# 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  $[ArC=0]^+$ .

ALTHOUGH the mass spectra of oxygen alkyl esters (R-CO-OR'),<sup>1</sup> 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,<sup>6</sup> 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,<sup>3</sup> 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

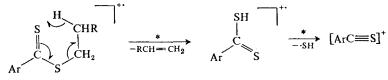
In every case, the base peak is the  $[C_6H_5C\equiv S]^+$  ion at m/e 121. The molecular peak is substantially more prominent than in the corresponding oxygen esters and S-alkyl thioesters. Other significant peaks are those of  $[C_6H_5]^+$  and  $[C_4H_3]^+$  ions at m/e 77 and 51 respectively. Thus,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

$$\begin{bmatrix} S \\ \\ C_6H_5 - C - SR \end{bmatrix}^{+} \xrightarrow{(a)} [C_6H_5C \equiv S]^{+} \xrightarrow{*} [C_6H_5]^{+} \xrightarrow{*} [C_4H_3]^{+} \xrightarrow{m/e \ 51} [C_6H_5]^{+} \xrightarrow{m$$

 $R = C_2 H_5, \, n - C_3 H_7, \, n - C_4 H_9.$ 

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.<sup>3</sup> A likely route to the base peak is via the ionized dithiobenzoic acid [ArCSSH]<sup>+</sup>, which can be formed by the McLafferty rearrangement of the molecular ion, followed by the elimination of a sulphydryl radical.



