Methoxide Ion Promoted Efficient Synthesis of 1,3-Oxathiolane-2-thiones by Reaction of Oxiranes and Carbon Disulfide

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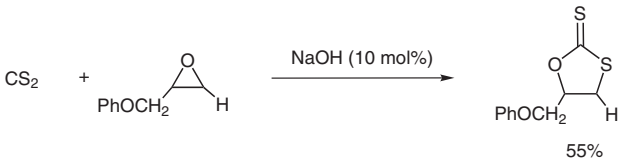
Abstract: An efficient one-pot synthesis of functionalized 1,3-oxathiolane-2-thiones is described via reaction of carbon disulfide with oxiranes in the presence of sodium hydride (10 mol%) and methanol.

Key words: oxathiolane, oxiranes, carbon disulfide, methoxide ion

O,*S*-Dialkyl dithiocarbonates (xanthates) are a versatile source of radicals,[1–4] intermediates in the synthesis of thiols,[5] thiocarbonates,[6,7] alkenes,[8] alkanes,[9] S-activated carbanions,[10] and photosensitizers[11] for the polymerization of vinyl monomers. They have also been used in the synthesis of natural products,[12] Claisen rearrangements,[13–16] and are also important for their biological activities.[17] There have been many reports on the reaction of oxiranes with carbon disulfide.[18,19] Depending on the catalysts and reaction conditions, five-membered cyclic dithiocarbonates, trithiocarbonates, and episulfides have been reported. Alkali-metal halides can effectively catalyze the reaction of carbon dioxide or carbon disulfide with oxiranes to form five-membered cyclic carbonates.[20] The earlier attempts for synthesis of 1,3-oxathiolane-2-thiones suffered from low yields and formation of byproducts.

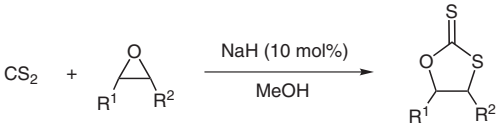
Our studies were initiated by treating a solution of carbon disulfide containing an oxirane derivative in the presence of sodium hydroxide (10 mol%). The efficiency of this reaction was low because hydroxide ion is a poor leaving group (Scheme 1).



Scheme 1

The nucleophile derived from methanol and carbon disulfide in the presence of sodium hydride (10 mol%) was found to undergo a clean and facile reaction with oxiranes at room temperature to afford **2** in excellent yields (Table 1).

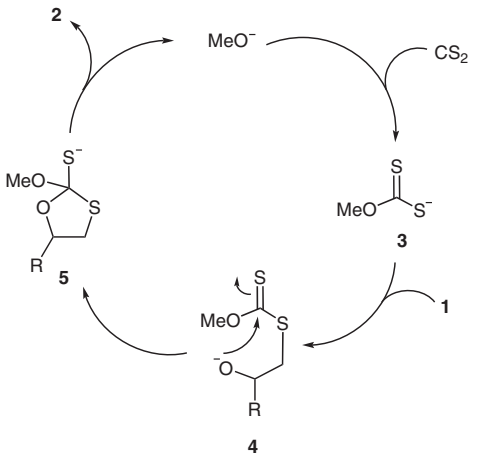
Table 1 Reaction of MeOH and CS_2 with Oxiranes in the Presence of NaH



1 **2**

1, **2**	R	R^1	Yield of **2** (%)
a	Me	H	96
b	Et	H	94
c	$(CH_2)_4$		96
d	Ph	H	95
e	$PhOCH_2$	H	94
f	$H_2C{=}CHCH_2OCH_2$	H	94
g	Me_2CHOCH_2	H	96
h	Ph	Ph (*cis*)	88
i	Ph	Ph (*trans*)	86

Structures of compounds **2a–i**[21] were confirmed by IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometric data. For example, the ^{1}H NMR spectrum of **2a** exhibited a doublet at 1.56 (^3J = 6.7 Hz) for the methyl proton, two doublet doublets at 3.62 (^2J = 11.9 Hz, ^3J = 7.4 Hz) and 3.98 (^2J = 11.9 Hz, ^3J = 6.4 Hz) for the CH_2 moiety and a multiplet at δ = 4.45–4.51 ppm for the CH group. The ^{13}C



Scheme 2

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NMR spectrum of **2a** shows a signal at δ = 228.5 ppm for the C=S group. The mass spectrum of **2a** displayed the molecular ion peak at *m/z* = 134.

A tentative mechanism for this transformation is proposed in Scheme 2. The first step may involve addition of methoxide ion to CS_2 and formations of the 1:1 adduct **3**. Subsequent nucleophilic attack of **3** to **1** yields **4**, which is converted to **2** by elimination of sodium methoxide.

In conclusion, the reaction of methanol and carbon disulfide with oxiranes in the presence of sodium hydride (10 mol%) leads to 1,3-oxathiolanes in excellent yields.

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(21) **General Procedure for the Preparation of Compounds 2**
To a stirred solution of CS_2 (0.35 g, 5 mmol) in MeOH (0.064 g, 2 mmol) containing NaH (10 mol%), was added, at r.t., the oxirane derivative **1** (2 mmol). The mixture was stirred for 12 h, and filtered to remove the white precipitates (presumably, NaOMe). The residue was purified by extraction with Et_2O to afford pure **2**.

