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MASS SPECTRA OF SOME DITHIOCARBOXYLIC ACID ESTERS

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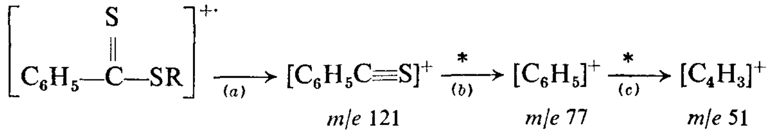
Abstract—The mass spectra of a variety of aliphatic esters of aromatic dithiocarboxylic acids are reported; their breakdown patterns are compared with those of the corresponding oxygen esters, O-alkyl thioesters and S-alkyl thioesters. Small quantities of O-alkyl thioesters present in alkyl dithioesters can be detected by the appearance of the peak $[ArC{\equiv}O]^+$.

ALTHOUGH the mass spectra of oxygen alkyl esters (R—CO—OR′),[1] S-alkyl thioesters (R—CO—SR′)[2,3] and O-alkyl thioesters (R—CS—OR′)[3,4,5] have been discussed, no information has been published on the fragmentation behaviour of dithioesters (R—CS—SR′) on electron-impact. Since a variety of new dithioesters have been prepared in this laboratory,[6] mass spectral studies of this group of compounds were carried out to determine their similarities with oxygen esters and thioesters.

The mass spectra of several dithioesters are presented in Table 1 and Fig. 1 shows the spectrum of propyl 2-furancarbodithioate. To facilitate comparisons with the data on thioesters reported by previous authors,[3] the molecular ion peaks in the spectra are normalized to 100%. Except for some isotope peaks, peaks of less than 3% relative intensity are not shown unless they have special significance.

Alkyl dithiobenzoates

In every case, the base peak is the $[C_6H_5C{\equiv}S]^+$ ion at *m/e* 121. The molecular peak is substantially more prominent than in the corresponding oxygen esters and S-alkyl thioesters. Other significant peaks are those of $[C_6H_5]^+$ and $[C_4H_3]^+$ ions at *m/e* 77 and 51 respectively. Thus, the most important successive fragmentations for alkyl dithiobenzoates are (a), (b) and (c), which are similar to those reported for alkyl benzoates,[7] O-alkyl thiobenzoates and S-alkyl thiobenzoates:[3]



$$\left[C_6H_5-\overset{\overset{\displaystyle S}{\|}}{C}-SR\right]^{+\cdot} \xrightarrow[(a)]{} \underset{m/e\ 121}{[C_6H_5C{\equiv}S]^+} \xrightarrow[(b)]{*} \underset{m/e\ 77}{[C_6H_5]^+} \xrightarrow[(c)]{*} \underset{m/e\ 51}{[C_4H_3]^+}$$

$R = C_2H_5$, n-C_3H_7, n-C_4H_9.

Ring substitution by methoxyl or nitro group or chlorine atom in the *para*- or *meta*-position does not alter the importance of fragmentations (a) to (c).

Interestingly, however, the metastable peak corresponding to the fragmentation (a) is not observed. This is in sharp contrast to the results from S-alkyl thiobenzoates but in agreement with those from O-alkyl thiobenzoates.[3] A likely route to the base peak is via the ionized dithiobenzoic acid $[ArCSSH]^{+\cdot}$, which can be formed by the McLafferty rearrangement of the molecular ion, followed by the elimination of a sulphydryl radical.

