Aluminium(salen) and Tetrabutylammonium Bromide Catalysed Synthesis of Cyclic Di- and Trithiocarbonates from Epoxides and Carbon Disulfide

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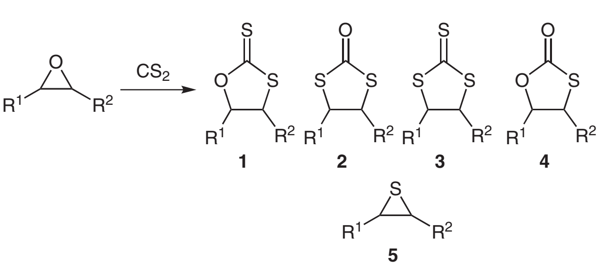
Dedicated to Professor Gerry Pattenden on the occasion of his 70th birthday

Abstract: The combination of a bimetallic aluminium(salen) complex and tetrabutylammonium bromide was found to catalyse the synthesis of cyclic di- and trithiocarbonates from epoxides and carbon disulfide. Reactions carried out at 50 °C produced 1,3-oxathiolane-2-thiones, whilst at 90 °C, 1,3-dithiolane-2-thiones were formed.

Key words: carbon disulfide, epoxide, aluminium, salen, dithiocarbonate, trithiocarbonate

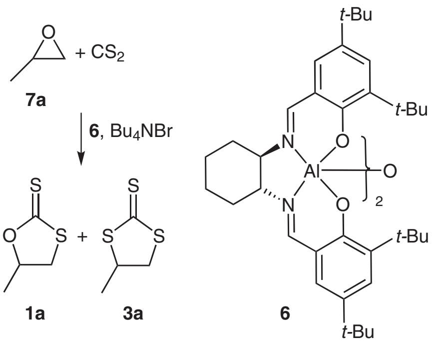
The reaction between epoxides and carbon disulfide is known to lead to a range of products[1] including 1,3-oxathiolane-2-thiones[2,3] **1**, 1,3-dithiolane-2-ones[4,5] **2**, 1,3-dithiolane-2-thiones[6] **3**, 1,3-oxathiolane-2-ones **4**, and thiiranes **5** (Scheme 1). Cyclic dithiocarbonates **1** have been shown to possess radioprotective activity[7] and have been used in polymer syntheses,[8] whilst isomers **2** have been incorporated into compounds which possess fungicidal[5] and antibacterial[9] properties, and trithiocarbonates **3** have been found to possess radioprotective[7] and insecticidal activity.[10]



Scheme 1 Reaction between epoxides and carbon disulfide

We have previously reported that the combination of bimetallic aluminium(salen) complex **6** and tetrabutylammonium bromide catalyses the synthesis of cyclic carbonates from epoxides and carbon dioxide under exceptionally mild conditions (room temperature and atmospheric pressure).[11] Therefore, to extend the scope of reactions catalysed by complex **6**,[12] we decided to study the use of this catalyst system for the synthesis of di- and trithiocarbonates from epoxides and carbon disulfide, and in this letter we report our first results.

Initial reactions were carried out using propylene oxide **7a** as substrate with up to seven equivalents of carbon disulfide in a sealed Young's tube for 16 hours under solvent-free conditions (Scheme 2). Results of this study are shown in Table 1. Entries 1 and 2 illustrate that neither catalyst **6** nor tetrabutylammonium bromide alone was capable of inducing a reaction at 50 °C and even at 90 °C they had negligible catalytic activity (entries 4 and 5). Entries 1–5 also show that even at 90 °C, there is no uncatalysed background reaction between epoxide **7a** and carbon disulfide.



Scheme 2 Synthesis of propylene di- and trithiocarbonates **1a** and **3a**

However, as shown in entries 6–13, the simultaneous use of complex **6** and tetrabutylammonium bromide was capable of catalysing the formation of di- and trithiocarbonates **1a** and **3a**. At 90 °C, using less than two equivalents of carbon disulfide, the reaction gave a 1:14 ratio of **1a/3a**, whilst using seven equivalents of carbon disulfide, the reaction gave a 2.4:1 ratio of **1a/3a** (entries 6 and 7). In the latter case, reducing the reaction temperature increased the **1a/3a** ratio to >13:1 at 45 °C, albeit at the expense of a lowered chemical yield (entries 7–9). By increasing the amount of both catalysts to 5 mol%, the yield was significantly improved, and under these conditions, the amount of carbon disulfide used could be reduced to less than two equivalents (entries 10–13) whilst retaining the preference for formation of product **1a**. A reaction temperature of 50 °C was found to be optimal both in terms of total yield and ratio of **1a/3a** (entry 12). In particular, further lowering of the reaction temperature significantly reduced

