complex, 67722-21-8; [2-^{15}N]phenylthiatriazole, 67688-23-7; [4-^{15}N]phenylthiatriazole, 67688-24-8.

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Methylthiolation of 2,3-Bis(methylthio)butanes

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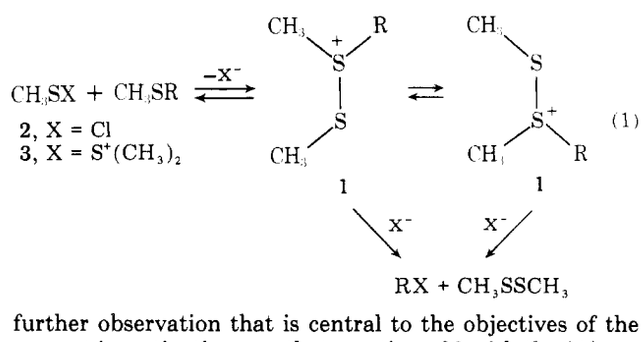
Reaction of dimethyl(methylthio)sulfonium fluoroborate with *meso*- and *dl*-2,3-bis(methylthio)butane appears to be a straightforward methylation of the sulfide to give a sulfonium salt of *retained* configuration. However, the product is actually formed in a multistep reaction involving C–S cleavage in the starting sulfide rather than in the starting salt. The initial step involves methylthiolation of 2,3-bis(methylthio)butane by the salt. This step reversibly forms methyl sulfide and a thiosulfonium ion that dissociates reversibly and stereospecifically to methyl disulfide and a thiiranium (episulfonium) ion with the result that methylthio exchange occurs. The thiiranium ion intermediate is trapped irreversibly by methyl sulfide to give the observed products of retained configuration.

In a previous study on the reaction of sulfides with sulfenyl compounds, we reported a degenerate rearrangement of an alkylthiosulfonium ion **1**.[1] For example, an ion of this type is evidently formed as an intermediate in the reaction of methyl 1-phenylethyl sulfide with methylthiolating agents such as methanesulfenyl chloride (**2**) and dimethyl(methylthio)sulfonium fluoroborate (**3**) (eq 1). The intermediate **1** is formed rapidly and reversibly in a displacement reaction at the sulfenyl sulfur of **3**.[2-4] Subsequently, **1** reacts irreversibly with the displaced nucleophile X to give the observed products. The rearrangement step was inferred from labeling studies in which a SCD_3 group in the starting sulfide was found to exchange with the SCH_3 group of the sulfenyl reagent. A



(1)

further observation that is central to the objectives of the current investigation was that reaction of **3** with the (+) en-

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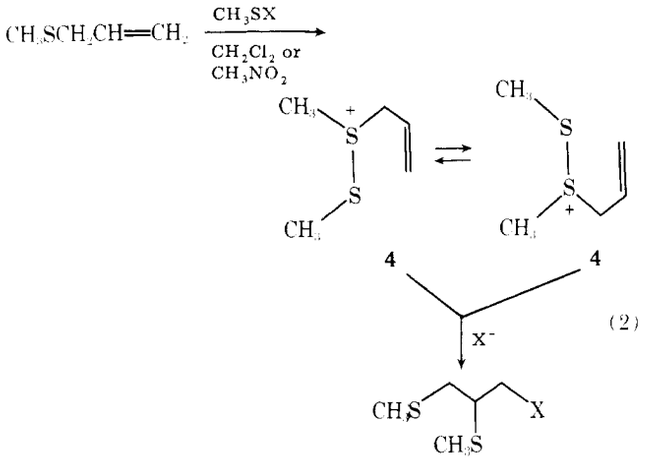
antiomer of chiral methyl 1-phenylethyl sulfide led to racemization of the sulfide at a rate faster than product was formed.[1] It was inferred from this result that the rearrangement step was a preequilibrium step involving an achiral transition state or intermediate.

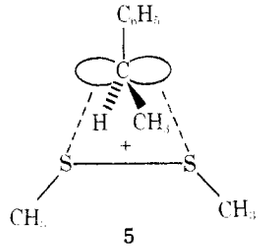
We subsequently found that allylic sulfides also react with sulfenyl compounds by alkylthiolation at sulfur and that the intermediate sulfonium ion **4** undergoes a degenerate 2,3 sigmatropic rearrangement (eq 2) prior to the product-forming



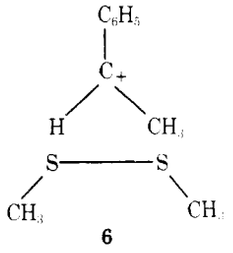
(2)

