KI-Tetraethylene Glycol Complex as an Effective Catalyst for the Synthesis of Cyclic Thiocarbonates from Epoxides and CS_2

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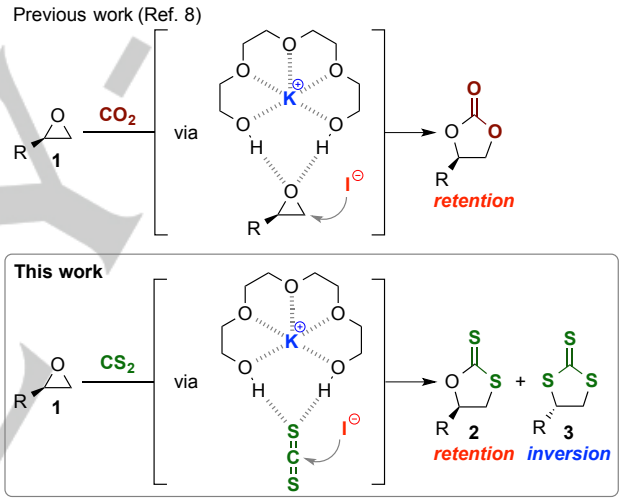
Abstract: An efficient synthesis of cyclic thiocarbonates from epoxides and CS_2 under mild reaction conditions was achieved when a KI-tetraethylene glycol complex was used as a readily available and economical catalyst. The effects of glycols and alkali metal halides were investigated in the present work to clarify the importance of both KI and tetraethylene glycol. The reaction mechanisms for the cyclic thiocarbonate synthesis are discussed based on the stereochemistry of products.

Introduction

Alkali metal halides, such as potassium and sodium halides, are among the most abundant and economical natural resources. Accordingly, the development of organic reactions using potassium and sodium halide catalysts, which are promoted by utilizing the ionic nature of these salts, is very attractive because it promotes the development of green and sustainable chemistry.[1] However, an alkali metal halide alone is a less-reactive catalyst in organic synthesis, due to its neutrality and to a low level of solubility in organic solvents. To solve these problems and to activate alkali metal halides, polyether compounds, such as crown ethers and polyethylene glycols, are often used with alkali metal halides in organic synthesis.[2] Polyether compounds are known to form complexes with potassium and sodium halides, and these complexes are soluble in organic solvents. Furthermore, the halide anions in these complexes exist in a more naked and nucleophilic version. By utilizing these properties, KI-polyether complex catalysts are applied to CO_2 fixation reactions with epoxides **1**, which are important reactions in green and sustainable chemistry.[3–5] The drawback of these catalytic systems has been the harsh reaction conditions (high pressure and high temperature) that are required to promote efficient CO_2 fixation.[3e,4,5] In our recent study on the CO_2 fixation reactions with epoxides **1** under mild reaction conditions,[6,7] we successfully developed a practical method for the synthesis of cyclic cabonates in the presence of a KI-tetraethylene glycol complex catalyst (Scheme 1).[8] Based on these findings, we were next interested in the synthesis of cyclic thiocarbonates by the reaction of epoxides **1** with CS_2, which is an isoelectronic analogue of CO_2.[9] Although these two reactions are similar, the reaction mechanisms are totally different. In the present article, we discuss and clarify the reaction mechanisms of the cyclic thiocarbonate synthesis based on the stereochemistry of products (Scheme 1).



Scheme 1. Synthesis of cyclic carbonates and thiocarbonates with a KI-tetraethylene glycol complex catalyst.

Results and Discussion

Our initial aim was to clarify the utility of a KI-tetraethylene glycol complex catalyst in the synthesis of cyclic thiocarbonates under mild conditions. The effects of glycols and alkali metal halides were investigated in a reaction with epoxide **1a** and CS_2 (Scheme 2). When a mixture of epoxide **1a**, CS_2 (1.2 equiv), and KI (10 mol %) was stirred for 5 h in the absence of tetraethylene glycol at room temperature (25 °C), cyclic dithiocarbonate **2a** was obtained in a low yield (2%). On the other hand, the KI-tetraethylene glycol complex catalyst efficiently promoted the reaction of **1a** and CS_2 under the same reaction conditions to give product **2a** in a high yield (88%). It is noteworthy that cyclic trithiocarbonate **3a** was also isolated as a minor product in this reaction (4%). To clarify the role of hydroxy groups in tetraethylene glycol, we also examined the reactions with tetraethylene glycol dimethyl ether and 18-crown-6. Very low

