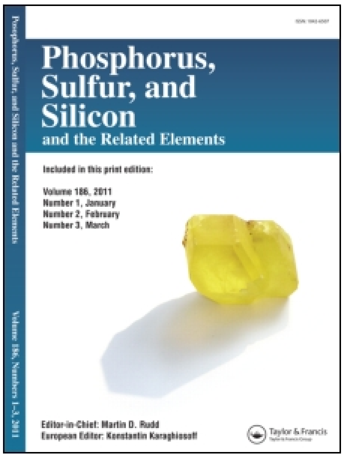

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Products of Sulfur Mustard Degradation: Synthesis and Characterization of 1-(2-Chloroethoxy)-2- [(2-chloroethyl)thio] Ethane, Related Compounds, and Derivatives

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Products of Sulfur Mustard Degradation: Synthesis and Characterization of 1-(2-Chloroethoxy)-2-[(2-chloroethyl)thio] Ethane, Related Compounds, and Derivatives

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A degradation product of sulfur mustard in ton storage containers 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane (little "t") has been synthesized and characterized along with a number of its derivatives and related compounds.

Keywords Degradation products; sulfone; sulfoxide; sulfur; sulfur mustard

INTRODUCTION

Since its introduction on the battlefield in WWI, sulfur mustard, bis(2-chloroethyl) sulfide, has been an important chemical warfare agent. In the years since WWI, there have been a number of suspected and recorded uses of sulfur mustard. Most recently, it was used during the Iran-Iraq war in the 1980s. Sulfur mustard's recent utilization, combined with its stockpiling by several countries, ease of production and potential use by terrorists has resulted in renewed interest and research. A search of Chemical Abstracts gives over 700 references to sulfur mustard[1] in the last five years alone.

The degradation of sulfur mustard in the environment, and in storage is complex. Numerous publications exist on the pathways and products of sulfur mustard degradation under a variety of field and laboratory conditions.[2] An analysis of sulfur mustard ton containers in the US stockpile showed in addition to sulfur mustard itself, by-products formed during manufacturing, and products formed from slow degradation reactions within the storage container. The analysis of these

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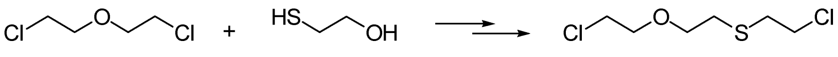
degradation products can be difficult due to their similarity and lack of easily distinguishable functional groups.

One compound 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane (**4**) has been observed[3] spectroscopically in ton container analysis for many years in concentrations up to 3%. To the best of our knowledge, no report of an authentic sample of **4** has been published in the open literature, only spectroscopic observations.[4] We would now like to report the synthesis and characterization of molecule **4**, along with a number of its direct derivatives.



RESULTS AND DISCUSSION

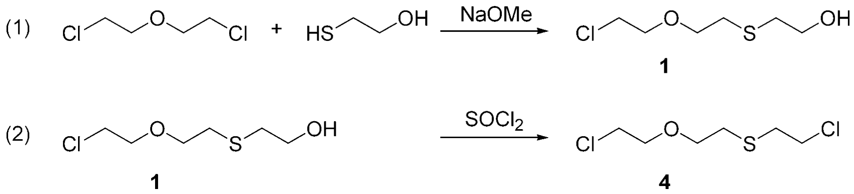
1-(2-Chloroethoxy)-2-[(2-chloroethyl)thio] ethane (**4**) was produced in two steps from bis(2-chloroethyl)ether and 2-mercaptoethanol (Scheme 1).

This simple route is vastly scalable and can be performed as a one-pot reaction with all purification and isolation performed at the end of the reaction sequence. Methanol, used as the solvent in equation 1 of Scheme 1 is removed prior to the use of benzene and thionyl chloride in equation 2 of Scheme 1.

