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Mass Spectra of 1,3-Dithiaspiranes and 2-Aryl-1,3-dithianes

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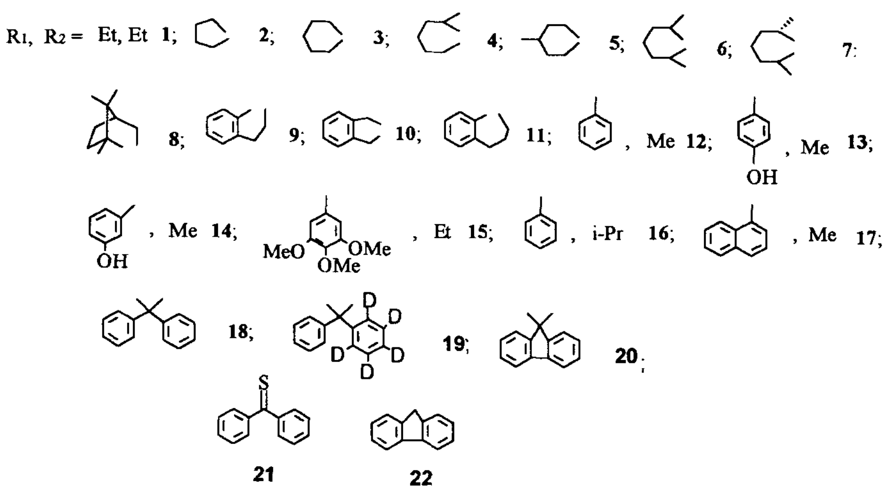
The mass spectra of 20 1,3-dithianes were studied. The fragmentation patterns including the loss of 74 u and 107 u and clearage of the substituent at C-2 depended strongly on the nature of the substituents at that position. 2,2-Diphenyl-1,3-dithiane undergoes an atypical fragmentation in which two hydrogens migrate from the phenyl ring, with the formation of a fluorene skeleton.

INTRODUCTION

Thioketals or thioacetals, resembling their oxygen counterparts, are widely used as intermediates or as protecting groups in organic synthesis.[1] Although the characterization of these derivatives is important during their preparation, only a few reports have appeared.[2] The fragmentations in the mass spectra of ketals and acetals are well known.[3] The presence of two alkoxy groups on the same carbon atom provides a powerful initiating site in electron impact mass spectrometry. The ionization energy and the critical energy for α-cleavage decreased substantially with resonance stabilization of the product ion.[4] Although the sulphur atom is able to stabilize the cation like the oxygen atom, the dissimilar electron density results in an altered degree of overlap between the carbon cation and the electron-donating atom, leading to an altered stability of the resulting ion.

In this work, we examined 18 1,3-dithianes and related compounds to investigate their fragmentation behaviour in the gas phase. The possible structure of the ion of m/z 165 from 2,2-diphenyl-1,3-dithianes was investigated by means of a linked-scan technique.



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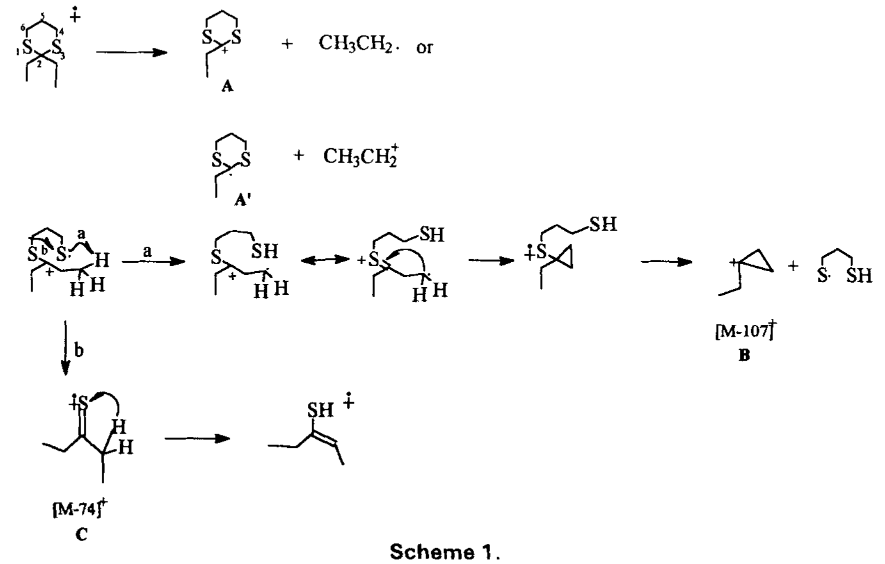


Scheme 1.