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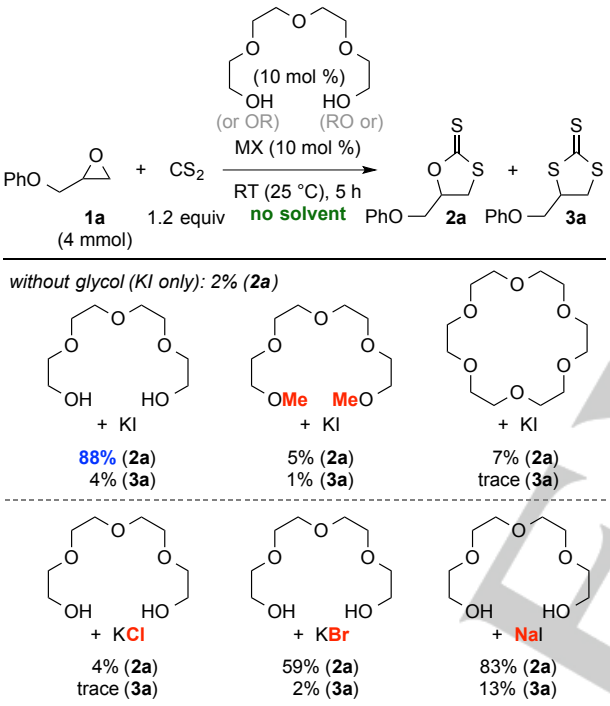
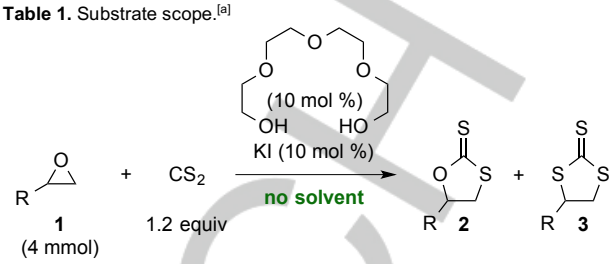
catalytic activities were observed in these reactions, which gave dithiocarbonate **2a** in low yields with trace amounts of trithiocarbonate **3a**. The effect of alkali metal halides was also investigated in the reaction with CS_2. Although a KCl complex with tetraethylene glycol showed quite low reactivity, a KBr-tetraethylene glycol complex catalyst moderately promoted the reaction to give **2a** in a 59% yield with **3a** in a 2% yield. The tendency of this reactivity with KBr is different from the reaction with CO_2.[8] The NaI complex showed comparable reactivity in the case of the KI complex, but the selectivity for dithiocarbonate **2a** to trithiocarbonate **3a** was lower (**2a**/**3a** = 6.4:1) than that attained with the KI complex (**2a**/**3a** = 22:1).



Scheme 2. Effects of glycols and alkali metal halides.

With the effective catalysts in hand, the substrate generality of epoxides **1** for the synthesis of thiocarbonates was examined using a KI-tetraethylene glycol complex catalyst (Table 1). The reactions were efficiently promoted under mild reaction conditions, and dithiocarbonate products **2** were obtained in good-to-high yields. The selectivities for dithiocarbonates **2** to trithiocarbonates **3** were also good-to-high (**2**/**3** = 4.3:1–>50:1).

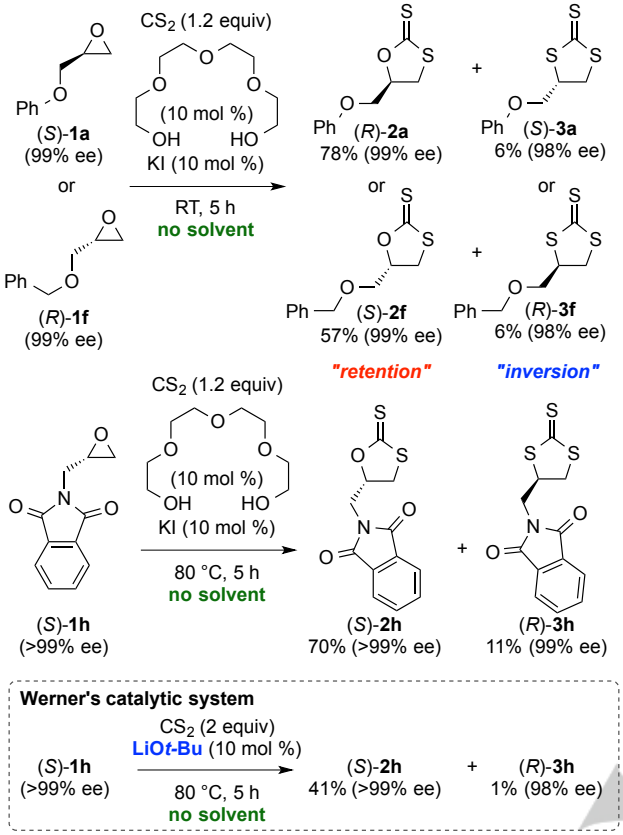
Table 1. Substrate scope.[a]

