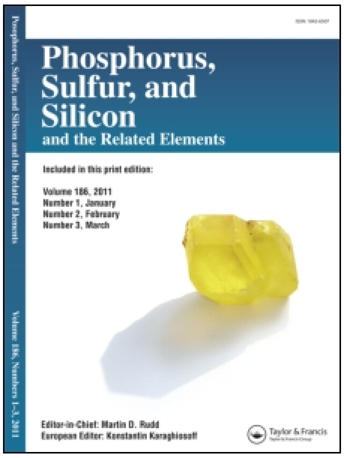

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MASS SPECTRAL FRAGMENTATION OF DISULFENAMIDES

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MASS SPECTRAL FRAGMENTATION OF DISULFENAMIDES[1a,b]

by

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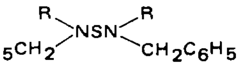
ABSTRACT

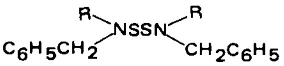
Five disulfenamides were prepared by reaction of benzylmethylamine and benzylisopropylamine with sulfur chlorides, (RSR, RSSR and RSSSR, R = $C_6H_5CH_2NCH_3$ or R = $C_6H_5CH_2NCH(CH_3)_2$). Their mass spectra are presented and discussed.

While there have been numerous studies of the mass spectral fragmentation of compounds containing divalent sulfur, most have been concerned with compounds with sulfur-carbon and sulfur-hydrogen bonds.[2-5] During the course of an investigation of the structural and stereochemical properties of sulfenamides we have had occasion to examine the mass spectra of several representative compounds bearing sulfur-nitrogen single bonds[6] (1-3). This series of compounds may be considered analogs of sulfides, disulfides and trisulfides in which nitrogen has replaced carbon as the element bonded to sulfur.