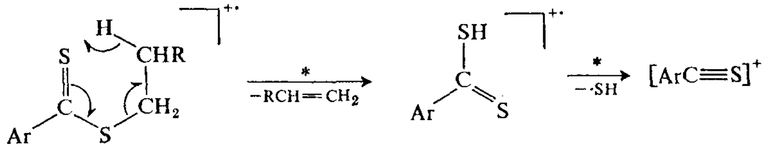


TABLE 1. MASS SPECTRA OF SOME DITHIOESTERS, RC(=S)R′

R = Ph; R′ = Me												
m/e	170	169	168	135	123	122	121	93	78	77	76	69
%	9·1	10	100	1·1	6·8	13	143	6·0	4·3	64	4·2	15
m/e	51	50	45	44								
%	30	7·9	10	7·9								
m^*: 87·2(168 → 121), 49·0(121 → 77), 33·8(77 → 51).												
R = Ph; R′ = Et												
m/e	184	183	182	181	179	178	156	155	154	149	123	122
%	9·4	12	100	3·6	4·2	27	1·6	1·8	18	2·6	12	22
m/e	121	110	89	78	77	76	69	62	61	52	51	50
%	250	6·0	4·0	5·0	48	5·0	7·3	5·0	2·2	1·6	17	5·0
m/e	45	44	39	29	28	27	26					
%	5·2	3·1	4·2	7·6	14	13	6·4					
m^*: 130·3(182 → 154), 122·0(182 → 149), 95·1(154 → 121), 49·0(121 → 77), 33·8(77 → 51).												
R = Ph; R′ = Pr												
m/e	198	197	196	179	178	163	156	155	154	123	122	121
%	9·5	13	100	2·9	17	1·6	7·6	8·8	84	25	41	480
m/e	110	109	94	93	82	78	77	76	75	74	69	66
%	14	5·5	4·0	6·4	3·6	14	136	11	5·0	5·0	20	5·2
m/e	65	63	52	51	50	47	45	44	43	42	41	40
%	4·8	6·4	4·8	52	12	6·4	18	9·5	13	11	30	5·2
m^*: 121·0(196 → 154), 95·1(154 → 121), 49·0(121 → 77).												
R = Ph; R′ = Bu												
m/e	212	211	210	180	179	178	177	156	155	154	123	122
%	10	14	100	13	78	14	8.5	10	15	102	20	35
m/e	121	110	91	90	89	88	78	77	76	75	69	63
%	415	6·5	3·5	13	12	4·6	8·0	68	10	4·0	8·0	5·0
m/e	61	57	56	55	51	50	47	45	44	43	41	39
%	5·0	9·0	43	13	22	7·5	7·5	9·0	4·0	7·5	51	17
m^*: 149·1(210 → 177), 112·9(210 → 154), 95·1(154 → 121), 49·0(121 → 77), 33·8(77 → 51).												
R = 4-ClC$_6$H$_4$; R′ = Et												
m/e	218	217	216	190	189	188	187	183	181	159	158	157
%	42	12	100	16	4·2	39	6·2	3·5	6·5	7·1	14	160
m/e	156	155	151	148	122	121	119	117	113	112	111	108
%	37	423	3·8	4·3	3·8	8·1	15	3·5	21	5·0	65	7·5
m/e	94	93	85	82	75	76	75	74	73	70	69	63
%	10	13	5·0	3·5	5·4	16	54	10	3·8	5·3	34	7·0
m/e	62	61	59	51	50	45	44	39	36			
%	5·4	4·6	5·0	11	19	16	9·6	7·0	4·3			
m^*: 163·6(216 → 188), 155·0(216 → 183), 127·8(188 → 155).												
R = 4-MeOC$_6$H$_4$; R′ = Et												
m/e	214	213	212	186	185	184	179	178	154	153	152	151
%	10	13	100	3·3	3·6	33	2·8	4·7	4·3	15	29	300
m/e	139	121	120	108	107	92	82	77	69	64	63	
%	6·9	19	4·7	22	4·3	6·9	4·9	15	6·9	6·0	6·5	
m^*: 159·6(212 → 184), 151·0(212 → 179), 123·8(184 → 151).												

TABLE 1. (*Continued.*)

R = 3-$NO_2C_6H_4$; R′ = Et

m/e	229	228	227	210	201	200	199	194	171	168	167	166
%	9·7	12	100	4·9	6·2	6·5	65	1·6	5·1	16	27	300
m/e	122	121	120	119	109	108	95	94	93	92	82	77
%	9·5	17	190	15	3·5	18	2·5	19	11	4·2	3·9	9·3
m/e	76	75	74	70	69	63	62	61	59	51	50	45
%	35	14	6·5	8·1	28	8·0	4·2	7·0	4·6	6·8	21	11
m/e	44	39	29	27								
%	4·2	9·8	15	15								

*m**: 174·5(227 → 199), 165·8(227 → 194), 138·5(199 → 166), 86·8(166 → 120).

