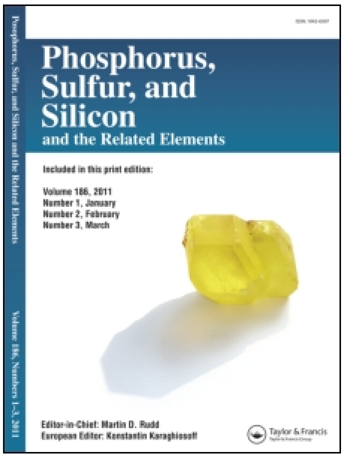

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Mass Spectrometry of Benzyl 2-Hydroxyethyl Oligosulfides, Dibenzyl di- and tri-Sulfides, Benzyl Phthalimido Disulfides, and Related Compounds

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MASS SPECTROMETRY OF BENZYL 2-HYDROXYETHYL OLIGOSULFIDES, DIBENZYL DI- AND TRI-SULFIDES, BENZYL PHTHALIMIDO DISULFIDES, AND RELATED COMPOUNDS

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Electron impact mass spectral data are reported and discussed for a range of benzyl 2-hydroxyethyl mono-, di-, tri-, and tetra-sulfides, dibenzyl di- and tri-sulfides, benzyl phthalimido disulfides, and a number of related compounds including benzyl acetyl disulfide, 2-hydroxyethyl phthalimido disulfide, and trichloromethyl phthalimido disulfide. The most abundant ions are in all cases formed by simple carbon-sulfur cleavage which gives the stable benzyl (or tropylium) and 2-hydroxyethyl (or protonated ethylene oxide) cations. Less abundant ions result in certain cases from carbon-sulfur cleavage with the elimination of a neutral benzyl radical, from sulfur-sulfur cleavage, possibly with hydrogen transfer, and from the elimination of sulfur. Additional characteristic ions are exhibited by the phthalimido derivatives.

Keywords: 2-hydroxyethyl; benzyl; fungicides; mass spectrometry; oligosulfides; phthalimido

INTRODUCTION

Benzyl 2-hydroxyethyl trisulfide (**1**) is an antimicrobial compound which occurs in the tropical plant *Petiveria alliacea*, commonly used in folk medicine. Its identity and its activity against various bacteria and human pathogenic fungi were established by Szczepanski et al.[1,2] The potential applications of this compound and

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Dedicated to the memory of Professor Max Pianka.

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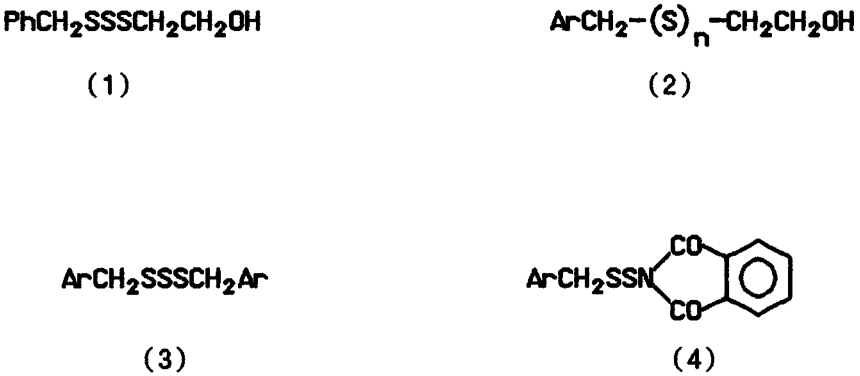


FIGURE 1 Structures 1–4.

of analogous benzyl oligosulfides (**2**) as antibacterial or antifungal pharmaceuticals,[3–6] as prophylactic and therapeutic agents in the treatment of liver disorders,[7,8] and as agrochemical fungicides[9] have been reported. We have also noted that the corresponding dibenzyl trisulfides (**3**) and benzyl phthalimido disulfides (**4**) (intermediates in the synthesis of trisulfides)[10,11] are significantly less active against *Fusarium* spp. than the benzyl 2-hydroxyethyl types.[12] (See Figure 1.)

It is known that the synthesis of unsymmetrical oligosulfides may be accompanied by the formation of the symmetrical analogues and also that di-, tri-, or tetrasulfides etc. may be formed concurrently. ^{1}H NMR spectroscopy may be useful for the identification and determination of individual components in reaction products on the basis of differences in chemical shift for the benzylic protons. Separation can be achieved by tlc or column chromatography,[5–9] although disproportionation of the tri- and tetra-sulfides may occur, especially in polar solvents.[5,6] Mass spectrometry has been used for identification to only a limited extent: thus, molecular ions were reported in the EI mass spectra of various benzyl disulfides[5,6] and a weak molecular ion, together with a number of fragment ions, were observed in connection with the original identification of benzyl 2-hydroxyethyl trisulfide.[1,2] Otherwise, to our knowledge, there are few mass spectrometric data for benzyl oligosulfides in the literature. Dialkyl monosulfides (thioethers) have, however, been studied in some detail, their EI mass spectra having been shown to be dominated by fragments arising from α-cleavage, carbon-sulfur fission, and olefin elimination.[13] In addition, hydrogen transfer to sulfur has been shown to occur via 4-, 5-, or 6-membered cyclic transition states.[14]