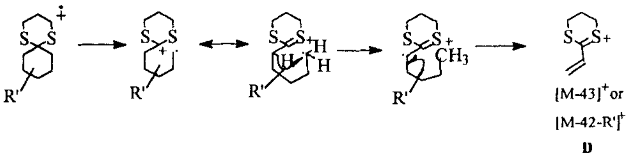
RESULTS AND DISCUSSION

In this series of dithianes, the sulphur atoms contain two unpaired electrons with small ionization energies (800 kJ mol^{-1} for compound **1** vs 1004 kJ mol^{-1} for its oxygen analogues); this S atom is expected to be both an ionization centre and a fragmentation centre.[4] In general, the molecular ions retain a relatively intense signal compared with their oxygen analogues. The main primary fragmentations include the loss of 74 u and 107 u and the cleavage of the substituent at C-2, depending on the nature of the substituents (Table 1).

Under the conditions of electron impact ionization, 2,2-diethyldithiane (**1**) underwent cleavage of the ethyl–C-2 bond and left a cation at the C-2 position as a base peak in which the positive charge is stabilized by the unpaired electrons of the two sulphur atoms (Scheme 1). The preference for a cation to be retained at C-2) instead of at the substituent is due to the relatively low ionization energy of radical **A'**[5] (776 vs 882 and 879 kJ mol^{-1} for ethyl and propyl radicals, respectively) (semi-empirical studies were performed using PM3 as implemented by the MOPAC package, version 5.0; all work was performed at the restricted Hartree–Fock SCF level; the software package was supplied by Biosym Technologies). Other important primary fragmentations involve rupture of the dithiane ring. The fission of the carbon–sulphur bond and migration of hydrogen from the methyl group to the sulphur radical must be followed by cleavage of C-2—S-1 after formation of a cyclopropane intermediate,[2a,b,d] affording $[M - 107]^+$ (**B**), whereas the fission of the C-2—S-3 bond followed by cleavage of C-6—S-1 afforded $[M - 74]^+$ (**C**) (Scheme 1) In contrast, the fragment with 74 u is a major ion instead of a radical and no ion **B** was observed in the monoalkyl-1,3-dithianes.[2c]

For the dithiaspirane series, accompanying the formation of $[M - 74]^+$ and $[M - 107]^+$, the fragments from cycloalkane ring rupture became the major fragmentation process. In order to lose the C_3H_7 radical from the cyclohexyl ring (or the C_4H_9 radical for methylcyclohexyl ring), cleavage of the carbon–carbon bond occurs with the positive charge retained at C-2, which is stabilized by the lone pair of electrons of the sulphur atom. Migration of hydrogen from the allylic position to the terminal methylene radical followed by loss of a propyl or butyl radical forms a butadiene-like cation (**D**) (Scheme 2). The abundance of $[M - 57]^+$ is larger than that of $[M - 43]^+$ for asymmetric methycyclohexenyl compound **4**. The substantial increase in the abundances of $[M - 57]^+$ for compound **7** is due to the formation of a more stable butyl radical. A six-membered transition structure seems to be essential for the formation of $[M - 43]^+$ because of the lack of this ion from the cyclopentyl derivative **2**. The highly strained ring of the norbornane derivative **8** underwent a loss of 110 u from the molecular ion i.e. forming a C_8H_{14} fragment and a dithiane cation as a base peak. This is a special case in this series. For a cycloalkane ring fused to a benzene ring, no product was formed from rupture of the cycloalkane ring owing to the lack of a suitable β-hydrogen available for migration after ring rupture and involving the cleavage of a π-bond of the benzene ring (compounds **9**, **10**, and **11**). Their fragmentation processes are mainly dominated by rupture of the dithiane ring.

