Preparation of 1,3-Oxathiolane-2-thiones by the Reaction of Oxirane and Carbon Disulfide

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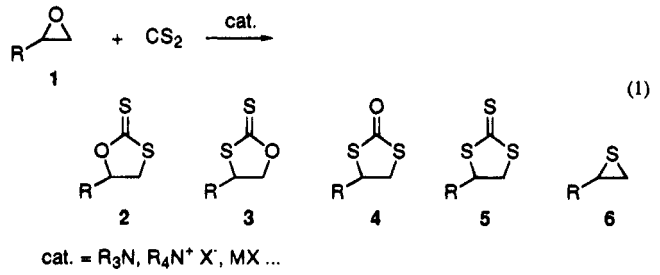
There have been many reports on the reaction of oxiranes **1** with carbon disulfide.[1–8] Depending on the catalysts and reaction conditions, five-membered cyclic dithiocarbonate **2**, its regioisomers **3** and **4**, trithiocarbonate **5**, and episulfide **6** have been reported to be formed. Although **5** or **6** can be selectively obtained at high temperature,[2,4,5,8] selective preparation of cyclic thiocarbonates **2**–**4** is rather difficult.[1,2,6,7]



(1)

Recently, we reported that alkali metal halides can effectively catalyze the reaction of carbon dioxide and oxiranes to form five-membered cyclic carbonates quantitatively at atmospheric pressure.[9] This reaction proceeds *via* nucleophilic attack of halide anion at the less substituted position of the oxiranes and cyclization of the resulting carbonate anion (Scheme 1).

Thus, the selective formation of cyclic dithiocarbonate **2** was expected from the reaction of oxiranes and carbon disulfide in the presence of the alkali metal halides as catalysts. Although LiCl-catalyzed reaction of oxirane and carbon disulfide in the gas-phase to afford **2** has been reported in a patent,[6] alkali metal halides have been reported to be inferior catalysts.[1,2] In this paper, we wish to report a novel, facile preparation of 1,3-oxathiolane-2-thione **2** at room temperature in high yield using alkali metal halides as catalysts. Since **2** can be a precursor of 2-mercaptoalkanols, regioselective preparation of **2** is an odorless method to prepare these species.

Scheme 1

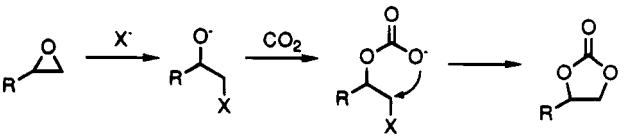
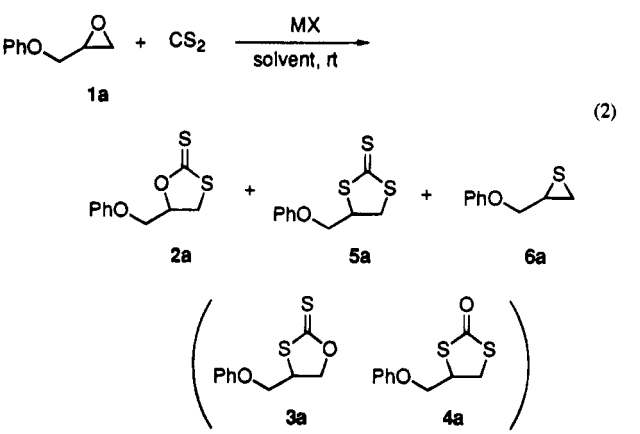


Table 1. Reaction of 1a and Carbon Disulfide[a]

solvent	catalyst	time (h)	yield (%)[b]	selectivity (%)[c]
THF	NaI	24	66	83
acetone	NaI	24	40	83
MeCN	NaI	24	26	87
DMF	NaI	24	6	60
NMP	NaI	24	1	25
methanol	NaI	24	37	38
THF	$PhCH_2N^+Me_3I^-$	24	0	–
THF	LiI	2	75	75
THF	LiBr	2	71	90
THF	LiCl	2	53	81
THF	LiCl	5	79	86

[a] The reaction was carried out at rt using 5 mol % of catalyst. [b] GLC yield. [c] (Yield of **2a**)/(conversion of **1a**) estimated by GC.

