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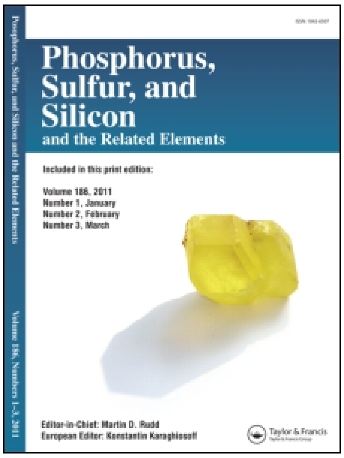

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Reaction of Epoxides with (Alkylthio)methyl Chloride

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Reaction of Epoxides with (Alkylthio)methyl Chloride

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The reaction of (methylthio)methylchloride with 1,2-epoxybutane and styrene oxide furnishes eleven and eight compounds, respectively. The probable mechanism of their formation and their mass spectral characterization are presented in this article.

Keywords Epoxide ring cleavage; formation of novel compounds; free radical reactions; (methylthio)methylchloride 1,2-epoxybutane; styrene oxide

Oxiranes comprise of an extremely versatile group of intermediates and as such have attracted considerable attention.[1] Due to their readlly availability and exceptional reactivity, the epoxides have found varied applications in synthetic organic chemistry. The oxirane ring can be opened under almost all conditions: electrophilic, nucleophilic, neutral, gas-phase, thermal, and free radical conditions (Figure 1(a)).[1a] The structures of the radical species generated from the oxiranes and thiiranes have been discussed (Figure 1(b)).[2] An excellent review on the preparation and synthetic applications of the oxiranes has appeared.[1f] Recently we investigated the free-radical cleavage of styrene oxide with

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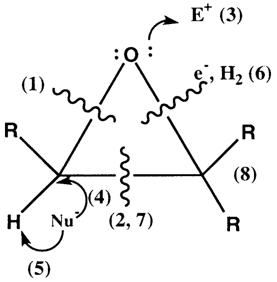

FIGURE 1(a) Types of oxirane cleavages and reactions. (1. 2) Homolytic cleavages (free radical, photolytic, and thermal); (3) electrophilic attack on the oxygen ring; (4) nucleophilic attack on the carbon ring; (5) nucleophilic attack on the hydrogen ring; (6) reactions with electrons and surface reactions; (7) cycloadditions; and (8) reactions of the substituent.

trifluoromethylthiocopper and dimethyl hydrogenphosphonate and reported the formation of products arising from the C—C and C—O bond fission.[3–6] Phosphorus compounds or *in situ*-generated intermediates are known to react with oxiranes as well.[7,8]

In continuation of our interest in the chemistry of the oxirane cleavage reactions[3–6] and with a view to examine whether this reaction can be applied to the decontamination and destruction of mustard, a blister agent,[9] the oxirane-ring-opening in the presence of (methylthio)methylchloride or (chloromethyl) methyl sulfide, has been examined. This article describes the probable mechanism of the formation of the various novel compounds formed during the course of the reaction and their GC-MS characterization.

RESULTS AND DISCUSSION

Recently we have shown that the oxirane ring can be cleaved with dimethyl hydrogen phosphonate[4,5] and trifluoromethylthiocoper and trifluoromethyl-sulfenyl chloride.[3,6] Sulfonium salts,[10a] trimethylsilyl halides,[10b] pheny trimethyl-silyl sulfides,[10c] and trimethylsilyl

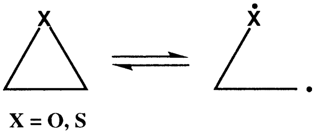

FIGURE 1(b) Structure of oxirane and thiirane and their diradicl equivalents.

