# The Generation of the Ethenethiolate Anion and Its Reaction with Several Chloromethyl Alkyl Ethers and Sulfides

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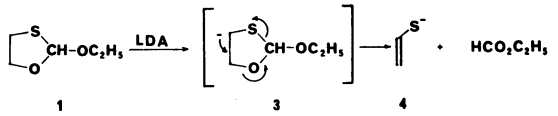
**Synopsis.** 2-Ethoxy-1,3-oxathiolane was deprotonated at the 4-position, followed by the cycloelimination of the resultant anion, leading to ethyl formate and the ethenethiolate anion. The anion was trapped by several chloromethyl alkyl ethers and sulfides to afford alkoxy(vinylthio)methanes and alkylthio(vinylthio)methanes respectively.

In a previous article[1] it was shown that 2-ethoxy-1,3-oxathiolane (**1**) undergoes ring cleavage on treatment with an excess of butyllithium in hexane, giving 5-nonanol together with 5-butyl-5-nonanol. By a similar treatment, 2-ethoxy-1,3-dithiolane (**2**) was also opened to produce 5-nonanethiol, along with 5-butyl-5-nonanethiol. Although the correct mechanism of these reactions is even now in doubt, it may involve three steps. The first step is the deprotonation at the 4-position of **1** or **2**. The second one is the cycloelimination of the resultant anion, leading to ethyl formate or *O*-ethyl thioformate, along with the ethenethiolate anion. The last step is the nucleophilic attack of 2 mol of butyllithium on the intermediate ethyl formate or *O*-ethyl thioformate to afford 5-nonanol or 5-nonanethiol.

Deprotonation at the 4-position of the 1,3-dithiolane ring by a strong base was initially confirmed by Wilson and his co-workers,[2] who reported that the reaction of 2-hexyl-1,3-dithiolane with an excess of butyllithium in ether gives 5-undecanethiol and 5-(butylthio)-undecane. More recently, we ourselves have found[3] that several 2-alkyl-2-aryl- and 2,2-diaryl-1,3-dithiolanes undergo predominant fragmentation by lithium diisopropylamide (LDA) in tetrahydrofuran, a process which is initiated by proton abstraction from C-4. Thus, it is conceivable that the reaction of **2** with butyllithium proceeds by a mechanism involving deprotonation at the 4-position in the first step. On the other hand, no description of deprotonation at the 4-position of the 1,3-oxathiolane ring by any one of the strong bases is available, although it is already well known that a few 1,3-oxathiolane derivatives are capable of proton abstraction from their C-2.[4] In order to verify the deprotonation at C-4 of the 1,3-oxathiolane ring by a strong base, we submitted **1** to a deprotonation-fragmentation sequence using LDA, since a hydrogen at C-4 seems to be more labile than that at C-2 in **1**. When **1** was treated with an excess of LDA in tetrahydrofuran at −78 °C, followed by the addition of an appropriate chloromethyl alkyl ether or sulfide, a series of alkoxy(vinylthio)methanes (**5**) or alkylthio(vinylthio)methanes (**6**) were obtained in moderate yields, suggesting the intermediary presence of the ethenethiolate anion (**4**) in the course of the reaction. The formation of the intermediate **4** is best explained by assuming that the initial deprotonation by LDA occurred not at the 2-position, but at the 4-position of **1**, and that it is followed by the fragmentation. On that occasion, there is no reaction between the less nucleophilic LDA and the ethyl formate which has been produced simultaneously.

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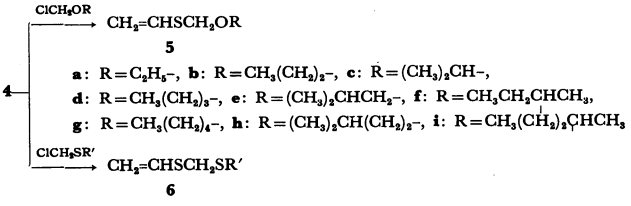