TABLE I Characteristic Ions in the EI Mass Spectra of Benzyl 2-Hydroxyethyl Monosulfides $\mathrm{ArCH_2{-}S{-}CH_2CH_2OH}$ (**5**)

Compound		*m/z* (%)[a]			
No.	$\mathrm{ArCH_2}$	$\mathrm{M}^{+\cdot}$	$\mathrm{ArCH_2S}]^{+}$	$\mathrm{ArCH_2}]^{+}$	$\mathrm{HOCH_2CH_2}]^{+}$
5a	$\mathrm{PhCH_2}$	168(27)	123(22)	91(100)	45(54)
5b	$\mathrm{2\text{-}ClC_6H_4CH_2}$	202(10)	157(9)	125(100)	45(61)
5c	$\mathrm{4\text{-}ClC_6H_4CH_2}$	202(12)	157(9)	125(100)	45(50)
5d	$\mathrm{2\text{-}MeC_6H_4CH_2}$	182(47)	137(6)	105(100)	45(48)
5e	$\mathrm{4\text{-}MeC_6H_4CH_2}$	182(42)	137(5)	105(100)	45(54)
5f	$\mathrm{4\text{-}MeOC_6H_4CH_2}$	198(30)	153(3)	121(100)	45(47)

[a] Data for chlorine-containing ions given for $^{35}\mathrm{Cl}$ only.

DISCUSSION

We have briefly reported mass spectral data for a range of benzyl 2-hydroxyethyl mono-, di-, tri-, and tetra-sulfides (**2**, n = 1–4).[9] These spectra are now discussed in more detail, together with data for dibenzyl disulfide (**6a**), benzyl acetyl disulfide (**6b**), symmetrical dibenzyl tri-sulfides (**10a–10f**), benzyl phthalimido disulfides (**8a–8f**), 2-hydroxyethyl phthalimido disulfide (**9a**) and trichloromethyl phthalimido disulfide (**9b**). Tables I–VIII show characteristic ions observed for the monosulfides (**5**), disulfides (**6**, **7**, **8**, **9**), trisulfides (**10**, **11**), and tetrasulfides (**12**) respectively. (See Figure 2.)

Molecular ions were generally weak under the conditions of our measurements, although certain exceptions include those derived from dibenzyl disulfide (**6a**) and benzyl acetyl disulfide (**6b**) for which relative intensities of 60% and 50%, respectively, were recorded (Table II). As a group, the benzyl 2-hydroxyethyl monosulfides (**5**) exhibited more intense molecular ions (M^{+}, 10–47%) than the benzyl 2-hydroxyethyl di- (**7**), tri- (**11**), or tetra-sulfides (**12**), for which the relative intensities

TABLE II Characteristic Ions in the EI Mass Spectra of Benzyl Disulfides $\mathrm{ArCH_2{-}S_2{-}R}$ (**6**)

Compound			*m/z* (%)[a]					
No.	$\mathrm{ArCH_2}$	R	$\mathrm{M}^{+\cdot}$	$\mathrm{M{-}S}]^{+\cdot}$	$\mathrm{ArCH_2S_2}]^{+}$	$\mathrm{ArCH_2S}]^{+}$	$\mathrm{ArCH_2}]^{+}$	$\mathrm{CH_3CO}]^{+}$
6a	$\mathrm{PhCH_2}$	$\mathrm{PhCH_2}$	246(60)	214(2)	155(19)	123(13)	91(100)	—
6b	$\mathrm{PhCH_2}$	$\mathrm{COCH_3}$	198(50)	—	—[b]	123(43)	91(80)	43(100)

[a] Data for chlorine-containing ions given for $^{35}\mathrm{Cl}$ only.

[b] *m/z* 156(12) indicates formation of $[\mathrm{PhCH_2S_2H}]^{+\cdot}$ by elimination of ketene.

$Ar{-}CH_2{-}S{-}CH_2CH_2OH$

(5)

Ar = Ph (5a); 2-Cl (5b); 4-Cl (5c);
2-Me (5d); 4-Me (5e); 4-MeO (5f)

$Ar{-}CH_2{-}S_2{-}R$

(6)

Ar = Ph, R = $PhCH_2$ (6a);
Ar = Ph, R = MeCO (6b)

$Ar{-}CH_2{-}S_2{-}CH_2CH_2OH$

(7)

Ar = Ph (7a); 2-Cl (7b); 4-Cl (7c);
4-F (7d); 2-Me (7e); 4-Me (7f);
4-MeO (7g)

$PhthN{-}S_2{-}CH_2Ar$

(8)