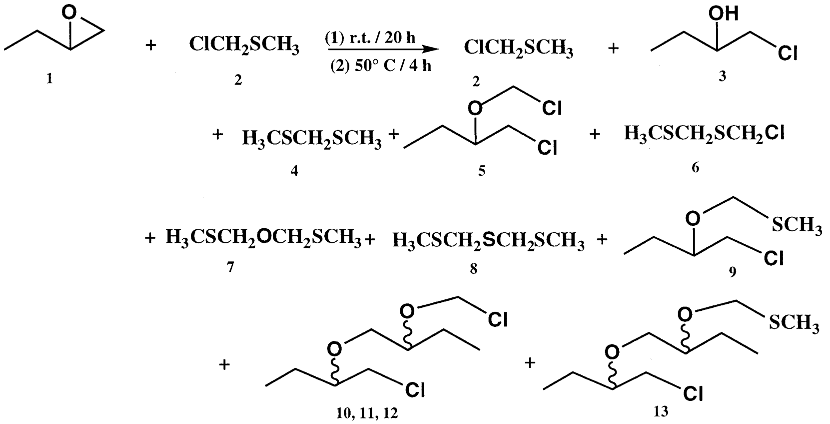

FIGURE 2 Products of the reaction of 1.2-epoxybutane with CH_3SCH_2Cl.

cyanides[10d–e] all have been used to cleave the oxirane ring. More interestingly, enantio-selective oxirane-ring-opening reactions have been described.[10g–h] It was considered interesting to investigate whether inexpensive oxiranes, such as ethylene oxide, can be employed successfully in the decontamination and destruction of mustard, [bis-(2-chloroethyl)sulfide], a known blister agent.[9] This expectation was supported by the fact that the oxiranes react with almost all kinds of reagents.[1]

The mixture of 1, 2-epoxybutane (**1**) and (methylthio)methylchloride (2) was stirred under dry nitrogen at an ambient temperature for 20 h and then heated at 50°C for 4 h. After the reaction mixture had come to room temperature, it was analyzed using GC and found to contain eleven components. This inference was further confirmed by the GC-MS analysis. A careful examination of the mass spectral breakdown pattern permitted the characterization of the following compounds (Figure 2): (1) (methylthio)methylchloride (**2**), (2) 1-chloro-2-hydroxybutane, (**3**), (3) bis-(methylthio)methane (**4**), (4) 1-chloro-2-(chloromethoxy)butane (**5**), (5) (chloromethylthio)(methylthio)methane (**6**), (6) bis-(methylthiomethyl) ether (**7**), (7) bis-(methylthiomethyl) sulfide (**8**), (8) 1-chloro-2-(methylthiomethoxy)butane (**9**), (9) three isomers (**10–12**) of 1-chlorobutyl-2-[(2-chloromethoxy)butyl] ether, and (10) 2-chlorobutyl-2-[(2-methylthiomethoxy)butyl] ether (**13**). The formation of the previously cited compounds can be directly attributed to the presence and participation of the free-radical reactions. This inference draws additional support from the observation on the formation of the thiyl radicals from sulfenyl halides.[11]