R = Ph;												
	$\mathbf{R'} = \mathbf{Me}$	:										
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								
	(168 → 12	1), 49.0(1	$21 \rightarrow 77$	), 33·8(	$77 \rightarrow 5$	1).						
R = Ph;	$\mathbf{R'} = \mathbf{Et}$											
m/e	184	183	182	181	179	178	156	155	154	149	123	12
%	9·4	105	102	3.6	4·2	27	1.6	1.8	134	2.6	125	2
m[e	121	110	89	78	77	76	69	62	61	52	51	5
%	250	6.0	4·0	5.0	48	5.0	7.3	5.0	2.2	1.6	17	5.
m/e	45	44	39	29	28	27	26			10	- /	5
%	5.2	3.1	4.2	7.6	14	13	6.4					
	3(182 → 1						), 49·0(	(121 →	77), 33	8.8(77 -	<b>→</b> 51).	
R = Ph;	$\mathbf{R'} = \mathbf{Pr}$											
m/e	198	197	196	179	178	163	156	155	154	123	122	121
<i>mie</i> %	198 9·5	137	190	2.9	178	1.6	7·6	8.8	84	25	41	480
∕∘ m e	110	109	94	93	82	78	77	76	75	74	69	
%	.14	5.5	4.0	6·4	3.6	14	136	11	5.0	5·0	20	5.3
m/e	65	63	52	51	50	47	45	44	43	42	41	4
%	4.8	6.4	4.8	52	12	6.4	18	9·5	13	11	30	5.
	D(196 → 1									~-		• •
<i>n</i> <sup>*</sup> . 1210	$J(190 \rightarrow 1)$	54), 95 1	$(134 \rightarrow 1)$	21), 49	0(121 -							
R = Ph;	$\mathbf{R'} = \mathbf{Bu}$											
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
					12	4.6	8.0	68	10	4.0	8.0	5·(
%	415	6.5	3.5	13			00		••			
m/e			3∙5 56	13 55	51	50	47	45	44	43	41	39
	415	6.5						45 9·0				
m e %	415 61	6·5 57 9·0	56 43	55 13	51 22	50 7·5	47 7•5	9.0	44 4·0	43 7·5	41 51	39 17
m/e % n*: 149·1	415 61 5∙0	6·5 57 9·0 77), 112·9	56 43	55 13	51 22	50 7·5	47 7•5	9.0	44 4·0	43 7·5	41 51	
m/e % n*: 149·1	$415$ $61$ $5.0$ $1(210 \rightarrow 1)$	6·5 57 9·0 77), 112·9	$56 \\ 43 \\ \Theta(210 \rightarrow$	55 13	51 22	50 7·5	47 7•5	9.0	44 4·0	43 7·5	41 51	17
$m/e$ % $m^*: 149.1$ $\overline{R} = 4-Clooperators m/e$	$415$ $61$ $5.0$ $1(210 \rightarrow 1)$ $C_{6}H_{4}; R'$ $218$	6.5 57 9.0 77), 112.9 = Et	56 43	55 13 154), 95	51 22 5·1(154	$50 \\ 7.5 \\ \rightarrow 121$	47 7·5 ), 49·0(	9·0 121 →	44 4·0 77), 33	43 7·5 9·8(77 -	41 51 → 51).	17
$m/e$ % $m^*: 149.1$ $R = 4-Cl($	$415$ $61$ $5.0$ $1(210 \rightarrow 1)$ $C_6H_4; R'$	$6.5 \\ 57 \\ 9.0 \\ 77), 112.9 \\ = Et \\ 217$	$56$ $43$ $9(210 \rightarrow 216$	55 13 154), 95 	51 22 5·1(154 189	$50 \\ 7.5 \\ \rightarrow 121$ $188$	47 7·5 ), 49·0( 187	9.0 121 → 183	44 4·0 77), 33 181	43 7·5 ··8(77 - 159	41 51 → 51).	17 157 160
m/e % $m^*: 149.1$ R = 4-Clo $m/e%m/e$	$415 \\ 61 \\ 5 \cdot 0 \\ 1(210 \rightarrow 1') \\ \hline C_6H_4; R' \\ 218 \\ 42$	6.5  57  9.0  77), 112.9  = Et  217  12	$56$ $43$ $9(210 \rightarrow 216$ $100$	55 13 154), 95 190 16	51 22 5·1(154 189 4·2	$50 \\ 7.5 \\ \rightarrow 121$ $188 \\ 39$	47 7·5 ), 49·0( 187 6·2	$9.0$ $121 \rightarrow$ $183$ $3.5$	44 4·0 77), 33 181 6·5	43 7·5 1·8(77 - 159 7·1	41 51 → 51). 158 14	17 157 160 108
