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Mass Spectral Studies of Some Dithioethers and Diamine–Dithioethers

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The mass spectra of bis(phenylthio)methane, 1,2-bis(phenylthio)ethane, 1,3-bis(phenylthio)propane, 1,6-bis(phenylthio)hexane, 1,8-bis(phenylthio)octane, cis-*1,2-bis(phenylthio)ethylene,* o-*phenylenebis(phenylthioether), some methyl-substituted analogues, and some tetradentate diamine–dithioethers are reported. The fragmentation patterns are illustrated and discussed with respect to differences between the ligands and the fragments derived from different ligands. The completely aliphatic ligands exhibit a complex fragmentation of α- and β-cleavages with and without hydrogen atom migration. A number of novel sulphur- and nitrogen-containing heterocycles have been detected.*

Introduction

As part of a study concerned with the effects of altering interdonor linkages in bi- and multidentate ligands upon the spectra and structure of their coordination complexes we have examined the mass spectra of several series of ligands [1–4]. In a previous study the fragmentation patterns of several tetrathioether ligands were discussed [5] and here we report the spectra of structurally similar diamine–dithioether ligands and of a series of dithioethers. In addition to their intrinsic interest the fragmentation of the dithioethers under electron impact have been studied to provide a comparison with the way these ligands fragment in S-dealkylation reactions when coordinated to various metal ions. Thus, the series of dithioethers was chosen to vary interdonor linkages in as systematic way as possible whilst retaining methyl or phenyl terminal groups. The mass spectra of thioethers, R_2S [6, 7], disulphides [8] and a comparison with some dithioethers [9] have been published.

Experimental

The syntheses of the diamine–dithioethers have been previously published [10]. The dithioethers were obtained by literature methods or by routes which will be published elsewhere, and were purified by recrystallisation or fractional distillation as appropriate.

Mass spectra were obtained using an A.E.I. MS902 mass spectrometer at 70 eV linked to a DS30 Data System.

Results and Discussion

Phenyl-substituted Dithioethers

The prominent ions in the fragmentation patterns of bis(phenylthio)methane, (I), 1,2-bis(phenylthio)ethane, (II), 1,3-bis(phenylthio)propane, (III), 1,6-bis(phenylthio)hexane, (IV), 1,8-bis(phenylthio)octane, (V), 1,12-bis(phenylthio)dodecane, (VI), *cis*-1,2-bis(phenylthio)ethylene, (VII), and *o*-phenylenebis(phenylthioether), (VIII), are listed in Table I.

The spectra of both (I) and (II) show moderately intense parent peaks and the base peaks are the products of α-cleavage of the backbone (M-SPh). The fragmentation patterns become more complicated with increasing backbone length. Thus, for (III), (IV) and (V) the intense parent ions undergo α-cleavage with and without hydrogen migration (M-PhS and M-PhSH), and (III) and (IV) also show peaks due to β-cleavage ($M\text{-}PhSCH_2$). Progressive loss of C_2H_4 from the alkane backbones is also indicated for the longer chain ligands. For (III) and (IV) the base peak is the product of β-cleavage, $PhSCH_2^{\bullet}$, but for (V) the observed base peak is composed of both PhSH and C_8H_{14} (Scheme I). The spectrum of (VI) is fairly similar except that the base peak is PhSH. In all these spectra other important peaks observed correspond to $PhSH^+$, PhS^+, $C_7H_7^+$ (probably benzyl, $PhCH_2^+$, rather than tropylium [5]) and CHS^+ (m/e = 45). The long backbones in (IV), (V) and (VI) also produce the expected alkane fragmentations, only the most important of which are shown in Table I. It is interesting that, in marked contrast to Group VB ligands [1–3], these thioethers show no tendency to eliminate the backbone and produce

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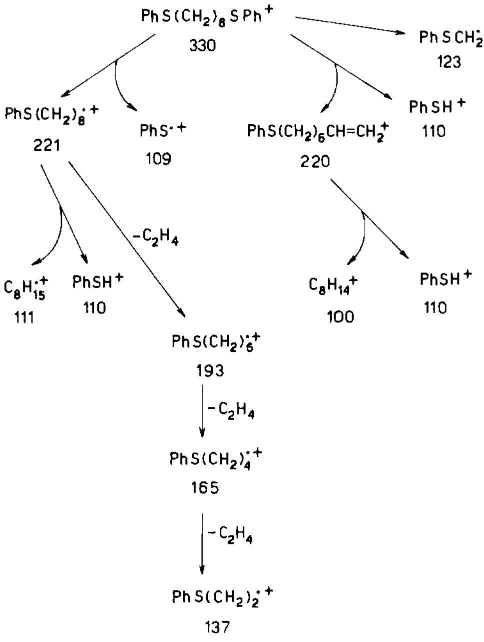
TABLE I.[a] Fragmentation Patterns of Phenyl-Substituted Dithioethers.