TABLE 1. REACTION PRODUCTS IN THE REACTION OF THE ETHENETHIOLATE ANION (**4**) WITH CHLOROMETHYL ALKYL ETHERS

| R in chloromethyl alkyl ether used | **5** Abbr. | Yield/%[a] | Bp $\theta_b$/°C (Torr)[b] | Found (Calcd)(%) C | H | $^1$H-NMR ($\delta$, in $CDCl_3$) |
|---|---|---|---|---|---|---|
| $C_2H_5$– | **5a** | 47 | 55—58(30) [lit[5], 41(17)] | 51.08 (50.81) | 8.61 (8.53) | 1.19 (t, 3H), 3.54 (q, 2H), 4.77 (s, 2H), 5.19 (d, 1H), 5.30 (d, 1H), 6.40 (dd, 1H) |
| $CH_3(CH_2)_2$– | **5b** | 39 | 64—70(27) [lit[5], 52(11)] | 54.26 (54.50) | 8.99 (9.15) | 0.91 (t, 3H), 1.3—1.8 (m, 2H), 3.42 (t, 2H), 4.78 (s, 2H), 5.18 (d, 1H), 5.28 (d, 1H), 6.42 (dd, 1H) |
| $(CH_3)_2CH$– | **5c** | 47 | 52—57(25.5) [lit[5], 47(15)] | 54.33 (54.50) | 9.04 (9.15) | 1.15 (d, 6H), 3.6—4.2 (m, 1H), 4.78 (s, 2H), 5.20 (d, 1H), 5.31 (d, 1H), 6.42 (dd, 1H) |
| $CH_3(CH_2)_3$– | **5d** | 58 | 71—75(23) | 57.28 (57.49) | 9.61 (9.65) | 0.90 (t, 3H), 1.2—1.8 (m, 4H), 3.46 (t, 2H), 4.76 (s, 2H), 5.16 (d, 1H), 5.27 (d, 1H), 6.37 (dd, 1H) |
| $(CH_3)_2CHCH_2$– | **5e** | 51 | 66—70(25) | 57.31 (57.49) | 9.40 (9.65) | 0.90 (d, 6H), 1.5—2.2 (m, 1H), 3.22 (d, 2H), 4.71 (s, 2H), 5.11 (d, 1H), 5.22 (d, 1H), 6.31 (dd, 1H) |
| $CH_3CH_2CHCH_3$ \| | **5f** | 50 | 64—68(23.5) | 57.19 (57.49) | 9.46 (9.65) | 0.89 (t, 3H), 1.12 (d, 3H), 1.1—1.7 (m, 2H), 3.3—3.9 (m, 1H), 4.75 (s, 2H), 5.19(d, 1H), 5.29 (d, 1H), 6.40 (dd, 1H) |
| $CH_3(CH_2)_4$– | **5g** | 60 | 91—97(22.5) | 59.77 (59.95) | 9.95 (10.06) | 0.89 (t, 3H), 1.1—1.8 (m, 6H), 3.47 (t, 2H), 4.76 (s, 2H), 5.20 (d, 1H), 5.31 (d, 1H), 6.39 (dd, 1H) |
| $(CH_3)_2CH(CH_2)_2$– | **5h** | 58 | 85—91(23) | 60.04 (59.95) | 10.09 (10.06) | 0.90 (d, 6H), 1.2—1.9 (m, 3H), 3.50 (t, 2H), 4.77 (s, 2H), 5.20 (d, 1H), 5.28 (d, 1H), 6.40 (dd, 1H) |
| $CH_3(CH_2)_2CHCH_3$ \| | **5i** | 56 | 79—85(22.5) | 59.82 (59.95) | 10.06 (10.06) | 0.90 (t, 3H), 1.19 (d, 3H), 1.2—1.8 (m, 4H), 3.4—3.9 (m, 1H), 4.80 (s, 2H), 5.20 (d, 1H), 5.28 (d, 1H), 6.41 (dd, 1H) |

a) Isolated yield (based on **1**). b) 1 Torr=133.322 Pa.

Table 2. Reaction products in the reaction of the ethenethiolate anion (4) with chloromethyl alkyl sulfides