m/e % $m^*: 149.1$ R = 4-Clo $m/e%$	$415 \\ 61 \\ 5 \cdot 0 \\ 1(210 \rightarrow 1') \\ \hline C_6 H_4; R' \\ 218 \\ 42 \\ 156 \\ \hline$	6.5  57  9.0  77), 112.9  = Et  217  12  155	$56$ $43$ $9(210 \rightarrow$ $216$ $100$ $151$	55 13 154), 95 190 16 148	51 22 5·1(154 189 4·2 122	$50$ $7 \cdot 5$ $\rightarrow 121$ $188$ $39$ $121$	47 7·5 ), 49·0( 187 6·2 119	$9.0$ $121 \rightarrow$ $183$ $3.5$ $117$	44 4·0 77), 33 181 6·5 113	43 7·5 1·8(77 - 159 7·1 112	41 51 → 51). 158 14 111	17 157 160 108 7.:
m/e % $m^*: 149.1$ R = 4-Clo $m/e%m/e%m/e$	$415 \\ 61 \\ 5 \cdot 0 \\ I(210 \rightarrow 1) \\ \hline C_6 H_4; R' \\ 218 \\ 42 \\ 156 \\ 37 \\ \hline $	6.5  57  9.0  77), 112-9  = Et  217  12  155  423	$56$ $43$ $9(210 \rightarrow$ $216$ $100$ $151$ $3 \cdot 8$	55 13 154), 95 190 16 148 4·3	51 22 5·1(154 189 4·2 122 3·8	$50$ $7 \cdot 5$ $\rightarrow 121$ $188$ $39$ $121$ $8 \cdot 1$	47 7·5 ), 49·0( 187 6·2 119 15	$\begin{array}{c} 9.0\\121 \rightarrow \end{array}$ $\begin{array}{c}183\\3.5\\117\\3.5\end{array}$	44 4-0 77), 33 181 6-5 113 21	43 7·5 1·8(77 - 159 7·1 112 5·0	41 51 → 51). 158 14 111 65	15 15 160 108 7.5
m/e % $m^*: 149.1$ R = 4-Clo $m/e%m/e%$	$415 \\ 61 \\ 5 \cdot 0 \\ I(210 \rightarrow 1') \\ \hline C_6 H_4; R' \\ 218 \\ 42 \\ 156 \\ 37 \\ 94$	6.5  57  9.0  77), 112-9  = Et  217  12  155  423  93	$56 \\ 43 \\ 9(210 \rightarrow 216 \\ 100 \\ 151 \\ 3 \cdot 8 \\ 85 \\ 5 \cdot 0$	55 13 154), 95 190 16 148 4-3 82 3-5	51 22 5·1(154 189 4·2 122 3·8 75	$50 \\ 7.5 \\ \rightarrow 121 \\ 188 \\ 39 \\ 121 \\ 8.1 \\ 76 \\ 76 \\ 8$	47 7·5 ), 49·0( 187 6·2 119 15 75	$\begin{array}{c} 9.0\\121 \rightarrow \\ 183\\3.5\\117\\3.5\\74\end{array}$	44 4·0 77), 33 181 6·5 113 21 73	43 7·5 1·8(77 - 159 7·1 112 5·0 70	$\begin{array}{c} 41 \\ 51 \\ \rightarrow 51). \end{array}$ $\begin{array}{c} 158 \\ 14 \\ 111 \\ 65 \\ 69 \end{array}$	157 160 108 7.5
m/e % $m^*: 149 \cdot 1$ $R = 4 \cdot Clo m/e%m/e%m/e%$	$415 \\ 61 \\ 5 \cdot 0 \\ I(210 \rightarrow 1') \\ \hline C_6 H_4; R' \\ 218 \\ 42 \\ 156 \\ 37 \\ 94 \\ 10 \\ \hline$	6.5  57  9.0  77), 112.9  = Et  217  12  155  423  93  13	$56 \\ 43 \\ 0(210 \rightarrow 216 \\ 100 \\ 151 \\ 3.8 \\ 85 \\ 85 \\ 85 \\ 85 \\ 85 \\ 85 \\ 85 \\ $	55 13 154), 95 190 16 148 4·3 82	51 22 5·1(154 189 4·2 122 3·8 75 5·4	$50 \\ 7.5 \\ \rightarrow 121 \\ 188 \\ 39 \\ 121 \\ 8.1 \\ 76 \\ 16 \\ 16 \\ 16 \\ 10 \\ 10 \\ 10 \\ 10 \\ 1$	47 7.5 0), 49.0( 187 6.2 119 15 75 54	9.0 $121 \rightarrow$ 183 3.5 117 3.5 74 10	44 4·0 77), 33 181 6·5 113 21 73 3·8	43 7·5 1·8(77 - 159 7·1 112 5·0 70	$\begin{array}{c} 41 \\ 51 \\ \rightarrow 51). \end{array}$ $\begin{array}{c} 158 \\ 14 \\ 111 \\ 65 \\ 69 \end{array}$	