The cleavage of 2-aryl-2-alkyldithianes depends strongly on both the substituents on the phenyl ring and the size of the alkyl group. The relatively weak $[M - 15]^+$ signals from compounds **12** and **17** indicate not a small tendency to lose a methyl radical but further fragmentation resulting in $[M - 15 - 74]^+$ as base peaks. If the alkyl group is ethyl or propyl, the $[M - R]^+$ ion became the base (or nearly the base) peak (compounds **15** and **16**). The ability of a substituent on the benzene ring to stabilize the cation at C-2 resulted from the fission of the C-2–alkyl bond and



Scheme 2.

Table 1. Electron impact mass spectra of 1,3-dithiaspiranes and 2-aryl-1,3-dithianes

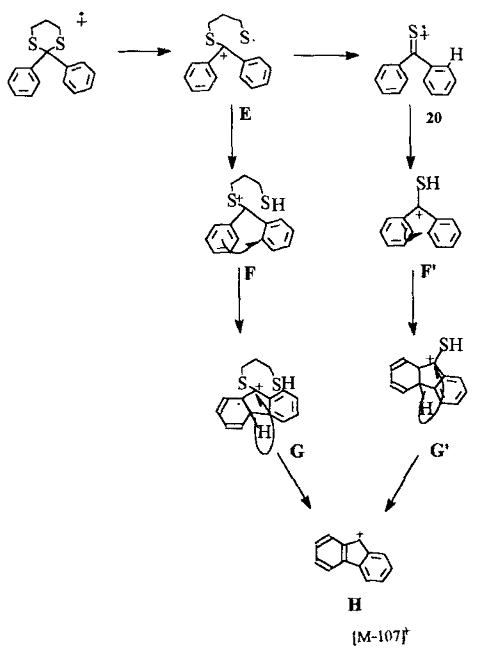
Compound	m/z (relative intensity (%))
1	178 (3), 177 (3), 176 (M, 32), 149 (10), 148 (8), 147 (100)[a], 103 (4), 102 (36)[b], 101 (4), 87 (4), 74 (10), 73 (70), 69 (16), 61 (6), 59 (8)[c], 55 (6), 47 (11), 46 (8), 45 (30), 41 (40)
2	176 (8), 175 (11), 174 (M, 82), 147 (4), 146 (6), 145 (43), 141 (28), 132 (13)[a], 127 (10), 114 (6), 113 (18), 107 (9), 106 (6), 101 (7), 100 (88)[b], 97 (9), 85 (19), 79 (10), 74 (10), 73 (15), 72 (10), 71 (50), 68 (6), 67 (100)[c], 65 (23), 59 (8), 58 (28), 53 (9), 47 (24), 46 (31)
3	190 (8), 189 (11), 188 (M, 95), 155 (26), 147 (6), 146 (9), 145 (73)[a], 141 (4), 116 (4), 115 (8), 114 (100)[b], 107 (8), 106 (19), 99 (11), 85 (9), 81 (11)[c], 79 (27), 77 (7), 73 (14), 71 (21), 67 (8), 58 (14), 53 (13), 46 (17)
4	204 (9), 203 (14), 202 (M, 100), 169 (16), 159 (31), 146 (15), 145 (93)[a], 132 (9), 128 (43)[b], 127 (14), 119 (13), 113 (10), 107 (9), 106 (43), 100 (6), 99 (10), 96 (7), 95 (79)[c], 94 (61), 93 (19), 81 (19), 79 (31), 68 (11), 67 (48), 65 (13), 60 (6), 59 (12), 58 (21), 55 (31), 53 (29), 51 (9), 47 (13), 46 (44)
5	204 (9), 203 (15), 202 (M, 100), 187 (4), 169 (17), 147 (8), 146 (9), 145 (95)[a], 132 (9), 129 (8), 128 (85)[b], 127 (18), 113 (15), 107 (17), 106 (21), 100 (11), 99 (16), 96 (6), 95 (84)[c], 94 (16), 93 (15), 91 (9), 87 (8), 86 (22), 85 (19), 81 (9), 79 (20), 78 (8), 77 (13), 74 (9), 73 (19), 72 (14), 71 (44), 69 (6), 68 (9), 67 (28), 65 (10), 59 (18), 58 (23), 55 (33), 53 (31), 51 (6), 47 (19), 46 (4)
6	218 (9), 217 (13), 216 (M, 100), 173 (4), 161 (7), 160 (9), 159 (88)[a], 142 (8)[b], 119 (14), 109 (22)[c], 106 (10), 93 (5), 85 (8), 79 (6), 71 (4), 67 (4), 55 (6), 46 (6)
7	218 (9), 217 (14), 216 (M, 95), 183 (3), 173 (6), 161 (11), 160 (13), 159 (100)[a], 148 (7), 146 (6), 145 (6), 142 (15)[b], 119 (21), 113 (4), 109 (38)[c], 106 (26), 99 (5), 97 (4), 95 (11), 93 (12), 91 (6), 87 (11), 85 (13), 81 (9), 79 (11), 77 (7), 71 (12), 67 (16), 59 (6), 55 (11), 46 (7)