Ar = Ph (8a); 2-Cl (8b); 4-Cl (8c);
2-Me (8d); 4-Me (8e); 4-MeO (8f)

$PhthN{-}S_2{-}R$

(9)

R = CH_2CH_2OH (9a); CCl_3 (9b)

$Ar{-}CH_2{-}S_3{-}CH_2{-}Ar$

(10)

Ar = Ph (10a); 2-Cl (10b); 4-Cl (10c);
2-Me (10d); 4-Me (10e); 4-MeO (10f)

$Ar{-}CH_2{-}S_3{-}CH_2CH_2OH$

(11)

Ar = Ph (11a); 2-Cl (11b); 4-Cl (11c);
2-Me (11d); 4-Me (11e); 4-MeO (11f)
2-furyl (11g)

$Ar{-}CH_2{-}S_4{-}CH_2CH_2OH$

(12)

Ar = Ph (12a); 4-Cl (12b); 2-Me (12c);
4-Me (12d); 4-MeO (12e); 2-furyl (12f)

FIGURE 2 Structures 5–12.

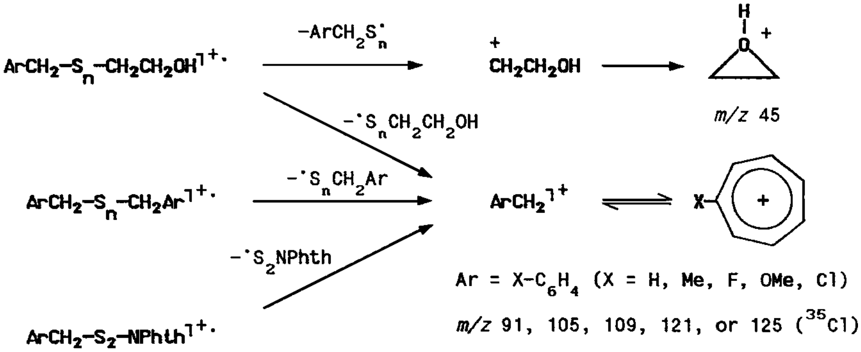
TABLE III Characteristic Ions in the EI Mass Spectra of Benzyl 2-Hydroxyethyl Disulfides $ArCH_2—S_2—CH_2CH_2OH$ (**7**)

Compound		m/z (%)[a]				
No.	$ArCH_2$	$M^{+\cdot}$	$M—S]^{+\cdot}$	$ArCH_2S]^{+}$	$ArCH_2]^{+}$	$HOCH_2CH_2]^{+}$
7a	$PhCH_2$	200(12)	168(2)	123(2)	91(100)	45(56)
7b	$2\text{-}ClC_6H_4CH_2$	234(5)	202(1)	157(3)	125(100)	45(53)
7c	$4\text{-}ClC_6H_4CH_2$	234(2)	202(1)	157(2)	125(100)	45(43)
7d	$4\text{-}FC_6H_4CH_2$	218(9)	186(2)	141(4)	109(100)	45(56)
7e	$2\text{-}MeC_6H_4CH_2$	214(4)	182(2)	137(6)	105(100)	45(48)
7f	$4\text{-}MeC_6H_4CH_2$	214(5)	182(3)	137(8)	105(100)	45(52)
7g	$4\text{-}MeOC_6H_4CH_2$	230(2)	198(1)	153(3)	121(100)	45(46)

[a] Data for chlorine-containing ions given for ^{35}Cl only.

were in no cases more than 12% and mainly around 2–3% (see Tables I, III, VII, and VIII).

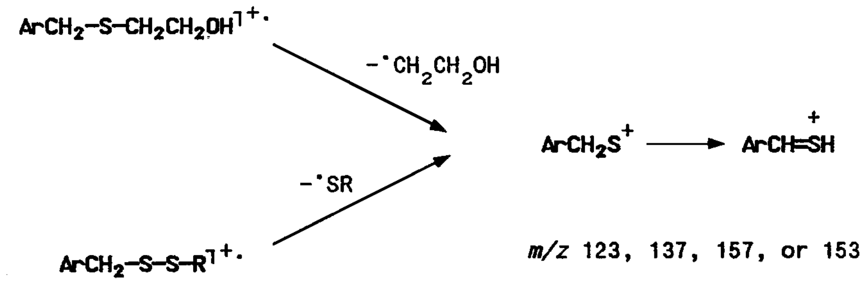
The most abundant ions in the spectra of all compounds were those derived from carbon-sulfur fission, viz., the resonance-stablized benzyl (or isomeric tropylium) cation[15] and, from the 2-hydroxyethyl derivatives, the 2-hydroxyethyl cation which may be stabilized by cyclization[16] to give protonated ethylene oxide (Scheme 1).