The reaction of **1a** with 1.2 equiv of carbon disulfide at room temperature in THF in the presence of sodium iodide afforded **2a** as the main product along with notable amounts of **5a** and **6a**; however, **3a** and **4a** were not formed (eq 2). To increase the selectivity for **2a**, the



(2)

reaction was carried out using various solvents and catalysts. The results are summarized in Table 1.

When the reaction was carried out in a less polar solvent, both the yield of **2a** and its proportion to other products increased. However, in the case of a protic solvent such as methanol, selectivity of **2a** decreased while the yields of **5a** and **6a** increased.[5,8] As shown in Table 1, THF is the best solvent, since alkali metal halides are nearly insoluble in less polar solvents than THF. Non-Lewis acidic quaternary ammonium salts show no catalytic activity, whereas Lewis acidic lithium salts show higher catalytic activity. We can conclude that Lewis acidity of the salts is essential for this reaction. The catalytic activity increased in the order of chloride < bromide < iodide, although selectivity decreased in the same order. Consequently, the selectivity and yield were highest when LiBr was used as a catalyst in THF.

The reactions of various oxiranes and carbon disulfide were examined using LiBr as a catalyst in THF, and the results are summarized in Table 2. Monosubstituted and *gem*-disubstituted oxiranes **1a**–**c**, **1e**–**h** gave desired dithiocarbonates **2a**–**c**, **2e**–**h** in high yields without the formation of possible byproducts **3**–**6**. Oxirane **1d** gave

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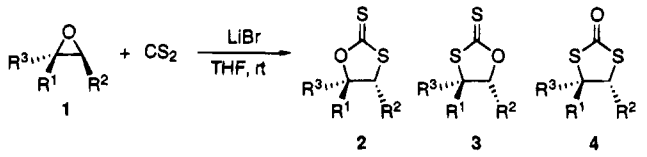
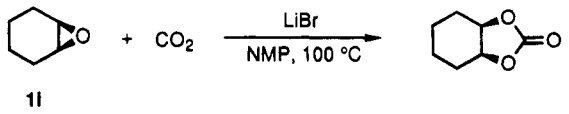
Table 2. Reaction of Various Oxiranes and Carbon Disulfide



oxirane	R^1	R^2	R^3	time (h)	product	yield (%)
1a	$PhOCH_2$	H	H	4.5	**2a**	97
1b	C_5H_{11}	H	H	19	**2b**	67
1c	C_6H_{13}	H	H	19	**2c**	67
1d	Ph	H	H	18	**2d+3d+4d**[a]	84 (67:12:21)[b]
1e	$PhCOOCH_2$	H	H	19	**2e**	95
1f	$CH_2=C(CH_3)COOCH_2$	H	H	17	**2f**	93
1g	Me	H	Me	17	**2g**	45
1h	$BnOCH_2$	H	Me	19	**2h**	89
1i	$-(CH_2)_4-$		H	17	**2i**	83
1j	H	$-(CH_2)_{10}-$		21	no reaction	0
1k	H	Ph	Ph	25	no reaction	0

[a] The isomers were not separable. [b] **2d**:**3d**:**4d** estimated by ^{1}H-NMR spectra.