X = Cl, $S^+(CH_3)_2$

step.[5] Related rearrangements of allylic groups are remarkably widespread and include the Stevens,[6] Pummerer,[7] Meisenheimer,[8] and Wittig rearrangements[9] as well as the sulfoxide–sulfenate rearrangements.[10] They are symmetry allowed six-electron pericyclic transformations.[11] By contrast, the 1,2 rearrangement of **1** (eq 1) would be a symmetry forbidden four-electron process by way of a Hückel-type transition state. Although 1,2 rearrangements of this type are not uncommon, none appear to be truly concerted.[11] A symmetry allowed process requires a transition state that would lead to *inversion* of configuration at carbon. In the case of **1**, a *reversible* rearrangement through a pericyclic transition state with inversion of configuration, as in **5**, could account for the observed loss of configuration at the chiral center of the migrating group. Alternatively, and perhaps more likely, the rearrangement could be a dissociative process by way of methyl disulfide and an achiral cation, as in **6**.



5

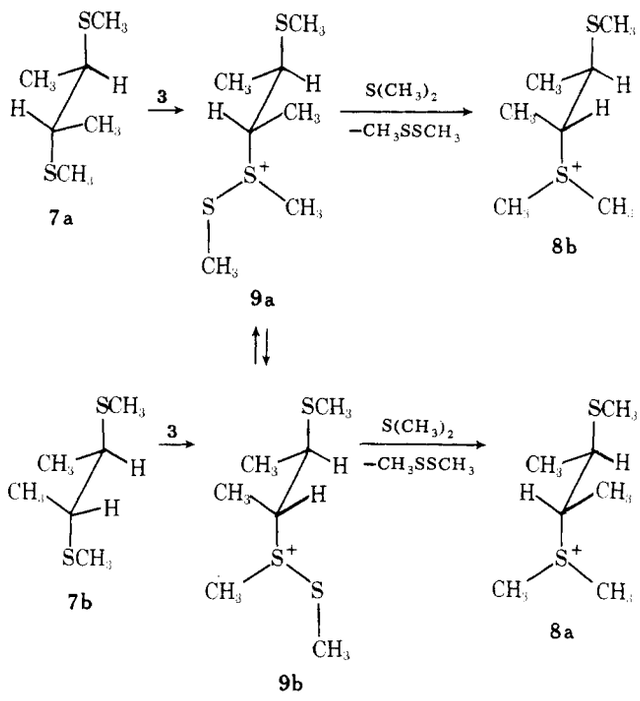


6

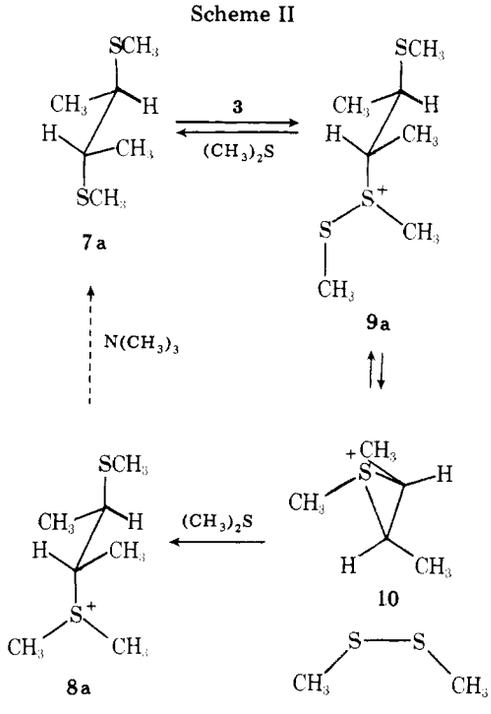
As a test of the pericyclic vs. the dissociative pathways for rearrangement in alkylthiosulfonium ions, a simple experiment was designed, which we now describe. The reaction of interest is the methylthiolation of meso and *dl* forms of 2,3-bis(methylthio)butane, **7a** and **7b**. Based on analogy with other sulfides, reaction of **7** with the sulfenyl salt **3** was expected to produce an alkyl dimethylsulfonium salt **8** by way of an intermediate thiosulfonium salt **9**. Should rearrangement of the intermediate **9** occur by way of a pericyclic transition state, the degeneracy is removed and inversion of configuration would occur at every pass, which would lead to a mixture of diastereomeric sulfonium salts **8a** and **8b** from either **7a** or **7b** (Scheme I).