m/e	I%	Fragment
$PhSCH_2SPh$, (I)		
233	25.5	$C_{13}H_{12}S_2$
123	100	C_7H_7S
110	12	C_6H_6S
109	13	C_6H_5S
91	4	C_7H_7
77	22	C_6H_5
65	9	C_5H_5
51	14	C_4H_3
45	50	CHS
$PhSCH_2CH_2SPh$, (II)		
246	25	$C_{14}H_{14}S_2$
137	100	C_8H_9S
135	9	C_8H_7S
123	11	C_7H_7S
110	10	C_6H_6S
109	50	C_6H_5S
91	4	C_7H_7
77	9.5	C_6H_5
65	13	C_5H_5
51	8	C_4H_3
45	11	CHS
$PhSCH_2CH_2CH_2SPh$, (III)		
260	91	$C_{15}H_{16}S_2$
183	5	$C_9H_{11}S_2$
151	84.5	$C_9H_{11}S$
150	48	$C_9H_{10}S$
149	34	C_9H_9S
137	16.5	C_8H_9S
135	61	C_8H_7S
123	100	C_7H_7S
110	39	C_6H_6S
109	82	C_6H_5S
105	15	$C_3H_6S_2$
91	26.5	C_7H_7
77	47	C_5H_5
65	42	C_5H_5
51	33.5	C_4H_3
45	98	CHS
$PhS(CH_2)_6SPh$, (IV)		
302	41.5	$C_{18}H_{22}S_2$
193	67.5	$C_{12}H_{17}S$
192	39	$C_{12}H_{16}S$
179	1.2	$C_{11}H_{15}S$
165	0.7	$C_{10}H_{13}S$
151	3.5	$C_9H_{11}S$
137	8	C_8H_9S
136	9	C_8H_8S
135	7	C_8H_7S
123	100	C_7H_7S
110	67.5	C_6H_6S
109	50	C_6H_5S
91	7	C_7H_7
$PhS(CH_2)_6SPh$, (IV) *(cont.)*		
83	38	C_6H_{11}
82	40	C_6H_{10}
77	18.5	C_6H_5
55	71.5	C_4H_7
45	43	CHS
$PhS(CH_2)_8SPh$, (V)		
330	58	$C_{20}H_{26}S_2$
221	21	$C_{14}H_{21}S$
220	9	$C_{14}H_{20}S$
193	0.5	$C_{12}H_{17}S$
165	3.5	$C_{10}H_{13}S$
151	1.5	$C_9H_{11}S$
137	8	C_8H_9S
136	3.5	C_8H_8S
135	6.5	C_8H_7S
123	84	C_7H_7S
111	18.5	C_8H_{15}
110	100	C_6H_6S & C_8H_{10}
109	39.5	C_6H_5S
91	7	C_7H_7
82	12.5	C_6H_9
77	13.5	C_6H_5
55	50	C_4H_7
45	36.5	CHS
$PhS(CH_2)_{12}SPh$, (VI)		
386	8.6	$C_{24}H_{34}S_2$
277	14.5	$C_{18}H_{29}S$
221	0.2	$C_{14}H_{21}S$
193	2	$C_{12}H_{17}S$
179	1	$C_{11}H_{15}S$
169	2	$C_{12}H_{25}$
165	3	$C_{10}H_{13}S$
151	1	$C_9H_{11}S$
137	5.5	C_8H_9S
135	2.5	C_8H_7S
123	62	C_7H_7S
110	100	C_6H_6S
109	18.5	C_6H_5S
97	10.5	C_7H_{13}
91	3	C_7H_7
83	18	C_6H_{11}
77	6	C_6H_5
69	54.5	C_5H_9
55	54	C_4H_7
45	18	CHS
cis-$PhSCH{=}CHSPh$, (VII)		
244	47	$C_{14}H_{12}S_2$
218	15	$C_{12}H_{10}S_2$
166	22	$C_8H_8S_2$
135	44	C_8H_7S
134	30	C_8H_6S