m/e % n*: 149·1 = 4-Clo m/e % m/e % m/e % m/e %	$415 \\ 61 \\ 5 \cdot 0 \\ I(210 \rightarrow 1') \\ \hline C_6H_4; \ R' \\ 218 \\ 42 \\ 156 \\ 37 \\ 94 \\ 10 \\ 62 \\ \hline $	6.5  57  9.0  77), 112.9  = Et  217  12  155  423  93  13  61  4.6	$56 \\ 43 \\ 9(210 \rightarrow 216 \\ 100 \\ 151 \\ 3.8 \\ 85 \\ 5.0 \\ 59 \\ 5.0 \\ 100 \\ $	55 13 154), 95 190 16 148 4·3 82 3·5 51 11	51 22 5·1(154 189 4·2 122 3·8 75 5·4 50 19	$50 \\ 7.5 \\ \rightarrow 121$ $188 \\ 39 \\ 121 \\ 8.1 \\ 76 \\ 16 \\ 45 \\ 16$	47 7.5 ), 49.0() 187 6.2 119 15 75 54 44 9.6	9.0 $121 \rightarrow$ 183 3.5 117 3.5 74 10 39	44 4·0 77), 33 181 6·5 113 21 73 3·8 36	43 7·5 1·8(77 - 159 7·1 112 5·0 70	$\begin{array}{c} 41 \\ 51 \\ \rightarrow 51). \end{array}$ $\begin{array}{c} 158 \\ 14 \\ 111 \\ 65 \\ 69 \end{array}$	17 157 160 108 7.5 63
$m/e \\ % \\ m^*: 149.1 \\ R = 4-Clo \\ m/e \\ % \\ m/e \\ % \\ m/e \\ % \\ m/e \\ % \\ m^*: 163.6 \\ R = 4-Me$	415 61 5.0 1(210 → 1' C6H4; R' 218 42 156 37 94 10 62 5.4 5(216 → 1) eOC6H4;	$6.5  57  9.0  77), 112.9  = Et  217  12  155  423  93  13  61  4.6  88), 155.0  \mathbf{R}' = Et$	$56 \\ 43 \\ 9(210 \rightarrow 216 \\ 100 \\ 151 \\ 3.8 \\ 85 \\ 5.0 \\ 59 \\ 5.0 \\ 9(216 \rightarrow 200) \\ $	55 13 154), 95 190 16 148 4-3 82 3-5 51 11 183), 12	51 22 5·1(154 189 4·2 122 3·8 75 5·4 50 19 27·8(18)	50 $7 \cdot 5$ → 121 188 39 121 $8 \cdot 1$ 76 16 45 16 $8 \rightarrow 15$	47 7·5 ), 49·0( 187 6·2 119 15 75 54 44 9·6 5).	9.0 $121 \rightarrow$ 183 3.5 117 3.5 74 10 39 7.0	44 4·0 77), 33 181 6·5 113 21 73 3·8 36 4·3	43 7·5 1·8(77 - 159 7·1 112 5·0 70	41 51 → 51). 158 14 111 65 69 34	157 160 108 7.5 63 7.0
$m/e \\ % \\ m^*: 149 \cdot 1 \\ = 4 - Clo \\ m/e \\ % \\ m/e \\ % \\ m/e \\ % \\ m/e \\ % \\ m^*: 163 \cdot 6 \\ c = 4 - Me \\ m/e \\ m/e \\ \end{cases}$	$415 \\ 61 \\ 5 \cdot 0 \\ 1(210 \rightarrow 1') \\ \hline C_6H_4; R' \\ 218 \\ 42 \\ 156 \\ 37 \\ 94 \\ 10 \\ 62 \\ 5 \cdot 4 \\ 6(216 \rightarrow 1) \\ \hline cOC_6H_4; \\ 214 \\ \hline $	$6.5  57  9.0  77), 112.9  = Et  217  12  155  423  93  13  61  4.6  88), 155.0  \mathbf{R'} = \mathrm{Et} 213$	$56 \\ 43 \\ 9(210 \rightarrow 216 \\ 100 \\ 151 \\ 3 \cdot 8 \\ 85 \\ 5 \cdot 0 \\ 59 \\ 5 \cdot 0 \\ 9(216 \rightarrow 212 \\ 212 \\ 212 \\ 3 \cdot 8 \\ 5 \cdot 0 \\ 5 \cdot $	55 13 154), 95 190 16 148 4·3 82 3·5 51 11 183), 12 186	51 22 5·1(154 189 4·2 122 3·8 75 5·4 50 19 27·8(18) 185	50 $7 \cdot 5$ → 121 188 39 121 $8 \cdot 1$ 76 16 45 16 $8 \rightarrow 15$ 184	47 7·5 ), 49·0( 187 6·2 119 15 75 54 44 9·6 5).	9.0 $121 \rightarrow$ 183 3.5 117 3.5 74 10 39 7.0 178	44 4·0 77), 33 181 6·5 113 21 73 3·8 36 4·3	43 7·5 1·8(77 - 159 7·1 112 5·0 70	$\begin{array}{c} 41 \\ 51 \\ \rightarrow 51). \end{array}$ $\begin{array}{c} 158 \\ 14 \\ 111 \\ 65 \\ 69 \end{array}$	157 160 108 7.5
$m/e \ % \ m^*: 149.1 \ x = 4-Cl(m/e) \ m/e \ % \ m/e \ m/e$	$415 \\ 61 \\ 5 \cdot 0 \\ 1(210 \rightarrow 1') \\ \hline C_6H_4; R' \\ 218 \\ 42 \\ 156 \\ 37 \\ 94 \\ 10 \\ 62 \\ 5 \cdot 4 \\ 6(216 \rightarrow 1) \\ \hline eOC_6H_4; \\ 214 \\ 10 \\ \hline eOC_6H_4; \\$	$6.5  57  9.0  77), 112.9  = Et  217  12  155  423  93  13  61  4.6  88), 155.0  \mathbf{R'} = \mathbf{Et} 2131313$	$56 \\ 43 \\ 9(210 \rightarrow 216 \\ 100 \\ 151 \\ 3.8 \\ 85 \\ 5.0 \\ 59 \\ 5.0 \\ 9(216 \rightarrow 212 \\ 100 \\ 212 \\ 100 \\ 3.8 \\ 5.0 $	55 13 154), 95 190 16 148 4·3 82 3·5 51 11 183), 12 186 3·3	51 22 5·1(154 189 4·2 122 3·8 75 5·4 50 19 27·8(18) 27·8(18) 185 3·6	50 $7 \cdot 5$ → 121 188 39 121 $8 \cdot 1$ 76 16 45 16 $8 \rightarrow 15$	47 7·5 ), 49·0( 187 6·2 119 15 75 54 44 9·6 5).	