R = 1-naphthyl; R′ = Et

m/e	234	233	232	231	205	204	203	199	173	172	171	170
%	10	16	100	11	4·9	8·7	48	2·8	14	34	269	10
m/e	166	129	128	127	126	120	101	77	32			
%	9·4	3·6	7·3	63	20	6·7	8·3	15	16			

*m**: 170·6(232 → 199), 177·6(232 → 203), 144·0(203 → 171), 94·3(171 → 127), 46·7(127 → 77).

R = 1-naphthyl; R′ = Pr

m/e	248	247	246	245	232	227	213	206	205	204	203	173
%	10	17	100	7·7	9·1	5·0	1·6	4·9	10	55	52	16
m/e	172	171	170	169	166	158	156	129	128	127	126	122
%	44	340	13	8·7	11	3·6	5·5	4·5	9·3	91	25	3·5
m/e	120	118	115	110	109	108	103	101	94	93	89	
%	8·2	25	5·4	16	9·1	73	25	11	6·4	5·0	15	

*m**: 169·6(246 → 204), 167·5 weak (246 → 203), 144·0 weak (203 → 177), 143·3(204 → 171), 94·3(171 → 127).

R = 1-naphthyl; R′ = Bu

m/e	262	261	260	227	217	206	205	204	203	173	172	171
%	10	19	100	2·6	2·8	6·5	14	77	50	19	49	380
m/e	170	169	158	129	128	127	115	101	77	76	75	74
%	13	7·0	3·6	6·9	11	81	4·3	9·8	17	4·0	6·9	3·5
m/e	69	63	56	55	51	45	41					
%	5·0	4·2	3·0	5·0	5·7	5·7	13					

*m**: 160·1(260 → 204), 143·3(204 → 171), 94·3(171 → 127).

R = 2-furyl; R′ = Me

m/e	160	159	158	113	112	111	83	82	76	71	69	45
%	9·2	8·2	100	7·3	9·8	155	10	5·8	5·2	3·5	4·8	8·4
m/e	44	39										
%	7·7	5·5										

*m**: 78·0(158 → 111), 62·1(111 → 83).

R = 2-furyl; R′ = Et

m/e	174	173	172	146	145	144	139	113	112	111	107	99
%	9·3	9·4	100	3·7	2·9	40	3·0	7·0	10	145	7·6	4·1
m/e	84	83	82	81	76	71	69	55	45	39	38	29
%	3·0	8·1	5·2	2·9	3·8	6·9	4·5	3·9	6·7	28	3·6	3·6

*m**: 120·6(172 → 144), 112·2(172 → 139), 85·6(144 → 111), 62·1(111 → 83).