TABLE I. *(Continued)*

m/e	I%	Fragment
cis-$PhSCH{=}CHSPh$, (VII) *(cont.)*		
123	19	C_7H_9S
110	89	C_6H_6S
109	100	C_6H_5S
91	23	C_7H_7
77	27	C_6H_5
65	36	C_5H_5
51	24	C_4H_3
45	28	CHS
o-$C_6H_4(SPh)_2$, (VIII)		
294	100	$C_{18}H_{14}S_2$
260	3	$C_{18}H_{12}S_2$
217	3.5	$C_{12}H_9S_2$
216	6.5	$C_{12}H_8S_2$
185	61	$C_{12}H_9S$
184	98.8	$C_{12}H_8S$
154	2.5	$C_{12}H_{10}$
152	14.5	$C_{12}H_8$
140	5	$C_6H_4S_2$
o-$C_6H_4(SPh)_2$, (VIII) *(cont.)*		
139	11.5	$C_6H_3S_2$
109	5	C_6H_5S
108	7	C_6H_4S
77	8	C_6H_5
65	4.5	C_5H_5
51	8.5	C_4H_3
45	2	CHS
cis-$PhCH_2SCH{=}CHSCH_2Ph$, (IX)		
272	15	$C_{16}H_{16}S_2$
181	1.5	$C_9H_9S_2$
123	1	C_7H_7S
121	1	C_7H_5S
91	100	C_7H_7
77	1.5	C_6H_6
65	13.5	C_5H_5
55	3	C_4H_3
45	5	CHS

[a] Peaks for ^{32}S only are quoted and relative intensities are uncorrected.



Scheme I.

PhSSPh; indeed, except for the parent ions, disulphur fragments are not of any importance.

The dithioether with the vinyl backbone, (VII), shows a base peak of PhS^+ and major peaks corresponding to the parent, PhSSPh, $PhSCH{=}CH_2$,

TABLE II. Fragmentation Patterns of Methyl-substituted Dithioethers.

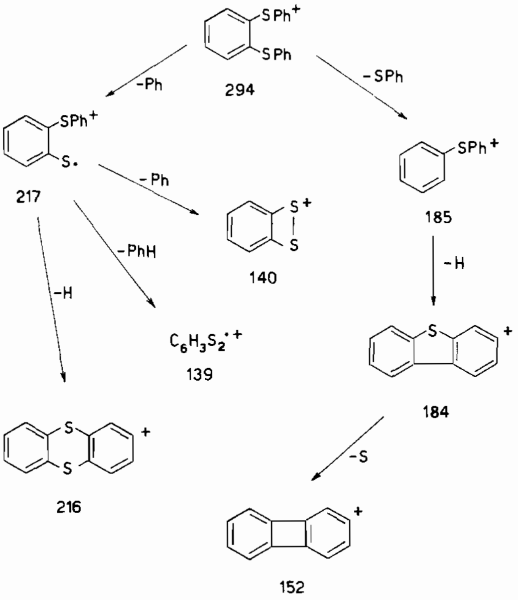
m/e	I%	Fragment
MeSCH$_2$SMe, (X)		
108	58.5	$C_3H_8S_2$
93	2	$C_2H_5S_2$
61	100	C_2H_5S
48	13.5	CH_4S
47	9.5	CH_3S
46	4	CH_2S
45	–	CHS
MeSCH$_2$CH$_2$SMe, (XI)		
122	75	$C_4H_{10}S_2$
120	11	$C_4H_8S_2$
107	1	$C_3H_7S_2$
92	3	$C_2H_4S_2$
75	43	C_3H_7S
74	21.5	C_3H_6S
61	100	C_2H_5S
59	14.5	C_2H_3S
48	6	CH_4S
47	23	CH_3S
46	18.5	CH_2S
45	23	CHS
MeSCH$_2$CH$_2$CH$_2$SMe, (XII)		
136	100	$C_5H_{12}S_2$
121	81.5	$C_9H_4S_2$
106	4.5	$C_3H_6S_2$
89	4.5	C_4H_9S
88	34	C_4H_8S
75	19	C_3H_7S
73	88	C_3H_5S
61	65	C_2H_5S
47	21	CH_3S
46	13	CH_2S
45	22.5	CHS
cis-MeSCH=CHSMe, (XIII)		
120	100	$C_4H_8S_2$
105	49	$C_3H_5S_2$
103	6.5	$C_3H_3S_2$
90	5	$C_2H_2S_2$
89	5	C_2HS_2
73	7	C_3H_5S
72	10	C_3H_4S
71	10	C_3H_3S
61	99.9	C_2H_5S
59	19.5	C_2H_3S
58	30.5	C_2H_2S
57	14	C_2HS
48	12.5	CH_4S
47	26	CH_3S
46	18.5	CH_2S
45	71.5	CHS
o-C$_6$H$_4$(SMe)$_2$, (XIV)		
170	61	$C_8H_{10}S_2$
168	4	$C_8H_8S_2$
o-C$_6$H$_4$(SMe)$_2$, (XIV) *(cont.)*		
155	26	$C_7H_7S_2$
154	100	$C_7H_6S_2$
153	14	$C_7H_5S_2$
140	27	$C_6H_4S_2$
124	46	C_7H_8S
123	8	C_7H_7S
122	8	C_7H_6S
121	16	C_7H_5S
110	6	C_6H_6S
109	40	C_6H_5S
108	16.5	C_6H_4S
91	95	C_7H_7
78	33	C_6H_6
77	45	C_6H_5
65	35	C_5H_5
45	98	CHS
o-C$_6$H$_4$(NH$_2$)(SMe), (XV)		
139	100	C_7H_9SN
138	9	C_7H_8SN
136	7	C_7H_6SN
125	18	C_6H_7SN
124	99.8	C_6H_6SN
109	6.5	C_6H_5S
108	10	C_6H_4S
97	28	C_5H_5S
96	11	C_5H_4S
93	25	C_6H_7N
92	9	C_6H_6N
91	14	C_7H_7
80	78	C_5H_6N
77	13.5	C_6H_5
o-H$_2$NC$_6$H$_4$SCH$_2$CH$_2$SC$_6$H$_4$NH$_2$-*o*, (XVI)		
276	19	$C_{14}H_{16}S_2N_2$
152	15	$C_8H_{10}SN$
151	23.5	C_8H_9SN
138	1.5	C_7H_8SN
136	6	C_7H_6SN
125	15.5	C_6H_7SN
124	100	C_6H_6SN
97	5	C_5H_5S
96	2	C_5H_4S
93	3	C_6H_7N
92	2	C_6H_6N
91	2.5	C_7H_7
80	24	C_5H_6N
o-H$_2$NC$_6$H$_4$SCH=CHSC$_6$H$_4$NH$_2$-*o*, (XVII)		
274	12	$C_{14}H_{14}S_2N_2$
150	31.5	C_8H_8SN
149	100	C_8H_7SN