8	244 (4), 243 (6), 242 (M, 37), 214 (6), 200 (3), 168 (9)[b], 167 (8), 134 (12), 133 (12), 132 (100), 125 (8), 119 (7), 113 (6), 108 (24), 107 (8), 106 (12), 95 (9), 93 (10), 91 (11), 85 (7), 79 (8), 77 (12), 67 (9), 55 (7), 45 (7), 41 (24)
9	224 (4), 223 (6), 222 (46), 189 (16), 175 (4), 150 (4), 149 (18), 148 (100)[b], 147 (63), 129 (7), 117 (6), 116 (13), 115 (52)[c], 107 (6), 106 (60), 89 (4), 77 (4), 73 (5), 69 (5), 63 (4), 45 (14), 41 (7)
10	224 (9), 223 (14), 222 (M, 100), 189 (5), 161 (7), 149 (6), 148 (38)[b], 147 (39), 129 (5), 128 (4), 116 (31), 115 (79)[c], 107 (12), 106 (19), 104 (14), 103 (8), 102 (4), 89 (6), 78 (5), 77 (8), 75 (7), 73 (9), 69 (5), 63 (7), 51 (12), 47 (8), 46 (6), 45 (19), 41 (22)
11	237 (6), 236 (M, 41), 203 (3), 163 (7), 162 (66)[b], 161 (13), 147 (8), 134 (14), 130 (11), 129 (100)[c], 128 (44), 127 (10), 115 (14), 77 (4), 51 (4), 45 (15), 41 (11),
12	212 (5), 211 (7), 210 (M, 62), 195 (3), 149 (43), 137 (6), 136 (52)[b], 135 (25), 122 (32), 121 (100), 105 (5), 104 (28), 103 (77), 102 (4), 77 (28), 59 (25), 51 (14), 45 (7), 41 (9)
13	228 (9), 227 (15), 226 (M, 91), 211 (10), 193 (14), 165 (7), 154 (5), 153 (12), 152 (100)[b], 138 (4), 137 (53), 121 (7), 120 (9), 119 (37)[c], 107 (3), 91 (11), 65 (9), 59 (8), 45 (6)
14	228 (11), 227 (20), 226 (M, 100), 211 (12), 193 (15), 183 (6), 165 (16), 154 (6), 153 (14), 152 (99)[b], 138 (8), 137 (79), 119 (19), 107 (6), 93 (12), 91 (19), 77 (6), 65 (15), 63 (6), 59 (18), 51 (4)
15	316 (6), 315 (11), 314 (M, 68), 287 (9), 286 (14), 285 (98), 253 (4), 242 (5), 241 (14), 240 (100)[b], 225 (11), 211 (42), 209 (37), 208 (11), 207 (27)[c], 195 (7), 193 (18), 181 (6), 177 (6), 176 (8), 168 (12), 167 (6), 166 (5), 165 (8), 161 (5), 150 (8), 135 (6), 133 (6), 121 (6), 107 (4), 106 (5), 105 (6), 91 (8), 86 (8), 84 (14), 79 (6), 77 (9), 73 (13), 45 (13), 41 (11)
16	238 (M, 10), 197 (9), 196 (12), 195 (100), 164 (3)[b], 136 (6), 131 (11)[c], 121 (31), 117 (6), 115 (4), 106 (3), 91 (5), 77 (4)
17	262 (5), 261 (10), 260 (M, 57), 245 (2), 199 (11), 187 (13), 186 (68)[b], 185 (83), 184 (22), 173 (4), 172 (11), 171 (100), 155 (4), 154 (20), 153 (59)[c], 152 (41), 127 (8), 115 (3), 77 (3), 59 (10), 51 (3), 45 (6), 41 (6)
18	274 (3), 273 (5), 272 (M, 32), 200 (5), 199 (16), 198 (100)[b], 197 (9), 178 (4), 166 (15), 165 (88)[c], 121 (29), 77 (5)
19	278 (5), 277 (M, 20), 276 (11), 204 (6), 203 (17), 202 (100), 201 (58), 199 (6), 170 (23), 169 (90), 168 (40), 167 (12), 126 (35), 125 (23), 122 (11), 121 (55), 82 (12), 77 (23), 45 (17), 41 (23)
20	272 (3), 271 (6), 270 (M, 32), 198 (5), 197 (21), 196 (100), 195 (12), 179 (2), 178 (5), 166 (10), 165 (47), 163 (6), 153 (2), 152 (17), 151 (5), 150 (3), 105 (3), 97 (4), 91 (2), 57 (13), 55 (8)
21	200 (19), 199 (68), 198 (M, 100), 197 (47), 167 (8), 166 (26), 165 (94), 153 (4), 152 (10), 123 (8), 122 (14), 121 (81), 105 (7), 77 (38), 69 (9), 64 (26), 63 (7), 52 (20)

