

Electron Impact Fragmentation of Some Tetramethyl Derivatives of Thiathrene and Phenoxathiin.

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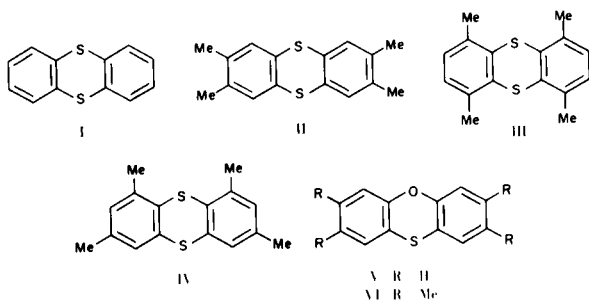
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Received December 10, 1973

Mass spectra of thiathrene and three tetramethylthiathrenes (II), (III) and (IV) are reported and discussed. The principal mode of fragmentation of these compounds consists of the loss of sulphur to give the corresponding dibenzothiophene ion. The general pattern of electrolytic decomposition among the tetramethylthiathrenes is, however, much more complex. The mass spectrum of 2,3,7,8-tetramethylphenoxathiin (VI) is also reported and compared with the spectrum of the corresponding thianthrene derivatives.

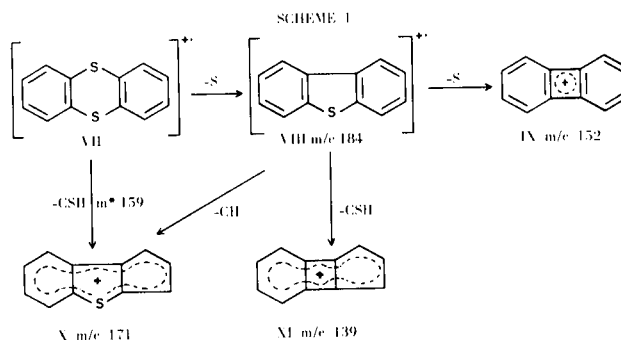
The mass spectrum of thiathrene (I) has been reported in the catalogue compiled by Cornu and Massot (1). But, apart from a study of the sulfone and sulfoxide derivatives by Heiss *et al.* (2), a general study on thiathrene and its derivatives under electron impact has not been reported hitherto.

In the framework of our studies on the *meso*-heterocyclic analogs of 9,10-dihydroanthracene (3), we undertook a comparative investigation of the fragmentation of thiathrene and 2,3,7,8- and 1,4,6,9- and 1,3,7,9-tetramethylthiathrenes under electron impact. We also investigated another analogous compound, *viz.* 2,3,7,8-tetramethylphenoxathiin, in order to make the comparison more comprehensive and complete.



We have reported in a preceding paper (4), the preparation of the isomeric tetramethylthiathrenes *viz.* by the action of sulphur on the three isomeric xylenes in the presence of aluminum chloride. 2,3,7,8-Tetramethylphenoxathiin has been prepared by the action of sulphur on 3,4,3',4'-tetramethyldiphenyl ether in the presence of aluminum chloride, and its structure has been established by examination of its nmr data.

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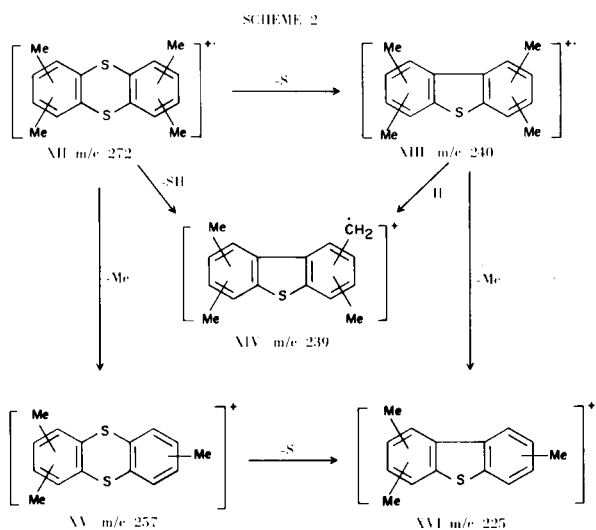
The fragmentation pattern of thiathrene (Figure 1 and Scheme 1) is relatively simple. The molecular ion (which is also the base peak) extrudes sulphur to give the dibenzothiophene ion (VIII), m/e 184, which in turn, loses S and CSH to give the stabilised species IX (m/e 152) and XI (m/e 139). The second mode of fragmentation of the molecular ion leads to the species X (m/e 171) through loss of CSH, as confirmed by the presence of metastable peak at m/e 159, corresponding to the transition $216^+ \rightarrow 171^+$. This ion might equally be formed from VIII through loss of CH.