SCHEME 1

In the case of monosulfides (**5**), loss of the 2-hydroxyethyl group as a neutral species also gave rise to an ion which may be formulated initially as $[ArCH_2S]^+$, but which is probably stabilized by hydrogen migration[13,14] to give the sulfonium species, $[ArCH{=}SH]^+$ (Scheme 2); and the same ion, formed by sulfur-sulfur cleavage, was observed in the mass spectra of di-, tri-, and tetra-sulfides (Scheme 2).

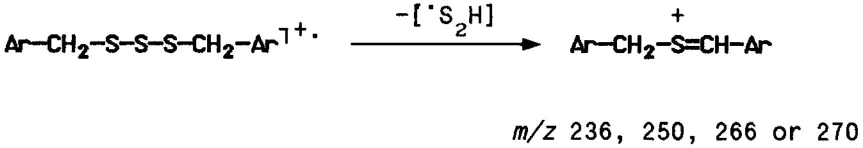
The elimination of S_2 or of S_2H in the mass spectrometry of aromatic disulfides has been recognized.[15] Prominent ions corresponding to the



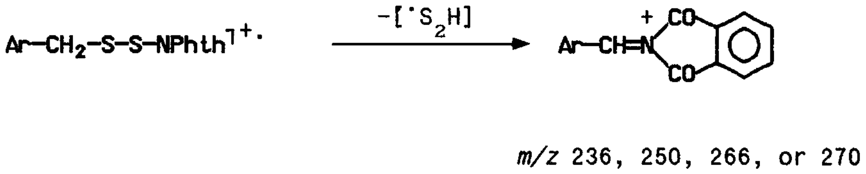
R = Ar, Bz, NPhth, SCH_2Ar,
or $S_nCH_2CH_2OH$ (n = 0, 1 or 2)

SCHEME 2

loss of S_2H were similarly observed in the spectra of symmetrical trisulfides (**10**) (Table VI) and phthalimido disulfides (**8**) (Table IV) and may be reasonably assigned as sulfonium or immonium ions (Schemes 3 and 4 respectively).



SCHEME 3



SCHEME 4

Benzyl 2-hydroxyethyl trisulfides (**11**) also gave rise to ions attributable to the loss of S_2H but these were generally of lower intensity (Table VII).

Other characteristic ions were formed by the loss of one or more sulfur atoms from the disulfides (**7**, **9**) trisulfides (**10**, **11**), and tetrasulfides (**12**) (Tables II, III, V, VI, VII, VIII). The mechanism by which individual sulfur atoms are eliminated is speculative but a possible route involves

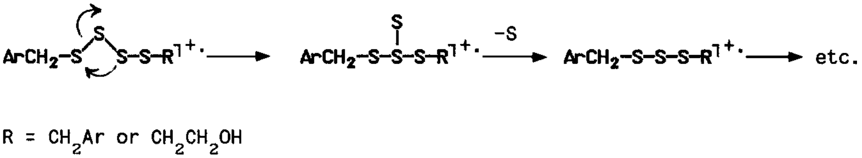
TABLE IV Characteristic Ions in the EI Mass Spectra of Benzyl Phthalimido Disulfides PhthN—S_2—CH_2Ar (**8**)

Compound		*m/z* (%)[a,b]				
No.	$ArCH_2$	$M^{+\cdot}$	$M—SSH]^+$	$ArCH_2S]^+$	$ArCH_2]^+$	$C_6H_4]^{+\cdot}$
8a	$PhCH_2$	301(24)	236(46)	123(43)	91(100)	76(15)
8b	$2\text{-}ClC_6H_4CH_2$	335(1)	270(19)	157(12)	125(92)	76(21)
8c	$4\text{-}ClC_6H_4CH_2$	335(2)	270(16)	157(8)	125(94)	76(18)
8d	$2\text{-}MeC_6H_4CH_2$	315(10)	250(12)	137(26)	105(100)	76(16)
8e	$4\text{-}MeC_6H_4CH_2$	315(13)	250(13)	137(21)	105(100)	76(23)
8f	$4\text{-}MeOC_6H_4CH_2$	331(12)	266(14)	153(27)	121(100)	76(28)

[a] Data for chlorine-containing ions given for ^{35}Cl only.

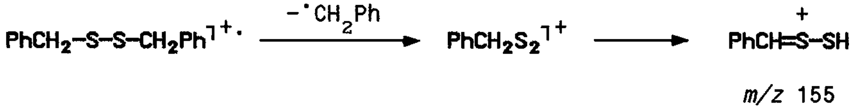
[b] The following ions derived from the phthalimide group were also observed: *m/z* 210 ($[PhthNS_2]^+$) (**8a**, 22; **8b**, 18; **8c**, 20; **8f**, 24%); *m/z* 178 ($[PhthNS]^+$) (**8a**, 22; **8b**, 16; **8c**, 18; **8d**, 12; **8e**, 2; **8f**, 13%); *m/z* 147 ($[PhthNH]^{+\cdot}$) (**8a**, 38; **8b**, 37; **8c**, 36; **8d**, 21; **8e**, 21; **8f**, 16%).