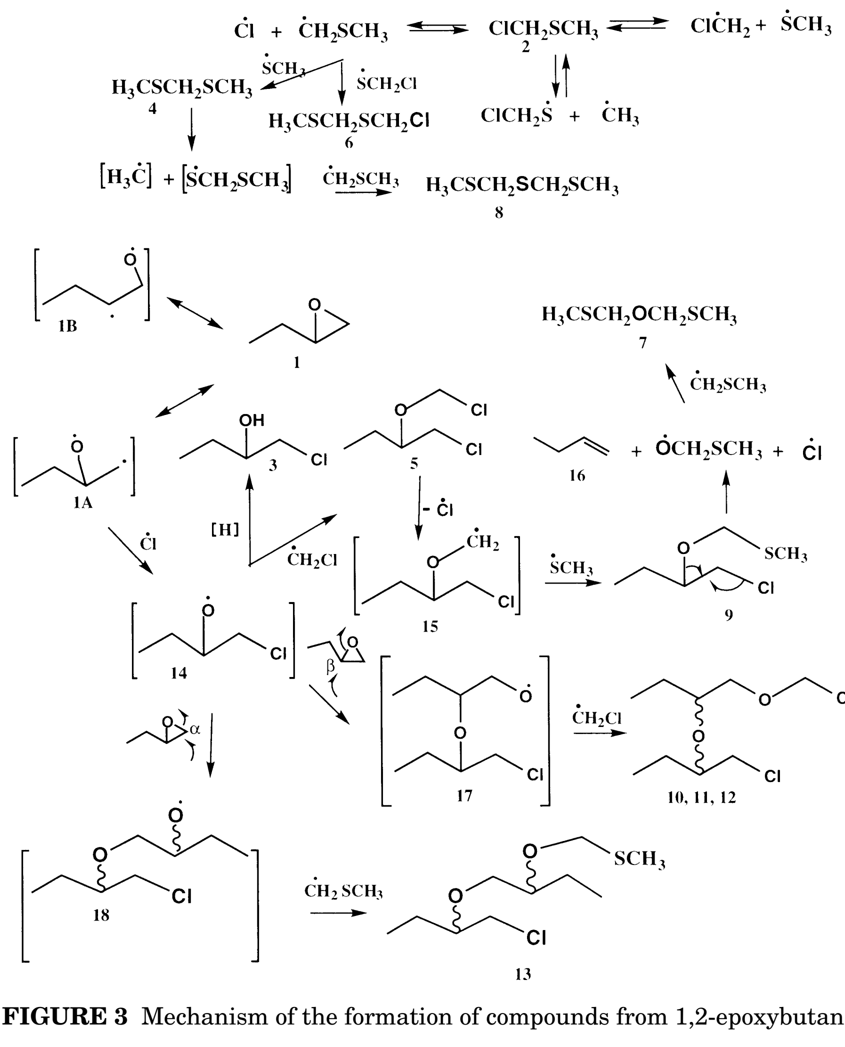

FIGURE 3 Mechanism of the formation of compounds from 1,2-epoxybutane.

Figure 3 endeavors to rationalize the probable mechanism of the formation of compounds **3–13**. It is conceivable that compound **2** undergoes free-radical fission according two pathways; first, to form chloromethyl and methylthiyl radicals, and second, to furnish chlorine and (methylthiomethyl) radicals. The combination of methylthiyl and (methylthio)methyl radicals results in the formation of bis-(methylthio)methane (**4**), while the reaction of (methylthio-methyl) and chlormethylthiyl radicals yields (chloromethylthio) (methylthio)-methane (**6**). Copmound **4** can undergo free-radical dissociation to give methyl and (methylthio)methylthiyl radicals. The latter then reacts with a (methylthio)methyl radical to form bis-(methylthiomethyl)sulfide (**8**). The substrate itself can undergo free radical fission to form diradical species, **1A** and **1B** (cf. ref. 2 and Figure 1(b)). The diradical **1A** thus generated can react with a $Cl^{\cdot}$ radical to form intermediate **14**, which has two options open to it: either to abstract hydrogen to form **3** or to react with $^{\cdot}CH_2Cl$ radical to yield **5**. Both **3** and **5** were characterized as products of the the reaction. The intermediate **14** also can arise from the direct attack of the $Cl^{\cdot}$ radical on the substrate (**1**). Compound **5** fragments of the $Cl^{\cdot}$ radical yield intermediate **15**, which then joins with the methylthiyl radical to furnish **9**, which in turn undergoes fission to form butylene (**16**) and $Cl^{\cdot}$ and (methylthio)methoxyl radicals. The latter then reacts with (methylthiyl)methyl radical to give bis-(methylthio)methyl ether (**7**).

The attack on the β-carbon atom of **1** by the radical intermediate (**14**) leads to the intermediate **17**, which would in turn react with the $^{\cdot}CH_2Cl$ radical to give three stereomers, namely **10**, **11**, and **12**. If on the other hand, **14** attacks the α-carbon, then that results in radical intermediate **18**, which then can join with a methylthiomethyl radical to yield compound **13**. In view of the similar mass spectral fragmentation patterns, it was not possible to unambiguously assign correct structures to the three isomers. If radical intermediate 14, formed either by the attack of $^{\cdot}Cl$ on the α-carbon of **1** or arising from the combination of $^{\cdot}Cl$ and **1A**, attacks the β-carbon of **1**, then that would lead to **17**, which on reacting with $^{\cdot}CH_2Cl$, furnishes the three isomeric compounds **10**, **11**, and **12**. If on the other hand **14** attacks the α-carbon, then that would result in **18**, which on reacting with (methylthio)methyl radical, goes on to give compound**13**. As previously mentioned, compounds **3**, **5**, **7**, and **9** have their origin in the intermediate **14**.

The mass spectral fragmentation behavior of the compounds **3–13** is rationalized in Table I. All compounds containing chlorine exhibit isotopic peaks as expected from their natural abundance. The fragmentation behavior of the compounds cited in the narrative is straightforward.

