A Simple and Novel Eco-Friendly Process for the Synthesis of Cyclic Dithiocarbonates from Epoxides and Carbon Disulfide in Water

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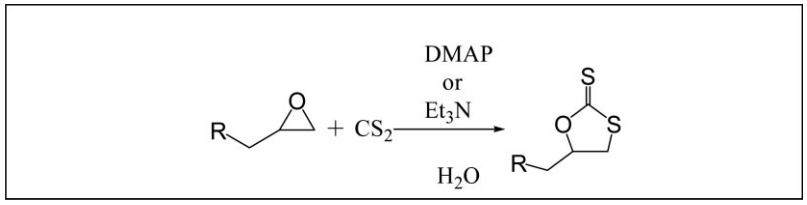

The reaction of oxiranes with carbon disulfide for preparation of cyclic dithiocarbonates was carried out in water under catalytic amount of an organic base such as dimethylaminopyridine or triethylamine. The reaction conditions are simple and give high yields of desired products.

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INTRODUCTION

Because it was reported that Diels–Alder reactions could be greatly accelerated by using water as a solvent instead of organic solvents [1], considerable attention has been directed toward the development of organic reactions in water. Besides Diels–Alder reaction, water was used in almost all of the useful organic reactions, even reactions involving water sensitive materials [2]. It is obvious that water is the most inexpensive and environmentally benign solvent. Thus, development of novel reactivity as well as selectivity that cannot be attained in conventional organic solvents is one of the challenging goals of aqueous chemistry [1].

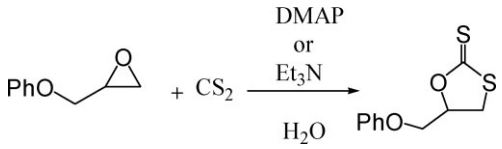
Tertiary amines- and pyridine-based organo catalysts were introduced to synthetic chemistry as a powerful nucleophilic group-transfer catalyst since more than 3 decades ago [3], because of their ability to catalyze important reactions such as acylation [4], esterification [5], macrolactonization [6], Baylis-Hillman [7], and silylation reactions [8]. Also, because of high potential of these compounds for developing of chiral acylating catalyst [9], several research groups are interested in this field of chemistry. 4-(Dimethylamino) pyridine (DMAP) is one of the standard catalysts for nucleophilic group-transfer reactions.

There are many reports on the reaction of epoxide with carbon disulfide [10]. Usually, high pressure and elevated temperature as well as long reaction times have been used for the synthesis of cyclic dithiocarbonates. Harsh reaction conditions have been reported for the synthesis and purification of five-membered cyclic dithiocarbonates, its regioisomers, and trithiocarbonates depending on the catalyst, temperature, and pressure. Shi and his coworkers studied the reaction between epoxy propane and carbon disulfide in the presence of DMAP and *p*-methoxyphenol as a catalyst at high temperature to afford the cyclic dithiocarbonate in 45% yield [11]. Recently, Maggi *et. al* reported a very interesting method for the synthesis of cyclic dithiocarbonates in the presence of hydrotalcite catalyst with good yields [12]. But there is no report for the preparation of cyclic dithiocarbonates in water therefore availability of a facile and green procedure to cover these drawbacks is interesting.

RESULTS AND DISCUSSION

Encouraged by our good experience to open the epoxide ring by nucleophiles such as amines [13] and dithiocarbamate anion [14] in water and in continuation of our previous work for the synthesis of dithiocarbamates in water and solvent-free conditions [15], we were interested to investigate the reaction of epoxides with CS_2 in the presence of Lewis bases in aqueous medium (Scheme 1). For this purpose, different Lewis bases such as Et_3N, DMAP, DABCO, and DBU were examined, and we have found that DMAP and Et_3N (10 mol %) gave the best results for the preparation of cyclic

Scheme 1. Synthesis of cyclic dithiocarbonate in water.



dithiocarbonates. We also tried the halide salts such as LiCl in water as catalyst, but we did not obtain good results (Table 1, entry 12). Also solvent effect was examined for the reaction of 2,3-epoxypropyl phenyl ether and CS_2 by using different organic solvents, but we did not obtain any desired products, except for ethanol, which gave only 10% yield (*ca*. Table 1).

After optimizing the reaction conditions, we tried to expand our results to other epoxides and the results are reported in Table 2. As shown in Table 2, 1,2-epoxides gave moderate to good yields but for cyclic epoxides such as cyclohexane epoxide, we obtained the product in low yield. For epichlorohydrin, 91% isolated yield was obtained. Only for styrene epoxide two regioisomers were obtained in 2:1 ratio and total yields of 52%. The ratio was determined by ^{1}H NMR with using the area of the peak of benzylic hydrogen in the two regioisomers (Entry 7, Table 2).

A plausible mechanism for this reaction is shown in Scheme 2. It is possible that the ability of water to give hydrogen bond with epoxides makes this transformation very efficient. We supposed that DMAP activates the CS_2 to dithiocarbamate anion **1**, which attacks to the water-activated epoxide to give compound **2**. In the next step, the epoxide's oxygen attacks the thiocarbonyl to remove DMAP and to form the cyclic dithiocarbonate 3.