| R′ in chloromethyl alkyl sulfide used | 6 | | | | | |
|---|---|---|---|---|---|---|
| | Abbr. | Yield/%[a] | Bp $\theta_b$/°C (Torr)[b] | Found (Calcd)(%) C | Found (Calcd)(%) H | $^1$H-NMR ($\delta$, in $CDCl_3$) |
| $CH_3$– | **6a** | 67 | 60—66 (26.5) [lit,[6] 48(7)] | 40.26 (39.96) | 6.75 (6.71) | 2.10 (s, 3H), 3.75 (s, 2H), 5.16 (d, 1H), 5.20 (d, 1H), 6.39 (dd, 1H) |
| $CH_3(CH_2)_2$– | **6b** | 62 | 94—99 (21.5) [lit,[6] 79—80(7)] | 48.72 (48.60) | 8.20 (8.16) | 0.98 (t, 3H), 1.3—1.9 (m, 2H), 2.61 (t, 2H), 3.77 (s, 2H), 5.10 (d, 1H), 5.19 (d, 1H), 6.42 (dd, 1H) |
| $(CH_3)_2CH$– | **6c** | 58 | 66—69 (9.5) [lit,[6] 67(7)] | 48.77 (48.60) | 8.09 (8.16) | 1.30 (d, 6H), 2.8—3.3 (m, 1H), 3.79 (s, 2H), 5.07 (d, 1H), 5.18 (d, 1H), 6.38 (dd, 1H) |
| $CH_3(CH_2)_3$– | **6d** | 56 | 96—102 (5) | 51.88 (51.80) | 8.61 (8.69) | 0.91 (t, 3H), 1.1—1.8 (m, 4H), 2.64 (t, 2H), 3.76 (s, 2H), 5.20 (d, 1H),5.24 (d, 1H), 6.26 (dd, 1H) |
| $(CH_3)_2CHCH_2$– | **6e** | 63 | 83—88 (4.5) | 52.03 (51.80) | 8.74 (8.69) | 0.98 (d, 6H), 1.5—2.2 (m, 1H), 2.50 (d, 2H), 3.76 (s, 2H), 5.20 (d, 1H), 5.23 (d, 1H), 6.40 (dd, 1H) |
| $C_6H_5CH_2$– | **6f** | 32 | 135—142 (4) | 61.09 (61.18) | 6.08 (6.16) | 3.55 (s, 2H), 3.76 (s, 2H), 5.19 (d, 1H), 5.24 (d, 1H), 6.37 (dd, 1H), 7.0—7.6 (m, 5H) |

a) Isolated yield (based on **1**). b) 1 Torr=133. 322 Pa.

The products obtained in this procedure are summarized in Tables 1 and 2, together with their physical properties. Some of these products have been already synthesized by other chemists *via* another route; therefore, our procedure provides an alternative method for the preparation of these acetals.

## Experimental

The starting compound **1** was prepared as previously reported.[1] The chloromethyl ethyl ether and chloromethyl methyl sulfide were commercially available and were distilled just before use. The other chloromethyl alkyl ethers and sulfides were made according to one of the published procedures.[7]

*Generation of Ethenethiolate Anion (4) from 2-Ethoxy-1,3-oxathiolane (1) with LDA and Trapping of 4 by Chloromethyl Alkyl Ethers and Sulfides. General Procedure*: A solution of diisopropylamine (5.0 g, 49.4 mmol) in tetrahydrofuran (40 ml) was cooled to −10—−5 °C under nitrogen, treated with a 1.56 molar solution (31 ml, 48.4 mmol) of butyllithium in hexane, and then stirred at the same temperature for 30 min. The solution of LDA thus prepared was cooled to −78 °C, and a solution of **1** (2.7 g, 20.1 mmol) in tetrahydrofuran (3 ml) was added. After an additional 30 min stirring at −78 °C, 40.8 mmol of a chloromethyl alkyl ether or a sulfide was stirred in. The stirring was continued for 30 min at −78 °C and then for a further 1—2 h at room temperature, after which the mixture was quenched with 60 ml of saturated aqueous $NH_4Cl$ and then extracted with ether (3×50 ml). The combined organic layer was washed repeatedly with a 10% aqueou NaOH solution saturated with $Na_2SO_4$ and once with saturated aqueous $Na_2SO_4$. The layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give a residue, which was then distilled. The distillate was further chromatographed on silica gel to provide a pure product. Five% ether–hexane was used as the eluent for **5**, and hexane, for **6**.

## References

1) S. Tanimoto, T. Miyake, and M. Okano, *Bull. Inst. Chem. Res., Kyoto Univ.*, **55**, 276 (1977).

2) S. R. Wilson, G. M. Georiadis, H. N. Khatri, and J. E. Bartmess, *J. Am. Chem. Soc.*, **102**, 3577 (1980); S. R. Wilson, P. Caldera, and M. A. Jester, *J. Org. Chem.*, **47**, 3319 (1982).

3) H. Ikehira, S. Tanimoto, T. Oida, and M. Okano, *J. Org. Chem.*, in press.

4) For example, M. Jones, P. Temple, E. J. Thomas, and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 433.

5) R. Kroker and H. Ringsdorf, *Makromol. Chem.*, **121**, 240 (1969).

6) K. D. Gollmer, F. H. Mueller, and H. Ringsdorf, *Makromol. Chem.*, **92**, 122 (1966).

7) H. R. Henze, V. B. Duff, W. H. Matthews, J. W. Melton, and E. O. Forman, *J. Am. Chem. Soc.*, **64**, 1222 (1942); H. Böhme, H. Fischer, and R. Frank, *Justus Liebigs Ann. Chem.*, **563**, 54 (1949); A. J. Hill and D. T. Keach, *J. Am. Chem. Soc.*, **48**, 257 (1926); J. W. Farren, H. R. Fife, F. E. Clark, and C. E. Garland, *ibid.*, **47**, 2419 (1925).