Alternatively, if methylthiolation of **7** at sulfur to give **9** leads to a dissociative rearrangement by heterolysis of the C–S^+ bond, the expected products are those of net retention of configuration at the reacting carbon (Scheme II). This route anticipates that the neighboring methylthio group will participate in the heterolysis step, for which there is ample precedent in related displacement reactions.[12] We therefore studied the stereochemistry of the methylation of **7** with the sulfenyl salt **3** in order to assess whether 1,2 rearrangement of alkylthiosulfonium ions is a concerted inversion process or otherwise.

Scheme I



Scheme II



Results and Conclusions

meso-2,3-Bis(methylthio)butane (**7a**) was prepared from *trans*-2-butene in two steps. In the first step, antarafacial

Table I. NMR Spectral Parameters of Reactants and Products[a]

compd	δ_{SCH_3}[b]	δ_{CH_3}	δ_{CH}	$\delta_{S^+(CH_3)_2}$
meso-**7a**	2.11 (6, s)	1.35 (6, d)[c]	2.80 (2, m)	
dl-**7b**	2.12 (6, s)	1.27 (6, d)[c]	2.96 (2, m)	
7[d]	2.12 (4.8, s)	1.27 (6, d)	2.96 (2, m)	
7[e]	2.12 (4.2, s)	1.27 (6, d)	2.96 (2, m)	
8a	2.25 (3, s)	1.53 (3, d)[c]	3.35 (1, m)	2.98 (3, s)
		1.62 (3, d)[c]	3.90 (1, m)	3.02 (3, s)
8b	2.23 (3, s)	1.47 (3, d)[c]	3.25 (1, m)	2.96 (3, s)
		1.63 (3, d)	3.83 (1, m)	2.98 (3, s)
8[f]	2.23 (2.5, s)	1.47 (3, d)	3.25 (1, m)	2.96 (1.5, s)
		1.63 (3, d)	3.83 (1, m)	2.98 (1.5, s)

[a] In CD_3NO_2. [b] Chemical shifts are in parts per million downfield from Me_4Si; signal area and multiplicity are in parentheses. [c] J = 7 Hz. [d] Recovered **7b** from the reaction of **7b** with **3**-d_6; MS gave M^+ at *m/e* 150, 153, and 156 in a ratio of 71.5:25.1:3.4. [e] Obtained from demethylation of **8** derived from the reaction of **7b** with **3**-d_6; MS gave M^+ at *m/e* 150, 153, and 156 in a ratio of 50.6:43.8:5.6. [f] Product from the reaction of **7b** with **3**-d_6.

addition of 1 equiv of **3** to *trans*-2-butene in nitromethane gave the *RS* sulfonium salt **8a** in good yield.[13] In the second step, demethylation of **8a** to **7a** was achieved by displacement with excess trimethylamine. In a like manner, addition of **3** to *cis*-2-butene gave (*RR*)- and (*SS*)-**8b**, which on demethylation gave racemic 2,3-bis(methylthio)butane (**7b**).

Reaction of the meso sulfide **7a** with an equivalent of **3** in nitromethane at 0 °C gave, as anticipated, methyl disulfide and a sulfonium salt as the only reaction products. The salt was isolated and shown to be identical with **8a** obtained from *trans*-2-butene and **3** by direct addition. No evidence was found for the formation of the diastereomeric salt **8b**, even though concentrations of **8b** as low as 3% could be detected easily in mixtures with **8a** by NMR (the chemical shifts of the diastereotopic $S^+(CH_3)_2$ groups in **8a** are well resolved from those of **8b**; Table I). Also, demethylation of the product salt with trimethylamine gave *meso*-2,3-bis(methylthio)butane (**7a**) with no detectable amount of the *dl* isomer by GC analysis.