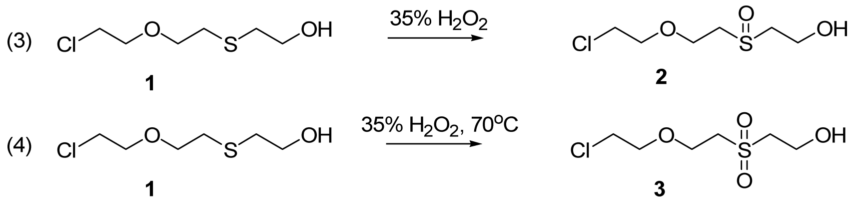
The sulfoxide and sulfone derivatives of sulfur mustard are well known[5] and the corresponding sulfoxide and sulfone derivatives for both 2-(2-chloroethoxy)ethyl 2-hydroxyethyl sulfide (**1**) and 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane (**4**) were easily prepared in reasonable yields using 35% hydrogen peroxide (Schemes 2 and 3).

Compounds **3** and **6** were prepared in identical procedures while compounds **2** and **5** differed only for reaction time required for oxidation.

The vinyl derivatives for sulfur mustard have also been reported in the literature.[6] The vinyl derivative **7** for 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio]ethane **4** was prepared in a yield of 29% and has not



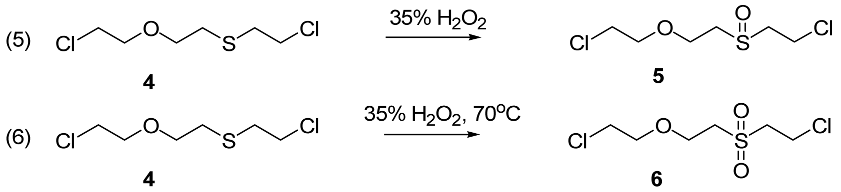
SCHEME 1 Short sequence to title product 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane **4.**



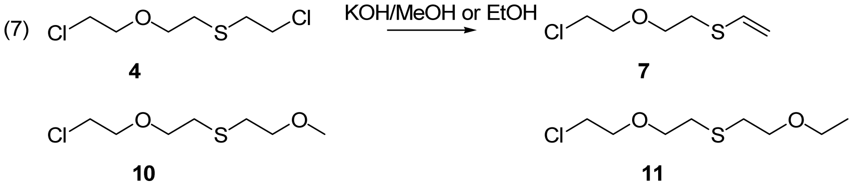
SCHEME 2 Conversion of **1** to its sulfoxide and sulfone derivatives.

been optimized. During the investigation of **7,** compounds **10** and **11** were isolated, depending on use of reaction solvent, as reaction side products and were spectroscopically characterized. (Scheme 4).

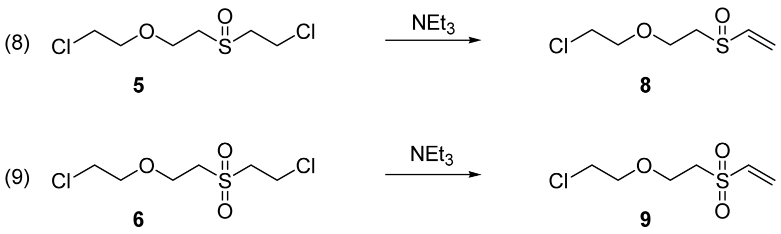
The vinyl derivatives of **5** and **6** were formed in reasonable yields by refluxing overnight in triethylamine, followed by chromatographic work-up (Scheme 5).



SCHEME 3 Conversion of **4** to its sulfoxide and sulfone derivatives.



SCHEME 4 Conversion of **4** to its vinyl derivative and two side products (**10** & **11**) isolated in the purification of **7**.



SCHEME 5 Conversion of **5** & **6** to vinyl derivatives **8** & **9**.

CONCLUSION

Overall, this paper describes the synthesis and spectroscopic (NMR and MS) characterizations of 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane **4** and the corresponding compounds that can be associated with several sulfur mustard degradation pathways. These short syntheses and corresponding characterizations may be relevant to ongoing investigations of sulfur mustard and its related compounds and it is our wish to share this information in a timely and relevant format.