1

a R = CH_3
b R = $CH(CH_3)_2$



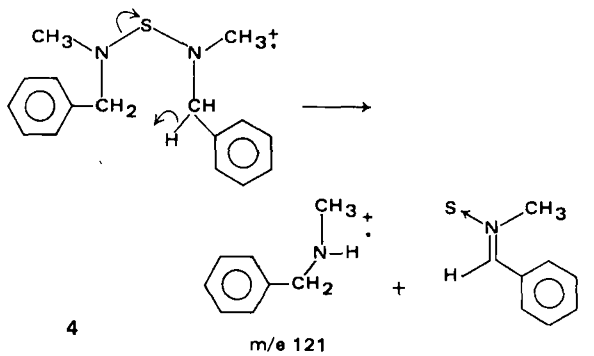
2

a R = CH_3
b R = $CH(CH_3)_2$

3

Bis-aminesulfides (Thiobisamines), 1

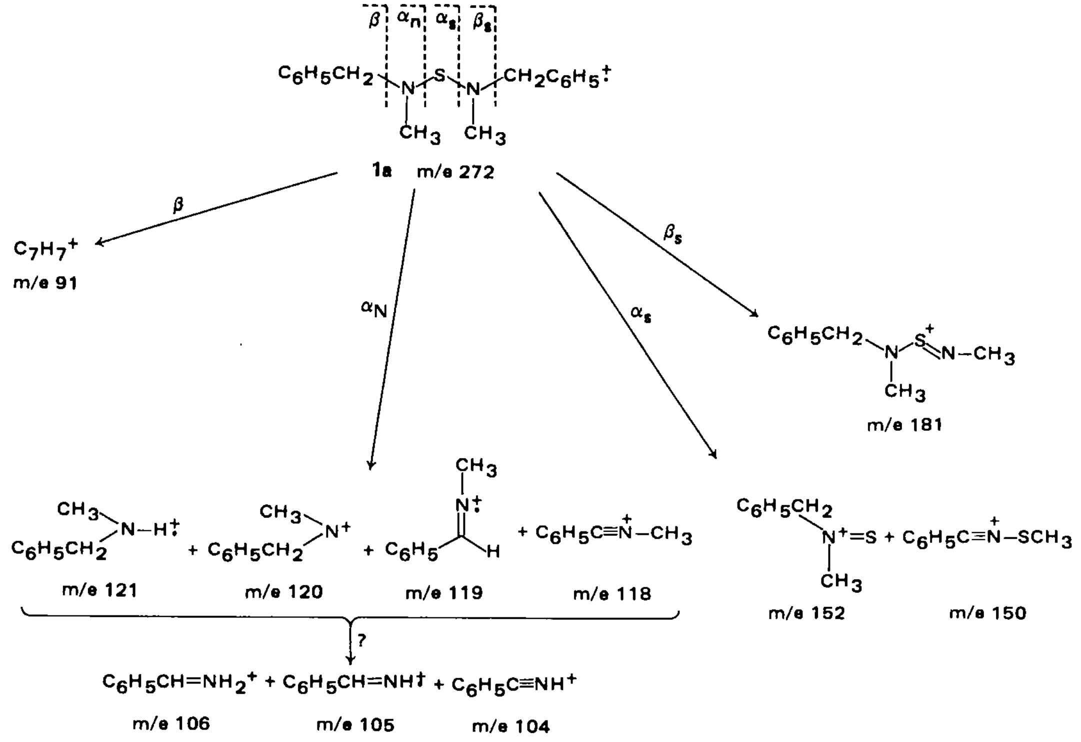
The bisaminesulfides 1, prepared by reaction of the corresponding amines with sulfur dichloride represent analogs of dialkyl sulfides. Their mass spectra like those of dialkyl sulfides, exhibit fairly intense ions for α and β-cleavage in addition to observable molecular ions (Figure 1, Scheme 1). The base peak for both **1a** and **1b**, as would be expected, is β-cleavage leading to the tropylium ion.[7] The tropylium ion accounts for 15.4% and 16.6% of the total ion current (t.i.c.) in **1a** and **1b** respectively. However, the most important type of fragmentation involves cleavage of the sulfur-nitrogen bond (α_N-cleavage) leading to the loss of sulfur (in the neutral fragment) and the formation of stable nitrogen containing cations. In compound **1a** α_N-cleavage can be associated with either the gain of a hydrogen atom, possibility *via* 4, expelling a thionitrone molecule as the neutral fragment, or with the loss of one or two benzyl or methyl hydrogen atoms giving ions with masses of 118 and 119. The latter even electron ion, for which either alkylated nitrile structures or an iminium ion can be proposed (only one of these is shown in Scheme 1), is the most intense of this group. In **1b** the corresponding loss of an isopropyl methyl group in place of a hydrogen atom is observed. These groups of ions, when summed, represent about one-third of the total ion current in both systems, 33.6% in **1a** and 32.7% in **1b**. Ions at m/e 104, 105 and 106, corresponding to protonated benzonitrile (m/e 104) and related ions are also evident in the