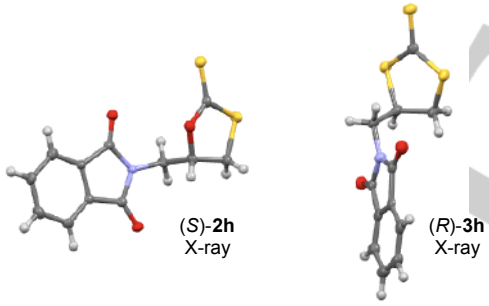


Entry	R	Conditions	Yield of **2** [%][b]	Yield of **3** [%][b]
1	*n*-Pr (**1b**)	40 °C, 24 h	65 (**2b**)	6 (**3b**)
2	$CH_3(CH_2)_5$ (**1c**)	40 °C, 16 h	65 (**2c**)	15 (**3c**)
3	CH_2=$CHCH_2CH_2$ (**1d**)	40 °C, 16 h	62 (**2d**)	12 (**3d**)
4	CH_2=$CHCH_2OCH_2$ (**1e**)	RT, 5 h	69 (**2e**)	4 (**3e**)
5	$PhCH_2OCH_2$ (**1f**)	RT, 5 h	63 (**2f**)	1 (**3f**)
6	$ClCH_2$ (**1g**)	RT, 24 h	78 (**2g**)	trace (**3g**)

[a] Reaction conditions: **1** (4.0 mmol), tetraethylene glycol (0.40 mmol, 10 mol %), KI (0.40 mmol, 10 mol %), CS_2 (4.8 mmol, 1.2 equiv). [b] Yield of isolated products **2** and **3**.

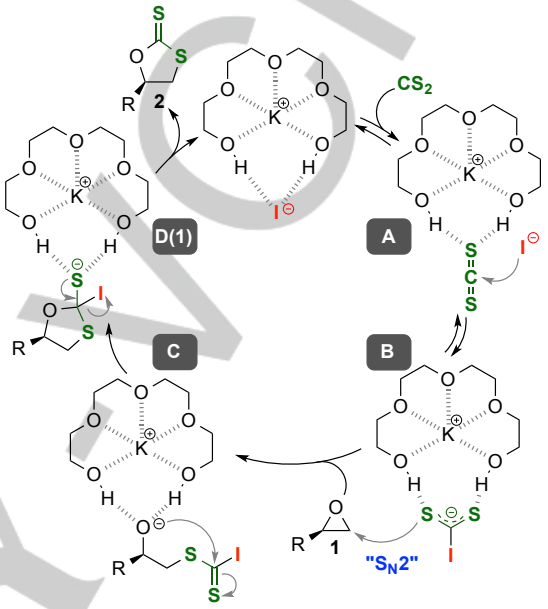
Enantiopure epoxides (**1a**, **1f**, and **1h**) were also submitted to the reaction with CS_2 under the influence of the KI-tetraethylene glycol complex catalyst (Scheme 3). To our delight, cyclic dithiocarbonates **2a**, **2f**, and **2h** were obtained in good yields with a complete "retention" of the stereochemistry. On the other hand, cyclic trithiocarbonates **3a**, **3f**, and **3h** were obtained in a complete "inversion" of the stereochemistry. The absolute configurations of the products **2** and **3** were determined by X-ray diffraction analysis of **2h** and **3h**.[10] Additionally, we proved that Werner's catalytic system that uses a Li*O*-*t*-Bu catalyst[9j,k] also showed the same stereochemistry tendency demonstrated in the present reaction. It should be noted that this is a valuable example of the determination of absolute configurations for thiocarbonates in the reaction of enantiopure epoxides and CS_2.



