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A Bimetallic Aluminum(salen) Complex for the Synthesis of 1,3-Oxathiolane-2-thiones and 1,3-Dithiolane-2-thiones

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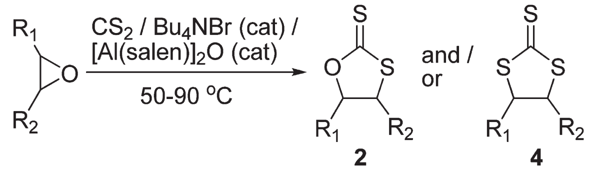

The combined use of the bimetallic aluminum(salen) complex [Al(salen)]$_2$O and tetrabutylammonium bromide (or tributylamine) is found to catalyze the reaction between epoxides and carbon disulfide. In most cases, at 50 °C, the reaction produces 1,3-oxathiolane-2-thiones, while at 90 °C, 1,3-dithiolane-2-thiones are the main product. The structure and stereochemistry of three of the 1,3-dithiolane-2-thiones is unambiguously determined by X-ray crystallographic analysis, and this is used to correct errors in the literature concerning the synthesis of cyclic di- and trithiocarbonates. The kinetics of 1,3-oxathiolane-2-thione synthesis are determined, and the resulting rate equation, along with a stereochemical analysis of the reaction and catalyst modification studies, is used to determine a mechanism for the synthesis of 1,3-oxathiolane-2-thiones which contrasts with the mechanism previously determined for cyclic carbonate synthesis using the same bimetallic aluminum(salen) complex.

Introduction

In 2003, Jacobsen first reported the use of bimetallic aluminum(salen) complex **1** as a catalyst for the asymmetric Michael addition of doubly stabilized carbanions to α,β-unsaturated imides.[1,2] Michael additions of azide,[2] nitroalkanes,[2] cyanide,[3] oximes,[4] and heterocycles[5] were also found to be catalyzed by complex **1**. Subsequently, Zhu showed that complex **1** would catalyze Passerini-type reactions between aldehydes, isocyanides, and hydrogen azide.[6] Building on our earlier work[7] involving bimetallic titanium(salen) complexes [Ti(salen)O]$_2$, we showed that the combined use of complex **1** as a Lewis acid and triphenylphosphine oxide as a Lewis base would catalyze the asymmetric addition of trimethylsilyl cyanide to aldehydes.[8,9] In addition, we have shown that a combination of complex **1** and tetrabutylammonium bromide forms an exceptionally active catalyst for the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide (Scheme 1), allowing cyclic carbonate synthesis to be carried

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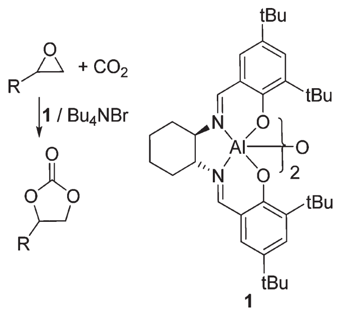
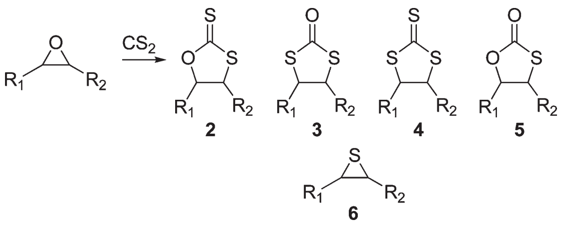
SCHEME 1. **Synthesis of Cyclic Carbonates**



SCHEME 2. **Reaction between Epoxides and Carbon Disulfide**



out at atmospheric pressure and room temperature[10] and to be integrated with oxyfuel combustion in a combined energy and chemical production unit.[11] Immobilized versions of complex **1** subsequently allowed cyclic carbonate synthesis to be carried out in a gas-phase flow reactor.[12]

In view of the high catalytic activity shown by complex **1** for the synthesis of cyclic carbonates, we decided to investigate its use in the related reaction between epoxides and carbon disulfide. This is known to be a more complex reaction as a variety of products can be formed[13] depending on the catalyst and reaction conditions, including 1,3-oxathiolane-2-thiones[14,15] **2**, 1,3-dithiolane-2-ones[16,17] **3**, 1,3-dithiolane-2-thiones[18] **4**, 1,3-oxathiolane-2-ones[13b] **5**, and thiiranes[14a] **6** as shown in Scheme 2. Previous work has shown that use of triethylamine (under high pressure)[13] as catalyst gave mixtures of products, while lithium bromide,[14a] hydrotalcite,[14e] sodium methoxide,[14f] tributylphosphine and lithium perchlorate,[14c,d] 4-methoxyphenol and DMAP at 120 °C,[14b] or triethylamine or DMAP in water[14g] selectively produced 1,3-oxathiolane-2-thiones, and potassium hydroxide or alkoxides,[18b−f] (2-propanolato)-titanatrane,[18g] or timethylamine (under high pressure)[18a] formed compounds **4** selectively. It is also known that compounds **2** can be isomerized to compounds **3** by potassium iodide[15] or by protic or Lewis acids,[19] that compounds **2** react with excess carbon disulfide to give trithiocarbonates **4**,[18g] and that compounds **4** can be converted into compounds **3** by treatment with lead tetraacetate,[17b] diaryltellurium species,[17c] or benzeneseleninic anhydride.[17d]