EXPERIMENTAL

General Procedures

Thin Layer Chromatography was performed using Analtech silica gel GF plates at 250 microns and were developed using iodine. All solvents and reagents were used as received except for acetone, which was distilled prior to chromatography. Flash chromatography was performed using 230–400 mesh silica gel. All NMR spectra were recorded in $CDCl_3$ and were referenced to the NMR solvent signal. ^1H and ^{13}C spectra were recorded on a JOEL ECX-400 NMR instrument. Mass spectra were recorded using a Hewlett-Packard 5975 series Mass Selective Detector coupled to a Hewlett-Packard 6890 gas chromatogram. Elemental analysis was performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer.

2-(2-Chloroethoxy)ethyl2-hydroxyethyl Sulfide (1)

In a 50-ml round bottom flask sodium (325 mg, 14.15 mmol) was reacted with 7.5 ml of dried MeOH while cooled in an ice bath. After reaction of the sodium, mercaptoethanol (1.00 g, 12.83 mmol) was added and the mixture allowed to stir for 15 min at room temperature. Bis(2-chloroethyl)ether (15.00 g, 104.9 mmol) was then added to the flask, and the reaction was stirred overnight. The resulting NaCl precipitate was filtered, the MeOH removed by rotary evaporation and the resulting oil was chromatographed using 20% acetone/petroleum ether ($R_f = 0.15$) to yield 1.86 g (79%) of **1**.

Alternatively, for scale-up purposes upon completion of the reaction, the NaCl was filtered off through a silica plug using a fine frit and acetone. The MeOH and acetone are removed by rotary evaporation and the resulting oil can be distilled at 110°C at a vacuum of 0.025 mm after first removing the bis(2-chloroethyl)ether at 35°C under the same vacuum using a bath temperature of 55–60°C. The receiver flask for the bis(2-chloroethyl)ether should be cooled in an ice bath for better recovery and reuse. NMR: ^{1}H ($CDCl_3$) δ 3.73–3.61 (m, 8H), 2.76–2.73 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 70.8, 70.7, 60.7, 42.5, 35.4, 31.1. MS (EI): m/z 61 (58), 75 (27), 91 (13), 105 (100), 148 (2), 166 (0.3), 168 (0.1). Anal. calcd. for $C_6H_{13}ClO_2S$: C 39.02; H 7.09; S 17.36. Found: C 38.79 H 6.93 S 17.76.

2-[[2-(2-Chloroethoxy)ethyl]sulfinyl]ethanol (2)

In a 5-ml round-bottom flask 2-(2-chloroethoxy)ethyl 2-hydroxyethyl sulfide (**1**) (504 mg, 2.73 mmol) was cooled to 0°C in an ice bath. The material was stirred rapidly and hydrogen peroxide (337 mg of 35%, 3.47 mmol of H_2O_2) was cooled to 0°C and added dropwise. The mixture was allowed to warm gradually to room temperature and stirred rapidly overnight. The product was purified on silica gel ($R_f = 0.11$) using 60% acetone/hexanes directly with no additional work-up to yield 413 mg (76%) of **2**.

NMR: ^{1}H ($CDCl_3$) δ 4.26 (br s, 1H), 4.10–4.03 (m, 2H), 3.95–3.87 (m, 2H), 3.73 (td, 2H, J = 4.1, 1.6 Hz), 3.61 (t, 2H, J = 4.1 Hz), 3.09–2.95 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 70.6, 62.8, 54.8, 54.5, 51.8, 42.4. MS (EI): m/z 63 (100), 76 (33), 107 (29), 128 (10), 130 (4), 147 (5), 165 (3), 183 (0.8), 187 (0.3). Anal. calcd. for $C_6H_{13}ClO_3S$: C 35.91; H 6.53; S 15.98. Found C 35.74 H 6.35 S 15.82.