5-Methyl-1,3-oxathiolane-2-thione (2a)
Yellow oil; yield 0.26 g (96%). IR (KBr): ν_{max} = 1700, 1439, 1414, 1370, 1143, 1073 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.56 (3 H, *d*, ^3J = 6.7 Hz, Me), 3.62 (1 H, dd, ^2J = 11.9 Hz, ^3J = 7.4 Hz, CH), 3.98 (1 H, dd, ^2J = 11.9 Hz, ^3J = 6.4 Hz, CH), 4.45–4.51 (1 H, m, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.1 (Me), 50.3 (CH_2), 55.5 (CH), 228.5 (C=S). MS (EI): *m/z* (%) = 134 (15) [M^+], 119 (78), 92 (100), 76 (64), 58 (48), 42 (56). Anal. Calcd (%) for $C_4H_6OS_2$ (134.21): C, 35.80; H, 4.51. Found: C, 35.90; H, 4.55.

5-Ethyl-1,3-oxathiolane-2-thione (2b)
Yellow oil; yield 0.28 g (94%). IR (KBr): ν_{max} = 1711, 1627, 1507, 1431, 1327, 1273 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.07 (3 H, *t*, ^3J = 7.4 Hz, Me), 1.91–1.97 (2 H, m, CH_2), 3.71 (1 H, dd, ^2J = 11.9 Hz, ^3J = 7.5 Hz, CH), 3.98 (1 H, dd, ^2J = 11.9 Hz, ^3J = 5.5 Hz, CH), 4.29−4.33 (1 H, m, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.1 (Me), 27.2 (CH_2), 48.3 (CH_2), 62.9 (CH), 228.5 (C=S). MS (EI): *m/z* (%) = 148 (10) [M^+], 119 (68), 92 (100), 76 (84), 56 (42), 29 (24). Anal. Calcd (%) for $C_5H_8OS_2$ (148.24): C, 40.51; H, 5.44. Found: C, 40.41; H, 5.49.

Hexahydro-1,3-benzoxathiole-2-thione (2c)
Yellow crystals; yield 0.33 g (96%); mp 176−178 °C. IR (KBr): ν_{max} = 1628, 1431, 1326, 1272, 1094 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.43–1.48 (2 H, m, CH_2), 1.68–1.75 (2 H, m, CH_2), 1.93–1.97 (2 H, m, CH_2), 2.17–2.22 (2 H, m, CH_2), 4.08–4.09 (1 H, m, CH), 4.09–4.11 (1 H, m, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 25.5 (2 CH_2), 29.5 (2 CH_2), 65.0 (2 CH), 227.6 (C=S). MS (EI): *m/z* (%) = 174 (5) [M^+], 118 (78), 92 (100), 82 (64), 76 (48), 56 (45). Anal. Calcd (%) for $C_7H_{10}OS_2$ (174.27): C, 48.24; H, 5.78; found: C, 48.18; H, 5.79.

5-Phenyl-1,3-oxathiolane-2-thione (2d)
Yellow crystals; yield 0.30 g (95%); mp 115–117 °C. IR (KBr): ν_{max} = 1568, 1470, 1438, 1413, 1357, 1048 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 4.03 (1 H, dd, ^2J = 12.0 Hz, ^3J = 5.7 Hz, CH), 4.17 (1 H, dd, ^2J = 12.0 Hz, ^3J = 11.8 Hz, CH), 5.65 (1 H, dd, ^2J = 10.3 Hz, ^3J = 5.7 Hz, CH), 7.37–7.44 (3 H, m, 3 CH), 7.50 (2 H, d, ^3J = 7.2 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 49.8 (CH_2), 64.2 (CH), 127.5 (2 CH), 129.2 (2 CH), 129.3 (CH), 135.3 (C), 227.2 (C=S). MS (EI): *m/z* 196 (10) [M^+], 119 (76), 104 (46), 92 (25), 77 (100). Anal. Calcd (%) for $C_9H_8OS_2$ (196.28): C, 55.07; H, 4.11. Found: C, 55.03; H, 4.08.

5-(Phenoxymethyl)-1,3-oxathiolane-2-thione (2e)
Yellow crystals; yield 0.42 g (94%); mp 55–57 °C. IR (KBr): ν_{max} = 1584, 1481, 1448, 1238, 1165, 1063 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 4.06 (1 H, dd, ^2J = 12.3 Hz, ^3J = 4.0 Hz, CH), 4.18–4.23 (2 H, m, CH_2), 4.36 (1 H, dd, ^2J = 12.2 Hz, ^3J = 4.5 Hz, CH), 4.61–4.66 (1 H, m, CH), 6.93 (2 H, d, ^3J = 7.9 Hz, 2 CH), 7.02 (1 H, *t*, ^3J = 7.3 Hz, CH), 7.33 (2 H, *t*, ^3J = 7.5 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 45.0 (CH_2), 57.4 (CH), 66.7 (CH), 114.7 (2 CH), 121.9 (CH), 129.7 (2 CH), 157.8 (C), 227.5 (C=S). MS (EI): *m/z* 226 (5) [M^+], 149 (78), 134 (64), 107 (94), 92 (46), 77 (100). Anal. Calcd (%) for $C_{10}H_{10}O_2S_2$ (226.31): C, 53.07; H, 4.45. Found: C, 53.05; H, 4.40.