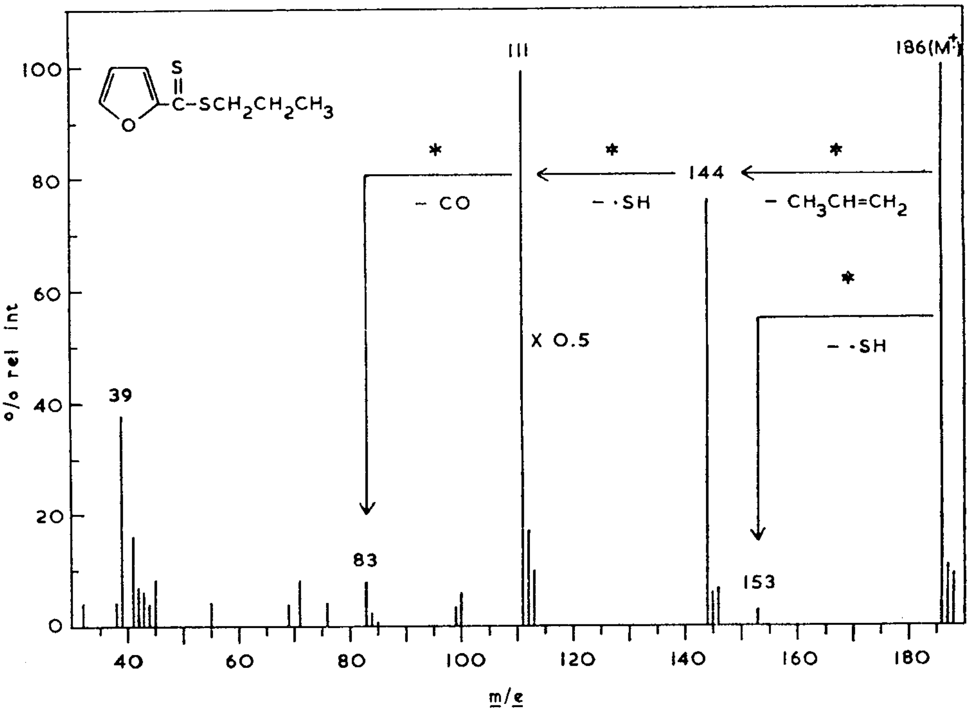


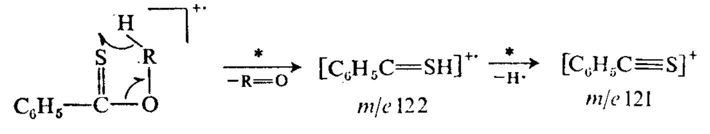
FIG. 1. Mass Spectrum of Propyl 2-Furancarbodithioate.

This is supported by the presence of a significant peak due to $[ArCSSH]^{+\cdot}$ as well as the appropriate metastable peaks.

The $[ArCSSH]^{+\cdot}$ peak arises only in compounds containing β-hydrogens. In the case of $PhC(=S)SCH_3$, where no such hydrogen is available, the metastable peak at *m/e* 87.2 ($121^2/168$) corresponding to fragmentation of molecular ion to base peak is apparent.

It has been reported that, in ethyl and higher alkyl benzoates, cleavage of oxygen-to-alkyl bond is accompanied by the rearrangement of two hydrogen atoms to form $[PhCOOH_2]^+$.[7] In alkyl dithiobenzoates such double hydrogen rearrangement is, however, absent or occurs to a very limited extent only (Table 2).

A novel rearrangement occurring to a significant extent involving the migration of a hydrogen from the alkoxyl group to the thiocarbonyl group has been observed in O-alkyl thiobenzoates:[3]



$$R = -CH_2-,\ -(CH_2)_2-.$$

In alkyl dithiobenzoates, this type of rearrangement is unlikely to occur. No appropriate metastable peaks can be detected; the peak *m/e* 122 can be accounted for as an isotopic peak of *m/e* 121.

TABLE 2. REARRANGEMENT OF ONE AND TWO HYDROGEN ATOMS DURING CLEAVAGE OF O- OR S-TO-ALKYL BOND[a]

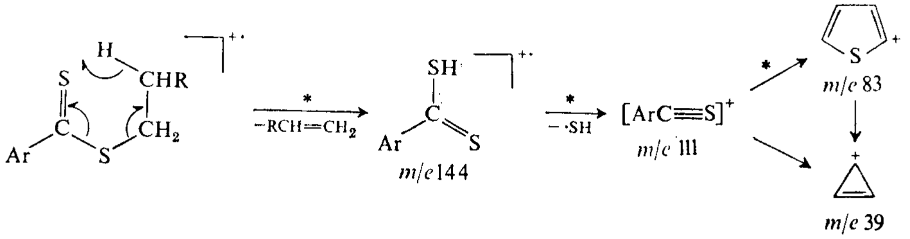
Ions	PhC(=X)XEt		PhC(=X)XBu	
	X = 0	X = S	X = 0	X = S
$[\mathrm{PhCXXH}]^{+\cdot}$	100	18	210	102
$[\mathrm{PhCXXH_2}]^{+}$[b]	35	ca. 0·2	820	ca. 5

[a] Peak heights expressed in per cent of the molecular ion peak.

[b] Corrected for the contribution of $[\mathrm{PhCXXH}]^+$ isotope peaks.

