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ORGANIC MASS SPECTROMETRY VI. FORMATION OF M-33 ION FROM THIOETHERS UPON ELECTRON IMPACT.

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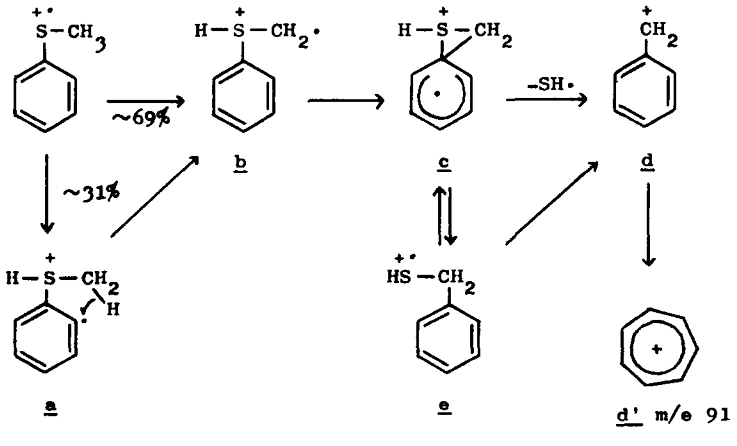
General fragmentation patterns of aliphatic thioethers have been investigated (1), but none of the thioethers have the fragment peak corresponding to M-33 (M-SH). Some of exceptions were recently reported (2). Mercaptans produce M-34 ion (M-SH_2). (3,4).

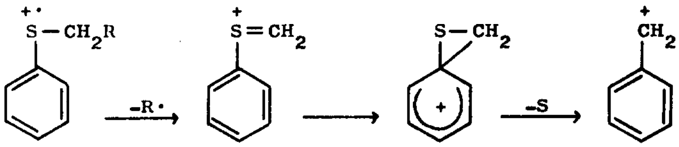
Pyrimidines and thiazolopyrimidines having an alkylthio group, especially methylthio group, on an aromatic carbon atom, however, show a characteristic M-33 peak in their mass spectra. Since the M-33 peak is also observed in the spectra of some of alkyl aryl sulfides (5), the peak may be used for characterization of alkyl aryl sulfides, though some exceptions are known (6). An interesting feature of this fragment is that the fragmentation involves skeletal rearrangement with formation of a new C-C bond (5,7,2).

The spectra of methyl phenyl sulfide and the heteroaromatic alkyl sulfides indicate that the M-33 peak in each case is directly produced (at least in part) from the molecular ion (metastable peak is observed) by expulsion of an SH radical. Mass spectrum of $C_6H_5SCD_3$ (Table 1) shows that, while other prominent peaks are produced by the expected processes (7), the m/e 91 peak (M-33) is shifted to m/e 93 (69%) and m/e 94 (31%), indicating that about 1/3 of hydrogen atom (8) of the SH radical, which is eliminated, comes from one of the hydrogens on the benzene ring. Since the M-CH_3 peak (m/e109) contains no deuterium atom, there is no possibility of exchange of hydrogens between methyl and phenyl groups before fragmentation occur. This result would suggest that the initial process is migration of a hydrogen atom from the methyl or the phenyl group to the sulfur atom (a and b).



If the radical-ion c is an intermediate of the process, benzyl mercaptan should give M-33 peak since c can be produced from benzyl mercaptan radical-ion (e). Indeed, benzyl mercaptan gives intense M-33 peak at m/e 91 (100%) in its mass spectrum. It is therefore suggested that the immediate precursor of the m/e 91 ion from methyl phenyl sulfide would be the ion c or e.

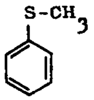
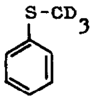
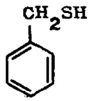
Recently Fisher and Djerassi (7) suggested the following process, but it would not be, if any, a predominant process since methyl phenyl sulfide gives intense m/e 91 ion (d, 26.5%) but weak M-1 ion (f, 8.8%), whereas in the spectrum of ethyl phenyl sulfide M-15 peak (f) is very intense (70%), but m/e 91 peak (d') is quite small (2%).



f g d

It may be concluded that M-33 peak is observed when the formation of a stabilized intermediate similar to c is possible (vinyl methyl sulfide, etc.) (9).

Table 1

m/e			
129		5.4	
128		9.2	
127		100.0	
126	5.3	4.6	2.1
125	9.7	9.2	3.6
124	100.0		36.6
123	8.8		1.2
109	38.9	41.3	
94		9.0	
93		16.8	
91	26.5		100.0
79	5.3	28.4	1.8
78	30.1	2.6	2.1
77	8.0		5.0
69	8.0	11.6	1.5
65	13.3	17.4	12.9
m*	124→91	127→94	124→91
	124→78	127→93	91→65
	109→65	127→79	
		109→65	

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5. J. Ø. Madsen, C. Nolde, S. -O. Lawesson, G. Schroll, J. H. Bowie and D. H. Williams, *Tetrahedron Letters*, **1965**, 4377.
6. Neopentyl phenyl sulfide gives no M-33 peak (7), whereas the peak is observed in the spectra of phenyl mercaptan (10%), benzyl mercaptan (100%), vinyl methyl sulfide (95%) (2), ethynyl methyl sulfide (10%) (2), and some of disulfides (5).
7. M. Fisher and C. Djerassi, *Ber*, **99**, 750 (1966).
8. Deuterium isotope effect is not taken into account.
9. The mass spectra were taken with a HITACHI Mass Spectrometer Model RMU-6D , using an all-glass inlet system. The ionizing potential was kept at 70 e.V. and the ionizing current at 80 μA.