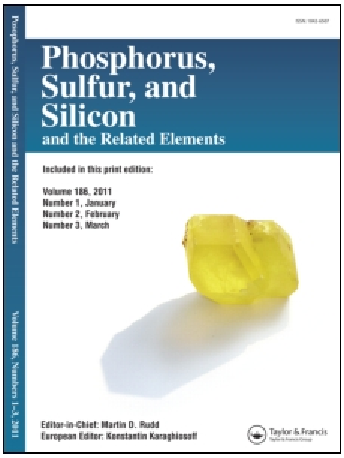

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Synthesis of Bis (Cyclic Dithiocarbonates) Bridged by a Polyoxyethylene Chain

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The reaction of bis-oxiranes 1 with carbon disulfide in the presence of lithium bromide as catalyst at reflux in dichloromethane affords selectively the corresponding polyoxyethylene bis (five-menbered cyclic dithiocarbonates) 2 in good yields. On the basis of the reaction conditions, an oriented mechanism for the reaction is proposed.

Keywords Carbon disulfide; cyclic dithiocarbonate; oxathiolane-2-thione; oxirane

INTRODUCTION

The synthesis of dithiocarbonate derivatives is of increasing interest[1–7] owing to their applications in polymer synthesis[8–11] and as biologically active compounds.[12–16] Recently, much attention has been paid to sulfur-containing polymers.[17] These polymers have superior optical and thermal properties[18–21] and are, therefore, expected to be useful as optical lenses and fibres.

As in the case of the synthesis of cyclic carbonates from oxiranes, cyclic dithiocarbonates may also be prepared using carbon disulfide instead of carbon dioxide.[22] Early attempts to react oxiranes and carbon disulfide resulted in either complex mixture or cyclic trithiocarbonates.[1–7] When LiBr was used as catalyst in appropriate solvent such as THF, selective formation of dithiocarbonates was acheived.[23–25]

More recently, we have reported the synthesis of a series of polyoxyethylene bis-oxazolidinones from polyoxyethylene diglycidyl ethers

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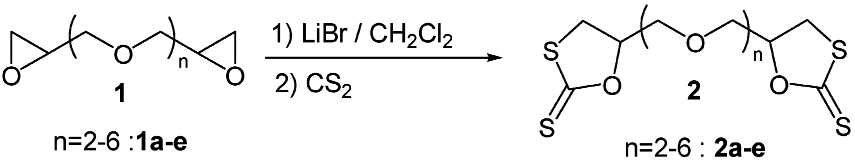
and simple isocyanates in the presence of lithium bromide as catalyst.[26] In this article, we describe the preparation of new polyoxyethylene bis(cyclic dithiocarbonates) **2** from the same diglycidyl ethers and carbon disulfide using the same catalyst. Only products **2** were obtained selectively as the single isomer.

RESULTS AND DISCUSSION

In the presence of catalytic amount of lithium bromide, bis-oxiranes **1** react with carbon disulfide in dichloromethane at reflux to give selectively polyoxyethylene bis (five-membered cyclic dithiocarbonate) **2** in 76–87% yield (Scheme 1). These new compounds were characterized by their IR, ^{1}H and ^{13}C NMR and HRMS spectra.



SCHEME 1

The structure of compounds **2** was confirmed by ^{1}H and ^{13}C NMR spectroscopy. For instance, the ^{1}H NMR spectra showed the absence of signals related to oxirane protons (2.5–3.2 ppm) and the presence of a new multiplet in the range 5.24–5.34 ppm assigned to cyclic protons and another multiplet at 3.79–3.85 due to the CH_2 protons of the CH_2—S—C=S moiety, confirming the formation of products **2**. Interestingly, the ^{13}C NMR spectra exhibited for the C=S group a signal at 212.18 ppm and another signal at 35.91 ppm assigned to the CH_2 carbon of the CH_2—S—C=S moiety, in good agreement with literature data obtained for similar compounds.[23,27] On the basis of the above NMR data, it appears that none of the other isomers of compounds **2** was formed as a reaction by-product. This may be interpreted by the choice of LiBr as catalyst and dichloromethane or THF as solvents, consistent with literature results reported for related compounds.[23]

It is worth to note that the same reaction was repeated in THF at room temperature; the yields and rates remain approximately the same as those obtained with refluxing dichloromethane.