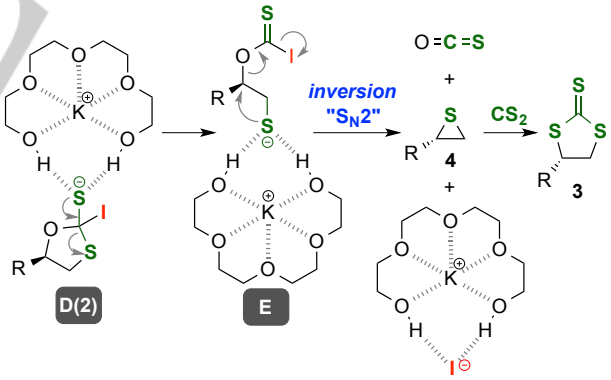


Scheme 3. Reaction with optically active epoxides.

Based on these results and those of previous related reports,[9] the assumed mechanisms for the reaction of epoxides **1** and CS_2 were proposed in Schemes 4 and 5. The first step of the reaction with CS_2 is known to differ from the reaction with CO_2.[9] At first, an iodide anion attacks CS_2, which was activated via hydrogen-bonding with the hydroxyl groups of tetraethylene glycol (intermediate **A**). Subsequently, a nucleophilic attack by the resultant iododithioformate anion in intermediate **B** on epoxide **1** led to intermediate **C**. Intramolecular cyclization (intermediate **C**) and the subsequent elimination of the iodide anion (intermediate **D(1)**) led to the attainment of cyclic dithiocarbonate **2** and to the retention of the stereochemistry. On the other hand, cyclic trithiocarbonate **3** was obtained via the ring opening in intermediate **D(2)** to form intermediate **E** (Scheme 5). The intramolecular S_N2 reaction of the thiolate anion in intermediate **E** afforded thiirane **4** with an inversion of the stereochemistry.[9j,11] The reaction of thiirane **4** with CS_2 under the influence of a KI-tetraethylene glycol complex gave product **3** in a catalytic cycle similar to that proposed for the reaction with epoxide **1** (Scheme 4).[9i,m,12] Note that trace amounts of thiiranes **4** were observed in the crude NMR spectra of several examples in Table 1.



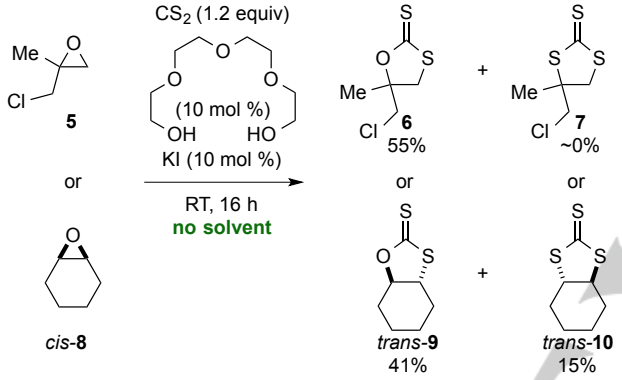
Scheme 4. Assumed catalytic cycle to produce cyclic dithiocarbonate **2**.



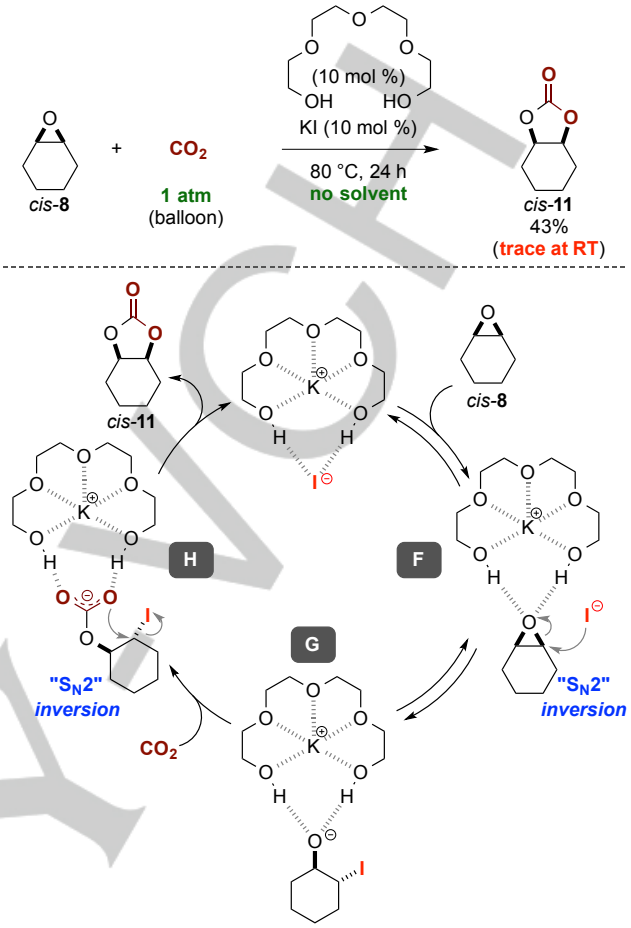
Scheme 5. Proposed mechanism to produce cyclic trithiocarbonate **3**.