TABLE II. *(Continued)*

m/e	I%	Fragment	m/e	I%	Fragment
o-H$_2$NC$_6$H$_4$SCH=CHSC$_6$H$_4$NH$_2$-*o*, (XVII) *(cont.)*					
136	24.5	C_7H_6SN	97	6	C_5H_5S
125	15.3	C_6H_7SN	93	5	C_6H_7N
124	13	C_6H_6SN	91	3.5	C_7H_7
117	19.5	C_8H_7N	80	21	C_5H_6N

PhSC≡CH – totally different behaviour from that of the dimethylene analogue. The replacement of phenyl by benzyl, (IX), produces a very simple fragmentation pattern dominated by the ion of m/e = 91, $PhCH_2^{\cdot+}$, weak peaks due to the parent, C_5H_5 and CHS, but no other peaks of any importance.

The completely aryl-substituted, *o*-$C_6H_4(SPh)_2$, (VIII), exhibits a simple fragmentation pattern (Scheme II), which shows some resemblance to that [1] of the corresponding diphosphine, *o*-$C_6H_4(PPh_2)_2$, especially in forming heterocyclic species such as $C_{12}H_8S$ and $C_{12}H_8S_2$.



Scheme II.

Methyl-substituted Dithioethers

The principle ions in the mass spectra of bis(methylthio)methane,* (X), 1,2-bis(methylthio)ethane, (XI), 1,3-bis(methylthio)propane, (XII), *cis*-1,2-bis(methylthio)ethylene, (XIII), and *o*-phenylenebis(methylthioether), (XIV), are shown in Table II.

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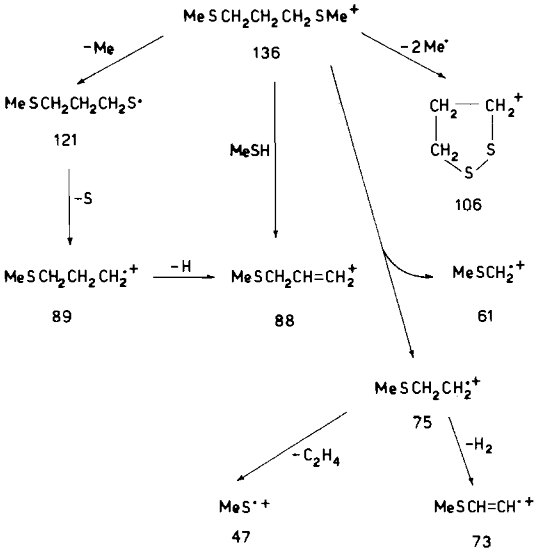
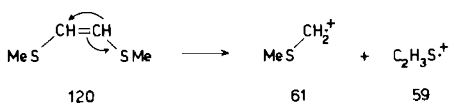
*Ligands (X), (XI), (XII) can also be named 2,4-dithiapentane, 2,5-dithiahexane and 2,6-dithiaheptane, respectively.