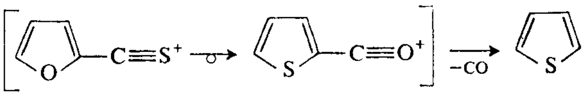
Alkyl 2-furancarbodithioates

The dominant fragmentation of alkyl 2-furancarbodithioates on electron-impact is again the formation of the $[\mathrm{ArC{\equiv}S}]^+$ ion as the base peak. When alkyl is higher than methyl, the route to this ion appears to be the same as for alkyl dithiobenzoates, i.e. via the ionized 2-furancarbodithioic acid, formed by the McLafferty rearrangement. This is evidenced by the appearance of the peak at *m/e* 144 and the appropriate metastable peaks. Other significant peaks are those of cyclopropenyl cation at *m/e* 39 and thienyl cation at *m/e* 83.



Ar = 2-furyl

It seems reasonable to explain the formation of thienyl cation by the following rearrangement:

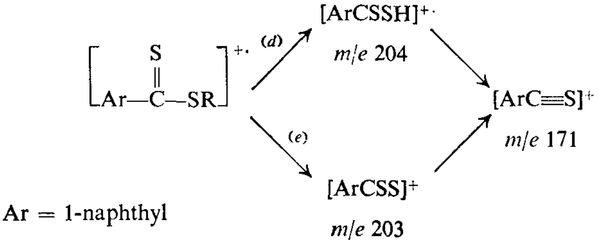


The fact that no furyl cation is observed is probably due to the preferential splitting of CO rather than CS.

As with alkyl dithiobenzoates, the rearrangement ions $[\mathrm{ArCSSH_2}]^+$ and $[\mathrm{ArC{=}SH}]^{+\cdot}$ in alkyl 2-furancarbodithioates are not observed. The above features are illustrated in the spectrum of propyl 2-furancarbodithioate (Fig. 1).

Alkyl 1-dithionaphthoates

The base peak is also the $[\mathrm{ArC{\equiv}S}]^+$ ion at *m/e* 171. While in alkyl (>Me) dithiobenzoates and 2-furancarbodithioates the path to the corresponding base peak is via the $[\mathrm{ArCSSH}]^{+\cdot}$ ion, in alkyl 1-dithionaphthoates an alternative path via the $[\mathrm{ArCSS}]^+$ ion is possible depending on the size of the alkyl moiety.



The relative intensities of the peaks at m/e 203 and 204 in alkyl 1-dithionaphthoates are illustrated in Table 3.

TABLE 3. RELATIVE INTENSITIES OF THE IONS m/e 203 AND 204 IN ALKYL 1-DITHIONAPHTHOATES[a]

m/e	Et	Pr	Bu
203	48	52	50
204[b]	2	48	71

[a] Peak heights expressed in per cent of the molecular ion peak.

[b] Corrected for the contribution of the peak m/e 203.

When R = Et, the low intensity of the [ArCSSH]$^{+\cdot}$ ion peak at m/e 204 together with the metastable peaks at m/e 177.6 ($203^2/232$) and 144.0 ($171^2/203$) suggest the path (e) instead of (d). When R = Pr, both paths (d) and (e) are apparently involved as indicated by the appearance of the metastable peaks at m/e 167·5 ($203^2/246$) and 144·0 ($171^2/203$) as well as 169·2 ($204^2/246$) and 143·3 ($171^2/204$), the latter two metastable peaks being more intense. When R = Bu, only metastable peaks at m/e 160·1 ($204^2/260$) and 143.3 ($171^2/204$) are in evidence, although the [ArCSS]$^+$ ion peak at m/e 203 is apparent.

The peak of [M — HS]$^+$ due to the elimination of a sulphydryl radical from the molecular ion is of low abundance and of comparable significance as in O-alkyl thiobenzoates. Metastable peaks for this reaction can be observed for most of the dithioesters studied.

Determination of Dithioesters

Dithioesters are oxidized slowly to the corresponding O-alkyl thioesters on prolonged storage. Owing to the formation of C=O function, the partially oxidized product will exhibit i.r. absorption at about 1690 cm^{-1} as well as an additional peak in its p.m.r. spectrum about 0·3 ppm upfield to the original —SCH_2— proton signal.[6] In addition to v.p.c., both i.r. and p.m.r. spectroscopy have been shown to be rapid and convenient methods for checking the purity of dithioesters.

