Reaction between Epoxides and Carbon Disulfide under Hydrotalcite Catalysis: Eco Compatible Synthesis of Cyclic Dithiocarbonates

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Abstract: Cyclic dithiocarbonates were prepared in good yield and excellent selectivity through an environmental acceptable methodology involving the reaction of substituted epoxides with carbon disulfide under hydrotalcite catalysis. The catalyst can be recovered by filtration and reused several times.

Key words: catalysis, green chemistry, heterocycles, heterogeneous catalysis, ring expansion.

The explosive development of heterogeneous catalysis over the past several years has led to a detailed re-examination of the most important synthetic processes by organic chemists.¹ In fact, the use of heterogeneous catalytic systems shows undoubted advantages from both an economic and environmental point of view;² these advantages are more noteworthy if the heterogeneous catalysis is applied to the preparation of fine chemicals, a chemistry sector showing an E-factor value (kg of byproducts/kg of product) up to 50.³

Cyclic dithiocarbonates **3** are important compounds utilized for the preparation of polymers;⁴ usually they are synthesized by reacting epoxides and carbon disulfide. The process can also afford the two isomers **4** and **5**, the trithiocarbonate **6**, and the episulfide **7** (Scheme 1).



Scheme 1 Possible products formed in the reaction between epoxides and carbon disulfide

By choosing convenient reaction conditions and by carrying out the process in the presence of basic catalysts, the selective production of 3 has been performed using homo-

SYNTHESIS 2008, No. 1, pp 0053–0056 Advanced online publication: 07.12.2007 DOI: 10.1055/s-2007-1000820; Art ID: T10707SS © Georg Thieme Verlag Stuttgart · New York geneous catalysis.^{4,5} Based upon these insights and due to the fact that, to the best of our knowledge, this process has never been studied under heterogeneous catalysis, the purpose of this work was to test the ability of commercially available basic solid catalysts to selectively promote the synthesis of dithiocarbonates **3**; the reaction shows 100% atom economy:⁶ all the atoms of the two starting reagents are incorporated into the final product.

The activity of two kinds of hydrotalcites,⁷ namely Pural MG30 and MG70, and two basic oxides, namely alumina and magnesium oxide (1.0 g each) was tested in a model reaction between 1,2-epoxy-3-phenoxypropane (**1a**, 10 mmol) and carbon disulfide (**2**, 3 mL, utilized as solvent and reagent) at 50 °C for three hours. The results are reported in Table 1.

Table 1Synthesis of 5-(Phenoxymethyl)-1,3-oxathiolane-2-thione(3a) Promoted by Heterogeneous Basic Catalysts



MgO/alumina (30:70)

6

All the catalysts were able to promote the reaction with high selectivity affording exclusively isomer **3a**, whose structure was assigned based on FT-IR, ¹H NMR, and MS data. Interestingly hydrotalcites MG30 and MG70, materials with magnesium oxide/alumina ratios of 30:70 and 70:30 respectively, performed the reaction in better yields than alumina, magnesium oxide, and a 30:70 mixture of magnesium oxide and alumina, confirming a synergic effect of the two oxides inside the hydrotalcite framework. In our opinion the plausible mechanism involves activation of carbon disulfide by nucleophilic attack from hy-

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98

drotalcite giving a supported xanthate anion that subsequently adds to the epoxide moiety.^{5c}

Before carrying out experiments to optimize the reaction conditions, we decided to perform the Sheldon test⁸ on the reaction carried out with hydrotalcite MG30 in order to verify the real heterogeneity of the process. Thus the reaction mixture was filtered at 50 °C after 1.5 hours (when **3a** was produced in 44% yield) and the filtrate was further heated at 50 °C for 1.5 hours. Product **3a** was detected in 46% total yield (44% + 2%). In contrast, addition of both 1,2-epoxy-3-phenoxypropane (**1a**, 10 mmol) and carbon disulfide (3 mL) to the recovered solid catalyst and heating at 50 °C for three hours afforded the dithiocarbonate **3a** in 83% yield: these results confirm that the reaction really occurs on the surface of the hydrotalcite catalyst.

The next step was to optimize the reaction conditions; to this end the following three parameters were considered: reaction time, reaction temperature, and amount of catalyst.

Firstly the model reaction was analyzed by examining the yield of product **3a** versus time; the reaction was carried out over six hours and GC analysis was performed every 30 minutes (Figure 1).