[a] Major fragment from cleavage of C-2 substituent.
[b] $[M-74]^+$.
[c] $[M-107]^+$.

Table 2. *B*/*E* scan spectra of *m*/*z* 165

Compound	*m*/*z* (Relative intensity (%))
18	165 (100), 164 (21), 163 (72), 162 (11), 161 (7), 139 (18), 138 (6), 137 (10), 134 (4), 122 (4), 115 (9), 113 (14), 111 (13), 110 (17), 109 (9), 108 (3), 99 (7), 98 (22), 97 (6), 89 (7), 88 (6), 87 (26), 85 (27), 84 (13), 75 (12), 74 (33), 73 (12), 63 (22), 62 (22), 61 (32), 60 (14), 51 (7), 50 (16), 49 (6), 43 (14)
20	165 (100), 164 (21), 163 (72), 162 (11), 161 (7), 139 (18), 138 (6), 137 (10), 134 (3), 126 (4), 122 (5), 115 (10), 113 (10), 111 (8), 110 (13), 109 (9), 99 (7), 98 (17), 97 (8), 89 (5), 88 (5), 87 (19), 86 (25), 84 (12), 75 (9), 74 (26), 73 (13), 63 (19), 62 (23), 61 (28), 60 (11), 51 (6), 50 (17), 49 (5), 43 (23), 42 (10)
21	165 (100), 164 (24), 163 (65), 162 (16), 161 (8), 139 (17), 138 (11), 137 (15), 134 (5), 122 (10), 120 (4), 115 (15), 113 (7), 111 (11), 110 (30), 109 (22), 108 (8), 99 (8), 98 (26), 97 (13), 89 (19), 88 (9), 87 (30), 86 (39), 85 (46), 84 (19), 75 (11), 74 (39), 73 (22), 72 (5), 63 (25), 62 (33), 61 (53), 60 (23), 51 (5), 50 (20), 49 (14), 43 (7)
22	65 (100), 164 (16), 163 (48), 162 (9), 161 (6), 139 (20), 138 (5), 137 (10), 134 (3), 126 (4), 122 (5), 115 (11), 113 (8), 111 (8), 110 (14), 109 (10), 99 (6), 98 (20), 97 (6), 89 (6), 88 (5), 87 (20), 86 (28), 85 (26), 84 (11), 76 (3), 75 (11), 74 (32), 74 (14), 72 (3), 63 (25), 62 (27), 61 (34), 60 (14), 51 (8), 50 (21), 49 (6)

