this process has been observed during the electron-induced fragmentations of *N*-substituted-*p*-toluenesulfonamides,[13] N-methyl-*N*-phenyl-2-thiophenesulfonamide[7] and some organosulfonyl chlorides.[12] This extrusion of SO_2 may be rationalized as involving the first step of route (iv), i.e. Th-S → Th-O rearrangement, from which the SO_2 may be lost:



$$Ph_3P{=}NSO_2Th^{7+} \rightarrow Ph_3P{=}N{-}\overset{\overset{\displaystyle O}{\|}}{S}{\diagdown}O\ \ Th^{7+} \rightarrow Ph_3P{=}NTh^{7+} + SO_2$$

From the $Ph_3P{=}NTh^+$ ion is then lost ThN, giving the m/e 262 ion, Ph_3P^+, which fragments further in the usual manner.[3]

EXPERIMENTAL SECTION

Compounds **Ia–Id** were prepared as previously described.[10,14] The mass spectra were obtained using an AEl MS12 and Micromass 7070F spectrometers at 70 evs with a source temperature of 200 °C.

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