Figure 1 Reactivity of 1,2-epoxy-3-phenoxypropane (1a) and carbon disulfide in the presence of hydrotalcite MG30 at 50 $^{\circ}$ C as a function of time

Results show that the maximum production of **3a** occurs during the first three hours (~84% yield, 99% selectivity); then the reaction proceeds slowly and the yield reaches its maximum value (~99% yield, 99% selectivity) after five hours.

In a second series of experiments the reaction temperature was examined. To this end the process was carried out at both 40 $^{\circ}$ C and 30 $^{\circ}$ C for five hours, but a dramatic drop in yield was observed (58% and 8%, respectively).

Finally, the effect of the amount of catalyst on the reaction yield was also taken into account with the aim of examining the possibility of using the minimum amount of hydrotalcite catalyst. To this end, comparative experiments with different amounts of MG30 were performed (Table 2).

As can be concluded from the results depicted in Table 2, lowering the amount of hydrotalcite MG30 from 1.00 to 0.75 g gives the same quantitative yield of **3a**, however, lowering the amount of catalyst further reduces the yield.

Entry	MG30 amount (g)	Yield (%) of 3a	Selectivity (%) of 3a
1	0.25	72	98
2	0.50	89	98
3	0.75	99	99
4	1.00	99	99

The process was then applied to various epoxides (Table 3) using 0.75 g of hydrotalcite MG30 for 10 mmol of epoxide and performing the reactions at 50 °C for five hours with carbon disulfide as solvent reagent (3 mL).

The corresponding dithiocarbonates 3a-d,g were obtained in good yields without the formation of possible byproducts 4–7. Only 1,2-epoxydodecane (1f) gave 3f in low yield (Table 3, entry 6); the low reactivity of such epoxides was already evidenced for reactions carried out under homogeneous conditions.^{5c} Interestingly, selective monofunctionalization of 1,2,3,4-diepoxybutane (1g) was observed and the corresponding 5-oxiran-2-yl-1,3-oxathiolane-2-thione (3g) was isolated in 87% yield and with 100% selectivity (Table 3, entry 7).

Table 3 Synthesis of Variously Substituted Dithiocarbonates Promoted by Hydrotalcite MG30

R ¹	+ R ²	CS ₂	MG30 50 °C, 5	\rightarrow O h \rightarrow R ¹	S S R ²	+ S R^1 R^2
1		2			3	4
Entry	R ¹		R ²	Products 3 , 4	Yield (%)	Ratio 3/4
1	CH ₂ OPh		Н	a	99	100:0
2	CH ₂ OBn		Н	b	94	100:0
3	CH ₂ O <i>i</i> -Pr		Н	c	80	100:0
4	-(CH ₂) ₄ -			d	75	
5	Ph		Н	e	83	62:38ª
6	$n-C_{10}H_{21}$		Н	f	25	100:0
7			Н	g	87	100:0

^a The isomers could not be separated. Ratio of **3e/4e** was estimated by ¹H NMR spectra.

Styrene oxide **1e** exhibited a particular reactivity, which can be ascribed to the presence of the phenyl group that accelerates ' α cleavage' through the formation of a stable benzylic cation.⁹ This reactivity is strongly dependent on the reaction temperature (Scheme 2).



Scheme 2 Product distribution as a function of temperature in the reaction between styrene oxide and carbon disulfide

At 50 °C **3e** and **4e** are obtained in 83% total yield (**3e**/ **4e** = 62:38), by carrying out the reaction at 75 °C, byproducts **6e** and **7e** were also produced (91% total yield, **3e**/**4e**/ **6e**/**7e** = 43:13:22:22) and by increasing the temperature up to 100 °C, the trithiocarbonate **6e** was isolated as the sole reaction product (98% yield).

Finally, we faced the problem of catalyst recycling; at the end of the model reaction the crude was filtered and the catalyst, after washing with carbon disulfide, was reused for at least four times affording product **3a** with the same high yield (reaction: 99%; 1st recycle: 98%; 2nd recycle: 97%; 3rd recycle: 99%; 4th recycle: 98%).

In conclusion we have shown for the first time that a heterogeneous catalyst, namely commercially available hydrotalcite MG30, can be successfully and efficiently utilized for the highly selective synthesis of cyclic dithiocarbonates. Moreover, the use of carbon disulfide as solvent-reagent, the high atom economy, and the possibility of recycling the catalyst for several runs, make this approach practical and environmentally acceptable.