9.0 $121 \rightarrow$ 183 3.5 117 3.5 74 10 39 7.0	44 4·0 77), 33 181 6·5 113 21 73 3·8 36 4·3	43 7·5 159 7·1 112 5·0 70 5·3	41 51 → 51). 158 14 111 65 69 34	157 160 108 7.5 63 7.0
m/e % $m^*: 149 \cdot 1$ $x = 4 \cdot Clo m/e%m/em/e%m/e%m/e%m/e%m/e%m/e%m/e%m/e%m/e%m/e%m/e%m/e%$	$415 \\ 61 \\ 5 \cdot 0 \\ 1(210 \rightarrow 1') \\ \hline C_6H_4; R' \\ 218 \\ 42 \\ 156 \\ 37 \\ 94 \\ 10 \\ 62 \\ 5 \cdot 4 \\ 6(216 \rightarrow 1) \\ \hline cOC_6H_4; \\ 214 \\ 10 \\ 139 \\ \hline $	$6.5  57  9.0  77), 112.9  = Et  217  12  155  423  93  13  61  4.6  88), 155.0  \mathbf{R'} = \mathbf{Et} 213131213121312131312131314151213141512131415121314151213141512131415141514151617171818181818181818$	$56 \\ 43 \\ 9(210 \rightarrow 216 \\ 100 \\ 151 \\ 3.8 \\ 85 \\ 5.0 \\ 59 \\ 5.0 \\ 9(216 \rightarrow 212 \\ 100 \\ 120 \\ 120 \\ 120 \\ 120 \\ 120 \\ 100 \\ 120 \\ 100 $	55 13 154), 95 190 16 148 4·3 82 3·5 51 11 183), 12 186	51 22 5·1(154 189 4·2 122 3·8 75 5·4 50 19 27·8(18) 27·8(18) 185 3·6 107	50 $7 \cdot 5$ → 121 188 39 121 $8 \cdot 1$ 76 16 45 16 45 16 $8 \rightarrow 15$ 184 33 92	47 7·5 ), 49·0( 187 6·2 119 15 75 54 44 9·6 5). 179 2·8 82	9.0 $121 \rightarrow$ 183 3.5 117 3.5 74 10 39 7.0 178 4.7 77	44 4·0 77), 33 181 6·5 113 21 73 3·8 36 4·3	43 7·5 159 7·1 112 5·0 70 5·3	$ \begin{array}{r} 41 \\ 51 \\ 51 \\ 158 \\ 14 \\ 111 \\ 65 \\ 69 \\ 34 \\ 152 \\ \end{array} $	17 160 108 7.4 62 7.4
$m/e \ % \ m^*: \ 149.1 \ x = 4-Cl(m/e) \ m/e \ % \ x = 4-Me \ m/e \ % \ x = 4-Me \ m/e \ % \ m/e \ % \ x = 4-Me \ m/e \ m/e \ % \ x = 4-Me \ m/e $	$415 \\ 61 \\ 5 \cdot 0 \\ 1(210 \rightarrow 1') \\ \hline C_6H_4; R' \\ 218 \\ 42 \\ 156 \\ 37 \\ 94 \\ 10 \\ 62 \\ 5 \cdot 4 \\ 6(216 \rightarrow 1) \\ \hline eOC_6H_4; \\ 214 \\ 10 \\ \hline eOC_6H_4; \\$	$6.5  57  9.0  77), 112.9  = Et  217  12  155  423  93  13  61  4.6  88), 155.0  \mathbf{R'} = \mathbf{Et} 2131313$	$56 \\ 43 \\ 9(210 \rightarrow 216 \\ 100 \\ 151 \\ 3.8 \\ 85 \\ 5.0 \\ 59 \\ 5.0 \\ 9(216 \rightarrow 212 \\ 100 \\ 212 \\ 100 \\ 3.8 \\ 5.0 $	55 13 154), 95 190 16 148 4·3 82 3·5 51 11 183), 12 186 3·3	51 22 5·1(154 189 4·2 122 3·8 75 5·4 50 19 27·8(18) 27·8(18) 185 3·6	50 $7 \cdot 5$ → 121 188 39 121 $8 \cdot 1$ 76 16 45 16 45 16 $8 \rightarrow 15$ 184 33	47 7·5 ), 49·0( 187 6·2 119 15 75 54 44 9·6 5).	9.0 $121 \rightarrow$ 183 3.5 117 3.5 74 10 39 7.0 178 4.7	44 4·0 77), 33 181 6·5 113 21 73 3·8 36 4·3 154 4·3	43 7·5 159 7·1 112 5·0 70 5·3	$41 \\ 51 \\ 51$ $158 \\ 14 \\ 111 \\ 65 \\ 69 \\ 34$ $152 \\ 29$	15 157 160 108 7.4 63 7.4