The substitution of **1** with styrene oxide (**19**) in the previously mentioned reaction with (methylthio)methylchloride (**2**) gave the following 10 compounds (cf. Figure 4): (1) bis-(chloromethyl)sulfide (**20**), (2) bis-(meththylthio)methane (**4**), (3) bis-(methylthio)ether (**7**), (4) benzaldehyde (**21**), (5) phenylacetaldehyde (**22**), (6) 1-chloro-2-hydroxy-2-phenylethane (**23**), (7) 1-hydroxy-2-chloro-2-phenylethane (**24**), (8) 1-hydroxy-2-methylthio-2-phenylethane (**25**), (9) 1-chloro-1-phenyl-2-(chloromethoxy)ethane (**26**), and (10) 1-chloro-1-phenyl-2-[(methylthio)methoxy]-ethane (**27**).

TABLE I Products Derived From Methylthio Methyl Chloride and 1, 2-Epoxybutane

1. (Methylthio)methyl chloride (**2**, r.t. = 2.06 min, 15.1%); M^+ = 96 (100%, ^{37}Cl:98); 81 (M-CH_3); 61 (M-Cl, 98%); 59 (C_2H_3S); 47 (SCH_3) and 46 (SCH_2).
2. 1-chloro-2-hydroxybutane (**3**, r.t. = 2.4 min, 5.7%); M^+ = 108 (not seen). 79 (M-C_2H_5); 59 (M-CH_2Cl, 100%); 55 (C_4H_7) and 49 (CH_2Cl).
3. Bis-(methylthio)methane (**4**, r.t. = 3.13 min, 34.2%): M^+ = 108 (100%); 93 (M-CH_3); 78 (93-CH_3 or CH_2S_2); 61 (CH_3SCH_2); 59 (C_2H_3S); 47 (SCH_3) and 46 (SCH_2).
4. 1-chloro-2-(chloromethoxy)butane (**5**, r.t. = 4. 28 min, 6.3%): M^+ = 156 (two chlorine isotope pattern seen); 127 (M-C_2H_5); 121 (M-Cl); 107 (M-CH_2Cl, 100%); 91 (107-O); 85 (121-HCl); 77 (91-CH_2); 71 (107-HCl); 55 (C_4H_7) and 49 (CH_2Cl).
5. (Chloromethylthio)(methylthio)methane (**6**, r.t. = 5.1 min, 0.4%): M^+ = 142 (100%, ^{37}Cl seen); 107 (M-Cl); 95 (M-SCH_3); 61 (CH_2SCH_3); 59 (C_2H_3S) and 49 (CH_2Cl).
6. Bis-(methylthiomethyl) ether (**7**, r.t. = 6. 13 min, 2.0%): M^+ = 138 (100%); 91 (M-SCH_3); 76 (91-CH_3); 64 (SS); 59 (C_2H_3S) and 47 (SCH_3).
7. Bis-(methylthiomethyl) sulfide (**8**, r.t. = 6. 87 min, 0.3%): M^+ = 154 (100%); 106 (M-$HSCH_3$); 93 (M-CH_2SCH_3); 78 (93-CH_3) and 61 (CH_2SCH_3).
8. 1-chloro-2-(methylthiomethoxy)butane (**9**, r.t. = 5. 73 min, 3.0%): M^+ = 168 (^{37}Cl seen); 132 (M-HCl); 121 (M-SCH_3); 119 (M-CH_2Cl); 103 (132-C_2H_5); 93 (M-CH_2-CH_2SCH_3); 91 (M-OCH_2SCH_3); 77 (OCH_2SCH_3); 75 (C_3H_4Cl); 63 (CH_2OS); 61 (CH_2SCH_3); 56(C_4H_6); 55 (C_4H_7, 100%); and 49 (CH_2Cl).
9. 1-chlorobutyl [(2-chloromethoxy)butyl] ether (**10**, r.t. = 8. 33 min, 22.0%): M^+ = 228 (two chlorine isotope pattern seen); 179 (M-CH_2Cl); 121 (179-C_3H_6O, 100%); 91 (121-OCH_2); 91 (121-OCH_2); 85 (121-HCl); 59 (C_3H_7O); 55 (C_4H_7 or OCH_2Cl) and 49 (CH_2Cl).
10. 1-chlorobutyl [(2-chloromethoxy)butyl] ether (**11**, r.t. = 8.38 min, 9.7%): M^+ = 228 (two chlorine isotope pattern seen); 179 (M-CH_2Cl); 149 (179-OCH_2); 121 (179-C_3H_6O, 100%); 85 (121-HCl); 59 (C_3H_7O); 55 (C_4H_7 or OCH_2Cl) and 49 (CH_2Cl).
11. 1-chlorobutyl [(2-chloromethoxy)butyl] ether (**12**, r.t. = 9.92 min, 1.1%): M^+ = 228 (two chlorine isotope pattern seen); 199 (M-C_2H_5); 179 (M-CH_2Cl); 121 (179-C_3H_6O, 100%); 91 (121-OCH_2); 85 (121-HCl); 59 (C_3H_7O); 55 (C_4H_7 or OCH_2Cl) and 49 (CH_2Cl).
12. 1-chlorobutyl [(2-(methylthiomethoxy)butyl] ether (**13**, r.t. = 9.68 min, 0.4%): M^+ = 240 (^{37}Cl seen); 179 (M-CH_2SCH_3); 147 (M-CH_3-C_2H_5-CH_2Cl); 133 (M-OC_4H_8Cl or $C_6H_{13}OS$, 100%); 121 ($C_5H_{10}ClO$); 118 (M-OC_4H_8Cl); 103 ($C_3H_6OCH_2SCH_3$); 91 (C_4H_8Cl); 85 (C_5H_9O); 75 (C_3H_4Cl); 61 (CH_2SCH_3); 55 (C_4H_7) and 47 (SCH_3).