The relatively important intensity of the peak at m/e 184, may be attributed, in part, to the conformation of the molecule of thiathrene, which is folded about the S-S axis (5). Loss of an atom of sulphur, under electron impact, allows it to pass to the more stable planar form of dibenzothiophene. The same phenomenon occurs in the case of its tetramethyl derivatives.

The mode of fragmentation of the three tetramethylthiathrenes (II, III, and IV), though reasonably identical, are however, endowed with a greater degree of complexity. Effectively, as it is shown in Table I and Scheme 2, the loss of S from the molecular ion takes place to an appreciable extent, but the loss of CS or CSH, on the other hand,

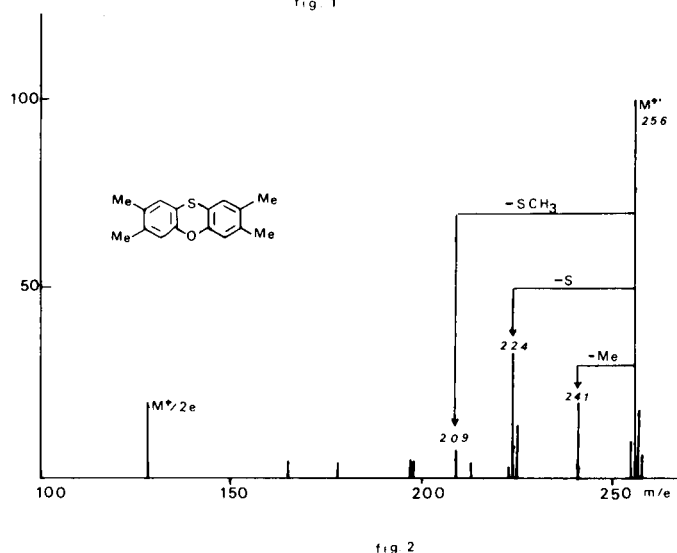
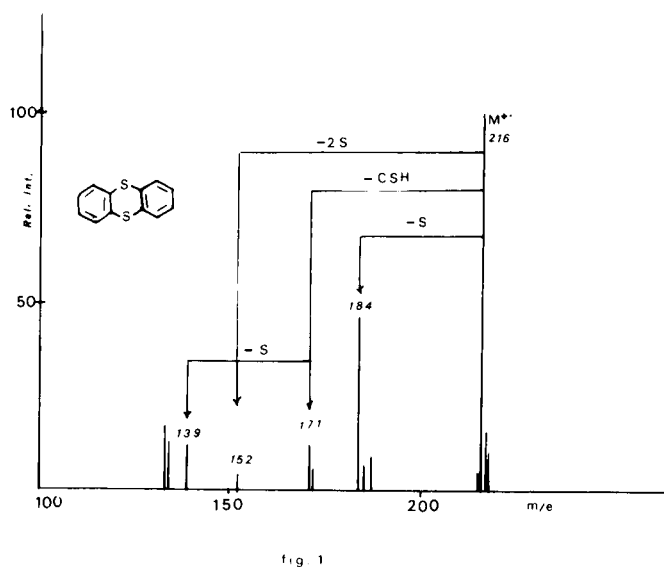
TABLE I
Significant Peaks Observed in Mass Spectra of
Tetramethylthianthrenes