All compounds were purchased from Aldrich and used without further purification. ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were recorded on a Bruker Avance 300 spectrometer. MS spectra were obtained with a HP 5971 A Mass Selective Detector.

1,3-Oxathiolane-2-thiones 3; General Procedure

Epoxide 1 (10 mmol), CS_2 (3 mL), and hydrotalcite MG 30 (0.75 g) were successively added to a test tube, which was stopped and the mixture was magnetically stirred (800 rpm) at 50 °C for 5 h. After cooling to r.t. the catalyst was separated by Büchner filtration, washed with CS_2 (10 mL), and the solvent removed under reduced pressure. The crude residue was column chromatographed (silica gel, hexane–EtOAc, 70:30) to afford the products. Spectral data of known dithiocarbonates **3a** and **3d–f** are in accordance with literature data.^{5c,10}

5-(Benzyloxymethyl)-1,3-oxathiolane-2-thione (3b)

Bp 55–56 °C/0.026 mbar.

¹H NMR (300 MHz, CDCl₃/TMS): δ = 3.58 (dd, ³*J* = 11.1, 7.2 Hz, 1 H, CH₂S), 3.67 (dd, ³*J* = 11.1, 8.1 Hz, 1 H, CH₂S), 3.76 (dd,

 ${}^{3}J$ = 10.8, 4.5 Hz, 1 H, OCH₂CH), 3.84 (dd, ${}^{3}J$ = 10.8, 4.9 Hz, 1 H, OCH₂CH), 4.58 (d, ${}^{3}J$ = 11.9 Hz, 1 H, CH₂Ph), 4.63 (d, ${}^{3}J$ = 11.9 Hz, 1 H, CH₂Ph), 4.63 (d, ${}^{3}J$ = 11.9 Hz, 1 H, CH₂Ph), 5.2–5.3 (m, 1 H, CH), 7.2–7.4 (m, 5 H, H_{arom}).

¹³C NMR (75 MHz; CDCl₃/TMS): δ = 36.1, 68.5, 73.7, 89.2, 127.8, 128.1, 128.5, 137.1, 211.9.

MS (EI, 70 eV): m/z (%) = 91 (100), 107 (40), 147 (10), 240 (3) [M⁺].

Anal. Calcd for $C_{11}H_{12}O_2S_2$: C, 43.60; H, 5.04; S, 26.72. Found: C, 43.42; H, 4.98; S, 26.56.

5-(Isopropoxymethyl)-1,3-oxathiolane-2-thione (3c) Bp 135–137 °C.

¹H NMR (300 MHz, CDCl₃/TMS): δ = 1.12 (dd, ³*J* = 6.1, 1.2 Hz, 6 H, 2 CH₃), 3.5–3.8 (m, 5 H, OCH₂CHCH₂S), 5.1–5.3 [m, 1 H, C*H*(CH₃)₂].

¹³C NMR (75 MHz, CDCl₃/TMS): δ = 21.9, 36.1, 66.7, 72.7, 89.9, 212.4.

MS (EI, 70 eV): m/z (%) = 57 (100), 74 (91), 131 (51), 192 (79) [M⁺].

Anal. Calcd for $C_7H_{12}O_2S_2;\,C,\,43.79;\,H,\,6.30;\,S,\,33.40.$ Found: C, 43.60; H, 6.38; S, 33.45.

5-Oxiran-2-yl-1,3-oxathiolane-2-thione (3g)

Bp 118–119.5 °C.

¹H NMR (300 MHz, CDCl₃/TMS): δ = 2.9–3.0 (m, 2 H, OCH₂), 3.3–3.4 (m, 1 H, OCH₂CH), 3.6–3.7 (m, 2 H, SCH₂), 5.0–5.2 (m, 1 H, SCH₂CH).

¹³C NMR (75 MHz, CDCl₃/TMS): δ = 35.9, 44.2, 51.0, 89.1, 210.9.MS (EI, 70 eV): m/z (%) = 57 (35), 71 (39), 162 (100) [M⁺].

Anal. Calcd for C₅H₆O₂S₂: C, 37.03; H, 3.73; S, 39.59. Found: C, 36.96; H, 3.65; S, 39.68.

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