4

SCHEME 1

Schematic Representation of Major Fragmentations in 1a



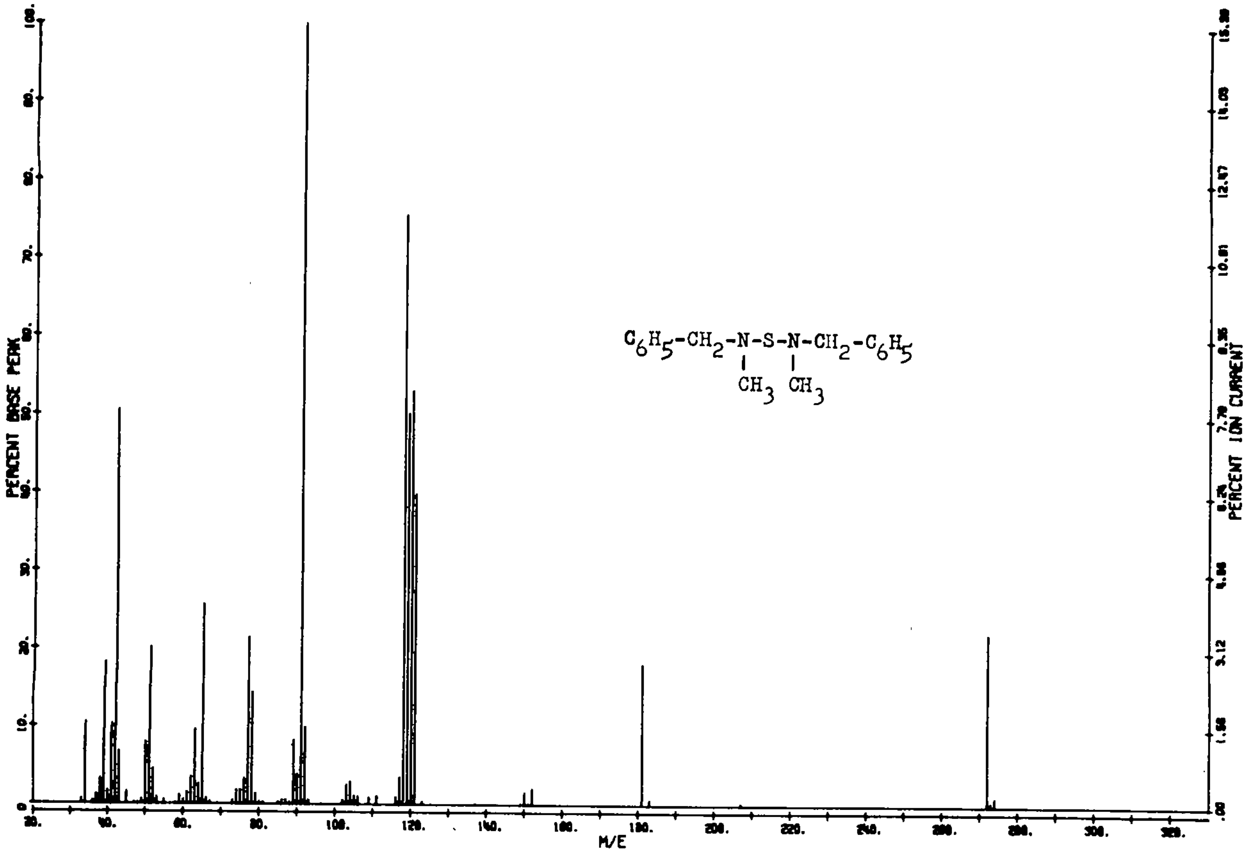
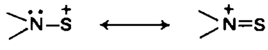


FIGURE 1

Mass spectrum of bis(benzylmethylamine)sulfide spectra of both compounds although they are of lesser importance, accounting for 1.3% t.i.c. (**1a**) and 7.3% t.i.c. (**1b**). These ions may also derive from α-cleavage followed by further fragmentation.

The finding that α-cleavage is the most important fragmentation pathway is in accord with the known behavior of simple alkyl sulfides. These, too, are known to exhibit, as their major ions, sulfur free fragments resulting from α-cleavage when this can result in the formation of stable cations[5,8] Thus, most simple secondary and tertiary sulfides afford the corresponding secondary or tertiary carbonium ions as base peaks.

Sulfur-containing cations resulting from cleavage of the same bonds were also observed. In order to avoid confusion we have termed these fragmentations α_s and β_s cleavages; the subscripts indicating that the charge is associated with the sulfur-containing fragment rather than with the sulfur-free portion as in the α_N and β cleavage fragmentations described above. The most important β_s fragmentation involves the loss of benzyl or tropylium radical. As indicated in Scheme 1, α_s fragmentation can be accompanied by the loss of 2 hydrogen atoms; a possible structure for the final ion m/e 150 involves rearrangement of an alkyl group from nitrogen to sulfur. The fraction of the total ion current resulting from α_s and β_s and cleavage is much smaller than that arising from cleavage of the same bonds with the loss of sulfur in the neutral fragment. Thus, the ratio of α_s/α was only 0.01 for **1a** and 0.03 for **1b**. We had expected that the presence of the nitrogen atom might have led to increased α_s cleavage since the lone pair on nitrogen can help to stabilize the sulfenyl cation (**5a** ↔ **5b**). This kind of overlap has been invoked to account for the nuclear magnetic resonance spectral behavior of sulfenamides.[9,10]