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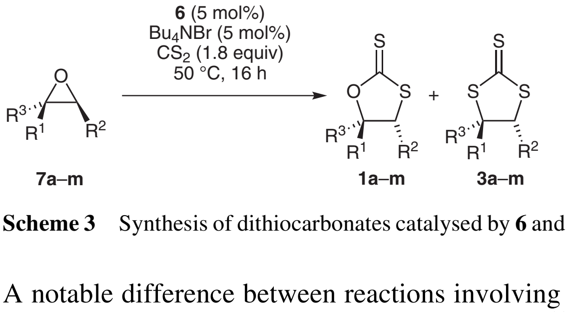
Table 1 Synthesis of Di- and Trithiopropylene Carbonates **1a** and **3a**

Entry	Catalyst (mol%)	Bu_4NBr (mol%)	CS_2 (equiv)	Temp (°C)	Yield (%)	**1a/3a**
1	5	0	7	50	0	0
2	0	5	7	50	0	0
3	0	0	1.8	90	0	
4	5	0	1.8	90	<1	
5	0	5	1.8	90	2	10:90
6	5	5	1.8	90	95	5:95
7	2.5	2.5	7	90	59	71:29
8	2.5	2.5	7	70	47	69:31
9	2.5	2.5	7	45	27	93:7
10	5	5	7	40	67	87:13
11	5	5	3.5	50	94	84:16
12	5	5	1.8	50	97	89:11
13	5	5	1.8	30	26	81:19

the chemical yield and also slightly reduced the product ratio (entry 13).

The conditions of Table 1, entry 12 were adopted as the optimal conditions for the synthesis of 1,3-oxathiolane-2-thiones, and the applicability of the chemistry to the synthesis of 1,3-oxathiolane-2-thiones derived from a range of epoxides was investigated under these conditions (Scheme 3). Results are summarized in Table 2 and in most cases good selectivities in favour of 1,3-oxathiolane-2-thiones **1a**–**k** were obtained. Terminal, aliphatic epoxides **7a**–**e** all gave predominantly the 1,3-oxathiolane-2-thione **1a**–**e**, though the **1/3** ratio decreased as the length of the alkyl chain increased (entries 1–5). Styrene oxide **7f** was exceptional in that, even at 50 °C, it gave 1,3-dithiolane-2-thione **3f** as the only product (entry 6). Functionalised epoxides **7g**,**h** both gave good results, with phenoxypropylene oxide **7h** giving a 99% yield of a 97:3 ratio of **1h**/**3h** (entries 7 and 8).



Scheme 3 Synthesis of dithiocarbonates catalysed by **6** and Bu_4NBr

A notable difference between reactions involving carbon disulfide and those we have previously reported[11a] using carbon dioxide is that vicinally disubstituted epoxides **7i**–**k** were converted into 1,3-oxathiolane-2-thiones **1i**–**k** and 1,3-dithiolane-2-thiones **3i**–**k** in moderate to good yields, though with variable levels of selectivity (entries 9–11); whereas they were inert to reaction with carbon dioxide. For each of substrates **7i**–**k**, the 1,3-oxathiolane-2-thiones **1i**–**k** were obtained with inversion of stereochemistry (*trans* product from *cis*-epoxide and vice versa). However, whilst cyclohexane derivative **3i** was also obtained as the stereoisomerically pure *trans* product (entry 9), acyclic 1,3-dithiolane-2-thiones **3j**–**k** were obtained as a virtually 1:1 mixture of *cis*- and *trans*-isomers (entries 10 and 11). When *trans*-epoxide **7k** was used as the starting material, 1,3-dithiolane-2-thione **3k** was the major product (entry 11) which may indicate that *cis*-disubstituted 1,3-oxathiolane-2-thiones, such as **1k**, are less stable than monosubstituted or *trans*-disubstituted 1,3-oxathiolane-2-thiones, such as **1a**–**j**. Attempts to extend the chemistry to geminally disubstituted substrate **1l** or trisubstituted epoxide **1m** were unsuccessful (entries 12 and 13).