Scheme 2



a mixture of regioisomers of dithiocarbonate, since a phenyl group accelerates "α-cleavage".[10] The lower yield of **2g** may be caused by the high volatility of **1g**. Oxygen-containing substituents on the oxirane-ring tend to increase the yield of **2**. Benzoate, methacrylate, and benzyl groups were not affected at all by these reaction conditions in spite of the presence of a highly nucleophilic xanthate anion intermediate (see below). *vic*-Disubstituted oxiranes are less reactive, and only **1i** gave the desired dithiocarbonate in high yield. It is noteworthy that *trans*-**2i** was obtained as a single product from **1i**.[11]

It is clear that the mechanism of the reaction of oxirane with carbon disulfide is different from that of the reaction with carbon dioxide (Scheme 1). Notably, the reaction of oxirane and alkali metal halide, which is the rate-determining step for the reaction of oxirane with carbon dioxide, did not proceed at room temperature, whereas the reaction of oxirane with carbon disulfide did proceed smoothly at room temperature. In addition, although *cis*-cyclic carbonate was obtained selectively from the reaction of **1i** with carbon dioxide by double S_N2 inversion on the oxirane ring (Scheme 2),[12] *trans*-cyclic dithiocarbonate **2i** was obtained selectively from the reaction of **1i** with carbon disulfide. The stereochemistry observed for **2i** indicates that S_N2 inversion on the oxirane ring occurred once during the formation of **2i**. The most plausible reaction mechanism[8], *i.e.*, reaction of xanthate anion (which can be formed from the alkali metal halide and carbon disulfide) with oxirane accompanied by S_N2 inversion and subsequent cyclization, is illustrated in Scheme 3. To test this hypothesis, this unusual equilibrium between an alkali metal halide and carbon disulfide was observed by ^{13}C-NMR spectra. Chemical shifts of

Scheme 3

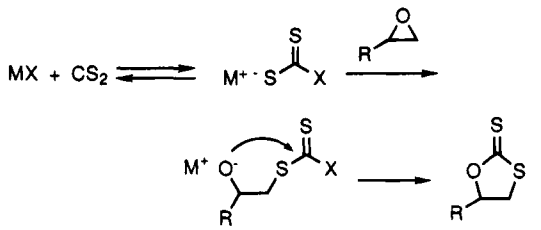


Table 3. Chemical Shift of Carbon Disulfide in the Presence of Lithium Salt[a]

salt[b]	chemical shift
none	193.36
lithium perchlorate	193.06
lithium iodide	192.67

[a] ^{13}C-NMR spectra (22.5 MHz) in THF-d_8 at 25 °C using TMS as an internal standard. [b] 1.0 equivalent.

the carbon of carbon disulfide in the presence of lithium salts are summarized in Table 3. That the chemical shift moved upfield in the presence of a lithium salt indicated an interaction between the lithium cation and carbon disulfide. Further, that the nucleophilic iodide anion caused a larger change than non-nucleophilic perchlorate anion suggested the presence of an equilibrium between lithium iodide–carbon disulfide and xanthate anion. It should be pointed out that this reaction mechanism is very similar to that presented for the reaction of oxirane and carbon dioxide under high pressure conditions.[9] Since carbon disulfide is highly electrophilic, it is not surprising that reaction of carbon disulfide with halide anion can occur at room temperature, although the Lewis acidity of the salt may play an essential role.

Experimental Section

Reaction of Oxiranes with Carbon Disulfide. To a solution of 4.3 mg (0.050 mmol) of LiBr and 158 mg (1.05 mmol) of **1a** in 0.20 mL of THF was added 75 μL (1.2 mmol) of carbon disulfide, and the reaction mixture was stirred at rt for 4.5 h. The reaction mixture was directly purified by preparative TLC (ethyl acetate/hexane 1/1 v/v, R_f = 0.44), and 231.3 mg (97%) of **2a** was obtained as yellow crystals: mp 55.5–56.0 °C (toluene); ^{1}H-NMR (60 MHz, CCl_4) δ 7.77–6.57 (m, 5H), 5.53–5.03 (m, 1H), 4.68–3.53 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 211.8, 157.6, 129.6, 121.7, 114.5, 88.2, 66.5, 36.0; Ir (KBr) 1597, 1494, 1190, 1049 cm^{-1}; MS 226 (M^+). Anal. Calcd for $C_{10}H_{10}O_2S_2$: C, 53.07; H, 4.45. Found: C, 53.38; H, 4.32.

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(11) The stereochemistry of **2i** was determined by X-ray crystallographic analysis. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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Other cyclic dithiocarbonates were synthesized in a similar manner.