5-(Vinyloxymethyl)-1,3-oxathiolane-2-thione (2f)
Yellow oil; yield: 0.36 g (94%). IR (KBr): ν_{max} = 1702, 1630, 1451, 1414, 1348 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.64 (1 H, dd, ^2J = 9.8 Hz, ^3J = 5.8 Hz, CH), 3.79–3.81 (1 H, m, CH), 3.94 (1 H, dd, ^2J = 12.1 Hz, ^3J = 4.7 Hz, CH), 4.04 (2 H, d, ^3J = 5.6 Hz, 2 CH), 4.07 (1 H, dd, ^2J = 12.1 Hz, ^3J = 5.7 Hz, CH), 4.44–4.49 (1 H, m, CH), 5.20–5.30 (2 H, m, 2 CH), 5.83–5.91 (1 H, m, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 45.4 (CH_2), 58.7 (CH), 69.4 (CH_2), 72.8 (CH_2), 118.4 (CH_2), 134.3 (CH), 227.9 (C=S). MS (EI): 190 (15) [M^+], 133 (74), 114 (58), 92 (46), 57 (100). Anal. Calcd (%) for $C_7H_{10}O_2S_2$ (190.27): C, 44.19; H, 5.30. Found: C, 44.15; H, 5.36.

5-(Isopropoxymethyl)-1,3-oxathiolane-2-thione (2g)
Pale yellow oil; yield 0.37 g (96%). IR (KBr): ν_{max} = 1703, 1643, 1452, 1417, 1372, 1332 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.12 (6 H, d, ^3J = 6.1 Hz, 2 Me), 3.53–3.62 (2 H, m, CH_2), 3.73 (1 H, m, CH), 3.89 (1 H, dd, ^2J = 12.0 Hz, ^3J = 4.9 Hz, CH), 4.01 (1 H, dd, ^2J = 12.0 Hz, ^3J = 5.7 Hz, CH), 4.36–44.40 (1 H, m, CH). ^{13}C NMR (125.7 MHz,

$CDCl_3$): δ = 21.7 (Me), 21.8 (Me), 44.7 (CH_2), 58.6 (CH_2), 67.0 (CH), 72.3 (CH), 227.3 (C=S). MS (EI): *m/z* 192 (5) [M^+], 149 (84), 119 (25), 116 (52), 92 (32), 43 (42), 73 (100). Anal. Calcd (%) for $C_7H_{12}O_2S_2$ (192.29): C, 43.72; H, 6.29. Found: C, 43.85; H, 6.26.

(4*S*,5*R*)-4,5-Diphenyl-1,3-oxathiolane-2-thione (2h)

Yellow crystals; yield 0.48 g (88%); mp 123−125 °C. IR (KBr): ν = 1475, 1435, 1140, 1050 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 4.41 (1 H, s, CH), 5.74 (1 H, s, CH), 7.13−7.17 (5 H, m, 5 CH), 7.31−7.33 (5 H, m, 5 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 44.5 (CH), 70.6 (CH), 127.6 (CH), 128.1 (2 CH), 128.5 (2 CH), 129.5 (2 CH), 129.6 (CH), 129.8 (2 CH), 133.6 (C), 135.5 (C), 225.3 (C=S). MS (EI): *m/z* (%) = 272 (15) [M^+], 196 (78), 180 (64), 92 (58), 77 (100). Anal. Calcd (%) for $C_{15}H_{12}OS_2$ (272.38): C, 66.15; H, 4.44. Found: C, 66.08; H, 4.39.

(4*R*,5*R*)-4,5-Diphenyl-1,3-oxathiolane-2-thione (2i)

Yellow crystals; yield 0.47g (86%); mp 127−129 °C. IR (KBr): ν_{max} = 1479, 1439, 1142, 1056 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 4.08 (1 H, s, CH), 5.76 (1 H, s, CH), 7.00 (2 H, d, ^3J = 7.4 Hz, 2 CH), 7.18 (2 H, t, ^3J = 7.8 Hz, 2 CH), 7.27−7.30 (3 H, m, 3 CH), 7.38 (2 H, t, ^3J = 7.5 Hz, 2 CH), 7.54 (1 H, d, ^3J = 7.4 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 45.9 (CH), 68.4 (CH), 126.9 (2 CH), 128.0 (CH), 128.8 (2 CH), 129.1 (2 CH), 129.2 (2 CH), 129.3 (CH), 133.5 (C), 137.7 (C), 227.9 (C=S). MS (EI): *m/z* (%) = 272 (15) [M^+], 196 (76), 180 (62), 92 (62), 77 (100). Anal. Calcd (%) for $C_{15}H_{12}OS_2$ (272.38): C, 66.15; H, 4.44. Found: C, 66.08; H, 4.46.