To expand the utility and further support the mechanism of the present reaction, 1,1- and 1,2-disubstituted epoxides **5** and *cis*-**8** were submitted to the reaction (Scheme 6). The reaction with 1,1-disubstituted epoxide **5** was promoted by the KI-tetraethylene glycol complex catalyst to give dithiocarbonate **6** in a moderate yield (55%) with high selectivity (trithiocarbonate **7**: ~0%). The reaction with 1,2-disubstituted epoxide *cis*-**8** and CS_2 proceeded at room temperature to afford dithiocarbonate *trans*-**9** (41%) and trithiocarbonate *trans*-**10** (15%).[9b,f,j,k] Notably, the

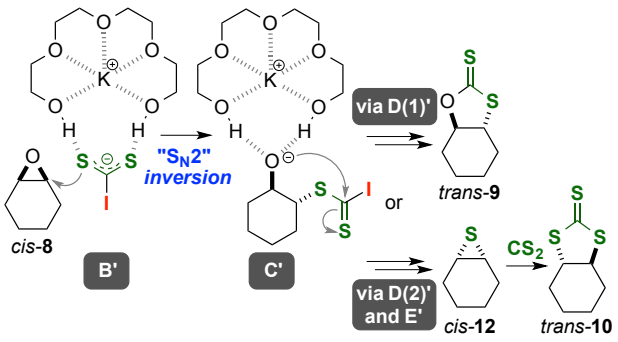
reactivity and stereoselectivity were completely different by comparison with the reaction of *cis*-**8** and CO_2 (Scheme 7). The reaction with CO_2 at 80 °C gave a *cis*-**11**, selectively, via double S_N2 inversions with activation of epoxide by the catalyst (intermediates **F** and **H** in Scheme 7). In sharp contrast, the product *trans*-**9** was formed as a result of the single S_N2 inversion in the conversion of intermediate **B'** to **C'** (Scheme 8). The *trans* selectivity of trithiocarbonate **10** could be explained by the formation of thiirane *cis*-**12**, which was formed in the same reaction mechanism for the formation of thiirane **4** in Scheme 5. The reaction of thiirane *cis*-**12** with CS_2 under the influence of the KI-tetraethylene glycol complex gave *trans*-**10** in a mechanism that was similar to that proposed for the reaction with epoxide *cis*-**8** (Scheme 8). These *trans* selectivities of thiocarbonates **9** and **10** from *cis*-**8** fully support the reaction mechanisms proposed in Schemes 4, 5, and 8.



Scheme 6. Reaction with 1,1-disubstituted and 1,2-disubstituted epoxides.



Scheme 7. Reaction with epoxide *cis*-**8** and CO_2.



Scheme 8. Proposed mechanism to produce cyclic thiocarbonates **9** and **10**.

Conclusions

We have successfully developed an efficient method for the synthesis of cyclic thiocarbonates via a reaction of epoxides and CS_2 under mild reaction conditions using a KI-tetraethylene glycol complex catalyst. The effects of glycols and alkali metal halides

were investigated to clarify the essential points of the catalytic activity. The importance of both the hydroxy groups of tetraethylene glycol and the iodide of the alkali metal halide was clearly observed in the cyclic thiocarbonate synthesis. The reactions of various epoxides and CS_2 provided cyclic dithiocarbonates in good yields. In these reactions, cyclic trithiocarbonates were also obtained as a minor product. The optically active epoxides and 1,2-disubstituted epoxides were also submitted to the reactions with CS_2 under the influence of a KI-tetraethylene glycol complex catalyst. Although the reaction with CO_2 gave cyclic carbonates in retention of the stereochemistry,[8,13] different trends were observed in the reaction with CS_2. Based on the stereochemistry of these two reactions, the reaction mechanisms were discussed, and assumed catalytic cycles were proposed. The proposed reaction mechanisms clearly explained the observed stereochemistry of cyclic thiocarbonates, and we concluded that the reactions with CO_2 and CS_2 proceeded via different mechanisms.