Table 1. Mass spectra of some dithioesters, RC(==S)R'

				TABLE	(		.)					
R = 3-NC	D₂C <sub>6</sub> H₄; ∃	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	20	00	12	, 0		00	21	• •
%	4.2	9.8	15	15								
	$7 \rightarrow 1$				38.5(19	$9 \rightarrow 16$	6), 86.8	3(166 -	× 120).			
	1 (1 . 1. D				1-110			4 - 1000 8 1000 104				
	phthyl; R											. – .
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			
n*: 170·€	$5(232 \rightarrow 1)$	99), 177·€	5(232 →	203), 14	44.0(20	$3 \rightarrow 17$	1), 94-3	8(171 -	× 127),	46.7(12	27 → 7 <sup>-</sup>	7).
k == 1-nai	ohthyl; R	$\mathbf{x}' = \mathbf{Pr}$										
m/e	248	247	246	245	232	227	213	206	205	204	203	173
		17	100	243 7.7	232 9·1	5.0	1.6	200 4·9	10	55	52	1/2
%	10					158						122
m e	172	171	170	169	166		156	129	128	127	126	
%	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	
	$\begin{array}{c} 6(246 \rightarrow 2 \\ (171 \rightarrow 12 \\ \hline \end{array})$		5 weak (2	246 → 2	.03), 14	4·0 wea	ak (203	i → 177	7), 143· 	3(204 -	→ 171),	
R = 1-naj	ohthyl; R	$\mathbf{X}' = \mathbf{B}\mathbf{u}$										
-		t′ = Bu 261	260	227	217	206	205	204	203	173	172	171
m/e	262	261				206 6·5	205 14	204 77	203 50	173 19	172 49	
m e %	262 10	261 19	100	2.6	2.8	6.5	14	77	50		49	380
m e % m e	262 10 170	261 19 169	100 158	2·6 129	2·8 128	6·5 127	14 115	77 101	50 77	19 76	49 75	380 74
m e % m e %	262 10 170 13	261 19 169 7·0	100 158 3·6	2·6 129 6·9	2·8 128 11	6·5 127 81	14 115 4·3	77	50	19	49	380 74
m/e % m/e	262 10 170	261 19 169	100 158	2·6 129	2·8 128	6·5 127	14 115	77 101	50 77	19 76	49 75	171 380 74 3·5
m e % m e % m e %	262 10 170 13 69	261 19 169 7·0 63 4·2	100 158 3·6 56 3·0	2.6 129 6.9 55 5.0	2·8 128 11 51 5·7	6·5 127 81 45 5·7	14 115 4·3 41 13	77 101	50 77	19 76	49 75	380 74
m e % m e % m/e % n*: 160·1	262 10 170 13 69 5.0	261 19 169 7·0 63 4·2 04), 143·3	100 158 3·6 56 3·0	2.6 129 6.9 55 5.0	2·8 128 11 51 5·7	6·5 127 81 45 5·7	14 115 4·3 41 13	77 101	50 77	19 76	49 75	380 74
m/e % m/e % m/e % n*: 160·1 R = 2-fur	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5 \cdot 0 \\ (260 \rightarrow 2 \\ yl; R' =$	261 19 169 7.0 63 4.2 04), 143.3 Me	$100$ $158$ $3 \cdot 6$ $56$ $3 \cdot 0$ $3(204 \rightarrow $	2.6 129 6.9 55 5.0 171), 94	2.8 128 11 51 5.7 4.3(171	$\begin{array}{c} 6.5\\ 127\\ 81\\ 45\\ 5.7\\ \rightarrow 127\end{array}$	14 115 4·3 41 13	77 101 9·8	50 77 17	19 76	49 75	380 74 3·5
$m/e$ % $m/e$ % $m/e$ % $n^*: 160.1$ $R = 2-fur$ $m/e$	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5.0 \\ (260 \rightarrow 2 \\ yl; R' = 160$	261 19 169 7.0 63 4.2 04), 143.3 Me	100 158 3·6 56 3·0	2.6 129 6.9 55 5.0	2·8 128 11 51 5·7	6·5 127 81 45 5·7	14 115 4·3 41 13	77 101	50 77	19 76 4·0	49 75 6·9	380 74 3.5
m/e % m/e % m': 160.1 x = 2-fur m/e %	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5 \cdot 0 \\ (260 \rightarrow 2 \\ yl; R' = 160 \\ 9 \cdot 2$	261 19 169 7.0 63 4.2 04), 143.3 Me 159	$100$ $158$ $3 \cdot 6$ $56$ $3 \cdot 0$ $3(204 \rightarrow 158)$	2.6 129 6.9 55 5.0 171), 94 113	2.8 128 11 51 5.7 4.3(171 112	$6.5$ $127$ $81$ $45$ $5.7$ $\rightarrow 127$ $111$	14 115 4·3 41 13 ).	77 101 9·8 82	50 77 17 76	19 76 4·0 71	49 75 6·9	380 74 3.5
m/e $%$ $m/e$ $%$ $m': 160.1$ $R = 2-fur$ $m/e$ $%$ $m/e$	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5.0 \\ (260 \rightarrow 2 \\ yl; R' = 160 \\ 9.2 \\ 44$	$261 \\ 19 \\ 169 \\ 7.0 \\ 63 \\ 4.2 \\ 04), 143.3 \\ \hline Me \\ 159 \\ 8.2 \\ 39 \\ \hline$	$100$ $158$ $3 \cdot 6$ $56$ $3 \cdot 0$ $3(204 \rightarrow 158)$	2.6 129 6.9 55 5.0 171), 94 113	2.8 128 11 51 5.7 4.3(171 112	$6.5$ $127$ $81$ $45$ $5.7$ $\rightarrow 127$ $111$	14 115 4·3 41 13 ).	77 101 9·8 82	50 77 17 76	19 76 4·0 71	49 75 6·9	380 74 3.5
m/e % m/e % m*: 160.1 x = 2-fur m/e % m/e %	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5 \cdot 0 \\ (260 \rightarrow 2 \\ yl; R' = 160 \\ 9 \cdot 2$	$261 \\ 19 \\ 169 \\ 7.0 \\ 63 \\ 4.2 \\ 04), 143.3 \\ Me \\ 159 \\ 8.2 \\ 39 \\ 5.5 \\ $	$   \begin{array}{r}     100 \\     158 \\     3.6 \\     56 \\     3.0 \\     3(204 \rightarrow 158 \\     100 \\   \end{array} $	2.6 129 6.9 55 5.0 171), 94 113 7.3	2.8 128 11 51 5.7 4.3(171 112	$6.5$ $127$ $81$ $45$ $5.7$ $\rightarrow 127$ $111$	14 115 4·3 41 13 ).	77 101 9·8 82	50 77 17 76	19 76 4·0 71	49 75 6·9	380 74