1,3-Oxathiolane-2-thiones **2** and 1,3-dithiolane-2-thiones **4** have both been shown to possess radioprotective activity.[20] Dithiocarbonates **2** have also been used in polymer syntheses,[14c,19,21] while trithiocarbonates **4** have been found to possess insecticidal activity.[22] In this paper, we give full details of the synthesis of compounds **2** and **4** from epoxides and carbon disulfide catalyzed by complex **1** and tetrabutylammonium bromide,[23] present the structures of three of the 1,3-dithiolane-2-thiones determined by X-ray crystallography, correct erroneous structural assignments in the literature, and report a kinetic analysis of the synthesis of dithiocarbonates **2** which allows a reaction mechanism to be determined.

Results and Discussion

Preliminary attempts to catalyze the reaction between epoxides and carbon disulfide using complex **1** and/or tetrabutylammonium bromide at atmospheric pressure and room temperature, the conditions used for the synthesis of cyclic carbonates[10] (Scheme 1), were unsuccessful. Therefore, reactions were carried out using propylene oxide **7a** as substrate with up to 7 equiv of carbon disulfide in a sealed Young's tube for 16 h under solvent-free conditions (Scheme 3). The results of

SCHEME 3. **Synthesis of Propylene Di- And Trithiocarbonates 2a and 4a**

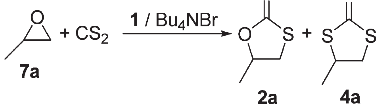


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TABLE 1. Synthesis of Di- and Trithiopropylene Carbonates 2a and 4a[a]

entry	**1** (mol %)	Bu_4NBr (mol %)	CS_2 (equiv)	*T* (°C)	yield (%)	**2a**/**4a**
1	0	0	1.8	90	0	
2	5	0	7	50	0	0
3	0	5	7	50	0	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
14	2.5	5	1.8	50	51	75:25
15	5	2.5	1.8	50	91	91:9
16	2.5	5	1.8	90	78	26:74
17	5	2.5	1.8	90	96	13:87

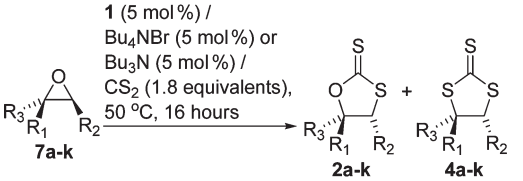
[a] All reactions were carried out for 16 h.

this optimization study are shown in Table 1. Entry 1 shows that, at 90 °C, there is no significant uncatalyzed background reaction between epoxide **7a** and carbon disulfide. Entries 2 and 3 illustrate that neither complex **1** nor tetrabutylammonium bromide alone is capable of inducing the reaction at 50 °C, and even at 90 °C they have negligible catalytic activity (entries 4 and 5).

However, the simultaneous use of complex **1** and tetrabutylammonium bromide was capable of catalyzing the formation of di- and trithiocarbonates **2a** and **4a** (entries 6−13). At 90 °C, using less than 2 equiv of carbon disulfide, the reaction gave **2a**/**4a** in a 1:14 ratio, while use of 7 equiv of carbon disulfide gave a 2.4:1 ratio of **2a**/**4a** (entries 6 and 7). In the latter case, reducing the reaction temperature increased the **2a**/**4a** 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 2 equiv (entries 10−13) while retaining the preference for formation of product **2a**. A reaction temperature of 50 °C was found to be optimal in terms of both total yield and **2a**/**4a** ratio (entry 12), since further lowering of the reaction temperature significantly reduced the chemical yield and also slightly reduced the product ratio (entry 13).

Entries 14−17 of Table 1 show that the amount of catalyst **1** used rather than the amount of tetrabutylammonium bromide principally determined the yield and chemoselectivity of reactions carried out at both 50 and 90 °C. Thus, at 50 °C, halving the amount of catalyst **1** significantly reduced both the yield and the **2a**/**4a** ratio (compare entries 12 and 14), while halving the amount of tetrabutylammonium bromide used only slightly reduced the chemical yield and had no significant effect on the **2a**/**4a** ratio (compare entries 12 and 15). Similarly, at 90 °C, halving the amount of catalyst **1** significantly reduced both the yield and the **4a**/**2a** ratio (compare entries 6 and 16), while halving the amount of tetrabutylammonium bromide used only slightly reduced the **4a**/**2a** ratio and had no effect on the chemical yield (compare entries 6 and 17).