CONCLUSIONS

In conclusion, we showed a very mild, facile, economical, and friendly method for the synthesis of cyclic dithiocarbonates in the presence of catalytic amount of DMAP. Also in large scale synthesis, extraction of products does not need to any organic solvent and only separation of organic phase from aqueous phase gives the crude products. Trying to do this reaction under asymmetrical conditions with chiral Lewis bases is undertaken in our laboratory.

EXPERIMENTAL

General. All chemicals were purchased and used without any further purification. NMR spectra were recorded at 500 MHz for proton and at 125 MHz for carbon nuclei in $CDCl_3$. The products were purified by column chromatography carried out on silica gel using ethyl acetate/petroleum ether mixtures. All compounds were characterized by their spectroscopic data (IR, ^{1}H NMR, and ^{13}C NMR) by comparison with those reported in the literature. Reactions were carried out at room temperature. Carbon disulfide, DMAP, and all epoxides are commercially available and used without further purification.

General procedure for the synthesis of the cyclic dithiocarbonates in water. In a round-bottomed flask equipped with magnet stirrer, epoxide (5 mmol), carbon disulfide (10 mmol) and water (20 mL) were added. To this mixture, DMAD or Et_3N (0.5 mmol) was added and stirred for 20 h. The progress of the reaction was checked by TLC. After completion of the reaction, the product was extracted with ethyl acetate and washed with water to remove the catalyst. The crude products were purified with column chromatography using silica gel as stationary phase and mixture of hexane and ethyl acetate (7:3) as an eluent to give the pure products with the yields shown in Table 2. Unreacted epoxides were recovered with column chromatography. Selected spectroscopic data for compounds are given in Table 2.

Compound (3a). Yellow crystal; mp 55–57°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78–3.85 (m, 2H, CH_2), 4.35 (m, 2H, CH_2), 5.48 (m, 1H, CH), 6.96 (d, J = 7.9 Hz, 2H, $2CH_{ar}$), 7.06 (t, J = 7.4, 1H, CH_{ar}), 7.36 (m, 2H, $2CH_{ar}$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 36.8, 66.7, 88.2, 114.9, 122.4, 130.2, 158.1, 211.9 ppm; IR (KBr): 1595, 1498, 1199, 1059 cm^{-1}.

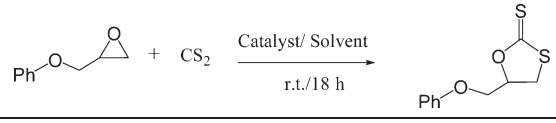
Compound (3b). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (d, J = 7.5 Hz, 6H, $2CH_3$), 3.60–3.65 (m, 3H, CH_2 and CH), 3.70 (m, 2H, CH_2), 5.16 (m, 1H, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 22.4, 36.6, 67.1, 73.2, 89.7, 211.8 (C=S) ppm. IR (KBr): 1703, 1452, 1417, 1372, 1332 cm^{-1}.

Compound (3c). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73–3.78(m, 2H, CH_2), 3.9 (m, 2H, CH_2), 5.3 (m, 1H, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 31.2, 37.3, 42.9, 88.4, 209.9 (C=S) ppm. IR (KBr): 1706, 1430, 1425, 1377, 1141, 1072 cm^{-1}.

Compound (3d). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.60–3.70 (m, 2H, CH_2), 3.73–3.83 (m, 2H, CH_2), 4.07 (d, J = 5.7 Hz, 2H, CH_2), 5.2–5.3 (m, 3H, CH and CH_2), 5.88 (m, 1H, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 36.5, 68.9, 72.9, 89.5, 118.3, 134.2, 211.2 (C=S) ppm. IR (KBr): 1702, 1638, 1423, 1419, 1354 cm^{-1}.

Table 1

Solvent and catalyst effects on the syntheis of cyclic dithiocarbonates.

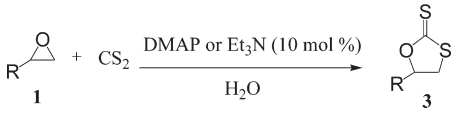


Entry	Solvent	Catalyst (mol %)	Yield (%)
1	H_2O	DMAP (50%)	84
2	H_2O	DMAP (10%)	76
3	H_2O	Et_3N (10%)	72
4	C_2H_5OH	DMAP (10%)	10
5	CH_2Cl_2	DMAP (10%)	0
6	$ClCH_2CH_2Cl$	DMAP (10%)	0
7	CH_3CN	DMAP (10%)	0
8	THF	DMAP (10%)	0
9	Toluene	DMAP (10%)	0
10	Acetone	DMAP (10%)	0
11	Solvent free	DMAP (10%)	50
12	H_2O	LiCl (10%)	0