m/e % m/e % $n^*: 160.1$ C = 2-fur m/e % m/e % $n^*: 78.0($	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5.0 \\ (260 \rightarrow 2) \\ \hline yl; R' = 160 \\ 9.2 \\ 44 \\ 7.7 \\ \hline $	$261 \\ 19 \\ 169 \\ 7.0 \\ 63 \\ 4.2 \\ 04), 143.3 \\ Me \\ 159 \\ 8.2 \\ 39 \\ 5.5 \\ 1), 62.1(1)$	$   \begin{array}{r}     100 \\     158 \\     3.6 \\     56 \\     3.0 \\     3(204 \rightarrow 158 \\     100 \\   \end{array} $	2.6 129 6.9 55 5.0 171), 92 113 7.3	2.8 128 11 51 5.7 4.3(171 112	$6.5$ $127$ $81$ $45$ $5.7$ $\rightarrow 127$ $111$	14 115 4·3 41 13 ).	77 101 9·8 82	50 77 17 76	19 76 4·0 71	49 75 6·9	380 74 3.5
m/e n/e m/e n/e $n^*: 160.1$ R = 2-fur m/e n	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5.0 \\ (260 \rightarrow 2) \\ yl; R' = 160 \\ 9.2 \\ 44 \\ 7.7 \\ (158 \rightarrow 11) \\ yl; R' = 100 \\ 1$	261 19 169 7.0 63 4.2 04), 143.3 Me 159 8.2 39 5.5 1), 62.1(1 Et	$100$ $158$ $3 \cdot 6$ $56$ $3 \cdot 0$ $8(204 \rightarrow 158$ $100$ $11 \rightarrow 83$	2.6 129 6.9 55 5.0 171), 94 113 7.3	2.8 128 11 51 5.7 4.3(171 112 9.8	6.5 127 81 45 5.7 $\rightarrow 127$ 111 155	14 115 4·3 41 13 ). 83 10	77 101 9·8 82 5·8	50 77 17 76 5·2	19 76 4·0 71 3·5	49 75 6·9 69 4·8	380 74 3.5 45 8.4
m/e m/e	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5.0 \\ (260 \rightarrow 2) \\ yl; R' = 160 \\ 9.2 \\ 44 \\ 7.7 \\ (158 \rightarrow 11) \\ yl; R' = 174$	261 19 169 7.0 63 4.2 04), 143.3 Me 159 8.2 39 5.5 1), 62.1(1 Et 173	$100$ $158$ $3 \cdot 6$ $56$ $3 \cdot 0$ $8(204 \rightarrow )$ $1158$ $100$ $11 \rightarrow 83$ $172$	2.6 129 6.9 55 5.0 171), 94 113 7.3 ).	2.8 128 11 51 5.7 4.3(171 112 9.8	6.5 127 81 45 5.7 - > 127 111 155 144	14 115 4·3 41 13 ). 83 10	77 101 9·8 82 5·8	50 77 17 76 5·2 112	19 76 4·0 71 3·5	49 75 6·9 69 4·8	380 74 3-5 45 8-4 999
m/e n/e n/e n/e n'*: 160.1 R = 2-fur m/e n''e n'e n'e n''e n'e n'e n'	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5 \cdot 0 \\ (260 \rightarrow 2 \\ yl; R' = 160 \\ 9 \cdot 2 \\ 44 \\ 7 \cdot 7 \\ (158 \rightarrow 111 \\ yl; R' = 174 \\ 9 \cdot 3 \\ 9 \cdot 3$	261 19 169 7.0 63 4.2 04), 143.3 Me 159 8.2 39 5.5 1), 62.1(1 Et 173 9.4	$ \begin{array}{r} 100\\ 158\\ 3.6\\ 56\\ 3.0\\ 8(204 \rightarrow 158\\ 100\\ 11 \rightarrow 83\\ 172\\ 100\\ \end{array} $	2.6 129 6.9 55 5.0 171), 94 113 7.3 ).	2.8 128 11 51 5.7 4.3(171 112 9.8 145 2.9	6.5 127 81 45 5.7 - > 127 111 155 144 46	14 115 4·3 41 13 ). 83 10 139 3·0	77 101 9·8 82 5·8 113 7·0	50 77 17 76 5·2 112 10	19 76 4·0 71 3·5	49 75 6·9 69 4·8	380 74 3.5 45 8.4 999 4.1
m/e m/e	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5 \cdot 0 \\ (260 \rightarrow 2 \\ yl; R' = 160 \\ 9 \cdot 2 \\ 44 \\ 7 \cdot 7 \\ (158 \rightarrow 111 \\ yl; R' = 174 \\ 9 \cdot 3 \\ 84$	261 19 169 7.0 63 4.2 04), 143-3 Me 159 8.2 39 5.5 1), 62.1(1 Et 173 9.4 83	$ \begin{array}{c} 100\\ 158\\ 3.6\\ 56\\ 3.0\\ 8(204 \rightarrow 158\\ 100\\ 11 \rightarrow 83\\ 172\\ 100\\ 82\\ \end{array} $	2.6 129 6.9 55 5.0 171), 94 113 7.3 ). 146 3.7 81	2.8 128 11 51 5.7 4.3(171 112 9.8 145 2.9 76	6.5 127 81 45 5.7 - > 127 111 155 144 46 71	14 115 4·3 41 13 ). 83 10 139 3·0 69	77 101 9·8 82 5·8 113 7·0 55	50 77 17 76 5·2 112 10 45	19 76 4·0 71 3·5 111 145 39	49 75 6·9 69 4·8	380 74 3.5 45 8.4 999 4.1 25
m/e n/e m/e n/e n'*: 160.1 x = 2-fur m/e n'': 78.0( x = 2-fur m/e n'' m/e n''' m/e n''''''''''''''''''''''''''''''''''''	$262 \\ 10 \\ 170 \\ 13 \\ 69 \\ 5 \cdot 0 \\ (260 \rightarrow 2 \\ yl; R' = 160 \\ 9 \cdot 2 \\ 44 \\ 7 \cdot 7 \\ (158 \rightarrow 111 \\ yl; R' = 174 \\ 9 \cdot 3 \\ 9 \cdot 3$	261 19 169 7.0 63 4.2 04), 143.3 Me 159 8.2 39 5.5 1), 62.1(1 Et 173 9.4 83 8.1	$ \begin{array}{c} 100\\ 158\\ 3.6\\ 56\\ 3.0\\ 8(204 \rightarrow 158\\ 100\\ 11 \rightarrow 83\\ 172\\ 100\\ 82\\ 5.2\\ \end{array} $	2.6 129 6.9 55. 5.0 171), 9 <sup>2</sup> 113 7.3 ). 146 3.7 81 2.9	2.8 128 11 51 5.7 4.3(171 112 9.8 145 2.9 76 3.8	6.5 127 81 45 5.7 $\rightarrow 127$ 111 155 144 46 71 6.9	14 115 4·3 41 13 ). 83 10 139 3·0 69 4·5	77 101 9·8 82 5·8 113 7·0 55 3·9	50 77 17 76 5·2 112 10 45 6·7	19 76 4·0 71 3·5	49 75 6·9 69 4·8	380 74 3.5 45 8.4