Experimental Section

Typical procedure for the reaction of epoxides 1 with CS_2 catalyzed by a KI-tetraethylene glycol complex: To a mixture of glycidyl phenyl ether **1a** (0.542 mL, 4.00 mmol), tetraethylene glycol (69.1 µL, 0.400 mmol, 10 mol %), and potassium iodide (66.4 mg, 0.400 mmol, 10 mol %) was added CS_2 (0.289 mL, 4.80 mmol) at room temperature. The reaction mixture was stirred for 5 h at room temperature (25 °C). The resultant reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1–2:1 as eluent) to afford cyclic dithiocarbonate **2a** (797 mg, 3.52 mmol; R_f = 0.42 in hexane/EtOAc = 2:1) and trithiocarbonate **3a** (38.8 mg, 0.16 mmol; R_f = 0.67 in hexane/EtOAc = 2:1).

2a:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.39–5.46 (m, 1H), 4.24–4.34 (m, 2H), 3.69–3.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.2, 157.7, 129.7, 121.9, 114.5, 87.7, 66.3, 36.3; IR (neat) 3060, 3038, 2924, 2870, 1597, 1587, 1494, 1240, 1228, 1181, 1042, 751, 689 cm^{-1}.

3a:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.61–4.67 (m, 1H), 4.37 (t, *J* = 9.6 Hz, 1H), 4.23 (dd, *J* = 5.8, 12.2 Hz, 1H), 4.20 (dd, *J* = 5.4, 9.8 Hz, 1H), 4.08 (dd, *J* = 4.0, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 226.4, 157.7, 129.7, 121.8, 114.6, 66.4, 57.2, 44.9; IR (neat) 3046, 1599, 1587, 1496, 1264, 1239, 1078, 1041, 732, 702, 690 cm^{-1}.

2b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.08–5.15 (m, 1H), 3.59 (dd, *J* = 6.6, 10.8 Hz, 1H), 3.40 (dd, *J* = 9.4, 11.0 Hz, 1H), 1.98–2.07 (m, 1H), 1.75–1.84 (m, 1H), 1.45–1.65 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 212.2, 91.6, 39.3, 35.7, 18.7, 13.7; IR (neat) 2959, 2932, 2872, 1182, 1046, 830, 647 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_6H_{10}OS_2$: 162.0173 ([M$^+$]), found 162.0172.

3b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.38–4.45 (m, 1H), 3.97 (dd, *J* = 5.6, 11.6 Hz, 1H), 3.71 (dd, *J* = 8.0, 12.0 Hz, 1H), 1.84–2.01 (m, 2H), 1.47 (sextet, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 228.0, 60.7, 48.2, 35.5, 21.5, 13.6; IR (neat) 2956, 2926, 2869, 1461, 1421, 1090, 1049, 874 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_6H_{10}S_3$: 177.9945 ([M$^+$]), found 177.9945.

2c:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.06–5.14 (m, 1H), 3.58 (dd, *J* = 6.6, 11.0 Hz, 1H), 3.40 (dd, *J* = 9.6, 11.2 Hz, 1H), 1.98–2.07 (m, 1H), 1.77–1.86 (m, 1H), 1.25–1.58 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 212.2, 91.9, 39.3, 33.6, 31.4, 28.8, 25.3, 22.4, 14.0; IR (neat) 2952, 2925, 2856, 1184, 1048 cm^{-1}.

3c:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.35–4.43 (m, 1H), 3.96 (dd, *J* = 5.2, 11.8 Hz, 1H), 3.71 (dd, *J* = 8.0, 12.0 Hz, 1H), 1.85–2.01 (m, 2H), 1.24–1.47 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 227.9, 61.0, 48.2, 33.5, 31.5, 28.8, 28.2, 22.5, 14.0; IR (neat) 2953, 2025, 2853, 1457, 1062, 873 cm^{-1}.