5a **5b**

However, the β_s/α_s cleavage ratios, 8.5 for **1a** and 2.5 for **1b**, were not very different from those which have been observed for simple sulfides: 1.7 for diethyl sulfide, 7.0 for dipropyl sulfide and 4.4 for diisopropyl sulfide.[5] It may be noted that α_s-cleavage in simple sulfides can occur with hydrogen rearrangement (6 → 7).[2] This mechanism for stabilization of the sulfur containing cation may be as effective as overlap with the nitrogen lone pair in **1**.

$$[\mathrm{RCH_2S} \mid \mathrm{R}]^{+\cdot} \xrightarrow{\alpha_s} \mathrm{RCH{=}\overset{+}{S}{-}H}$$

6 **7**

In accord with the behavior of simple sulfides and in contrast with that of the disulfides 2 and trisulfide 3, no $(M{-}S)^{+\cdot}$ peak was observed for either **1a** or **1b**.

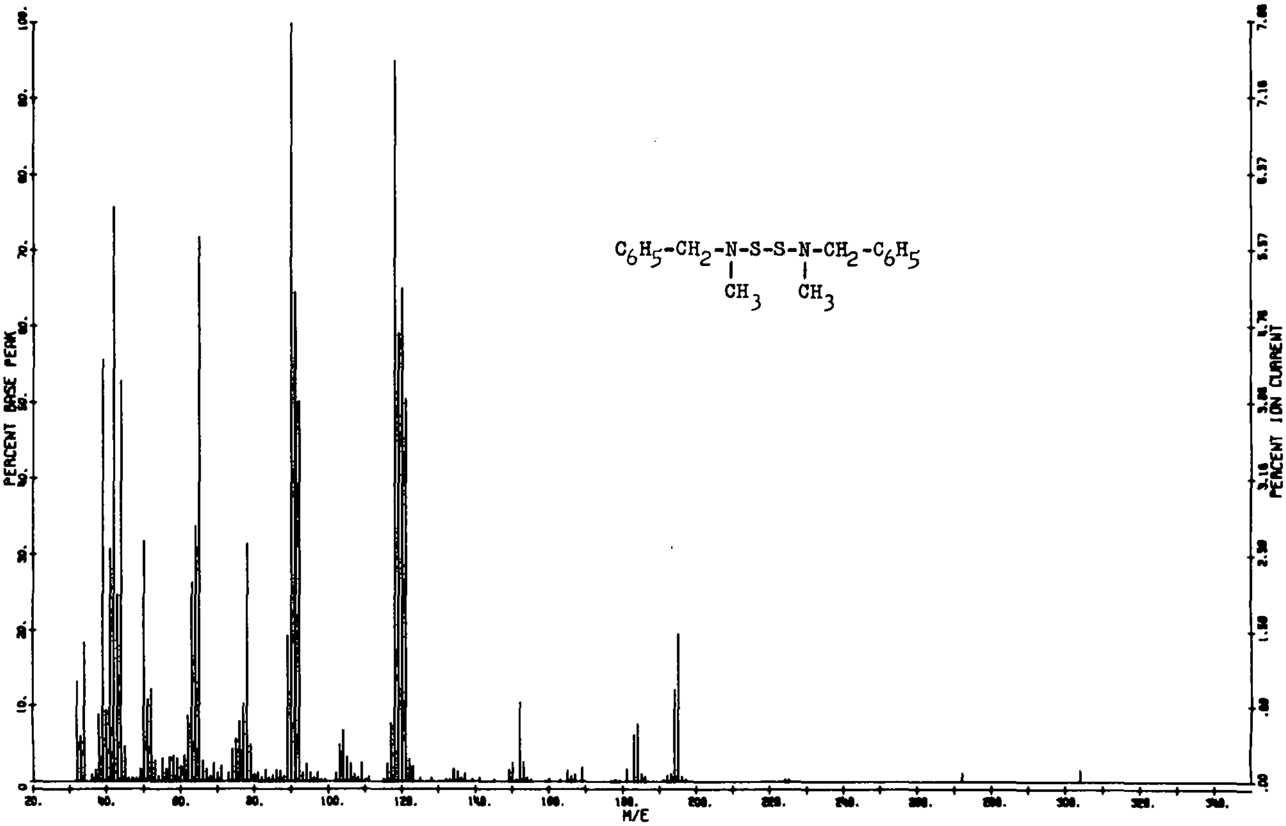


FIGURE 2

Mass spectrum of bis(benzylmethylamine)disulfide

Bisaminedisulfides, 2

The bisaminedisulfides 2 were obtained upon reaction of the appropriate amines with S_2Cl_2 (sulfur monochloride). Like 1a and 1b they exhibit peaks characteristic of α and β cleavage as well as observable molecular ions. In this case, however, loss of sulfur represents an important fragmentation pathway. The $[M-S]^{+\cdot}$ ion accounts for 0.09% t.i.c. for 2a (Figure 2) and 0.42% t.i.c. for 2b. This is not the case for simple dialkyl disulfides,[5] although aryl disulfides also exhibit substantial $[M-S]^{+\cdot}$ fragmentation.[11,12]