prior rearrangement to give a branched-chain structure, followed by fission of the side-chain sulfur-sulfur bond (e.g., Scheme 5).*



SCHEME 5

In the case of dibenzyl disulfide (**6a**) simple cleavage of a carbon-sulfur bond, with loss of a neutral benzyl radical, gives an ion at *m/z* 155, corresponding to $[PhCH_2S_2]^+$ (Table II), although it is likely that stabilization by hydrogen transfer occurs (Scheme 6) as for the monosulfides. In contrast, benzyl acetyl disulfide (**6b**) gives the radical cation $[PhCH_2S_2H]^{+\cdot}$, *m/z* 156, most probably by direct elimination of the stable ketene molecule (Scheme 7).*



SCHEME 6

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*Intramolecular rearrangements in Schemes 5, 7, and 8 are shown for convenience as heterolytic processes, although the precise mechanism in each case will be influenced by the location of the unpaired electron.

TABLE V Characteristic Ions in the EI Mass Spectra of 2-Hydroxyethyl and Trichloromethyl Phthalimido Disulfide PhthN—S_2—R (**9**)

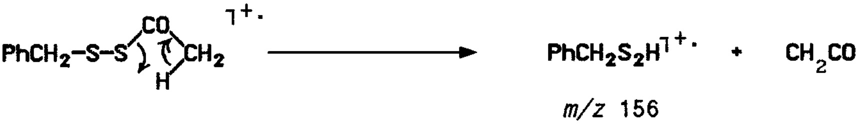
Compound		m/z (%)[a]						
No.	R	$M^{+\cdot}$	M—S$]^{+\cdot}$	M—$S_2]^{+\cdot}$	$PhthNS_2H]^{+\cdot}$	$PhthNSH]^{+\cdot}$	$PhthNH]^{+\cdot}$	$C_6H_4]^{+\cdot}$
9a	CH_2CH_2OH	255(23)	—	—	211(14)	179(41)	147(76)	76(100)[b]
9b	CCl_3	316(48)	284(11)	252(19)	—	—	—[c]	76(100)[d]

[a] Data for chlorine-containing ions given for ^{35}Cl only.

[b] m/z 45($[CH_2CH_2O]^+$) also recorded.

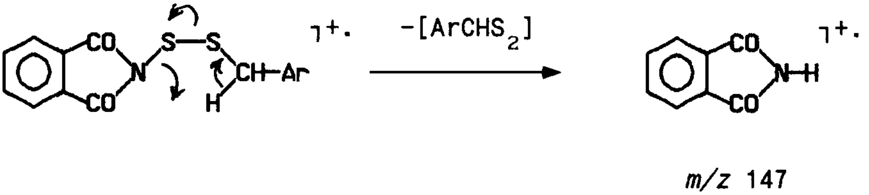
[c] m/z 146(26) assigned to $[PhthN]^+$.

[d] Also m/z 106(27), tentatively assigned to $[S_2NCO]^+$.

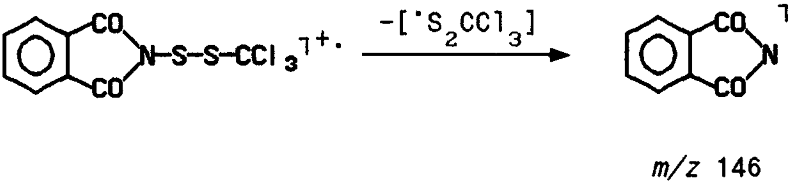


SCHEME 7

The phthalimido disulfides generate additional characteristic fragments. Thus, cleavage of the sulfur-nitrogen bond is accompanied by hydrogen transfer to nitrogen, giving the phthalimide radical cation (*m*/*z* 147) which appears as a prominent peak with relative intensity 16–38% for the benzyl compounds (Table IV) and 76% for 2-hydroxyethyl phthalimido disulfide (Table V). In the case of benzyl derivatives (**8a–f**) the proton can only originate from the benzylic methylene group and it is reasonable to assume that a cyclic transition state is involved (Scheme 8).* The 2-hydroxyethyl derivative (**9a**) could in principle transfer either the hydroxyl proton or a methylene group proton to nitrogen, although the higher acidity of the former makes this the more likely choice; the relatively high intensity of the resulting phthalimide cation (76%) also supports the view that this is a facile rearrangement involving a labile hydrogen atom. No hydrogen transfer is possible in trichloromethyl phthalimido disulfide (**9b**), and in this case the ion at *m*/*z* 147 is not observed but is replaced by *m*/*z* 146, which is thought to be the phthalimido cation (Scheme 9). In addition, the trichloromethyl compound (**9b**) exhibited a prominent peak at *m*/*z* 106 which is tentatively assigned to the fragment ion $S_2NCO^{\urcorner +}$.