Table 2 Synthesis of Dithiocarbonates **1a**–**k** and **3a**–**k** at 50 °C

Entry	R^1	R^2	R^3	Products **1**, **3**	Yield (%)	Ratio **1/3**
1	Me	H	H	**a**	97	89:11
2	Et	H	H	**b**	54	85:15
3	Bu	H	H	**c**	56	66:34
4	C_6H_{13}	H	H	**d**	61	70:30
5	C_8H_{17}	H	H	**e**	49	56:44
6	Ph	H	H	**f**	62	0:100
7	CH_2Cl	H	H	**g**	76	85:15
8	CH_2OPh	H	H	**h**	97	97:3
9	$-(CH_2)_4-$		H	**i**	35	58:42
10	Me	Me	H	**j**	96	95:5[a]
11	H	Me	Me	**k**	71	22:78[b]
12	Me	H	Me	**l**	0	–
13	Me	Me	Me	**m**	0	–
14	Me (*R*)	H	H	**a**	94	82:18

[a] The minor product is a 2:3 ratio of **3j** and **3k**.

[b] The major product is a 40:38 ratio of **3j** and **3k**.

To further investigate the stereochemistry of this reaction and to extend the chemistry to the synthesis of nonracemic dithiocarbonates, the use of enantiomerically pure (*R*)-**7a** as substrate was investigated (entry 14). The yield and **1a**/**3a** ratio were similar to those obtained with the racemic epoxide (compare entries 1 and 14). Compounds **1a** and **3a** were separable by column chromatography, and both were found to be optically active {(*R*)-**1a**: $[\alpha]_D^{20}$ –29.2 (*c* 2.5, $CHCl_3$); (*R*)-**3a**: $[\alpha]_D^{20}$ –35.9 (*c* 2.5, $CHCl_3$)}. Unfortunately, the enantiomers of **1a** and **3a** were not separable by chiral HPLC (ADH or ASH columns) and attempted analysis by chiral GC resulted in thermal decomposition to mixtures of compounds **1a**–**5a**.

From the results shown in Table 1 (especially compare entries 6 and 12), it appeared that whilst reactions carried out at 50 °C produced 1,3-oxathiolane-2-thiones **1** preferentially, reactions conducted at 90 °C should predominantly produce 1,3-dithiolane-2-thiones **3**. Therefore, the synthesis of compounds **3** from epoxides **7** was investigated (Scheme 2) by carrying out the reaction between the epoxide and carbon disulfide at 90 °C under the conditions of Table 1, entry 6. The results of this study are shown in Table 3.

Table 3 Synthesis of Dithiocarbonates **1a–k** and **3a–k** at 90 °C

Entry	Substrate	Yield (%)	Ratio **1/3**
1	**7a**	94	5:95
2	**7b**	90	47:53
3	**7c**	87	43:57
4	**7d**	81	39:61
5	**7e**	85	45:55
6	**7f**	91	0:100
7	**7g**	84	36:64
8	**7h**	87	71:29
9	**7i**	76	19:81
10	**7j**	99	83:17[a]
11	**7k**	85	77:23[b]
12	**7l**	0	–
13	**7m**	0	–

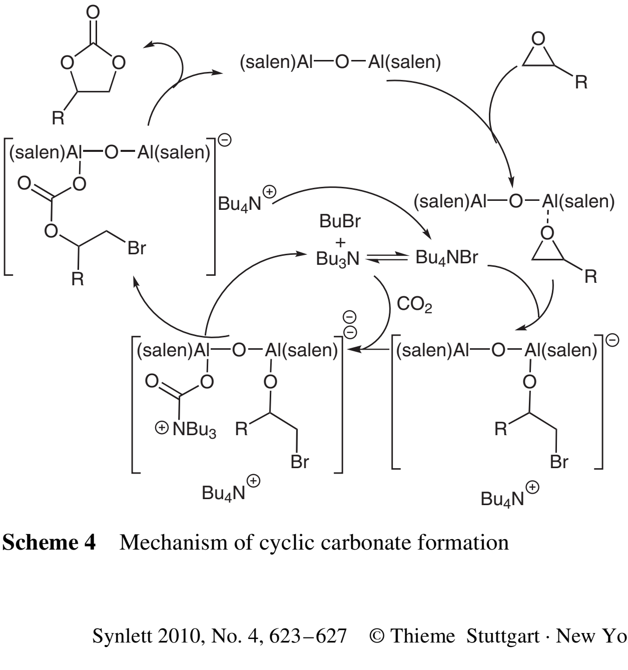
[a] The minor product is a 14:3 ratio of **3j** and **3k**.