It has now been shown that mass spectrometry, used in conjunction with the above methods, can greatly facilitate the determination of dithioesters. In the mass spectrum of the partially oxidized product, a peak corresponding to [ArC≡O]$^+$ will be observed.

The sensitivity of the method is based on the fact that the ratio of base peak to molecular ion peak in S-alkyl thioesters is generally much higher than that in alkyl dithioesters. For example, under normal experimental conditions (70 eV, source inlet temperature at 50 to 100°) the ratios for ethyl dithiobenzoate and S-ethyl thiobenzoate are 2·5 and 8·6 respectively. Furthermore, the peak $[C_6H_5C{\equiv}S]^+$ derived from S-ethyl thiobenzoate is negligible, $[C_6H_5C{\equiv}S]^+/[C_6H_5COSEt]^{+\cdot}$ being 0·04. By comparing the relative intensity of the peaks $[C_6H_5C{\equiv}S]^+$ (*m*/*e* 121) and $[C_6H_5C{\equiv}O]^+$ (*m*/*e* 105) with standards, the presence of S-ethyl thiobenzoate in a sample of ethyl dithiobenzoate containing 0·5% of the former has been successfully detected.

EXPERIMENTAL

Mass spectra were recorded on an AEI MS-12 spectrometer at 70 eV. Source inlet temperatures were varied, according to the sample, between 50 and 100°.

PMR spectra were recorded at ambient temperature for solutions in CCl_4 and integrated with a JEOL JNM-PS-100 (100 MHz) spectrometer with TMS as internal standard.

Dithiocarboxylic acid esters were freshly prepared as described previously.[6] The following two new compounds were obtained similarly:

n-Propyl 1-dithionaphthoate. Orange prisms, m.p. 42 to 44°; p.m.r.: δ7·1 to 8·4 (*m*, 7H, ArH), 3·42 (*t*, J = 7·0 Hz, 2H, SCH_2), 1·83 (sextet, J = 7·0 Hz, CH_2CH_3), 1·08 (*t*, J = 7·0 Hz, 3H, CH_3). (Found: C, 68·1; H, 5·7; S, 25·9. $C_{14}H_{14}S_2$ requires: C, 68·25; H, 5·7; S, 26·0%).

n-Butyl 1-dithionaphthoate. Red oil, b.p. 150°/0·05 mm; p.m.r.: δ7·3 to 8·4 (*m*, 7H, ArH), 3·37 (*t*, J = 7·0 Hz, 2H, SCH_2), *ca.* 1·6 (*m*, 4H, $(CH_2)_2CH_3$), 0·92 (*t*, J = 7·0 Hz, 3H, CH_3). (Found: C, 69·2; H, 6·1; S, 24·5. $C_{15}H_{16}S_2$ requires: C, 69·2; H, 6·2; S, 24·6%).

Methyl dithioesters were prepared as follows:

Methyl 2-furancarbodithioate. Methyl mercaptan was passed into a soln of carboxymethyl 2-furancarbodithioate[8] (10·1 g) in 1 N NaOH (50 ml) under external ice-cooling for about 10 mins; a red oil separated out gradually as the colour of the aq soln was discharged. Work-up by the standard method[6] gave 7·4 g (94%) of methyl 2-furancarbodithioate as a mobile red liquid, b.p. 64°/0·3 mm; p.m.r.: δ7·59 (*m*, 1H, ArH in 3-position), 7·31 (*d*, J = 5 Hz, 1H, ArH in 5-position), 6·47 (*m*, 1H, ArH in 4-position), 2·64 (*s*, 3H, CH_3). (Found: C, 45·7; H, 3·9; S, 40·2. $C_6H_6OS_2$ requires: C, 45·5; H, 3·8; S, 40·5%).

Methyl dithiobenzoate was prepared similarly in 93% yield. The mobile red liquid had b.p. 100°/1 mm (Lit.[9] b.p. 105°/1 mm); p.m.r.: δ8·02 (*m*, 2H, ArH *ortho* to C=S), 7·36 (*m*, 3H, ArH *meta* and *para* to C=S), 2·86 (*s*, 3H, CH_3).

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