Figure 5 attempts to rationalize the probable mechanism of the formation of the previously mentioned compounds. Structures **19A** and **19B** represent the equivalent diradical forms of styrene oxide (**19**) (sf. Figure 2).[2] Phenyacetaldehyde (**22**) is the result of the known keto-epoxide rearrangement.[1] The reaction of the $Cl^{\cdot}$ radical with the diradical **19A** gives the intermediate **28**, which has two options open to it: First, it can fragment off a $^{\cdot}CH_2Cl$ moiety to yield benzaldehyde (**21**), and second, it can go on to abstract hydrogen to furnish

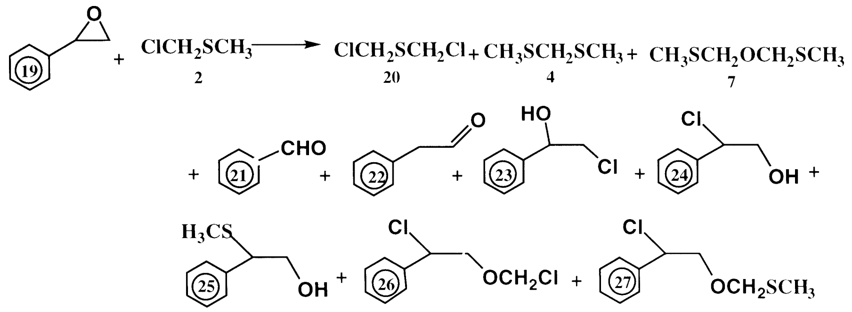

FIGURE 4 Compounds from the reaction of styrene oxide with CH_3SCH_2Cl.

1-chloro-2-phenyl-2-hydroxyethane (**23**). Indeed, both of these compounds have been characterized by their mass spectra.

On the other hand, if the diradical **19B** reacts with the Cl rad-ical, it will form intermediate **29**, which has three options available to it, namely to (1) abstract hydrogen to give 1-chloro-1-phenyl-(2-hydroxy)ethane (**24**), (2) react with the CH_2Cl moiety to