The fragmentation modes of the methyl-substituted ligands are more complex than their phenyl analogues, but do show the predominant route to be *via* α- and β-cleavage at the sulphur. For (X) and (XI) the base peak is m/e = 61 ($C_2H_5S^+$), whilst for (XII) the base peak is the parent ion. The main fragmentation routes of XII are shown in Scheme III.

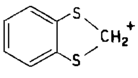


Scheme III.

The fragmentation of the vinylic dithioether, (XIII), is complicated. The parent ion is once again the base peak, with m/e = 61 ($C_2H_5S^+$) of almost the same intensity (I = 99.9%); in this case this ion must be produced by a rearrangement



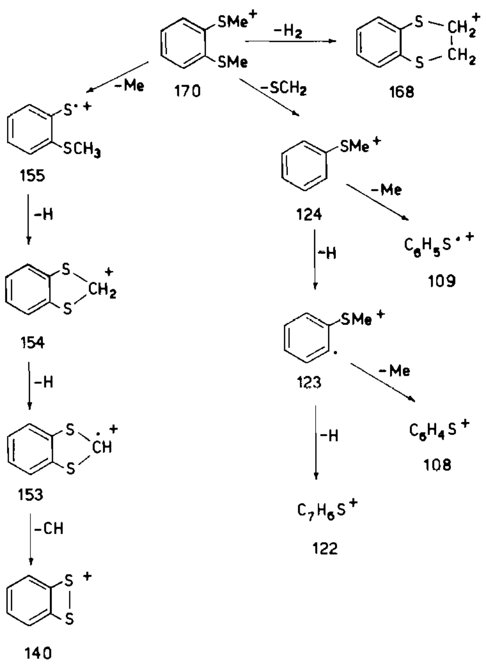
The fragmentation of o-$C_6H_4(SMe)_2$, (XIV), Scheme IV, is similar to that of the tetrathioether, o-$MeSC_6H_4SCH_2CH_2SC_6H_4SMe$-$o$, the base peak being the cyclic ion (XVIII). The importance of ions of m/e = 91 ($C_7H_7^+$) and 45 (CHS^+) should be noted.



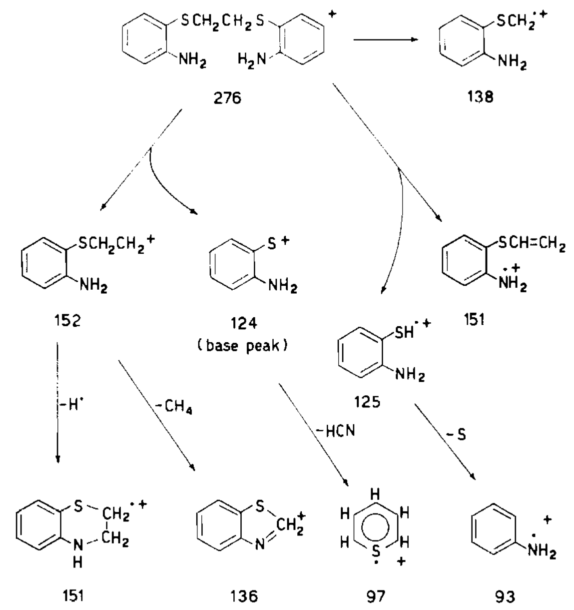
(XVIII)

Sulphur-Nitrogen Ligands

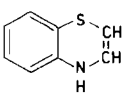
o-Methylthioaniline, (XV), and the diamine–dithioethers (XVI) and (XVII) exhibit interesting fragmentation patterns. All exhibit parent ions and this is also the base peak for (XV) the α-cleavage of the S-alkyl linkage followed by the formation of various S,N species, probably cyclic ions, is the main fragmentation route, Scheme V. The fragmentation of (XVII) is similar, the base peak is m/e = 149, (XIX), and a strong ion at m/e = 117 is probably (XX), which do not occur in (XVI) or (XVII).



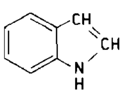
Scheme IV.



Scheme V.



(XIX)



(XX)

For (XV) the main route is *via* m/e = 124, *o*-C_6H_4-$(NH_2)S^+$, and m/e = 124, *o*-$C_6H_4(NH_2)SH$, which lose HCN and S, respectively, to give m/e = 97 and 93. The ion m/e = 80, C_5H_6N, is prominent in all three spectra.

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