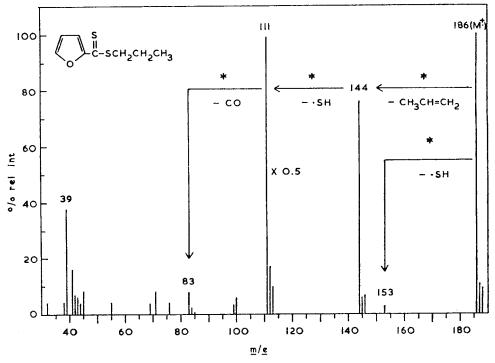


FIG. 1. Mass Spectrum of Propyl 2-Furancarbodithioate.

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

The [ArCSSH]<sup>+</sup> peak arises only in compounds containing  $\beta$ -hydrogens. In the case of PhC(=S)SCH<sub>3</sub>, where no such hydrogen is available, the metastable peak at m/e 87.2 (121<sup>2</sup>/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 oxygento-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:<sup>3</sup>

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.

#### Mass spectra of some dithiocarboxylic acid esters

Ions	PhC(=	=X)XEt	PhC(=X)XBu		
	$\mathbf{X} = 0$	X = S	X = 0	X = S	
[PhCXXH]+·	100	18	210	102	
[PhCXXH <sub>2</sub> ] <sup>+b</sup>	35	ca. 0·2	820	ca. 5	

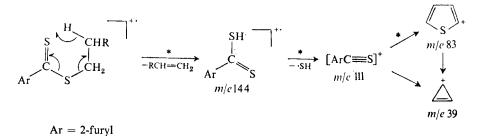
TABLE 2. REARRANGEMENT OF ONE AND TWO HYDROGEN ATOMS DURING CLEAVAGE OF O- OR S-TO-ALKYL BOND<sup>a</sup>

<sup>a</sup> Peak heights expressed in per cent of the molecular ion peak.

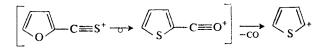
<sup>b</sup> Corrected for the contribution of [PhCXXH]<sup>+</sup> isotope peaks.

# Alkyl 2-furancarbodithioates

The dominant fragmentation of alkyl 2-furancarbodithioates on electron-impact is again the formation of the  $[ArC=S]^+$  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.



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

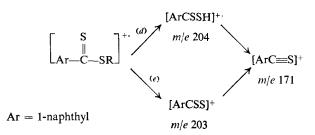


The fact that no furyl cation is observed is probably due to the preferential splitting of CO rather than CS.

As with alkyl dithiobenzoates, the rearrangement ions  $[ArCSSH_2]^+$  and  $[ArC=SH]^+$  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  $[ArC \equiv S]^+$  ion at m/e 171. While in alkyl (>Me) dithiobenzoates and 2-furancarbodithioates the path to the corresponding base peak is via the  $[ArCSSH]^+$  ion, in alkyl 1-dithionaphthoates an alternative path via the  $[ArCSS]^+$  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<sup>a</sup>

m/e	Et	Pr	Bu
203	48	52	50
204 <sup>b</sup>	2	48	71

<sup>a</sup> Peak heights expressed in per cent of the molecular ion peak. <sup>b</sup> Corrected for the contribution of the peak *m/e* 203.

When R = Et, the low intensity of the [ArCSSH]<sup>+,</sup> ion peak at m/e 204 together with the metastable peaks at m/e 177.6 (203<sup>2</sup>/232) and 144.0 (171<sup>2</sup>/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<sup>2</sup>/246) and 144.0 (171<sup>2</sup>/203) as well as 169.2 (204<sup>2</sup>/246) and 143.3 (171<sup>2</sup>/204), the latter two metastable peaks being more intense. When R = Bu, only metastable peaks at m/e 160.1 (204<sup>2</sup>/260) and 143.3 (171<sup>2</sup>/204) are in evidence, although the [ArCSS]<sup>+</sup> 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<sup>-1</sup> as well as an additional peak in its p.m.r. spectrum about 0.3 ppm upfield to the original  $-SCH_2$ - proton signal.<sup>6</sup> 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  $[ArC=0]^+$  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  $[C_6H_5C\Longrightarrow S]^+$  derived from S-ethyl thiobenzoate is negligible,  $[C_6H_5C\Longrightarrow S]^+$  (m/e 121) and  $[C_6H_5C\Longrightarrow O]^+$  (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<sub>4</sub> 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.<sup>6</sup> The following two new compounds were obtained similarly:

*n*-Propyl 1-dithionaphthoate. Orange prisms, m.p. 42 to 44°; p.m.r.:  $\delta$ 7·1 to 8·4 (*m*, 7H, ArH), 3·42 (*t*, J = 7.0 Hz, 2H, SCH<sub>2</sub>), 1·83 (sextet, J = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1·08 (*t*, J = 7.0 Hz, 3H, CH<sub>3</sub>). (Found: C, 68·1; H, 5·7; S, 25·9. C<sub>14</sub>H<sub>14</sub>S<sub>2</sub> requires: C, 68·25; H, 5·7; S, 26·0%).

*n-Butyl* 1-dithionaphthoate. Red oil, b.p.  $150^{\circ}/0.05$  mm; p.m.r.:  $\delta7.3$  to 8.4 (*m*, 7H, ArH), 3.37 (*t*, J = 7.0 Hz, 2H, SCH<sub>2</sub>), *ca*. 1.6 (*m*, 4H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.92 (*t*, J = 7.0 Hz, 3H, CH<sub>3</sub>). (Found: C, 69.2; H, 6.1; S, 24.5. C<sub>15</sub>H<sub>16</sub>S<sub>2</sub> 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<sup>8</sup> (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<sup>6</sup> gave 7·4 g (94%) of methyl 2-furancarbodithioate as a mobile red liquid, b.p. 64°/0·3 mm; p.m.r.:  $\delta 7\cdot59$  (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<sub>3</sub>). (Found: C, 45·7; H, 3·9; S, 40·2. C<sub>6</sub>H<sub>6</sub>OS<sub>2</sub> 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.  $100^{\circ}/1 \text{ mm}$  (Lit.<sup>9</sup> b.p.  $105^{\circ}/1 \text{ mm}$ ); p.m.r.:  $\delta 8.02 (m, 2H, ArH ortho to C=S)$ , 7.36 (m, 3H, ArH meta and para to C=S), 2.86 (s, 3H, CH<sub>3</sub>).

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