2-[[2-(2-Chloroethoxy)ethyl]sulfonyl]ethanol (3)

In a flask 2-(2-chloroethoxy)ethyl 2-hydroxyethyl sulfide (**1**) (501 mg, 2.71 mmol) was mixed with hydrogen peroxide (1.61 g of 35%, 16.53 mmol of H_2O_2) and stirred rapidly. The mixture was heated in a 70°C water bath for 40 min at which time GC/MS analysis showed the absence of starting material. The solution was cooled and extracted with $CHCl_3$. The organics were combined and dried with $MgSO_4$ to yield an oil which was purified on silica gel ($R_f = 0.33$) using 60% acetone/hexanes. Yield 287 mg, 49%) **3**. NMR: ^{1}H ($CDCl_3$) δ 3.99 (t, 2H, J = 4.1 Hz), 3.86 (t, 2H, J = 4.1 Hz), 3.68 (t, 2H, J = 4.1 Hz), 3.59 (t, 2H, J = 3.3 Hz), 3.33–3.29 (m, 4H), 3.11 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 70.8, 64.3, 56.7, 55.9, 54.3, 42.7. MS (EI): m/z 63 (73), 109 (58), 137 (100), 155 (5), 167 (30). Anal. calcd. for $C_6H_{13}ClO_4S$: C 33.26; H 6.05; S 14.80. Found: C 32.89 H 5.96 S 14.85.

1-(2-Chloroethoxy)-2-[(2-chloroethyl)thio]ethane (4)

A solution of **1** (1.75 g, 9.5 mmol) in 20 ml of dried benzene was stirred at room temperature and thionyl chloride (2.28 g, 19.2 mmol) was added dropwise. The reaction was stirred for an additional hour and the benzene was removed by rotary evaporation. Chromatography

($R_f = 0.83$) using 20% acetone/petroleum ether gave **4** (1.89 g, 98%) as a clear colorless oil. NMR: ^1H ($CDCl_3$) δ 3.79–3.61 (m, 8H), 2.92 (t, 2H, J = 5.9 Hz), 2.76 (t, 2H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) δ 71.2, 70.9, 43.0, 42.6, 34.6, 31.7. MS (EI): m/z 63 (66), 93 (15), 109 (21), 123 (100), 125 (39), 166 (8), 168 (3). Anal. calcd. for $C_6H_{12}Cl_2OS$: C 35.48; H 5.95; S 15.79. Found: C 35.84 H 5.88 S 16.07.

For scale-up, upon completion of the procedure for **1**, the NaCl was filtered off through silica gel and the MeOH and acetone were removed. The oil was taken up in benzene and assuming complete conversion, the requisite amount of thionyl chloride was added dropwise and the reaction stirred for 1 h at room temperature. The solution was once again filtered through a silica gel plug and distillation was similar to **1**. Removal of the bis(2-chloroethyl)ether was followed by distillation of **4** at 93–95°C at 0.025 mm of pressure.

1-(2-Chloroethoxy-2[(2-chloroethyl)sulfinyl]ethane (5)

In a 5 ml round-bottomed flask **4** (501 mg, 2.47 mmol) was cooled to 0°C and stirred rapidly while hydrogen peroxide (263 mg of 35%, 2.70 mmol of H_2O_2) also cooled to 0°C was added dropwise. The mixture was stirred rapidly at room temperature overnight. GC/MS analysis indicated a lack of starting material the following morning and the solution was filtered through silica gel and washed with acetone. The acetone was removed by rotary evaporation and the oil was purified on silica gel ($R_f = 0.45$) using 40% acetone/hexanes to yield 431 mg (80%) of **5**. NMR: ^1H ($CDCl_3$) δ 3.84–3.79 (m, 4H), 3.63 (t, 2H, J = 4.2 Hz) 3.52 (t, 2H, J = 4.2 Hz), 3.11–2.99 (m, 3H), 2.84 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 70.8, 62.6, 54.8, 51.8, 42.4, 36.8. MS (EI): m/z 63 (100), 65 (30), 76 (9), 83 (7), 107 (13), 139 (2), 169 (1). Anal. calcd. for $C_6H_{12}Cl_2O_2S$: C 32.89; H 5.52; S 14.63. Found: C 32.56 H 5.33 S 14.51.