SCHEME 4. Synthesis of Dithiocarbonates Catalyzed by 1 and Bu_4NBr or Bu_3N



Since the conditions of Table 1, entry 12, gave the best chemical yield and a high **2a**/**4a** ratio, they were adopted as the standard 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 epoxides **7a**−**k** was investigated (Scheme 4). The results are summarized in Table 2, and in most cases, good selectivities in favor of 1,3-oxathiolane-2-thiones **2a**−**i** were obtained. Terminal, aliphatic epoxides **7a**−**e** all gave predominantly the 1,3-oxathiolane-2-thione **2a**−**e**, though the **2**/**4** 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 **4f** as the only product (entry 6). Functionalized epoxides **7g,h** both gave good results, with phenoxypropylene oxide **7h** giving a 99% yield of a 97:3 ratio of **2h**/**4h** (entries 7 and 8).

A notable difference between reactions involving carbon disulfide and those we have previously reported using carbon dioxide is that vicinally disubstituted cyclohexene oxide **7i** was converted into an almost 1:1 ratio of 1,3-oxathiolane-2-thione **2i** and 1,3-dithiolane-2-thione **4i** in moderate yield (entry 9), whereas vicinally disubstituted epoxides were inert to reaction with carbon dioxide.[10a] Compounds **2i** and **4i** were both obtained exclusively as the *trans*-isomer, corresponding to inversion of configuration having occurred during the synthesis of **2i** and **4i** from *cis*-cyclohexene oxide. Attempts to extend the chemistry to geminally disubstituted substrate **7j** or trisubstituted epoxide **7k** were unsuccessful (entries 10 and 11).

Determination of the structure of compounds **2a**−**i** and **4a**−**i** was far from straightforward as the spectroscopic data present in the literature contained numerous errors and inconsistencies. A full tabulation of all of the literature data for compounds **2a**−**i** and **4a**−**i** is given in the Supporting Information. However, as an example, the ^1H and ^{13}C NMR spectra we recorded for the crystalline product obtained from styrene oxide matched the literature data for **4f**[24] but also matched the data in two papers claiming to have prepared **2f**.[14f,g] A third paper19b on the synthesis of **2f**, however, had spectroscopic data which differed from those we recorded. The high-resolution mass spectrum of our material was entirely consistent with structure **4f**, but to confirm this unambiguously, a single-crystal X-ray analysis of our product was undertaken, which clearly showed that the product was indeed trithiocarbonate **4f** (Figure 1). This, combined with numerous other spectroscopic inconsistencies detailed in the Supporting Information, suggests that some of the previously reported[14f,g] syntheses of 1,3-oxathiolane-2-thiones **2** actually synthesized 1,3-dithiolane-2-thiones **4**. This will be discussed later in this manuscript.

Products **2i**/**4i** obtained from cyclohexene oxide **7i** were separable by careful column chromatography. The structure and *trans*-stereochemistry of compound **2i** have previously been determined by Endo using X-ray analysis.[14a] Again, however, some,[13a,14g] but not all,[14f] of the literature data

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TABLE 2. **Synthesis of Dithiocarbonates 2a−i and Trithiocarbonates 4a−i**[a]

					50 °C (Bu_4NBr)		90 °C (Bu_4NBr)		50 °C (Bu_3N)	
entry	R[1]	R[2]	R[3]	products **2**, **4**	yield (%)	**2**/**4**	yield (%)	**2**/**4**	yield (%)	**2**/**4**
1	CH_3	H	H	**a**	97	89:11	94	5:95	89	80:20
2	C_2H_5	H	H	**b**	54	85:15	90	47:53	40	78:22
3	C_4H_9	H	H	**c**	56	66:34	87	43:57	38	58:42
4	C_6H_{13}	H	H	**d**	61	70:30	81	39:61	41	87:13
5	C_8H_{17}	H	H	**e**	49	56:44	85	45:55	35	91:9
6	Ph	H	H	**f**	62	0:100	91	0:100	71	0:100
7	CH_2Cl	H	H	**g**	76	85:15	84	36:64	66	85:15
8	CH_2OPh	H	H	**h**	97	97:3	87	71:29	100	98:2
9	$-(CH_2)_4-$		H	**i**	35	58:42	76	19:81	25	66:33
10	CH_3	H	CH_3	**j**	0		0			
11	CH_3	CH_3	CH_3	**k**	0		0			
12	CH_3 (*R*)	H	H	**a**	94	82:18				

[a]All reactions carried out for 16 h.