As shown in Table I, both the reaction time and yields increase with increasing polyoxyethylene chain length. The more extended reaction time may be related to a difficulty in accessing the center involved in the cyclization reaction, whereas the higher yields may be explained by the

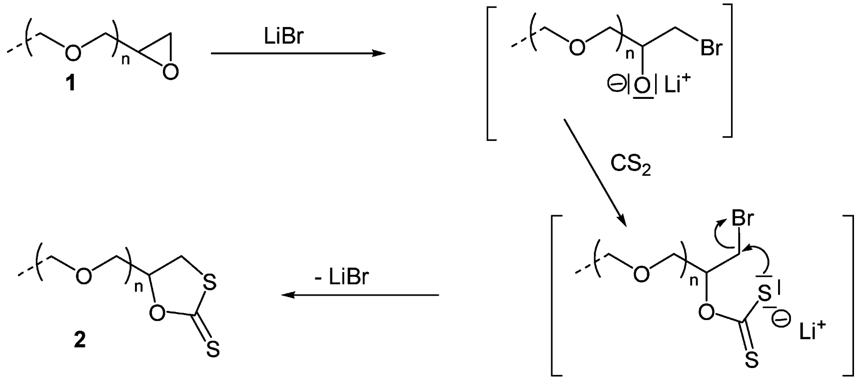
TABLE I Reaction Rates and Yields of the Different Bis-Dithiocarbonates 2

Bis-oxathiolane-2-thione	**2a**	**2b**	**2c**	**2d**	**2e**
Time (h)	10	16	21	24	28
Yield (%)	76	79	81	84	87

stronger nucleophilic character of the dithiocarbonate anion as a result of a better solvation of the lithium ion when the chain is lengthened.

Sanda et al.[11] and Kihara et al.[23] have shown that the reaction of oxiranes with carbon disulfide proceeds via a single S_N2 inversion process in contrast to the reaction with CO_2, which occurs via a double S_N2 inversion. They explained the difference in the mechanism by a difference in initial steps. This means that in the case of carbonate synthesis, the reaction proceeds via a ring opening of oxiranes by catalysts, nucleophilic addition to carbon dioxide and cyclization, whereas in the case of dithiocarbonate synthesis, the reaction steps are nucleophilic addition of catalysts to carbon disulfide leading to the formation of xanthate salts, ring opening of oxirane by xanthate salts and cyclization.

In our case, however, the reaction conditions were different since bis-oxiranes and LiBr are mixed and left for two hours before carbon disulfide was added (see Experimental section). This leads to the initial formation of a bromohydrine salt. The latter undergoes thereafter a nucleophilic attack of carbon disulfide leading to an oriented mechanism as shown in Scheme 2.



SCHEME 2

CONCLUSION

Starting from bis-oxiranes **1**, we have selectively prepared new bis(dithiocarbonates) containing a polyoxyethylene chain. The existence of the latter is expected to introduce new properties to these bis(dithiocarbonates). As with other bifunctional dithiocarbonates separated by a phenyl-containing group,[28] the polyaddition reaction carried out on bis (oxathiolane-2-thione) **2c** afforded readily the corresponding poly(thiourethanes). The extension of this reaction to other polyoxyethylene dithiocarbonates and the structural determination of this novel polyoxyethylene polymer series, as well as the study on the reactivity of these new bis(cyclic dithiocarbonates) **2** are under investigation.

EXPERIMENTAL

The IR spectra were recorded on Perkin-Elmer PARAGON 1000 PC. The ^{1}H, ^{13}C NMR were realized on Bruker AC 300 at 300 and 75 MHz, respectively, using $CDCl_3$ as a solvent and referenced to TMS. HRMS spectra were obtained from MAT 95 SBE. Analytical TLC was conducted using percolated aluminium TLC plates: silica gel/UV 254. Column chromatography was performed on silica gel (Merck 7734). The oligoethylene glycol diglycidyl ethers were synthesized, in phase transfer catalysis conditions, from epichlorohydrin and polyoxyethylene glycols as previously described.[29]

Preparation of bis-Oxathiolane-2-thiones 2: General Procedure

To a solution of diglycidyl ether **1** (7.6 mmol) dissolved in 20 mL of dry dichloromethane was added 0.52 g (0.6 mmol) of lithium bromide. After stirring the mixture at reflux for 2 h, a solution of carbon disulfide 1.73 g (22.8 mmol) was added dropwise. The reaction mixture was then refluxed over 10–28 h (see Table I) and monitored with TLC (ethyl acetate). At the end of the reaction, the mixture was cooled, diluted with water (40 mL) and then extracted with dichloromethane (4 × 40 mL). It was washed with water (2 × 30 mL) and dried on $MgSO_4$. The solvent was removed and the residue purified on column chromatography with ethyl acetate as eluent to obtain bis-oxathiolane-2-thiones **2** as yellow viscous oils.