2d:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77–5.87 (m, 1H), 5.06–5.16 (m, 3H), 3.61 (dd, *J* = 6.6, 10.8 Hz, 1H), 3.42 (dd, *J* = 9.8, 11.0 Hz, 1H), 2.22–2.37 (m, 2H), 2.11–2.20 (m, 1H), 1.87–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 212.0, 136.1, 116.3, 90.9, 39.2, 32.7, 29.4; IR (neat) 3076, 2977, 2935, 2849, 1640, 1437, 1350, 1182, 1047, 914, 847, 647 cm^{-1}.

3d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73–5.83 (m, 1H), 5.05–5.12 (m, 2H), 4.37–4.43 (m, 1H), 3.99 (dd, *J* = 5.4, 11.8 Hz, 1H), 3.71 (dd, *J* = 7.2, 12.0 Hz, 1H), 2.14–2.30 (m, 2H), 1.96–2.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 227.5, 136.1, 116.7, 59.9, 48.1, 32.6, 32.1; IR (neat) 3074, 2976, 2920, 2848, 1639, 1444, 1434, 1421, 1059, 914, 870 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_7H_{10}S_3$: 189.9945 ([M$^+$]), found 189.9945.

2e:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85–5.94 (m, 1H), 5.21–5.34 (m, 3H), 4.08–4.09 (m, 2H), 3.82 (dd, *J* = 5.4, 10.6 Hz, 1H), 3.77 (dd, *J* = 4.4, 10.8 Hz, 1H), 3.70 (dd, *J* = 8.4, 11.2 Hz, 1H), 3.62 (dd, *J* = 7.2, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.9, 133.5, 117.7, 89.1, 72.4, 68.3, 35.9; IR (neat) 3079, 3010, 2979, 2921, 2859, 1345, 1228, 1183, 1093, 1043, 924, 843 cm^{-1}.

3e:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85–5.95 (m, 1H), 5.22–5.34 (m, 2H), 4.44–4.50 (m, 1H), 4.09 (dd, *J* = 5.8, 8.4 Hz, 1H), 4.04–4.07 (m, 2H), 3.97 (dd, *J* = 4.4, 12.4 Hz, 1H), 3.84 (dd, *J* = 9.2, 10.0 Hz, 1H), 3.65 (dd, *J* = 5.8, 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 227.2, 133.8, 118.0, 72.4, 69.0, 58.1, 44.9; IR (neat) 2924, 2853, 1421, 1265, 1068, 1035, 997, 928, 864, 735 cm^{-1}.

2f:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.40 (m, 5H), 5.21–5.28 (m, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 3.84 (dd, *J* = 5.0, 10.6 Hz, 1H), 3.78 (dd, *J* = 4.6, 10.6 Hz, 1H), 3.69 (dd, *J* = 8.4, 10.8 Hz, 1H), 3.60 (dd, *J* = 7.2, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.8, 137.0, 128.5, 128.0, 127.7, 89.0, 73.7, 68.4, 36.0; IR (neat) 2922, 2863, 1731, 1453, 1343, 1228, 1185, 1095, 1038, 913, 848, 737, 697 cm^{-1}.

3f:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.40 (m, 5H), 4.59 (s, 2H), 4.44–4.50 (m, 1H), 4.07 (dd, *J* = 6.0, 12.4 Hz, 1H), 3.95 (dd, *J* = 4.8, 12.0 Hz, 1H), 3.85 (dd, *J* = 9.2, 9.4 Hz, 1H), 3.69 (dd, *J* = 5.8, 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 227.2, 137.2, 128.6, 128.1, 127.7, 73.5, 69.0, 58.2, 44.9; IR (neat) 2923, 2855, 1453, 1361, 1068, 1034, 864, 736, 696 cm^{-1}.

2g:[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.35–5.42 (m, 1H), 3.85–3.96 (m, 2H), 3.70–3.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.7, 88.2, 42.7, 36.7; IR (neat) 3047, 2954, 1438, 1428, 1338, 1265, 1179, 1038, 732, 701 cm^{-1}.