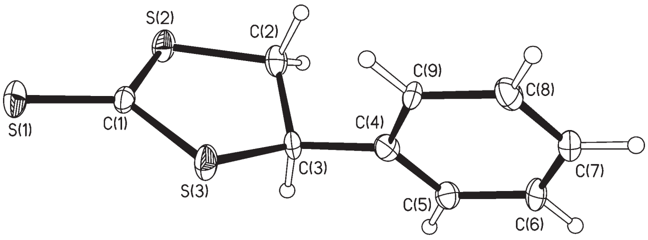


FIGURE 1. Molecular structure of compound **4f** with 40% probability ellipsoids.

were consistent with those reported by Endo. Our spectroscopic data were also consistent with those of Endo, and analysis of the ^{1}H NMR spectrum allowed the three-bond coupling constant between the two methine hydrogen atoms to be determined as 11.9 Hz which is also consistent with a *trans*-ring fusion. The symmetrical nature of trithiocarbonate **4i** meant that its stereochemistry could not be unambiguously determined from its spectroscopic data, though our data were consistent with those previously reported.[24a] Therefore, the single-crystal X-ray analysis of compound **4i** was undertaken, and this confirmed the *trans* nature of the ring fusion (Figure 2). The analysis was complicated by the extremely small size of the crystals, necessitating the use of synchrotron radiation, and by the fact that the molecule is disordered across a crystallographic mirror plane passing through atoms S(1) and C(1) and bisecting the two fused rings; this disorder has been satisfactorily resolved with the aid of some refinement restraints, clearly indicating a *trans* ring fusion, essentially planar heterocycle, chair conformation for the cyclohexane ring, and a racemic mixture of the *R*,*R* and *S*,*S* enantiomers.

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 (Table 2, entry 12). The yield and **2a**/**4a** ratio were similar to those obtained with the racemic epoxide (compare Table 2, entries 1 and 12). Compounds **2a** and **4a** were separable by column chromatography, and both were found to be optically active ((*R*)-**2a**: $[\alpha]^{20}_{D}$ −29.2 (c = 2.5, $CHCl_3$); (*R*)-**4a**: $[\alpha]^{20}_{D}$ −35.9 (c = 2.5, $CHCl_3$)). Unfortunately, the enantiomers of **2a** and **4a** were not separable by chiral HPLC (ADH or ASH columns), and attempted analysis by chiral GC resulted in thermal decomposition to mixtures of compounds **2a**−**6a**.

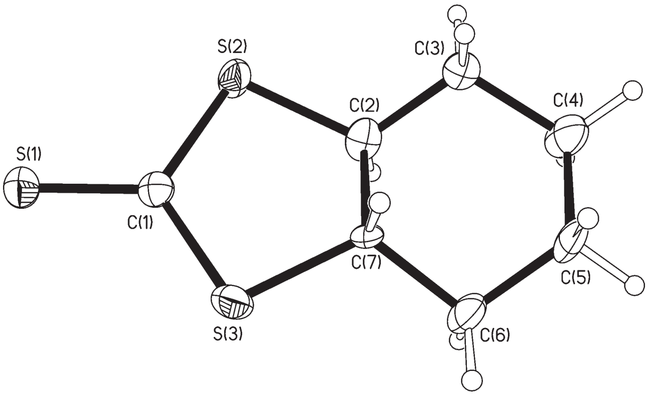


FIGURE 2. Molecular structure of compound **4i** with 40% probability ellipsoids.

From the results shown in Table 1 (especially comparing entries 6 and 12), it appeared that, while reactions carried out at 50 °C produced predominantly 1,3-oxathiolane-2-thiones **2**, reactions conducted at 90 °C should produce 1,3-dithiolane-2-thiones **4** as the major product. Therefore, the synthesis of compounds **4** from epoxides **7** was investigated (Scheme 4) 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 also shown in Table 2.

Even at 90 °C, geminally substituted epoxides **7j**,**k** failed to undergo any reaction (entries 12 and 13) while styrene oxide **7f**, which had given trithiocarbonate **4f** as the sole product at 50 °C, also gave trithiocarbonate **4f** as the only isolated product at 90 °C (entry 6). At 90 °C, monosubstituted epoxides **7a**−**e**,**g** did produce trithiocarbonates **4a**−**e**,**g**, though, with the exception of propylene oxide **7a**, there was only a slight preference for formation of trithiocarbonate **4** over dithiocarbonate **2** (entries 1−5 and 7). Cyclohexene oxide **7i** gave the *trans*-diastereomers of **2i** and **4i** in a 1:4 ratio (entry 9). Epoxide **7h** was unique among the terminal epoxides in that, at 90 °C, the major product was still the dithiocarbonate **2h**, though the **2h**/**4h** selectivity was reduced from that obtained at 50 °C (entry 8). To confirm this unexpected result, since there were only melting point and infrared data for compound **4h** in the literature,[18d] and the literature data for compound **2h** contained inconsistencies,[14a,f,g] compounds **2h** and **4h** were separated by column chromatography. The major product had high-resolution mass spectral data consistent with structure **2h**. The minor product was a crystalline