1-(2-Chloroethoxy-2[(2-chloroethyl)sulfonyl]ethane (6)

In a 5 ml round-bottomed flask **4** (501 mg, 2.47 mmol) was mixed with hydrogen peroxide (1.88 g of 35%, 19.35 mmol of H_2O_2) and stirred rapidly. The mixture was heated in a 70°C water bath for 40 minutes at which time GC/MS analysis showed the absence of starting material. The solution was cooled and added directly to a silica gel column where the product was eluted ($R_f = 0.46$) using 30% acetone/hexanes to yield 382 mg (66%) of **6**. NMR: ^1H ($CDCl_3$) δ 3.87–3.81 (m, 4H), 3.69 (m, 2H), 3.60–3.54 (m, 4H), 3.24 (t, 2H, J = 4.0Hz); ^{13}C NMR ($CDCl_3$) δ 70.9, 64.3, 56.5, 54.2, 42.6, 35.5. MS (EI): m/z 63 (100), 65 (36), 106 (31), 127 (12), 129 (4), 155 (71), 157 (27), 185 (27) 187 (10). Anal. calcd. for $C_6H_{12}Cl_2O_3S$: C 30.65; H 5.14; S 13.64. Found: C 30.78 H 5.06 S 13.95.

[[2-(2-Chloroethoxy-ethyl]thio]ethene (7)

A solution of **4** (305 mg. 1.50 mmol) in 8.1 ml of ethanol was mixed with potassium hydroxide (639 mg, 11.39 mmol) and stirred rapidly overnight. The ethanol was removed under vacuum and the product was extracted with ether followed by methylene chloride. The organics were dried with $MgSO_4$ and the solvents removed using rotary evaporation. Purification on silica gel ($R_f = 0.75$) using 15% ether/hexanes gave **7** as a colorless oil. (73.8 mg, 29%). NMR: ^1H ($CDCl_3$) δ 6.35 (dd, 1H, J = 12.8, 7.6 Hz), 5.20 (d, 1H, J = 7.6 Hz), 5.15 (d, 1H, J = 12.8 Hz), 3.73–3.68 (m, 4H), 3.61 (t, 2H, J = 4.1 Hz), 2.90 (t, 2H, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$) δ 131.8, 111.4, 71.0, 69.9, 42.6, 30.9. MS (EI): m/z 63 (100), 73 (59), 87 (75), 93 (19), 106 (19), 120 (13), 166 (17), 168 (6). Anal. calcd. for $C_6H_{11}ClOS$: C 43.24; H 6.65; S 19.24. Found: C 43.31 H 6.76 S 19.48.

[[2-(2-Chloroethoxy)-ethyl]sulfinyl]ethene (8)

A mixture of 1-(2-chloroethoxy-2[(2-chloroethyl)sulfinyl]ethane **5** (400 mg, 1.83 mmol) and triethylamine (1.70 g, 16.79 mmol) in 10 ml of benzene was refluxed overnight. The resulting solids were filtered and the solvents removed by rotary evaporation. The resulting oil was purified on silica gel ($R_f = 0.45$) using 40% acetone/hexanes to yield 320 mg (96%) of **8**. NMR: ^1H ($CDCl_3$) δ 6.50 (dd, 1H, J = 12.6, 7.4 Hz), 5.75 (d, 1H, H = 12.4 Hz), 5.64 (d, 1H, J = 7.4 Hz) 3.63–3.55 (m, 2H), 3.46–3.38 (m, 2H), 3.33 (t, 2H, J = 4.0 Hz), 2.78 (ddd, 1H, J = 10.3, 6.2, 4.0 Hz), 2.55 (ddd, 1H, J = 10.1, 3.5, 3.5); ^{13}C NMR ($CDCl_3$) δ 140.5, 120.4, 70.2, 62.5, 52.9, 42.1. MS (EI): m/z 63 (100), 65 (33), 76 (36), 107 (28), 109 (9), 118 (3), 133 (2), 17 (1). Anal. calcd. for $C_6H_{11}ClO_2S$: C 39.45; H 6.07; S 17.55. Found: C 39.15 H 6.29 S 17.69.