2b: yellow oil; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 5.26–4.79 (m, 1H), 3.80–3.11 (m, 2H), 2.36–0.67 (m, 11H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 212.3, 92.0, 39.4, 33.7, 31.3, 25.1, 22.4, 13.9; IR (NaCl) 1190, 1049 cm^{-1}; MS 190 (M^+). Anal. Calcd for $C_8H_{14}OS_2$: C, 50.49; H, 7.41. Found: C, 50.20; H, 7.32.

2c: yellow oil; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 5.33–4.78 (m, 1H), 3.80–3.17 (m, 2H), 2.43–0.67 (m, 13H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 212.3, 92.0, 39.4, 33.7, 31.5, 28.8, 25.3, 22.5, 14.0; IR (NaCl) 1192, 1053 cm^{-1}; MS 204 (M^+). Anal. Calcd for $C_9H_{16}OS_2$: C, 52.90; H, 7.89. Found: C, 52.86; H, 7.98.

2e: yellow crystals; mp 69.0–70.5 °C; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 8.14–7.16 (m, 5H), 5.69–5.18 (m, 1H), 4.58 (d (J = 5.0 Hz), 2H), 3.95–3.35 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 211.5, 165.8, 133.6, 129.7, 128.9, 128.5, 87.8, 63.6, 36.0; IR (KBr) 1722, 1186, 1061 cm^{-1}; MS 254 (M^+). Anal. Calcd for $C_{11}H_{10}O_3S_2$: C, 51.95; H, 3.96. Found: C, 51.73; H, 4.02.

2f: yellow crystals; mp 43.5–44.0 °C (methanol); ^{1}H-NMR (90 MHz, $CDCl_3$) δ 6.25–6.07 (m, 1H), 5.71–5.60 (m, 1H), 5.55–5.22 (m, 1H), 4.57–4.42 (m, 2H), 3.89–3.41 (m, 2H), 2.04–1.88 (m, 3H); ^{13}C-NMR (22.5 MHz, acetone-d_6) δ 213.2, 166.8, 136.4, 126.7, 89.4, 64.3, 36.3, 18.2; IR (KBr) 1722, 1196, 1052 cm^{-1}; MS 218 (M^+). Anal. Calcd for $C_8H_{10}O_3S_2$: C, 44.02; H, 4.62. Found: C, 43.64; H, 4.50.

2g: colorless oil. ^{1}H-NMR (60 MHz, acetone-d_6) δ 3.60 (s, 2H), 1.65 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 211.2, 97.1, 45.5, 26.2; IR (NaCl) 1252, 1134 cm^{-1}; MS 148 (M^+). Anal. Calcd for $C_5H_8OS_2$: C, 40.51; H, 5.44. Found: C, 40.81; H, 5.28.

2h: colorless oil; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 7.23 (s, 5H), 4.53 (s, 2H), 3.90–3.06 (m, 4H), 1.59 (s, 3H); ^{13}C-NMR (22.5 MHz, acetone-d_6) δ 212.7, 138.8, 129.1, 128.4, 128.3, 99.1, 74.0, 73.6, 41.3, 22.2; IR (KBr) 1219, 1105 cm^{-1}; MS 255 (M^+). Anal. Calcd for $C_{12}H_{14}O_2S_2$: C, 56.66; H, 5.55. Found: C, 57.01; H, 5.58.

2i: yellow crystals; mp 53.5–55.0 °C methanol); ^{1}H-NMR (60 MHz, $CDCl_3$) δ 4.70–3.47 (m, 2H), 2.40–0.60 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 212.4, 94.6, 56.3, 29.7, 28.1, 24.9, 23.6; IR (KBr) 1188, 1042 cm^{-1}; MS 174 (M^+). Anal. Calcd for $C_7H_{10}OS_2$: C, 48.24; H, 5.78. Found: C, 48.06; H, 5.72.

Supplementary Material Available: ORTEP drawing of **2i** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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