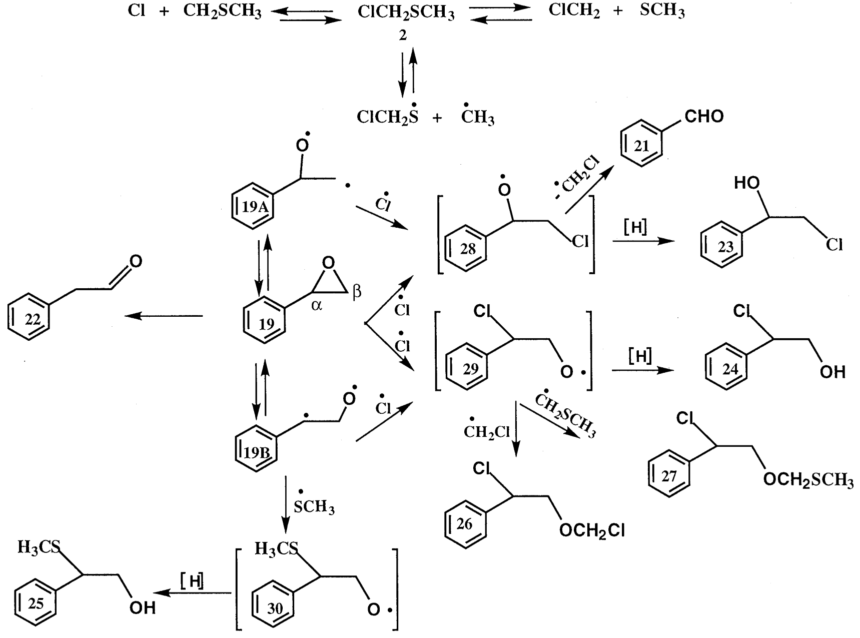

FIGURE 5 Mechanism of the formation of compounds from styrene oxide.

form 1-chloro-1-phenyl-2-(chloromethoxy)ethane (**26**), and (3) react with a (methylthio)methyl radical to furnish 1-chloro-1-phenyl-2-[(methylthio)methoxy]ethane (**27**). It is interesting to observe that all of these three possibilities have materialized: The previously mentioned compounds, **24**, **26**, and **27** all have been found to be present in the reaction product and have been identified by their mass spectra. The diradical intermediate (**19B**) also can react with a methylthiyl radical to form intermediate **30**, which then can abstract hydrogen to yield 1-hydroxy-2-(methylthio)-2-phenylethane (**25**). This compound also was identified.

With lithium chloride and acetic acid in tetrahydrofuran, 1-hydroxy-2-chloro-2-phenyl ethane and 1-hydroxy 1-phenyl-2-{1-chloroethoxy)ethane were found to be the major and minor products, respectively.[12] Silica-supported lithiumhalides have been shown to react with styrene oxide and give isomeric alcohols, depending on the nature of the halides.[12d] The suggested formation of the compounds of the type of cycloalkyl(methylthio)ether has precidents.[13] 1-hydroxy-2-phenyl-2-trifluoro-methylthioethane, similar to a compound, has been described.[3] The treatment of styrene oxide (**19**) with mixed lithiocopper halides is known to yield 1-halogeno-2-phenyl-2-hydroxyethane as the primary product.[14] Styrene oxide (**19**) also reacts with alkyl- and arylthioalkylsilanes, which represent "a powerful combination of organophiles and strong nucleophiles under mild conditions in aprotic solvents and in the presence of mild Lewis acid catalysts" to furnish 1-hydroxy-2-phenyl-2-(phenylthio)ethane and 1-hydroxy-1-phenyl-2-(phenylthio)-ethane.[10b]

The origin of bis-(methylthio)methane (**4**) and bis-(methylthiomethyl)ethane (**7**) can be traced to the free-radical reactions of (methylthio)methylchloride (**2**). The same is true for bis-(chloromethyl)sulfide (**20**), in particular, to the reaction of a $^{\cdot}SCH_2Cl$ radical with $^{\cdot}CH_2Cl$ radical. The mass spectral fragmentation of compounds **2**, **4**, **7**, and **20–27** is given in Table II. The mass spectrum of benzaldehyde has been discussed in detail.[15] The mass spectrum of phenylacetaldehyde (**22**) has also been described.[16] In fact, compound **22** was identified as one of the artifacts during the GC-MS analysis of styrne oxide.[16] In spite of these promising results, (ethylthio)ethylchloride, [ethyl (2-chloroethyl)sulfide], a simulant of the blister agent, mustard, was found not to react with epoxides even under forcing conditions. This failure to react can be attributed, at least in part, to the increased distance between sulfur and chlorine. In other words, it appears that the influence of sulfur on the reactivity of chlorine tends to decrease as the distance between the two increases.