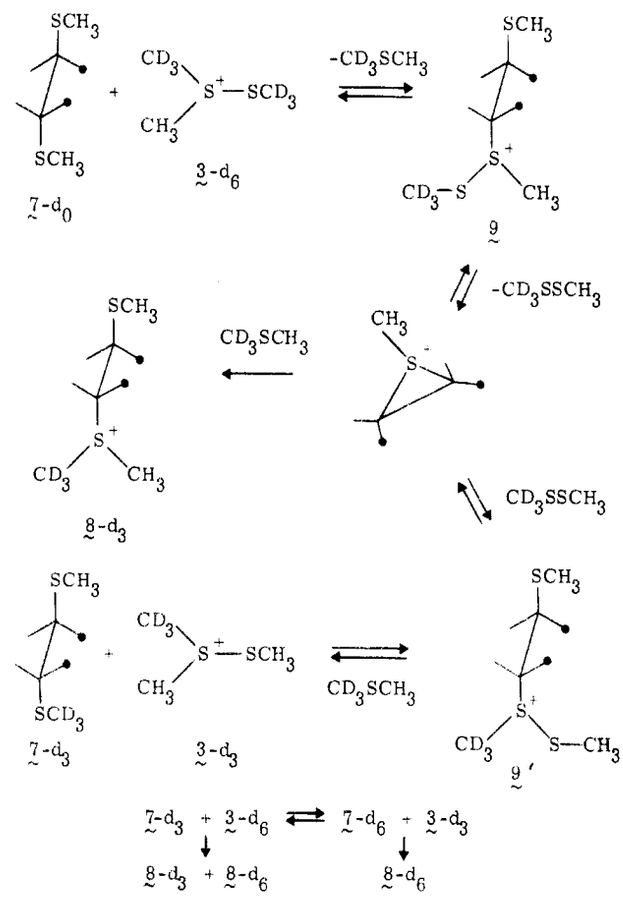
A similar series of experiments starting with *dl*-2,3-bis(methylthio)butane (**7b**) gave entirely comparable results. Thus, methylthiolation of **7b** with **3** gave methyl disulfide and the sulfonium salt **8b** of retained configuration. No evidence was found for the presence of the diastereomer **8a**, and demethylation led only to **7b**.

While these results are certainly inconsistent with Scheme I, they provide equivocal support for the process of Scheme II because the rearrangement in question is not evident. That is to say, the stereochemical outcome of the reaction does not require that rearrangement occur. The products can be very simply explained as the result of S_N2 attack of the sulfide on a methyl group of the salt. If this were the case, the C–S bonds in the sulfide would not participate directly in the reaction and retention of configuration would be the expected outcome. Alternatively, the sequence of steps in Scheme II may be a valid description of the reaction, but if intermediate **9** dissociates *irreversibly*, rearrangement will not be observed.

In order to distinguish between direct methylation of the sulfide by the salt as opposed to the more involved alkylation sequence of Scheme II, it proved necessary to employ the deuterium-labeled salt **3**-d_6 prepared from CD_3SSCD_3 and trimethyloxonium fluoroborate. We have shown previously[14] that a degenerate 1,2 rearrangement of methyl from S^+ to S does not occur in **3** under the reaction conditions employed in this work. Therefore, with the integrity of the methyl labels assured, **3**-d_6 was chosen as a suitable reagent with which to probe further the nature of the reaction between **7** and **3**.

The alternate pathways suggested can be distinguished by the degree of incorporation of SCD_3 into the products and starting reagents. Thus, direct methylation of **7** with **3**-d_6 would be expected to give comparable amounts of **8**-d_0 and

Scheme III[a]



[a] Filled-in circles (•) represent CH_3.

8-d_3 and no exchange of SCH_3 for SCD_3 in the starting sulfide. Alkylation according to Scheme II would lead only to **8**-d_3, provided that **9** dissociates *irreversibly*. However, a mixture of **8**-d_3, **8**-d_6, **7**-d_0, **7**-d_3, and **7**-d_6 would be formed if both formation and dissociation of **9** are *reversible* (Scheme III). Accordingly, a slight excess of **7b** was reacted with **3**-d_6, and the excess sulfide was recovered and analyzed. By NMR, the intensity of the *S*-methyl singlet of recovered **7** was only 80% of that of the *C*-methyl doublet, indicating some 20% deuterium incorporation. By mass spectrometry, the appearance of molecular ions at *m/e* 150, 153, and 156 in a ratio of 72:25:3 confirms the presence of **7b**-d_0, -d_3, and -d_6 and implies about

16% deuterium incorporation. The NMR and mass spectral results are in reasonable agreement.

The product salt **8b** obtained in the reaction of **7b** with labeled **3** showed that the intensity of the neutral *S*-methyl ^{1}H NMR resonance was only 83% of the sulfonium methyl resonance, indicating the presence of 17% *neutral* SCD_3 groups. (In the absence of exchange, the SCH_3/S^+CH_3 ratio is expected to be 1:1.) No deuterium exchange was evident in the positive *S*-methyl groups because the intensity ratio of S^+CH_3 to $C\text{-}CH_3$ at C-3 was 1:1, which is within experimental error of that expected in the absence of exchange.

Treatment of the salt product **8** with excess trimethylamine gave the neutral sulfide **7b**, which by NMR analysis showed that 30% of the *S*-methyl groups were present as SCD_3. Mass spectral analysis showed the presence of molecular ions at *m/e* 150, 153, and 156 in a ratio of 51:44:6, corresponding to ions from **7b**-d_0, -d_3, and -d_6, which implies 28% incorporation of SCD_3. Again, the NMR and mass spectral results agree within experimental error.