SCHEME 8



SCHEME 9

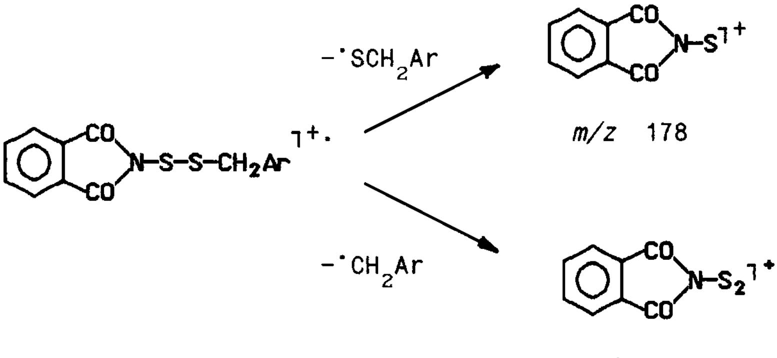
TABLE VI Characteristic Ions in the EI Mass Spectra of Symmetrical Dibenzyl Trisulfides $ArCH_2—S_3—CH_2Ar$ (**10**)

Compound		*m*/*z* (%)[a]				
No.	$ArCH_2$	$M^{+\cdot}$	$M—S]^{+\cdot}$	$M—SSH]^{+}$	$ArCH_2S]^{+}$	$ArCH_2]^{+}$
10a	$PhCH_2$	278(8)[b]	246(12)	213(54)	123(36)	91(100)
10b	$2\text{-}ClC_6H_4CH_2$	346(9)	314(1)	281(12)	157(7)	125(100)
10c	$4\text{-}ClC_6H_4CH_2$	346(4)	314(1)	281(13)	157(11)	125(100)
10d	$2\text{-}MeC_6H_4CH_2$	306(17)	274(1)	241(43)	137(17)	105(100)
10e	$4\text{-}MeC_6H_4CH_2$	306(2)	274(1)	241(12)	137(5)	105(100)
10f	$4\text{-}MeOC_6H_4CH_2$	338(11)	306(1)	273(29)	154(58)	121(41)

[a] Data for chlorine-containing ions given for ^{35}Cl only.

[b] *m*/*z* 277(31) ($[M\text{-}1]^+$) also observed.

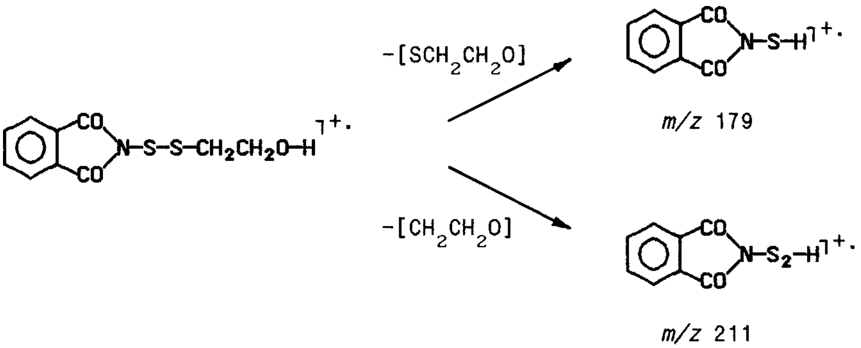
In addition to the formation of benzyl cations by carbon-sulfur cleavage (Scheme 1), the benzyl phthalimido disulfides (Table IV) also gave prominent ions at *m*/*z* 210 due to the loss of a benzyl radical (except for **8d** and **8e**), and at *m*/*z* 178 due to the loss of benzylthio (Scheme 10). In the case of 2-hydroxyethyl phthalimido disulfide (**9a**) hydrogen transfer also occurred, presumably from the hydroxyl group, giving the corresponding ions at *m*/*z* 211 and 179, respectively (Scheme 11). A further peak at *m*/*z* 76 is assigned to the phenylene radical cation, $C_6H_4^{+\cdot}$ (Tables IV and V), also seen as an intense ion in the spectra of phthalimide and phthalic acid.[17]



SCHEME 10

EXPERIMENTAL

Starting materials, solvents, and reagents were obtained from Aldrich Chemical Company or Lancaster Synthesis. Analysis and spectroscopy



SCHEME 11

were carried out as described previously.[9] The EI mass spectra were recorded on a Kratos Profile spectrometer by direct injection and with an ionizing energy of 70 eV. Relative intensities of chlorine-containing ions are given for ^{35}Cl only.