As illustrated in Scheme 2, three sorts of α-cleavage can occur for disulfides 2, cleavage of the S–N bond (α_s, leaving the charge on the sulfur containing fragment; α_N leaving the charge on the sulfur free fragment), in addition to cleavage of the S–S bond (α_{sym}). Overall, the combination of the three types of α cleavage contribute 19.7% t.i.c. and 20.4% t.i.c. for 2a and 2b respectively. The most important of these three modes is α_N, while α_{sym}accounts for only 0.80% in 2a and 0.75% in 2b (i.e. about 4% of the total α-cleavage). The α_s/α ratios for 2a and 2b were small, 0.02 and 0.03, about the same as those for 1. Formation of the tropylium ion *via* β-cleavage was less important than for 1, 4.7% and 4.1%. β_s-cleavage was not observed for either disulfide. Fairly intense ions were observed at m/e 64 and m/e 65. While these might be due to $S_2^{+\cdot}$ and HS_2^+, ions of the same mass are produced in the secondary fragmentation of the tropylium ion, e.g. $C_5H_5^+$. The intensity of m/e 65 is fairly high in all of the compounds investigated, supporting the latter assignment. However, m/e 64 is intense only for the disulfides and the trisulfide supporting the assignment of $S_2^{+\cdot}$ for this ion.

Bisaminetrisulfide, 3

Bisaminetrisulfide, 3, prepared by reaction of the amine with S_3Cl_2, exhibits comparable fragmentation to that seen for the sulfide and disulfide analogs, 1a and 2a, including α and β cleavages. Loss of sulfur, resulting in odd electron ions, is also an important process. In agreement with the previous observations, loss of S_1 (0.6% t.i.c.) and S_2 (2.0% t.i.c.) are important while loss of S_3 was not observed.