Clearly, the reaction is not a simple S_N2 displacement. The labeling results are entirely consistent with the sequence in Scheme III, in which the intermediate thiosulfonium ion is formed *reversibly* from the starting reagents and dissociates *reversibly* prior to the product-forming step. It is the reversible dissociation step that amounts to a 1,2 rearrangement of the type specified in eq 1.

Summary

The fact that extensive methylthio exchange occurs in the reaction of the labeled sulfenyl salt **3**-d_6 with 2,3-bis(methylthio)butane means that the product **8** is not formed by direct methylation at sulfur. Rather, the reaction is initially one of methylthiolation at sulfur to give an intermediate alkylthiosulfonium ion **9** that rearranges with *retention* of configuration by migration of the alkyl group from positive sulfur to neutral sulfur. The stereochemical result eliminates the interesting possibility of concerted rearrangement with inversion by way of a pericyclic Möbius transition state. Thus, the four-electron 1,2 sigmatropic migration with inversion of configuration continues to elude detection. The present rearrangement is best explained as a reversible dissociation of **9** (inversion) by way of the thiiranium ion **10**, which on reaction with methyl sulfide rather than disulfide is trapped irreversibly (inversion) as the observed product **8** with net retention of configuration.

Experimental Section

2,3-Bis(methylthio)butane (7) was prepared as either the *dl* or meso diastereomer in two steps by the addition of dimethyl(methylthio)sulfonium fluoroborate **3**, respectively, to an excess of either *cis*- or *trans*-2-butene in nitromethane at 0 °C followed by demethylation of the sulfonium salt product, **8a** or **8b**, with excess trimethylamine. The procedure followed in the addition step was that of Helmkamp and co-workers,[13] who have established that **3** reacts with alkenes by a stereospecific antarafacial addition. The diastereomeric salts, **8a** from *trans*-2-butene and **8b** from *cis*-2-butene, can be isolated as crystalline solids in yields up to 95%. They can be distinguished most easily by their respective NMR spectra (Table I). Demethylation of **8** was accomplished by condensing excess trimethylamine into a stirred solution of either **8a** or **8b** in nitromethane at 0 °C. White crystals of tetramethylammonium fluoroborate separated almost immediately. Stirring was continued for 8–12 h at room temperature, after which excess amine and the solvent were evaporated under vacuum. The residual oil was dissolved in ether or dichloromethane and extracted twice with 2 N hydrochloric acid and twice with water. The organic layer was dried ($MgSO_4$) and distilled to give either **7a** or **7b** (bp 71–73 °C, 6 mm).[13] Methylation of **7a** or **7b** with trimethyloxonium fluoroborate in dichloromethane regenerated the starting sulfonium salt, **8a** or **8b**, uncontaminated by the other diastereomer.

Reaction of *meso*-Bis(methylthio)butane (7a) with Dimethyl(methylthio)sulfonium Fluoroborate (3). The reaction was performed by adding a solution of **3** in nitromethane (1 g per mL) to a stirred solution containing an excess of **7a** in nitromethane (1 g per mL) at 0–5 °C. The ratio of sulfide to salt was varied from 1.3:1 to 2:1 equiv with comparable results. Stirring was continued for at least 1 h at room temperature, after which the solvent and unreacted sulfide were collected by vacuum flash distillation. The distillate was analyzed by MS, GC, and NMR, which confirmed that no isomerization of **7a** to **7b** had occurred during reaction. The residual solid was recrystallized from acetone–ether and analyzed by NMR (Table I). The product **8a**, mp 58–60 °C, was obtained in 74% isolated yield and was identical with that obtained by direct methylation of **7a** with trimethyloxonium fluoroborate. The recrystallized salt **8a** was reconverted to **7a** by demethylation with excess trimethylamine, as described above. No **7b** was detected in the product.

A comparable reaction of the *dl* diastereomer **7b** with **3** in nitromethane gave **8b** only, mp 96–97 °C, which on demethylation reverted to **7b** free of **7a**.

The deuterium-labeled salt **3**-d_6 was prepared as previously reported.[14] The reaction of **3**-d_6 with **7b** was performed as described for the unlabeled salt using 1:3 molar equiv of **7b**/**3**, and the product salt was demethylated as before. Both the recovered sulfide and the product salt were analyzed for deuterium content by NMR and/or GC. The results are summarized in Table I.

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Registry No.—**3**, 5799-67-7; *meso*-**7a**, 1556-19-0; *dl*-**7b**, 67889-87-6; **8a**, 67827-34-3; **8b**, 67827-35-4, *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

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