(*S*)-**2h:** HPLC analysis: Daicel Chiralcel OD-3, haxane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 37.0 min (minor) and 40.1 min (major). $[\alpha]^{28}_{D}$ = –57.6 (*c* = 1.0, $CHCl_3$; >99% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.91 (m, 2H), 7.76–7.80 (m, 2H), 5.41–5.48 (m, 1H), 4.27 (dd, *J* = 6.8, 14.0 Hz, 1H), 4.06 (dd, *J* = 5.4, 14.2 Hz, 1H), 3.75 (dd, *J* = 7.6, 11.2 Hz, 1H), 3.60 (dd, *J* = 7.0, 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.3, 167.7, 134.5, 131.6, 123.7, 86.6, 39.5, 37.3; IR (neat) 3062, 3027, 2997, 2952, 1773, 1704, 1414, 1393, 1370, 1309, 1238, 1167, 1055, 1034, 1004, 957, 721, 712 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{12}H_9NO_3S_2$: 279.0024 ([M$^+$]), found 279.0007.

(*R*)-**3h:** HPLC analysis: Daicel Chiralcel OD-3, haxane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 33.2 min (major) and 43.1 min (minor). $[\alpha]^{20}_{D}$ = +193.2 (*c* = 1.0, $CHCl_3$; 99% ee). Spectral data completely matched with reported data.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.92 (m, 2H), 7.77–7.81 (m, 2H), 4.64–4.71 (m, 1H), 4.28 (dd, *J* = 8.4, 14.0 Hz, 1H), 4.12 (dd, *J* = 5.2, 12.0 Hz, 1H), 4.08 (dd, *J* = 5.6, 14.0 Hz, 1H), 3.77 (dd, *J* = 4.4, 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 225.6, 168.0, 134.5, 131.6, 123.8, 57.2, 45.9, 39.2; IR (neat) 3058, 2979, 2929, 1770, 1706, 1424, 1391, 1359, 1098, 1065, 715 cm^{-1}.

6: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (d, *J* = 12.0 Hz, 1H), 3.84 (d, *J* = 11.6 Hz, 1H), 3.69 (d, *J* = 12.0 Hz, 1H), 3.44, (d, *J* = 11.2 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.0, 96.5, 47.3, 41.5, 22.9; IR (neat) 2982, 2951, 2931, 2853, 1436, 1381, 1268, 1197, 1166, 1107, 1058, 1037, 854, 792, 745 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_5H_7ClOS_2$: 181.9627 ([M$^+$]), found 181.9627.

trans-**9:**[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.35 (td, *J* = 4.0, 11.6 Hz, 1H), 3.73 (td, *J* = 4.0, 12.0 Hz, 1H), 2.41–2.47 (m, 1H), 2.17–2.23 (m, 1H), 1.97–2.03 (m, 1H), 1.88–1.94 (m, 1H), 1.72–1.82 (m, 1H), 1.58–1.69 (m, 1H), 1.32–1.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 212.3, 94.6, 56.3, 29.7, 28.1, 25.0, 23.6; IR (neat) 2941, 2862, 1454, 1444, 1266, 1254, 1214, 1206, 1179, 1146, 1084, 1058, 1038, 1000, 959, 902, 862, 833, 637, 614 cm^{-1}.

trans-**10:**[9] Spectral data completely matched with reported data. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.05–4.14 (m, 2H), 2.20–2.24 (m, 2H), 1.91–2.01 (m, 2H), 1.68–1.78 (m, 2H), 1.40–1.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 227.1, 64.4, 29.0, 25.0; IR (neat) 2939, 2856, 1445, 1441, 1280, 1265, 1100, 1058, 1035, 863, 740 cm^{-1}.

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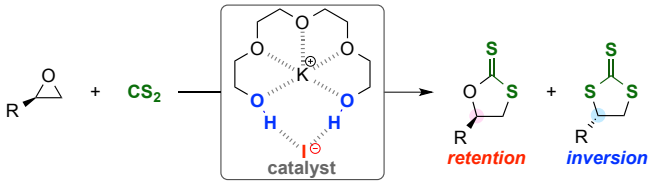

Efficient synthesis of cyclic thiocarbonates from epoxides and CS_2 was achieved when a KI-tetraethylene glycol complex was used as an economical catalyst. The mechanism for this reaction was discussed based on the stereochemistry of products.

Sustainable Catalyst

*M. Okada, R. Nishiyori, S. Kaneko, K. Igawa, S. Shirakawa**

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KI-Tetraethylene Glycol Complex as an Effective Catalyst for the Synthesis of Cyclic Thiocarbonates from Epoxides and CS_2