[b] The major product is a 22:55 ratio of **1j** and **1k**; the minor product is a 8:15 ratio of **3j** and **3k**.

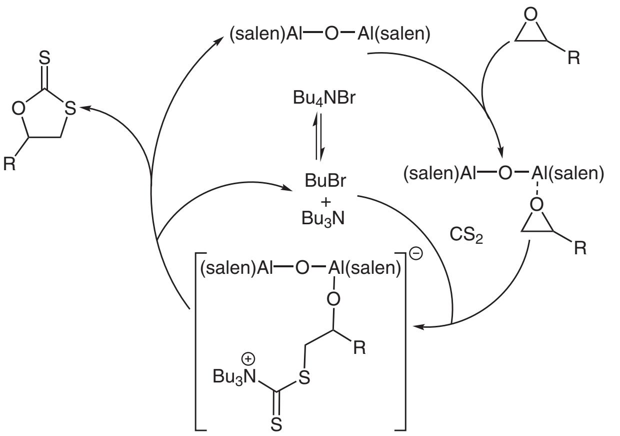
Even at 90 °C, geminally substituted epoxides **7l,m** failed to undergo any reaction (entries 12 and 13) whilst styrene oxide **7f**, which had given trithiocarbonate **3f** as the sole product at 50 °C (Table 2, entry 6), also gave trithiocarbonate **3f** as the only isolated product at 90 °C (Table 2, entry 6). Monosubstituted epoxides **7a–e,g** gave predominantly trithiocarbonates **3a–e,g**, although, with the exception of propylene oxide **3a**, there was only a slight preference for formation of trithiocarbonate **3** over dithiocarbonate **1** (entries 1–5, 7). Epoxide **7h** was unique amongst the terminal epoxides in that, at 90 °C, the major product was still the dithiocarbonate **1h**, although the **1h/3h** selectivity was reduced from that obtained at 50 °C (compare Table 2 entry 8 with Table 3 entry 8).

Cyclohexene oxide **7i** gave the *trans*-diastereomers of **1i** and **3i** in a 1:4 ratio (entry 9). However, the 1,2-dimethyl-substituted epoxides **7j,k** were less stereoselective. *cis*-Epoxide **7j** gave only a slightly lower ratio of dithiocarbonate to trithiocarbonate to that observed at 50 °C (compare Table 2 entry 10 with Table 3 entry 10). However, whilst the dithiocarbonate was again obtained exclusively as the *trans*-diastereomer **1j**, the **3j/3k** ratio changed from 2:3 at 50 °C to 14:3 at 90 °C. In contrast, at 90 °C *trans*-epoxide **7k** gave both dithiocarbonate and trithiocarbonate products as a mixture of *cis*- and *trans*-isomers. From these results it can be concluded that the synthesis of trithiocarbonates **3** is not a stereoselective process and that whilst the synthesis of dithiocarbonates **1** is stereoselective at 50 °C, this selectivity is lost at 90 °C, at least for *trans*-disubstituted epoxide **7k**.

We have previously proposed[11b] the catalytic cycle shown in Scheme 4 for the synthesis of cyclic carbonates from epoxides and carbon dioxide catalysed by complex **6** and tetrabutylammonium bromide. However, this mechanism is not consistent with the stereochemical results obtained in the reaction of disubstituted epoxides **7i–k** with carbon disulfide. In particular, the mechanism shown in Scheme 4 involves double inversion at one end of the epoxide (formation of the bromide intermediate followed by its displacement) and so overall retention of stereochemistry should be observed. However, the conversion of epoxides **7i–k** into 1,3-oxathiolane-2-thiones **1i–k** was found to result in inversion of stereochemistry. The same inversion of stereochemistry was previously observed by Endo et al.[2a] and explained on the basis of a mechanism in which the epoxide ring is opened by a sulfur-based nucleophile. The mechanism shown in Scheme 4 can similarly be modified to the rather simpler catalytic cycle shown in Scheme 5 which is consistent with the observed stereochemical outcome. The difference in the mechanisms for carbonate and dithiocarbonate formation is explained on the basis of sulfur being a better nucleophile than bromide which is, in turn, a better nucleophile than oxygen. This also explains why vicinally disubstituted epoxides are substrates for the reaction with carbon disulfide but not for reaction with carbon dioxide. Only the most reactive sulfur-based nucleophile is able to react with the vicinally disubstituted epoxides under the reaction conditions.