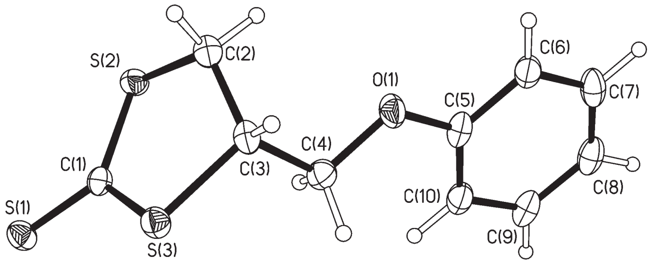
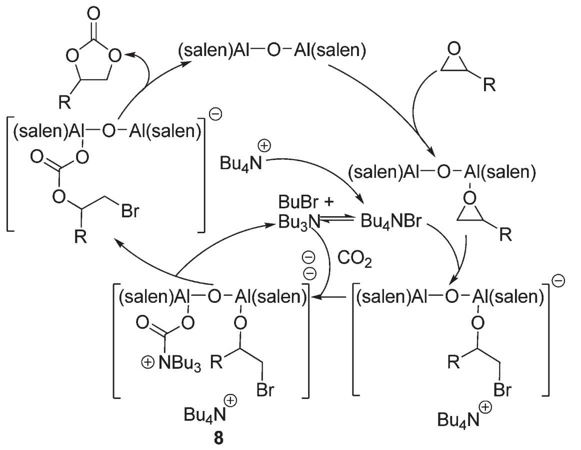
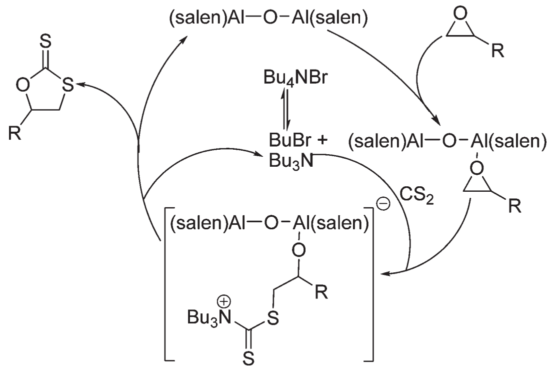


FIGURE 3. Molecular structure of compound **4h** with 40% probability ellipsoids.

SCHEME 5. **Catalytic Cycle for Cyclic Carbonate Synthesis**



SCHEME 6. **Catalytic Cycle for 1,3-Oxathiolane-2-Thione Synthesis**



solid, and its high-resolution mass spectral data and single-crystal X-ray structure (Figure 3) confirmed that it was indeed the trithiocarbonate. Compound **4h** also gave very small crystals which required synchrotron radiation to allow the X-ray structure to be determined. In addition, the crystals were found to be twinned, though this was resolved satisfactorily. The NMR data for the major isomer matched the data in two of the previous reports of the synthesis of compound **2h**.[14a,g] However, a third paper[14f] claiming the synthesis of compound **2h** contained different spectroscopic data, and these were found to be identical to those we obtained for trithiocarbonate **4h**. Thus, we were able to confirm unambiguously the structure of products **2h** and **4h** and correct the literature data.

We have previously proposed[10b] the catalytic cycle shown in Scheme 5 for the synthesis of cyclic carbonates from epoxides and carbon dioxide catalyzed by complex **1** and tetrabutylammonium bromide. The key features of this mechanism are that complex **1** acts as a Lewis acid, activating the epoxide toward ring-opening by bromide. A second tetrabutylammonium bromide molecule decomposes in situ by a reverse Menschutkin reaction[25] to form butyl bromide and tributylamine. The latter species can act as a Lewis base and activate the carbon dioxide as a carbamate. The bimetallic nature of complex **1** allows this also to coordinate to an aluminum ion to give key intermediate **8**. Formation of the aluminum-coordinated carbonate can then occur intramolecularly and is followed by cyclization to form the cyclic carbonate and regenerate the catalytic species.