Preparations

Preparations of benzyl and substituted benzyl 2-hydroxyethyl mono-, di-, tri-, and tetra-sulfides (**2**, n = 1–4) were as reported previously.[9] The following compounds were also prepared by described methods: dibenzyl disulfide (**6a**), m.p. 71–72°C (lit.[18,19] 71°C), acetyl benzyl disulfide (**6b**), m.p. 56–57°C (lit.[20] 55–57°C), benzyl phthalimido disulfide (**8a**), m.p. 135–137°C (lit.[21] m.p. 134–136°C), trichloromethyl phthalimido disulfide (**9b**), m.p. 129–130°C (lit.[22,23] 130–132°C), dibenzyl trisulfide (**10a**), m.p. 50–51°C (lit.[20] 48.5–49.5°C), di(2-chlorobenzyl) trisulfide (**10b**), m.p. 75–76°C (lit.[20] 75°C), di(4-chlorobenzyl) trisulfide (**10c**), m.p. 81–82°C (lit.[20] 82–83°C), di(2-methylbenzyl) trisulfide (**10d**), m.p. 48–49°C (lit.[20] 47–49°C), di(4-methylbenzyl) trisulfide (**10e**), m.p. 54–55°C (lit.[20] 55–57°C), and di(4-methoxybenzyl) trisulfide (**10f**), m.p. 172–173°C (lit.[20] 171–173°C).

By an analogous procedure to that described for the preparation of benzyl phthalimido disulfide (**8a**)[21] the following new compounds were obtained (recrystallized twice from ethanol):

*2-Chlorobenzyl phthalimido disulfide (**8b**).* (10.6 g, 90%), as white needles, m.p. 148–149°C, (Found: C, 53.71; H, 2.96; N, 4.18; S, 19.10. $C_{15}H_{10}ClNO_2S_2$ requires: C, 53.65; H, 3.01; N, 4.17; S, 19.08%); δ_H ($CDCl_3$) 4.32 (CH_2, s, 2H), 7.23 (Ar—H, m, 4H), 7.84 (Ar—H, m, 4H); δ_C ($CDCl_3$) 43.13 (CH_2), 124.07 (ArC-1), 126.82 (ArC-3), 129.70 (ArC-2), 126.7 (ArC-5), 129.6 (ArC-6), 131.9 (ArC-4), 132.21 (ArC-3′,4′), 134.09 (ArC-2′,5′), 134.83 (ArC-1′,6′), 167.82 (C=O); *m/z* (^{35}Cl) 335 (M^+, 1).

TABLE VII Characteristic Ions in the EI Mass Spectra of Benzyl 2-Hydroxyethyl Trisulfides $ArCH_2—S_3—CH_2CH_2OH$ (**11**)

Compound		*m/z* (%)[a]					
No.	$ArCH_2$	$M^{+\cdot}$	$M—S]^{+\cdot}$	$M—SSH]^{+}$	$ArCH_2S]^{+}$	$ArCH_2]^{+}$	$HOCH_2CH_2]^{+}$
11a	$PhCH_2$	232(12)	200(4)	167(14)	123(23)	91(100)	45(68)
11b	$2\text{-}ClC_6H_4CH_2$	266(1)	234(2)	201(2)	157(3)	125(17)	45(59)
11c	$4\text{-}ClC_6H_4CH_2$	266(2)	234(1)	201(2)	157(1)	125(23)	45(62)
11d	$2\text{-}MeC_6H_4CH_2$	246(2)	214(3)	181(3)	137(3)	105(100)	45(58)
11e	$4\text{-}MeC_6H_4CH_2$	246(2)	214(2)	181(7)	137(10)	105(100)	45(65)
11f	$4\text{-}MeOC_6H_4CH_2$	262(2)	—	197(4)	153(2)	121(29)	45(53)
11g	$2\text{-}furylCH_2$	222(2)	—	157(1)	—	81(100)	45(49)

[a] Data for chlorine-containing ions given for ^{35}Cl only.

TABLE VIII Characteristic Ions in the EI Mass Spectra of Benzyl 2-Hydroxyethyl Tetrasulfides $ArCH_2{-}S_4{-}CH_2CH_2OH$ (**12**)

Compound		m/z (%)[a]						
No.	$ArCH_2$	$M^{+\cdot}$	$M{-}S]^{+\cdot}$	$M{-}2S]^{+\cdot}$	$M{-}3S]^{+\cdot}$	$ArCH_2S]^{+}$	$ArCH_2]^{+}$	$HOCH_2CH_2]^{+}$
12a	$PhCH_2$	264(2)	—	200(11)	167(3)	123(29)	91(100)	45(53)
12b	4-$ClC_6H_4CH_2$	298(3)	266(8)	234(3)	201(5)	157(4)	125(100)	45(59)
12c	2-$MeC_6H_4CH_2$	278(2)	—	214(9)	—	137(4)	105(100)	45(60)
12d	4-$MeC_6H_4CH_2$	278(2)	—	214(11)	—	137(5)	105(100)	45(49)
12e	4-$MeOC_6H_4CH_2$	294(2)	—	230(8)	198(5)	153(5)	121(100)	45(62)
12f	2-furylCH_2	254(4)	222(5)	190(9)	158(3)	113(6)	81(100)	45(47)

[a] Data for chlorine-containing ions given for ^{35}Cl only.