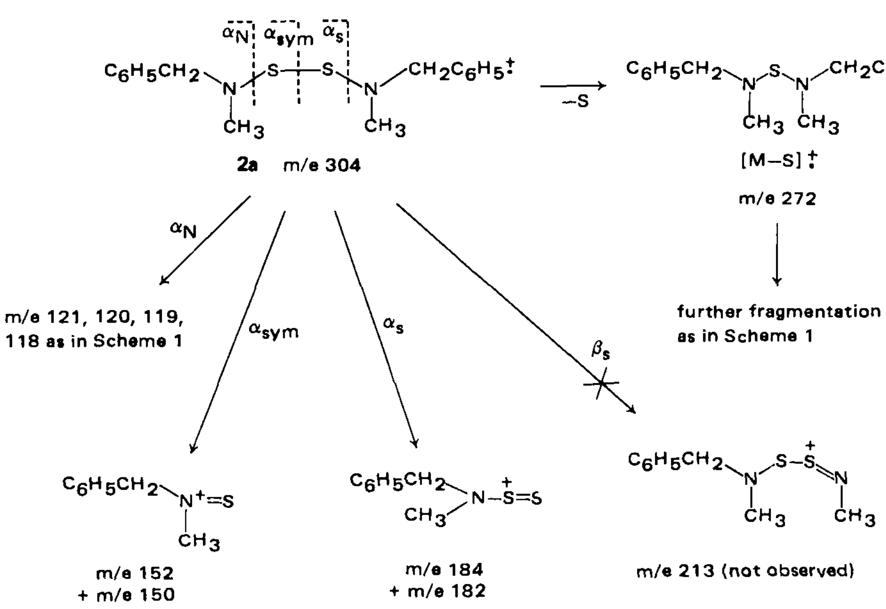
The tropylium ion formed by β-cleavage was again the base peak (21.9% t.i.c.) while β_s-cleavage was again absent. Cleavage of bonds to sulfur (S–S and S–N bonds) leading to sulfur containing cations was quite important, in contrast to the behavior exhibited by 1 and 2. Four such types of cleavage are possible, α_N, α_s, α_{ss} and α_{sss} depending on the number of sulfur atoms in the ion fragment (Scheme 3). The first three of these, appearing at m/e 120, 152 and 184, were fairly intense, while α_{ss} (m/e 216) was not observed.

Experimental Section

Experimental analyses were performed by Midwest Microlab, Inc. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Mass spectra were recorded