Scheme 4 Mechanism of cyclic carbonate formation



Scheme 5 Proposed mechanism for 1,3-oxathiolane-2-thione formation

In conclusion, we have shown that bimetallic aluminium(salen) complex **6** in conjunction with tetrabutylammonium bromide is an effective catalyst system for the formation of 1,3-oxathiolane-2-thiones and 1,3-dithiolane-2-thiones. The stereochemical and reactivity differences between cyclic carbonate and cyclic dithiocarbonate formation can be explained on the basis of the established mechanism for cyclic carbonate synthesis.

Synthesis of 1,3-Oxathiolane-2-thiones and 1,3-Dithiolane-2-thiones

CS_2 (0.18 mL, 2.98 mmol), an epoxide (1.67 mmol), catalyst **6** (74 mg, 0.083 mmol) and TBAB (28 mg, 0.083 mmol) were placed in a sealed Young flask and stirred at 50 °C or 90 °C for 16 h. Then, the solution was evaporated and the residue purified by column chromatography ($CHCl_3$–hexane, 1:1) to give compounds **1a**–**k** and/or **3a**–**k**.

Characterisation Data for New Compounds

Compound 1c

IR: ν_{max} = 1191 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (3 H, t, *J* = 6.7 Hz), 1.20–1.30 (2 H, m), 1.30–1.50 (2 H, m), 1.50–1.70 (2 H, m), 3.45 (1 H, dd, *J* = 9.5, 6.2 Hz), 3.60 (1 H, dd, *J* = 11.0, 6.5 Hz), 5.00–5.20 (1 H, m, CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.4, 33.5, 36.4, 39.5, 44.1, 92.1, 212.4. ESI-MS: *m/z* = 199 [M + Na^+]. ESI-HRMS: *m/z* calcd for $C_7H_{13}S_2O$ [MH^+]: 177.0408; found: 177.0405.

Compound 1j

IR: ν_{max} = 1192 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (3 H, d, *J* = 6.7 Hz), 1.51 (3 H, d, *J* = 6.3 Hz), 3.70–3.80 (1 H, m), 4.70–4.80 (1 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.6, 18.0, 52.5, 93.5, 211.6. ESI-MS: *m/z* = 171 [M + Na^+]. ESI-HRMS: *m/z* calcd for $C_5H_8S_2ONa$ [M + Na^+]: 170.9914; found 170.9911.

Compound 1k

IR: ν_{max} = 1192 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (3 H, d, *J* = 6.7 Hz), 1.46 (3 H, d, *J* = 6.7 Hz), 3.80–3.90 (1 H, m), 5.10–5.20 (1 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.7, 15.6, 49.5, 89.8, 212.0. ESI-MS: *m/z* = 171 [M + Na^+]. ESI-HRMS: *m/z* calcd for $C_5H_8S_2ONa$ [M + Na^+]: 170.9914; found 170.9906.

Compound 3c

IR: ν_{max} = 1061 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (3 H, t, *J* = 6.7 Hz), 1.20–1.40 (4 H, m), 1.70–1.90 (2 H, m), 3.64 (1 H, dd, *J* = 11.9, 8.0 Hz), 3.89 (1 H, dd, *J* = 11.9, 5.4 Hz), 4.20–4.40 (1 H, m, CHS). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 22.4, 30.5, 33.2, 48.3, 61.0, 228.5. ESI-MS: *m/z* = 215 [M + Na^+]. ESI-HRMS: *m/z* calcd for $C_7H_{13}S_3$ [M^+]: 192.0101; found: 192.0095.

Compound 3e

IR: ν_{max} = 1068 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (3 H, t, *J* = 6.8 Hz), 1.10–1.40 (12 H, m), 1.80–2.00 (2 H, m), 3.65 (1 H, dd, *J* = 10.8, 6.1 Hz), 3.88 (1 H, dd, *J* = 11.0, 6.4 Hz), 4.30–4.40 (1 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 22.7, 28.7, 29.2, 29.3, 29.4, 31.9, 33.6, 48.3, 61.1, 228.1. ESI-MS: *m/z* = 271 [M + Na^+]. ESI-HRMS: *m/z* calcd for $C_{11}H_{21}S_3$ [MH^+]: 249.0805; found: 249.0793.

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