TABLE II Products Derived From (Methylthio)methyl Chloride and Styrene Oxide

1. Styrene oxide* (**19**), r.t. = 4.83 min, 58.5%): $M^+ = 120$; 119 (M-H); 104 IM-O); 92 (M-C_2H_4 or M-CO); 91 (M-CHO, 100%); 89 (M-OCH_3); 77 (C_6H_5); 65 (C_5H_5) and 51 (C_4H_3).
2. Methylthio methyl chloride (**2**, r.t. = 2.08 min, 10.6%); $M^+ = 96$ (100%, ^{37}Cl:98); 81 (M-CH_3); 61 (M-Cl, 98%); 59 (C_2H_3S); 47 (SCH_3) and 46 (SCH_2).
3. Bis-(chloromethyl) sulfide (**20**, r.t. = 2. 82 min, 0.7%): $M^+ = 130$ (^{37}Cl peak seen); 115 (M-CH_3); 95 (M-Cl, 100%); 83 ($CH_3S(H)Cl$); 59 (C_2H_3S) and 49 (CH_2Cl).
4. Bis-(methylthio)methane (**4**, r.t. = 3.15 min, 2.4%): $M^+ = 108$ (100%); 93 (M-CH_3); 78 (93-CH_3 or CH_2S_2); 61 (CH_3SCH_2); 59 (C_2H_3S) and 47 (SCH_3).
5. Bis-(methylthiomethyl) ether (**7**, r.t. = 6.14 min, 0.4%): $M^+ = 138$ (100%); 91 (M-SCH_3); 76 (91-CH_3); 64 (SS); 59 (C_2H_3S) and 47 (SCH_3).
6. Benzaldehyde (**21**, r.t. = 3.78 min, 0.2%): $M^+ = 106$; 105 (M-H, 100%); 77 (C_6H_5); 51 (C_4H_3) and 50 (C_4H_2).
7. Phenylacetaldehyde (**22**, r.t. = 4.59 min, 12.5%): $M^+ = 120$; 91 (M-CHO, 100%); 65 (C_5H_5) and 51 (C_4H_3).
8. 1-chloro-2-phenyl-2-ethane (**23**, r.t. = 6.66 min, 0.7%): $M^+ = 156$; 107 (M-CH_2Cl, 100%); 105 (C_6H_5CO); 91 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5) and 51 (C_4H_3).
9. 1-hydroxy-2-chloro-2-phenylethane (**24**, r.t. = 6.86 min, 0.7%): $M^+ = 156$; 126 (M-CH_2O); 125 (M-CH_2OH, 100%); 121 (M-Cl); 103 (121-H_2O); 91 (C_7H_7); 89 (125-HCl); 79 (C_6H_7); 77 (C_6H_5); 63 (C_5H_3) and 51 (C_4H_3).
10. 1-hydroxy-2-phenyl-2-methylthioethane (**25**, r.t. = 8.48 min, 0.6%): $M^+ = 168$; 137 (M-CH_2OH, 100%); 121 (C_7H_5S); 103 (C_8H_7); 91 (C_7H_7 or C_3H_8OS); 77 (C_6H_5); 65 (C_5H_5); 59 (C_2H_3S) and 51 (C_4H_3).
11. 1-chloro-21-phenyl-2-chloromethoxyethane (**26**, r.t. = 8.88 min, 1.1%): $M^+ = 204$; 169 (M-Cl); 138 (M-HCl-OCH_2); 125 (M-CH_2OCH_2Cl, 100%); 103 (C_8H_7); 77 (C_6H_5) and 51 (C_4H_3).
12. 1-chloro-1-pheny1-2- (methylthiomethoxy) ethane (**27**, r.t. = 10. 13 min, 2.8%): $M^+ = 216$; 186 11. (M-OCH_2); 168 (M-$HSCH_3$); 151 (186-Cl); 138 (186-$HSCH_3$); 125 (C_6H_5CHCl); 103 (C_8H_7); 91 (C_7H_7); 61 (CH_2SCH_3) and 51 (C_4H_3).

*The mass spectrum of styrene oxide has been described [cf. Chemical Concept (1995)].