m/e	Relative Abundance (%)			Nature of the ion
	II	III	IV	
274	10	5.9	9.9	$M^+ + 2$
273	20	20	18.5	$M^+ + 1$
272	100	100	100	M^+
271	5	1	3.6	$M^+ - 1$
258	7.3	4.5	4.5	
257	13.6	12.3	9.9	$[M - CH_3]^+$
256	4.2	7.7	6.2	
255	3	5	7.4	
242	4.5	2.4	3.6	$[M - 2 CH_3]^+$
241	7.3	7.3	9.9	
240	22	15	33.6	$[M - S]^+$
239	38	45.5	68	$[M - HS]^+$
238	3	6.3	2	
237		7.7		
225	10	7.3	9.9	$[M - SCH_3]^+$
224	5	10	7.3	
223	6	7.7	7.4	
149	5		9.9	
136	16.4	25	17.3	M^{2+}
112	8.2		8.7	



is practically negligible. The major fragmentation pattern, consists of the loss of sulphur and hydrogen from the molecular ion to give XIV; this may take place in either one or two steps, passing through XIII. Though the latter path might appear most likely, the presence of a metastable peak at m/e 210, corresponding to the transition $M^+ \rightarrow 239^+$, corroborates a single step transition.

Another point of identity in the mode of decomposition of the three compounds consists of the loss of a methyl radical from the molecular ion to give XV, and the fact that the loss of two methyl radicals appears to be as uncertain. Finally, another fragment which evokes interest, is the corresponding to the ion XVI. This might form directly



through out the loss of SCH_3 or passing through the intermediates XII or XV. The absence of metastable peaks renders the choice between the two impossible.

For comparative purposes we have also examined the mode of fragmentation of 2,3,7,8-tetramethylphenoxathiin, where one of the two sulphur atoms of the thianthrene nucleus has been replaced by oxygen. Mass spectroscopic data of phenoxathiin, as reported by Calder *et al.* (6), have revealed the stability of the molecule under electron impact. The principal fragments are formed by the loss of S and CHO and thus through the loss of CO from the molecular ion, which is also the base peak. The mass spectrum of the tetramethyl derivative (Figure 2) equally reveals its stability under electron impact. This is clearly demonstrated by the prominent peak corresponding to the doubly charged molecular ion. Its fragmentation pattern is also quite simple. The only important peaks are at m/e 224 and at m/e 241, resulting from the loss of sulphur and

the methyl radical, respectively, from the molecular ion. The two metastable peaks at m/e 195 and m/e 227 corresponds to the transeions $M^+ \rightarrow 224^+$ and $M^+ \rightarrow 241$, respectively. A third peak at m/e 207 (7.5% of the base peak) probably corresponds to the loss of SCH_3 . On the other hand, contrary to the observation noted in the course of electronolysis of phenoxathiin, there is no loss of either CO or CHO.

It is, therefore, pertinent to conclude that in a general way the presence of methyl substituents on the nucleus of thianthrene of phenoxathiin modifies in an understandable way the mass spectrum of these heterocycles. However, the position of the substituents does not appear to influence the electronolysis of these compounds to any significant extent.

EXPERIMENTAL

The mass spectrometer used was a CH-4 apparatus (70 eV), with direct introduction. The experimental condition used were: for compound I, $t^\circ = 150^\circ$; for compound II, $t^\circ = 180^\circ$; for compound III, $t^\circ = 150^\circ$, for compound IV, $t^\circ = 100^\circ$ and for compound VI, $t^\circ = 172^\circ$.

2,3,7,8-Tetramethylphenoxathiin (VI).

This compound was prepared according to the method of Suter

and Maxwell (7). A mixture of 3,4,3',4'-tetramethyldiphenyl ether (6.8 g.), of sulphur (0.74 g.) and aluminum chloride (1.54 g.) was heated on a water bath. After cooling, the reaction mixture was extracted with ether, the ether fraction was washed with water, dried over sodium sulfate and vacuum evaporated. The residue (5.4 g.) was recrystallized from benzene giving colorless microprisms, m.p. 172° ; nmr (8) $\delta = 6,8$ (4H, singlet, aromatic) and $\delta = 2,18$ (12H, singlet, methyls).

Anal. Calcd. for $C_{16}H_{16}OS$: C, 75.0; H, 6.3. Found: C, 75.1; H, 6.3.

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