*4-Chlorobenzyl phthalimido disulfide (**8c**).* (16.0 g, 95%), as white needles, m.p. 153–154°C, (Found: C, 53.69; H, 2.99; N, 4.17; S, 19.20. $C_{15}H_{10}ClNO_2S_2$ requires: C, 53.65; H, 3.01; N, 4.17; S, 19.08%); δ_H ($CDCl_3$) 4.38 (CH_2, s, 2H), 7.25 (Ar—H, m, 4H), 7.85 (Ar—H, m, 4H); δ_C ($CDCl_3$) 43.48 (CH_2), 124.21 (ArC-1), 126.79 (ArC-3,5), 129.67 (ArC-2,6), 131.26 (ArC-4), 132.18 (ArC-3′,4′), 134.48 (ArC-2′,5′), 135.08 (ArC-1′,6′), 169.57 (C=O); *m/z* (^{35}Cl) 335 (M^+, 2).

*2-Methylbenzyl phthalimido disulfide (**8d**).* (10.9 g, 85%), as white needles, m.p. 147–148°C, (Found: C, 60.76; H, 4.21; N, 4.44; S, 20.21. $C_{16}H_{13}NO_2S_2$ requires: C, 60.94; H, 4.16; N, 4.44; S, 20.33%); δ_H ($CDCl_3$) 2.33 (CH_3, s, 3H), 4.37 (CH_2, s, 2H), 7.25 (Ar—H, m, 4H), 7.85 (Ar—H, m, 4H); δ_C ($CDCl_3$) 20.98 (CH_3), 45.67 (CH_2), 124.47 (ArC-1), 129.12 (ArC-3), 128.90 (ArC-5), 129.46 (ArC-6), 130.11 (ArC-2), 132.36 (ArC-4), 133.37 (ArC-3′,4′), 134.68 (ArC-2′,5′), 138.01 (ArC-1′,6′), 167.90 (C=O); *m/z* 315 (M^+, 10).

*4-Methylbenzyl phthalimido disulfide (**8e**).* (11.2 g, 89%), as white needles, m.p. 131–132°C, (Found: C, 60.89; H, 4.25; N, 4.34; S, 20.21. $C_{16}H_{13}NO_2S_2$ requires: C, 60.94; H, 4.16; N, 4.44; S, 20.33%); δ_H ($CDCl_3$) 2.30 (CH_3, s, 3H), 4.30 (CH_2, s, 2H), 7.25 (Ar—H, m, 4H), 7.85 (Ar—H, m, 4H); δ_C ($CDCl_3$) 21.17 (CH_3), 45.21 (CH_2), 124.03 (ArC-3, 5), 129.32 (ArC-2, 6), 129.35 (ArC-1), 132.25 (ArC-4), 133.35 (ArC-3′,4′), 134.77 (ArC-2′,5′), 137.43 (ArC-1′,6′), 169.06 (C=O); *m/z* 315 (M^+, 13).

*4-Methoxybenzyl phthalimido disulfide (**8f**).* (14.1 g, 85%), as white needles, m.p. 148–149°C, (Found: C, 58.06; H, 3.97; N, 4.26; S, 19.40. $C_{16}H_{13}NO_3S_2$ requires: C, 58.00; H, 3.96; N, 4.23; S, 19.36%.; δ_H ($CDCl_3$) 3.78 (CH_3O, s, 3H), 4.30 (CH_2, s, 2H), 6.85 (Ar—H, m, 2H), 7.35 (Ar—H, m, 2H), 7.85 (Ar—H, m, 4H); δ_C ($CDCl_3$) 25.78 (CH_3O), 45.29 (CH_2), 125.75 (ArC-3, 5), 130.32 (ArC-2,6), 113.72 (ArC-1), 154.34 (ArC-4), 134.37 (ArC-3′,4′), 135.03 (ArC-2′,5′), 138.58 (ArC-1′,6′), 167.64 (C=O); *m/z* 331 (M^+, 12).

*2-Hydroxyethyl phthalimido disulfide (**9a**).* (7.2 g, 76%), m.p. 214–216°C (Found: C, 47.05; H, 3.51; N, 5.72; S, 25.10. $C_{10}H_9NO_3S_2$ requires: C, 47.06; H, 3.56; N, 5.49; S, 25.13%); δ_H ($CDCl_3$) 2.59 (OH, s, 1H), 2.89 ($\mathrm{HOCH_2C}H_2\mathrm{S}$, t, 2H, $^3J_{HCCH}$ 5 Hz), 3.79 ($\mathrm{HO}C\mathrm{H_2CH_2S}$, t, 2H, $^3J_{HCCH}$ 5 Hz), 7.28 (Ar—H, m, 4H); δ_C ($CDCl_3$) 41.37 ($\mathrm{CH_2}C\mathrm{H_2S}$), 42.86 ($\mathrm{Ar}C\mathrm{H_2S}$), 60.14 ($\mathrm{HO}C\mathrm{H_2}$), 133.76 (ArC-3,4), 134.96 (ArC-2,5), 138.16 (ArC-1,6); *m/z* 225 (M^+, 23).

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