EXPERIMENTAL

All solvents were dry and freshly distilled prior to use. Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m × 0.25 mm. i.d. DB-5 capillary column (J and W Scientific, Folsom, California, USA) or a Finnigan 5100 GC/MS equipped with a 15 m × 0.25 mm. i.d.Rtx-5 capillary column (Restek, Bellefonte, Pennsylvania, USA). The conditions on 5100 were the following: oven temperature 60–270°C at 10°C/min, injection temperature was 210°C, interface temperature 230°C, electron energy 70 eV, emission current 500 μA, and scan time 1 s. The conditions on the TSQ-7000 were the following: oven temperature 60–270°C at 15°C/min, injection temperature 220°C, interface temperature 250°C, source temperature 150°C, electron energy 70 eV

(EI) or 200 eV (CI), emission current 400 μA (EI) or 300 μA (CI), and scan time 0.7 s. Data was obtained in both the electron ionization mode (range 45–450 da) and chemical ionization mode (mass range 60–450 da). Ultrahigh purity methane was used as the CI agent gas with a source pressure of 0.5 Torr (5100) or 4 Torr (TSQ-7100). Routine GC analyses were accomplished with a Hewlett Packard 5890 A gas chromatograph equipped with a J and W Scientific 30 m × 0.53 mm i.d. DB-5 column (J and W Scientific).

Reaction of 1,2-Epoxybutane (1) with (Methylthio) Methylchloride (2)

A mixture of 1,2-epoxybutane (**1**, 4 g) and stoichimetric amounts of (methylthio) methylchloride (**2**) were stirred under a current of dry nitrogen for 20 h and then the reaction mixture was heated with stirring at 50°C for 4 h. The mixture was allowed to come to an ambient temperature. The GC analysis of the reaction product showed it to consist of a complex mixture of 11 compounds. Attempts to fractionate the mixture to separate the components via vacuum distillation were not successful. The GC-MS analysis of the reaction product permitted the characterization of the following compounds: (1) (methylthio)methylchloride (**2**, r.t. = 2.06 min, 15.1%); (2) 1-chloro-2-hydroxy-butane (**3**, r.t. = 2.4 min, 5.7%); (3) bis-(methylthio)methane (**4**, r.t. = 3.13 min, 34.2%); (4) 1-chloro-2-(chloromethoxy)butane (**5**, r.t. = 4.28 min, 6..3%); (5) (chloromethylthio)-(methylthio)methane (**6**, r.t. = 5.1 min, 0.4%); (6) bis-(methylthiomethyl) ether (**7**, r.t. = 6.13 min, 2.0%); (7) bis-(methylthiomethyl) sulfide (**8**, r.t. = 6.87 min, 0.3%); (8) 1-chloro-2-(methylthiomethoxy)butane (**9**, r.t. = 5.73 min, 3.0%); (9) three isomers (**10–12**) 1-chlorobutyl-2-[(2-chloromethoxy)butyl]ether; (**10**, r.t. = 8.33 min, 22.0%; **11**, r.t. = 8.38 min, 9.7% and **12**, r.t. = 9.92 min, 1.1%) and (10) 1-chlorobutyl-2-[(2-methylthiomethoxyl)butyl]ether (**13**, r.t. = 9.68 min, 0.4%).

Reaction of Styrene Oxide (19) with (Methylthio) Methylchloride (2)

A mixture of styrene oxide (**19**, 3.0 g) and stoichimetric amounts of (methylthio) methylchloride (**2**) was stirred under a current of dry nitrogen for 20 h and the reaction mixture was then heated with stirring at 50°C for 4 h. The mixture was allowed to come to room temperature. The GC analysis of the reaction mixture showed it to contain eight compounds. Attempts to distil the mixture under reduced pressure to separate it into pure components were not successful. The

GC-MS analysis of the reaction product permitted the characterization of the following compounds: (1) bis-(chloromethyl)sulfide (**20**, r.t. = 2.82 min, 0.7%), (2) bis-(meththylthio)methane (**4**, r.t. = 3.15; 2.4%), (3) bis-(methylthio)ether (**7**, r.t. = 6.14 min; 0.4%), (4) benzaldehyde (**21**, r.t. = 3.78; 0.2%), (5) phenylacetaldehyde (**22**, r.t. = 4. 59; 12.5%), (6) 1-chloro-2-hydroxy-2-phenylethane (**23**, r.t. = 6.66 min; 0.7%), (7) 1- hydroxy-2- chloro -2-phenylethane (**24**, r.t. = 6.86 min; 0.7%), (8) 1-hydroxy-2-methylthio-2-phenylethane (**25**, r.t.= 8.48 min; 0.6%), (9) 1-chloro-1-phenyl-2-(chloro-methoxy)ethane (**26**, r.t. = 8.48 min; 0.6%), and (10) 1-chloro-1-phenyl-2-(methylthiomethoxy)ethane (**27**, r.t. = 10.13 min; 2.8%).

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