However, this mechanism is not consistent with the stereochemical results obtained in the reaction of cyclohexene oxide **7i** with carbon disulfide. In particular, the mechanism shown in Scheme 5 involves double inversion at one end of the epoxide (formation of the bromide intermediate followed by its displacement during the cyclic carbonate forming step) and so overall retention of stereochemistry should be observed. However, the conversion of epoxide **7i** into 1,3-oxathiolane-2-thione **2i** was shown to involve inversion of stereochemistry. The same inversion of stereochemistry was previously observed by Endo et al.[14a] and was explained on the basis of a mechanism in which the epoxide ring is opened by a sulfur-based nucleophile. The mechanism shown in Scheme 5 can similarly be modified to the rather simpler catalytic cycle shown in Scheme 6, which is consistent with the observed stereochemical outcome.

In the mechanism shown in Scheme 6, the tetrabutylammonium bromide still decomposes in situ to form butyl bromide and tributylamine. The tributylamine reacts as a Lewis base with carbon disulfide to form a dithiocarbamate,[13,18a,24a] which acts as a nucleophile and ring opens the aluminum-coordinated epoxide. Subsequent cyclization directly forms the 1,3-oxathiolane-2-thione and regenerates the Lewis acid and Lewis base catalysts. This suggests that the only role for the tetrabutylammonium bromide is to provide an in situ source of tributylamine and that bromide is not involved in ring-opening the epoxide. An experiment carried out at 50 °C under the conditions of Table 2 with epoxide **7h** as substrate but using tributylamine instead of tetrabutylammonium bromide supported this hypothesis as a quantitative yield of **2h**/**4h** in a 98:2 ratio was obtained. In view of this success, this procedure was extended to all epoxides **7a**−**i**, and the results are included in Table 2. In each case, epoxide **7a**−**i** was converted into products **2**/**4a**−**i**, though in most cases, the yields and/or **2**/**4** ratios were lower than those obtained using tetrabutylammonium bromide as an in situ source of tributylamine, suggesting that too high a concentration of amine may inhibit the catalytic activity of aluminum complex **1**. The exceptions were epoxides **7d,e,i** which all contain long alkyl groups attached to the epoxide and which all gave better **2**/**4** ratios with tributylamine than with tetrabutylammonium bromide, though with lower chemical yields, and styrene oxide **7f** which gave a higher chemical yield (exclusively of trithiocarbonate **4f**) with tributylamine as cocatalyst.

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[25] (a) Hofman, A. W. *Proc. R. Soc. London* **1860**, *10*, 594–596. (b) Collie, N.; Schryver, S. B. *J. Chem. Soc.* **1890**, 767–782. (c) Zaki, A.; Fahim, H. *J. Chem. Soc.* **1942**, 270–272. (d) Gordon, J. E. *J. Org. Chem.* **1965**, *30*, 2760–2763.

TABLE 3. Synthesis of Compounds 2h and 4h Using Monometallic Aluminum(salen) Complexes

catalyst	yield (%)	ratio of **2h**/**4h**
9	93	91:9
10	80	78:22
11	98	90:10

To provide additional evidence to support the catalytic cycle shown in Scheme 6, the reaction kinetics were monitored. These reactions were carried out using epoxide **7h** as substrate so that dithiocarbonate **2h** was formed essentially as the sole product, without coformation of trithiocarbonate **4h** complicating the kinetic analysis. It was found that the kinetics could be monitored by ^{1}H NMR spectroscopy using $CDCl_3$ as solvent at 50 °C. The concentration of each component of the reaction was varied, allowing the rate equation (eq 1) to be derived. This can be compared with the rate equation previously determined[10b,c] for cyclic carbonate synthesis (eq 2).

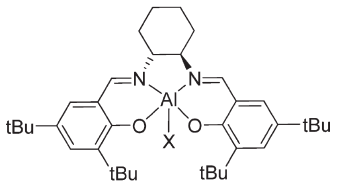
$$\text{rate} = k[\mathbf{1}][\mathbf{7h}] \text{ and zero order in both } [CS_2] \text{ and } [Bu_4NBr] \quad (1)$$

$$\text{rate} = k[\mathbf{1}][\text{epoxide}][CO_2][Bu_4NBr]^2 \quad (2)$$

Clearly, the two processes follow very different rate equations, which is consistent with them occurring by different mechanisms. The zero-order dependence of the rate of dithiocarbonate synthesis on the concentrations of both carbon disulfide and tetrabutylammonium bromide is particularly notable. This suggests that these species are only involved in the mechanism after the rate-determining step and is consistent with the mechanism in Scheme 6 provided formation of the catalyst−epoxide complex is rate-limiting. This is reasonable since the high nucleophilicity of sulfur will ensure that the subsequent epoxide ring-opening is rapid and the final step of the catalytic cycle is intramolecular (5-*exo-trig* cyclization).