Spectral Data for Compounds 2a–e

1,6-Bis(oxathiolane-2-thione-5-yl)-2,5-dioxahexane (2a)

IR ($CHCl_3$): ν = 1188 (C=S) cm^{-1}.^1H NMR ($CDCl_3$): δ = 5.33–5.25 (m, 2H, 2CHOC=S), 3.94–3.81 (m, 4H, $2CH_2SC=S$), 3.75–3.71 (m, 4H, $2C\underline{H}_2OCHO$), 3.67–3.64 (m, 4H, $2CH_2O$).^{13}C NMR ($CDCl_3$): δ = 212.19 (s, 2C, 2C=S), 89.44 (s, 2C, $2\underline{C}HOC=S$), 71.27-69.79 (m, 4C, $4CH_2O$), 35.91 (s, 2C, $2\underline{C}H_2SC=S$). ESI-HRMS:M^+ calcd. 325.9774, found 325.9769, Δ (mmu) = 0.5.

1,9-Bis(oxathiolane-2-thione-5-yl)-2,5,8-trioxanonane (2b)

IR ($CHCl_3$): ν = 1184 (C=S) cm^{-1}.^1H NMR ($CDCl_3$): δ = 5.34–5.24 (m, 2H, 2CHOC=S), 3.95–3.79 (m, 4H, $2CH_2SC=S$), 3.74–3.70 (m, 4H, $2C\underline{H}_2OCHO$), 3.68–3.64 (m, 8H, 4 CH_2O).^{13}C NMR ($CDCl_3$): δ = 212.18 (s, 2C, 2C=S), 89.42 (s, 2C, $2\underline{C}HOC=S$), 71.27–69.74 (m, 6C, $6CH_2O$), 35.86 (s, 2C, $2\underline{C}H_2SC=S$). ESI-HRMS:M^+ calcd. 370.0037, found 370.0034, Δ (mmu) = 0.3.

1,12-Bis(oxathiolane-2-thione-5-yl)-2,5,8,11-tetraoxadidecane (2c)

IR ($CHCl_3$): ν = 1186 (C=S) cm^{-1}.^1H NMR ($CDCl_3$): δ = 5.32–5.26 (m, 2H, 2CHOC=S), 3.93–3.80 (m, 4H, $2CH_2SC=S$), 3.73–3.71 (m, 4H, $2C\underline{H}_2OCHOC=S$), 3.67–3.65 (m, 12H, 6 CH_2O).^{13}C NMR ($CDCl_3$): δ = 212.18 (s, 2C, 2C=S), 89.46 (s, 2C, $2\underline{C}HOC=S$), 71.27–69.83 (m, 8C, $8CH_2O$), 35.85 (s, 2C, $2\underline{C}H_2SC=S$). ESI-HRMS:M^+ calcd. 414.0299, found 414.0292, Δ(mmu) = 0.7.

1,15-Bis(oxazothiolane-2-thione-5-yl)-2,5,8,11,14-pentaoxapentadecane (2d)

IR ($CHCl_3$): ν = 1182 (C=S) cm^{-1}.^1H NMR ($CDCl_3$): δ = 5.35–5.28 (m, 2H, 2CHOC=S), 3.96–3.82 (m, 4H, $2CH_2SC=S$), 3.75–3.73 (m, 4H, $2C\underline{H}_2OCHOC=S$), 3.69–3.66 (m, 16H, 8 CH_2O).^{13}C NMR ($CDCl_3$): δ = 212.22 (s, 2C, 2C=S), 89.49 (s, 2C, $2\underline{C}HOC=S$), 71.22–68.76 (m, 10C, $10CH_2O$), 35.95 (s, 2C, $2\underline{C}H_2SC=S$). ESI-HRMS:M^+ calcd. 458.0561, found 458.0557, Δ (mmu) = 0.4.

1,18-Bis(oxathiolane-2-thione-5-yl)-2,5,8,11,13,17-hexaoxaoctanonane (2e)

IR ($CHCl_3$): ν = 1189 (C=S) cm^{-1}.^1H NMR ($CDCl_3$): δ = 5.34–5.25 (m, 2H, 2CHOC=S), 3.92–3.78 (m, 4H, $2CH_2SC=S$), 3.73–3.69 (m, 4H, $2C\underline{H}_2OCHO$), 3.66–3.63 (m, 20H, 10 CH_2O).^{13}C NMR ($CDCl_3$): δ = 212.17 (s, 2C, 2C=S), 89.47 (s, 2C, $2\underline{C}HOC=S$), 71.25–69.73 (m, 12C, $12CH_2O$), 35.89 (s, 2C, $2\underline{C}H_2SC=S$). ESI-HRMS:M^+ calcd. 502.0823, found 502.0815, Δ (mmu) = 0.8.

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