[[2-(2-Chloroethoxy)ethyl]sulfonyl]ethene (9)

In a 25-ml round-bottomed flask 1-chloro-2-[2-(2-chloroethanesulfonyl)-ethoxy]-ethane (**6**) (394 mg, 1.68 mmol) was dissolved in 10 ml of benzene with triethylamine (851 mg, 8.43 mmol) and refluxed overnight. The resulting solids were filtered and the solvents removed by rotary evaporation. The oil was chromatographed using 30% acetone/hexanes ($R_f = 0.58$) to give **9** (238 mg, 72%). NMR: ^1H ($CDCl_3$) δ 6.73 (dd, 1H, J = 12.6, 7.6 Hz), 6.30 (d, 1H, J = 12.6 Hz), 6.03 (d, 1H, J = 7.6 Hz), 3.83 (t, 2H, J = 4.1 Hz), 3.65 (t, 2H, J = 4.1 Hz), 3.55 (t, 2H, J = 4.0 Hz), 3.20 (t, 2H, J = 4.3 Hz); ^{13}C NMR ($CDCl_3$) δ 137.5, 128.7, 70.9, 64.3, 54.5, 42.5. MS (EI): m/z 63 (55), 91 (100), 106 (32), 119 (73), 134 (11), 149 (35). Anal. calcd. for $C_6H_{11}ClO_3S$: C 36.27; H 5.58; S 16.14. Found: C 36.30 H 5.56 S 15.91.

1-(2-Chloroethoxy-2[(2-methoxyethyl)thio]ethane (10)

This product was isolated during an attempted synthesis of (**7**) as a by-product, it had an $R_f = 0.67$ using 28% acetone/hexanes. NMR: ^1H ($CDCl_3$) δ 3.62 (t, 2H, J = 4.3 Hz), 3.58 (t, 2H, J = 5.0 Hz), 3.53 (t, 2H, J = 4.1 Hz), 3.46 (t, 2H, J = 5.0 Hz), 3.26 (s, 3H), 2.66 (td, 4H, J = 5.0, 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 71.9, 70.8, 70.6, 58.3, 42.4, 31.6, 31.4. MS (EI): m/z 58 (45), 63 (48), 75 (81), 87 (10), 103 (23), 119 (100), 198 (0.2). Anal. calcd. for $C_7H_{15}ClO_2S$: C 42.31; H 7.61; S 16.14. Found: C 41.93 H 7.27 S 16.30.

1-(2-Chloroethoxy-2[(2-ethoxyethyl)thio]ethane (11)

This product was isolated during the synthesis of (**7**) as a byproduct, it had an $R_f = 0.51$ using 30% ether/hexanes.

NMR: ^1H ($CDCl_3$) δ 3.72 (t, 2H, J = 4.3 Hz), 3.68 (t, 2H, J = 5.0 Hz), 3.63–3.57 (m, 4H), 3.50 (q, 2H, J = 5.2 Hz), 2.78–2.73 (m, 4H), 1.19 (t, 3H, J = 5.2Hz); ^{13}C NMR ($CDCl_3$) δ 71.0, 70.9, 70.2, 66.3, 42.6, 32.0, 31.7, 15.1. MS (EI): m/z 59 (74), 63 (65), 72 (74), 75 (100), 88 (20), 103 (25), 133 (79), 167 (4), 212 (0.1). Anal. calcd. for $C_8H_{17}ClO_2S$: C 45.17; H 8.05; S 15.07. Found: C 44.73 H 7.86 S 14.62.

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