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, however, a better nucleophile than oxygen. This also explains why cyclohexene oxide is a substrate 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 epoxide under the reaction conditions. It is also notable that the mechanism shown in Scheme 5 exploits the bimetallic nature of complex **1** to preorganize both the ring-opened epoxide and carbamate for intramolecular reaction. In contrast, the mechanism in Scheme 6 involves no such preorganization, which may explain why reactions involving carbon disulfide require a higher reaction temperature (50−90 °C) than those involving carbon dioxide (20 °C).

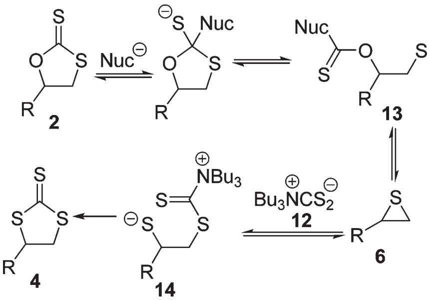
Since the mechanism shown in Scheme 6 involves only one aluminum atom in the catalytic cycle, the catalytic activity of complexes **9**−**11** was investigated. These complexes had all previously been shown to be inactive for cyclic carbonate synthesis,[10c] but in the presence of tetrabutylammonium bromide and under the conditions of Table 1, entry 12, all were found to catalyze the reaction between epoxide **7h** and carbon disulfide to form dithiocarbonate **2h** and trithiocarbonate **4h**, again with dithiocarbonate **7h** as the major product (Table 3). This clearly demonstrates that the bimetallic nature of complex **1** is not essential for its catalytic activity and provides further evidence to support the mechanism shown in Scheme 6.



9: X = Cl
10: X = Et
11: X = OEt

The mechanism by which 1,3-dithiolane-2-thiones **4** are formed has previously been discussed on the basis that they are formed from 1,3-oxathiolane-2-thiones **2**. The accepted mechanism[13,18a,b,d] (Scheme 7) involves reaction of a nucleophile (bromide or dithiocarbamate **12** in our case) with the thiocarbonyl bond of 1,3-oxathiolane-2-thione **2**.

SCHEME 7. Mechanism for the Synthesis of 1,3-Dithiolane-2-thiones 4



Subsequent cleavage of the carbon−sulfur bond within the five-membered ring establishes intermediate **13** in which the oxygen is part of a good leaving group and the thiolate is a good nucleophile. Thus, intermediate **13** can cyclize to thiirane **6**, which can then be ring-opened by dithiocarbamate **12** to give intermediate **14** which can cyclize to 1,3-dithiolane-2-thione **4**. The fact that (*R*)-**2a** is converted into optically active **4a** implies that, for this substrate at least, the formation of thiirane **6** occurs by an S_N2 reaction. However, the extremely facile formation of 1,3-dithiolane-2-thione **4f** is consistent with an S_N1-type mechanism for the synthesis of thiirane **6**, which in this case would be facilitated by the benzylic nature of the intermediate carbenium ion.

To resolve some of the inconsistencies in the literature, we repeated the synthesis of some of 1,3-oxathiolane-2-thiones **2a**−**i** using the literature procedures. Yavari et al.[14f] have reported a method for the synthesis of oxathiolane-2-thiones **2a**,**b**,**f**,**h**,**i** using sodium methoxide (generated in situ from sodium hydride) in methanol. We repeated this work (using commercial sodium methoxide) and found that it did give oxathiolane-2-thiones **2a**,**b**,**f**,**h**,**i** as the major product, but some of the corresponding 1,3-dithiolane-2-thione **4a**,**b**,**f**,**h**,**i** was also formed as a minor product. The spectroscopic data of the reaction mixtures (see Supporting Information) clearly showed that the major product had spectra which matched those we report for **2a**,**b**,**f**,**h**,**i**, while the minor product gave the spectroscopic data reported in the literature. Saidi et al. reported a synthesis of oxathiolane-2-thiones **2a**,**b**,**e**−**i** using triethylamine in water.[14g] We repeated their synthesis using epoxides **7a**,**b**,**f**−**i** and again found that the oxathiolane-2-thiones **2a**,**b**,**f**−**i** were the major product in each case but that the spectroscopic data again matched our data rather than those reported by the authors. In some cases, a mixture of oxathiolane-2-thione **2** and 1,3-dithiolane-2-thione **4** was again formed. Thus, styrene oxide **7f** gave a 9:1 ratio of **2f**/**4f**, 3-chloropropylene oxide **7g** gave a 98:2 ratio of **2g**/**4g**, and cyclohexene oxide **7i** gave a 3.5:1 ratio of **2i**/**4i**.