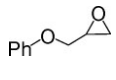
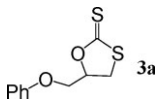
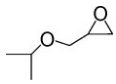
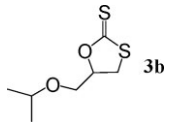
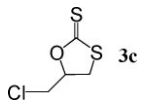
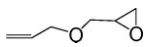
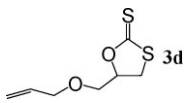
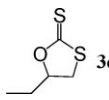
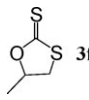
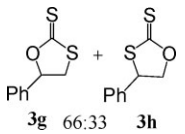
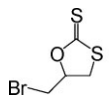
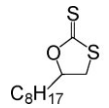
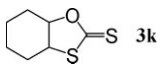
Compound (3e). Yellow oil ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08 (t, J = 7.5 Hz, 3H, CH_3), 1.85 (m, 1H, one proton of CH_2), 2.00 (m, 1H, one proton of CH_2), 3.39 (dd, J = 11.7, 7.2 Hz, 1H, one proton of CH_2), 3.61 (dd, J = 11.7, 5.4 Hz, 1H, one proton of CH_2), 5.05 (m, 1H, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 10.2, 27.2, 39.4, 93.2, 212.1 (C=S) ppm. IR (KBr): 1714, 1619, 1511, 1426, 1332, 1268 cm^{-1}.

Table 2

Synthesis of cyclic dithiocarbonates by reaction of epoxide and carbon sisulfide in water.

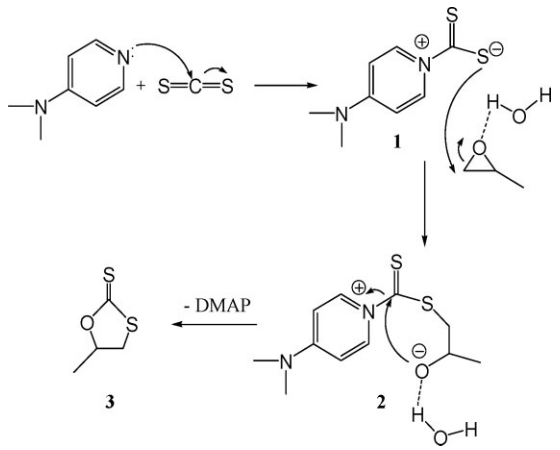


1 3

Entry	Epoxide	Product	Yield (%)[a]
1		 **3a**	76[16]
2		 **3b**	79 [16]
3		 **3c**	91
4		 **3d**	77(56)[b] [16]
5		 **3e**	50 [16]
6		 **3f**	30(45)[b] [16]
7		 **3g** 66:33 **3h**	52 [10j]
8		 **3i**	26
9		 **3j**	24
10		 **3k**	18 [16]

[a] Isolated yield.
[b] Triethyl amine as catalyst.

Scheme 2. Proposed mechanism for the synthesis of cyclic dithiocarbonate.



Compound (3f). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66 (d, J = 6.3 Hz, 3H, CH_3), 3.39 (dd, J = 11.7, 7.2 Hz, 1H, one proton of CH_2), 3.66 (dd, J = 11.7, 4.5 Hz, 1H, one proton of CH_2), 5.27 (m, 1H, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 19.8, 41.2, 88.0, 211.6 (C=S) ppm. IR (KBr): 1703, 1439, 1417, 1370, 1141, 1079 cm^{-1}.

Compound (3g). Yellow crystal; mp 115–117°C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 4.03 (1 H, dd, J = 12.0 Hz, J = 5.7 Hz, CH), 4.17 (1 H, dd, J = 12.0 Hz, J = 11.8 Hz, CH), 5.65 (1 H, dd, J = 10.3 Hz, J = 5.7 Hz, CH), 7.37–7.50 (5H_{Ar}). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 49.8 (CH2), 64.2 (CH), 127.5 (2 CH), 129.2 (2 CH), 129.3 (CH), 135.3 (C), 227.2 (C=S). IR (KBr): 1568, 1470, 1438, 1413, 1357, 1048 cm^{-1}.

Compound (3h). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.70–3.88 (2 H, CH_2), 5.35 (1 H, dd, J = 10.3 Hz, J = 5.7 Hz, CH), 7.37–7.44 7.50 (5 H_{Ar}). IR (KBr): 1560, 1461, 1445, 1410, 1351, 1049 cm^{-1}.

Compound (3i). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.63–3.73(m, 2H, CH_2), 3.8 (m, 2H, CH_2), 5.25 (m, 1H, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 30.3, 36.3, 41.9, 87.4, 206.9 (C=S) ppm. IR (KBr): 1700, 1425, 1370, 1143, 1071 cm^{-1}.

Compound (3j). Yellow oil; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.79–1.68 (15 H), 1.80 (1 H, m, CH_2), 1.98 (1H, m, CH_2), 3.44–3.79 (2H, CH2), 5.12 (1H, CH). IR (KBr): 1701, 1455, 1417, 1374, 1338 cm^{-1}.

Compound (3k). Yellow crystal; mp 176–178°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.6–2.4 (m, 8H, 4CH_2), 3.47–4.70 (m, 2H, 2CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.6, 24.9, 28.1, 29.7, 56.3, 94.6, 212.4(C=S) ppm; IR (KBr): 1628, 1431, 1326, 1272, 1094 cm^{-1}.

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