SCHEME 2

Schematic Representation of α- and β-cleavage Fragmentations in 2a



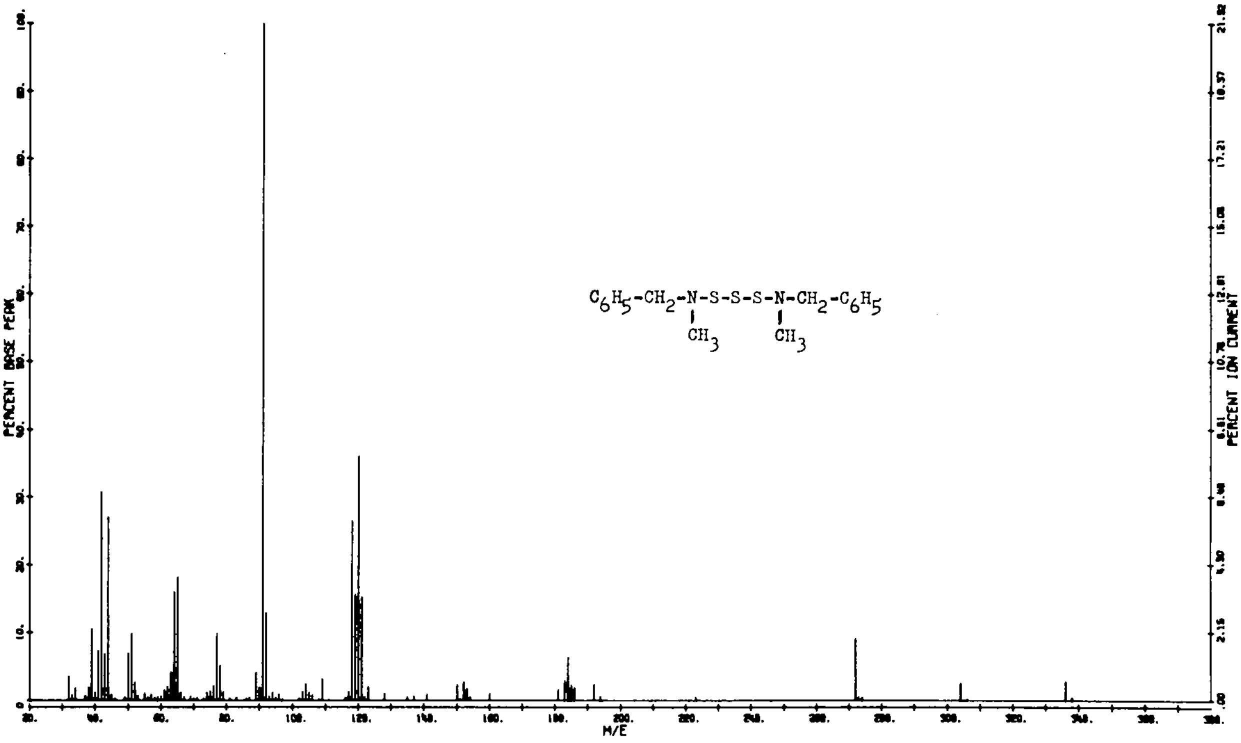
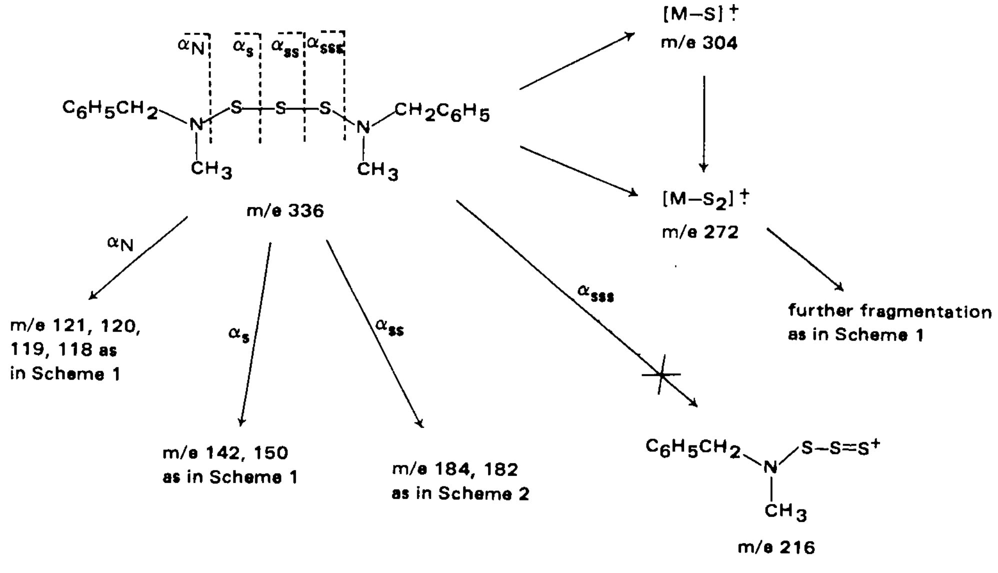


FIGURE 3

Mass spectrum of bis(benzylmethylamine)trisulfide

SCHEME 3

Schematic Representation of α-cleavage Fragmentation in 3



on an AEI mass spectrometer model MS-902 at 70 eV with an accelerating voltage of 8 KV. Nmr spectra were measured on a Varian A-60A spectrometer and are reported in δ-units relative to tetramethylsilane as internal standard.

Bis(N-benzyl-N-alkylamine)sulfides, 1

Commercial SCl_2 was purified by treatment with chlorine gas (to convert any sulfur monochloride present to the dichloride), followed by distillation at 57°C, and stored over a small amount of PCl_5. Purified SCl_2 (0.075 moles) was added dropwise to a cooled (−78°C), stirred solution of the appropriate N-benzyl-N-alkylamine (0.30 moles) in petroleum ether or hexane (400 ml). After being allowed to react at −78°C for one hour, the reaction mixture was allowed to warm to room temperature and filtered. The solvent was removed in vacuo and the crude product recrystallized from methanol. Analytical and nmr spectroscopic data were in agreement with the assigned structures. **1a**, mp 37–38°C; nmr (CCl_4): δ 2.80 *s*, (3H), $C\mathit{H}_3$; δ 4.30 *s*, (2H), $C\mathit{H}_2$, δ 7.18, *s*, (5H), $C_6\mathit{H}_5$.