Conclusions

In conclusion, we have shown that bimetallic aluminum(salen) complex **1** 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 synthesis of 1,3-oxathiolane-2-thiones **2** is a stereospecific process which proceeds with inversion of configuration. The structures and stereochemistry of three of the 1,3-dithiolane-2-thiones has been unambiguously determined by single-crystal X-ray analysis, and this has allowed structural assignments in the literature to be corrected. 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 and the greater nucleophilicity of sulfur-based nucleophiles than their oxygen counterparts. This mechanistic analysis is supported by an analysis of the reaction kinetics and by modification of the catalyst structure.

Experimental Section

Synthesis of 1,3-Oxathiolane-2-thiones and 1,3-Dithiolane-2-thiones. Carbon disulfide (0.18 mL, 2.98 mmol), an epoxide (1.67 mmol), catalyst **1** (74 mg, 0.083 mmol), and tetrabutylammonium bromide (28 mg, 0.083 mmol) or tributylamine (15 mg, 0.083 mmol) were placed in a sealed Young flask and stirred at 50 or 90 °C for 16 h. The solution was evaporated and the residue purified by column chromatography (chloroform/hexane 1/1) to give compounds **2a**−**i** and/or **4a**−**i**. Compounds **2a**,**c**−**e** and **4g** could not be separated from the other reaction product in any solvent system tried. In each case, however, the other reaction product (**4a**,**c**−**e** and **2g**) was obtained pure, and spectra of compounds **2a**,**c**−**e** and **4g** showed that no other impurities were present. A sample of compounds **4f**, **4i**, and **4h** was dissolved in MeOH (2 mL) and left in a refrigerator for 48 h to produce crystals suitable for X-ray analysis.

In those cases where compounds **2** and **4** could be separated, full spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, low- and high-resolution mass spectra, and X-ray data for **4f**,**h**,**i**) are given in the Supporting Information. Copies of the ^{1}H and ^{13}C NMR spectra of all pure compounds and/or the mixture of compounds **2** and **4** are also given in the Supporting Information. Spectroscopic data for new compounds are given below.

5-Butyl-1,3-oxathiolane-2-thione 2c: ν_{max} 1191 cm^{-1}; δ_H (CDCl$_3$) 0.87 (3H, t J = 6.7 Hz), 1.2−1.4 (3H, m), 1.4−1.5 (1H, m), 1.7−1.8 (1H, m), 1.9−2.0 (1H, m), 3.35 (1H, dd J = 9.5, 6.2 Hz), 3.52 (1H, dd J = 11.0, 6.5 Hz), 5.0−5.1 (1H, m); δ_C (CDCl$_3$) 13.8, 22.3, 27.4, 33.4, 39.3, 91.8, 212.1; m/z (ESI) 199 (M + Na$^+$) found 177.0405, ($C_7H_{13}S_2O$, MH$^+$) requires 177.0408.

4-Butyl-1,3-dithiolane-2-thione 4c: ν_{max} 1061 cm^{-1}; δ_H (CDCl$_3$) 0.86 (3H, t J = 6.7 Hz), 1.2−1.4 (4H, m), 1.7−2.0 (2H, m), 3.64 (1H, dd J = 11.9, 8.0 Hz), 3.90 (1H, dd J = 11.9, 5.4 Hz), 4.2−4.4 (1H, m); δ_C (CDCl$_3$) 13.8, 22.3, 30.3, 33.2, 48.2, 60.9, 227.9; m/z (ESI) 215 (M + Na$^+$) found 192.0095, ($C_7H_{13}S_3$, M$^+$) requires 192.0101.

4-Octyl-1,3-dithiolane-2-thione 4e: ν_{max} 1068 cm^{-1}; δ_H (CDCl$_3$) 0.82 (3H, t J = 6.8 Hz), 1.1−1.4 (12H, m), 1.8−2.0 (2H, m), 3.64 (1H, dd J = 10.8, 6.1 Hz), 3.90 (1H, dd J = 11.0, 6.4 Hz), 4.2−4.4 (1H, m); δ_C (CDCl$_3$) 14.0, 22.6, 28.3, 29.1, 29.2, 29.3, 31.7, 33.5, 48.2, 61.0, 227.9; m/z (ESI) 271 (M + Na$^+$) found 249.0793, ($C_{11}H_{21}S_3$, MH$^+$) requires 249.0805.

Reaction Kinetics. Complex **1**, tetrabutylammonium bromide, and epoxide **7h** were dissolved in CDCl$_3$ (0.75 mL) to give the concentrations required for a particular experiment. The solution was added to an NMR tube followed by addition of the required amount of carbon disulfide. The tube was sealed and inserted into the NMR spectrometer with the probe heated to 50 °C. A ^{1}H NMR spectrum was collected every ca. 30 min for ca. 10 h.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **2**,**4a**−**i**; a tabulated comparison of all of the literature data for compounds **2**,**4a**−**i**; crystallographic information files for compounds **4f**,**h**,**i**; details of all kinetic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.