from rupture of the dithiane ring that retards further fragmentation (i.e. formation of an intense signal of $[M - R]^+$ and $[M - 74]^+$ ions) (Scheme 3). The fragmentation from 2,2-diphenyldithiane (**18**) that resulted in $[M - 74]^+$ and $[M - 107]^+$ (**H**, 165 u) is an interesting case. The formation of the former can be rationalized as above. The formation of ion **H** must be a complicated process. The *B*/*E* scan spectrum of this ion (165 u) resembled those obtained from thiabenzophenone (**20**) the 1,3-dithiane derivative of 9-fluorenone (**21**) and fluorene (**22**) (Table 2). Hence the structure of ion **H** is a fluorenium ion. From the B^2/E scan spectrum of ion **H**, we found that fragments of *m*/*z* 272 and 180 are their parent ions (Table 3). From these results, a possible fragmentation process is shown in Scheme 3, in which the mechanism included cleavage of the sulphur–carbon bond, hydrogen migration from the phenyl ring to the sulphur radical, formation of a fluorene skeleton and migration of a second hydrogen with loss of an SH or $HS(CH_2)_3S$ radical to rearomatize. A hydrogen migration from the phenyl ring to the sulphur radical resulting in loss of $HS(CH_2)_3S$ was verified from the fragmentation of 2-pentadeuteriophenyl-2-phenyldithiane (**19**), which forms *m*/*z* 169 ($[M - 107]^+$, 90%) and *m*/*z* 168 ($[M - 108]^+$, 40%). The latter is a radical of $DS(CH_2)_3S$. The significant difference in abundances between *m*/*z* 169 and 170 implies a larger isotopic effect resulting in more hydrogen migration to sulphur radical.



Scheme 3.

Table 3. B^2/E scan spectra of *m*/*z* 165 ion

Compound	*m*/*z* (relative intensity (%))
18	165 (100), 198 (4.4), 272 (0.4)
20	165 (100), 198 (1.5)
21	165 (100), 197 (0.6), 210 (0.4), 270 (0.3)

EXPERIMENTAL

The electron impact mass spectra were obtained on a JEOL Model JMX-DX 300 double-focusing mass spectrometer. Samples were introduced via a direct insertion probe; the source temperature was kept at 45 °C. The trap current for the 70 eV mass spectra was maintained at 300 μA and the accelerating voltage was maintained at 3 kV. All mass spectra were obtained at resolution 5000 (10% valley definition). The reported relative intensities of peaks are averages from two runs. The linked-scan spectra were measured on the same mass spectrometer. The metastable peaks produced in the first field-free region were recorded by combined scan (B/E = constant and B^2/E = constant) techniques.[6] The pressure of helium in the collision cell was sufficient to decrease the main beam signal by 80%.

General procedure for preparation of 1,3-dithianes

BF_3 etherate (0.5 ml) was added to a solution of diethyl ketone (0.5 g) and propane-1,3-dithiol (0.38 g) dissolved in chloroform (10 ml). The reaction mixture was stirred at 0 °C for 3 h. Excess water (50 ml) was poured into the solution to decompose BF_3, and then the mixture was extracted with chloroform (3 x 10 ml). The combined chloroform solution was treated according to the usual method and purified by chromatography on a silica gel column to yield 2,2-diethyl-1,3-dithiane (**1**) (96.5% yield).

Compound **21** was prepared according to the literature.[7]

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