Anal. Calcd. for $C_{16}H_{20}N_2S$: C, 70.55; H, 7.40; N, 10.28; S, 11.77. Found: C, 70.54; H, 7.35; N, 10.20; S, 11.81.

1b, mp 59–60°C; nmr (CCl_4): δ 1.13, *d*, J = 6.7 Hz, $CH(C\mathit{H}_3)_2$, δ 3.27, heptet, J = 6.7 Hz, $C\mathit{H}(CH_3)_2$, δ 4.16, *s*, $C\mathit{H}_2$, δ 7.16, *s*, $C_6\mathit{H}_5$.

Anal. Calcd. for $C_{20}H_{28}N_2S$: C, 73.12, H, 8.59, N, 8.53, S, 9.76. Found, C, 72.96; H. 8.62; N, 8.41; S, 9.51.

Bis-(N-benzyl-N-alkylamine)disulfides, 2

A solution of sulfur monochloride (S_2Cl_2, 0.0125 moles) in benzene was added dropwise to a stirred benzene solution of the appropriate N-alkyl-N-benzylamine (0.05 moles). After reaction at room temperature for 20 hr the reaction mixture was filtered, washed with water and conc. NaCl, dried over anhydrous magnesium sulfate and the solvent removed by distillation in vacuo. The resultant pale oils gave satisfactory analytical data and had nmr spectra in accord with their structures. **2a**, nmr (toluene-d_8): δ 2.45, *s*, (3H), $C\mathit{H}_3$, δ 3.81, *s*, (2H), $C\mathit{H}_2$; δ 7.16, s, (5H), $C_6\mathit{H}_5$.

Anal. Calcd for $C_{16}H_{20}N_2S_2$: C, 63.12; H, 6.62; N, 9.20. Found: C, 63.38; H, 6.48; N, 8.92.

2b, nmr (neat), δ 1.02, *d*, j = 6.2, $CH(C\mathit{H}_3)_2$; δ 3.05, *heptet*, J = 6.1, $C\mathit{H}(CH_3)_2$; δ 4.14, *s*, $C\mathit{H}_2$; δ 7.16, *s*, C_6H_5.

Anal. Calcd for $C_{20}H_{28}N_2S_2$: C, 66.62; H, 7.83; N, 7.77; S, 17.78. Found, C, 66.90; H, 7.81; N, 7.63; S, 17.52.

Bis(N-benzyl-N-methylamine)trisulfide, 3

A mixture of sulfur chlorides was obtained by treatment of sulfur monochloride with I_2 followed by distillation to obtain a fraction rich in S_3Cl_2. The mixture of sulfur chlorides (0.11 moles) was added dropwise to a cooled (0°C) stirred solution of benzylmethylamine (0.4 moles) in petroleum ether (500 ml). After reaction for 1 hr at 0°C, the reaction mixture was filtered and the solvent removed in vacuo. The resulting mixture was chromatographed and the fraction corresponding to trisulfide was recrystallized from hexane, mp. 85–86°C. Nmr (toluene-d_8): δ 2.54, *s*, (3H), $C\mathit{H}_3$; δ 3.92, *s*, (2H), $CH_2\ C_6\mathit{H}_5$; δ 7.10, *s*, (5H), $C_6\mathit{H}_5$.

Anal. Calcd for $C_{16}H_{20}N_2S_3$: C, 57.11; H, 5.99; N, 8.32; S, 28.58. Found: C, 57.13; H, 6.09; N, 8.45; S, 28.73.

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