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Synthesis of 1,4-oxathian-2-ones by Triton B-catalyzed one-pot reaction of epoxides with ethyl mercaptoacetate

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Abstract: A rapid one-pot reaction of epoxides with ethyl mercaptoacetate furnishing 1,4-oxathian-2-ones in the presence of a catalytic amount of eco-friendly Triton B is reported. High regioselectivity is due to the nucleophilic attack on the less sterically hindered carbon atom of the aliphatic unsymmetrical epoxide.

Keywords: 1,4-oxathian-2-ones; eco-friendly; epoxide; ethyl mercaptoacetate; intramolecular transesterification; Triton B.

Introduction

Benzyltrimethylammonium hydroxide (Triton B) is an ecofriendly basic phase-transfer catalyst employed in many chemical reactions [1–3]. The recent increasing interest in this catalyst is due to its physical and chemical properties, ecological effect, availability and low cost [4].

1,4-Oxathian-2-ones are an important class of heterocyclic compounds [5] with many applications in medicinal chemistry [6–8] and industrial fields [9]. The increasing interest in these compounds has led to the development of many synthetic methods using different substrates [10] and catalysts [4]. 1,4-Oxathian-2-one derivatives can be synthesized by many methods [11–16] including transformation of epoxides [17–19]. Many synthetic protocols involve opening of epoxides into the corresponding β -hydroxy sulfides [20–25]. As part of our work on the use of Triton B as a catalyst for diverse organic transformations [3], we report in this paper, a new method for the synthesis of 1,4-oxathian-2-one derivatives by a one-pot reaction of epoxides with ethyl mercaptoacetate using, for the first time, Triton B as a commercially available and inexpensive base catalyst.

Results and discussion

The reaction of equimolar amounts of epoxide **1** and ethyl 2-mercaptoacetate **2** in the presence of Triton B (2.5%) was carried out at 25°C for 10 min and afforded a mixture of β -hydroxythioacetate **3** and 1,4-oxathian-2-one **4** in good yield with predominance of compound **3**. This result is consistent with the ring opening reaction of the epoxide, leading to **3**, while the cyclic compound **4** is formed via the partial lactonization of the intermediate product **3** (Scheme 1).

Previously, the Lewis acid LiBr has been used as a catalyst in the reaction of thio acids with epoxides to yield the corresponding α -mercaptocarboxylic acids through attack of the thiol on the more substituted carbon atom of the epoxide ring [8]. In our case, the β -hydroxythioacetates **3b-g** were formed through the nucleophilic attack of the thiolate anion on the less substituted carbon atom of the epoxide 1. Generation of thiolate is facilitated in the presence of basic Triton B. The thiolate attacks the less substituted epoxide carbon atom, via an S₂ mechanism. In the case of epichlorohydrin **1e** bearing both epoxide and alkyl halide moieties, the reaction is regio- and chemo-selective affording exclusively the corresponding β -hydroxythioacetate **3e**, and no chloride substitution product is observed [3, 22]. The reaction of the styrene oxide **1g** gave a mixture of two regioisomers 3g and 3g', which results from competitive nucleophilic attacks on carbon atoms β and α of the epoxide, respectively (Scheme 1). Compound **3g** is the major product resulting from the nucleophilic attack on the less sterically hindered carbon atom β . The two regioisomers **3g** and 3g' undergo cyclization yielding the corresponding 1,4-oxathian-2-ones 4g (13%) and 4g' (9%), respectively. It

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Scheme 1

appears that the intramolecular transesterification reaction is not complete at room temperature and reaches a dynamic equilibrium, as the ratio of 3/4 does not change even after extending the reaction time from 10 min to 24 h.

The lactonization/transesterification reaction was also studied in the presence of NEt, as a base (Table 1). In the first attempts, under solvent-free conditions, the reaction of ethyl 2-mercaptoacetate 2 (1 equiv) with the symmetrical epoxide **1a** (1 equiv) in the presence of Et₂N (2 equiv) was investigated at room temperature and at 100°C. In these cases, the uncyclized compound **3a** was obtained exclusively after 24 h in 75% and 67% yields, respectively (Table 1, entries 1 and 2). Under similar conditions, but in refluxing toluene using a Dean-Stark apparatus, 1,4-oxathian-2-one 4a was the only isolated product after 18 h (Table 1, entry 3). The yield was 60% in both cases. On the other hand, under solvent-free conditions, the reaction of ethyl 2-mercaptoacetate 2 (1 equiv) with epoxide **1a** (1 equiv) in the presence of a catalytic amount (2.5%) of Triton B both at room temperature and at 100°C, afforded after 10 min a mixture of compounds **3a** and **4a** in excellent yields in ratios of 3a/4a = 57/43and 3a/4a = 54/46, respectively (Table 1, entries 4 and 5).

Interestingly, in the presence of Triton B in refluxing toluene using a Dean-Stark apparatus, the reaction was clean and rapid, affording exclusively 1,4-oxathian-2-one **4a** within 10 min in 97% yield (Table 1, entry 6).

After the successful one-pot conversion of epoxide **1a** into 1,4-oxathian-2-one **4a** in the presence of Triton B as catalyst at refluxing toluene (Table 1), the scope of the reaction with epoxides **1b–g** was explored (Scheme 2). Thus, the use of Triton B as a catalyst allows the one-pot synthesis of lactones **4b–g** in short reaction times (10 min) and in excellent yields.

Products **3** and **4** were characterized using proton nuclear magnetic resonance (¹H NMR), carbon-13 nuclear magnetic resonance (¹³C NMR) and elemental analysis or high resolution mass spectrometry (HRMS). All results are in agreement with the previous spectral studies of 1,4-oxathian-2-ones [26]. In particular, in ¹H NMR spectra, the protons of the S-CH₂-CO₂ group in compounds **3** and **4** show different patterns. In the acyclic compounds **3**, the two protons are magnetically equivalent and give a singlet. In thiolactones **4**, these two equatorial/axial protons are no longer magnetically equivalent and appear as an *AB* system with a coupling constant ²*J*_{HH} = 15 Hz.

Entry	Base	T (°C)	Solvent	Time, min (h)	Ratio 3a/4a (%)ª	Yield (%)
1	Et ₃ N (2 eq)	rt	Neat	(24)	100/0	75
2	Et ₃ N (2 eq)	100	Neat	(24)	100/0	67
3	Et ₃ N (2 eq)	110	Toluene	(18)	0/100	60
4	Triton B (2.5%)	rt	Neat	10	57/43	95 ^ь
5	Triton B (2.5%)	100	Neat	10	54/46	90 ^b
6	Triton B (2.5%)	110	Toluene	10	0/100	97

 Table 1
 Base-catalyzed reaction with epoxide 1a with ethyl 2-mercaptoacetate 2.

^aThe ratios were determined by ¹H NMR; ^btotal yield of products.





Conclusion

A new eco-friendly and time-efficient one-pot protocol for the preparation of 1,4-oxathian-2-ones involves ring opening of epoxides by the reaction with ethyl mercaptoacetate followed by intramolecular transesterification of the intermediate products. The synthesis of 1,4-oxathian-2-ones *via* an epoxide ring-opening-ring-closing reaction cascade was carried out for the first time in the presence of eco-friendly and inexpensive Triton B as a base catalyst.

Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker AC 300 spectrometer in $CDCl_3$ at 300 MHz and 75 MHz, respectively. HRMS spectra were recorded on a Finnigan MAT 95 mass spectrometer operating in chemical ionization mode (CI).

Synthesis of hydroxythioacetates 3

Ethyl 2-mercaptoacetate **2** (1.80 g, 15 mmol) was added dropwise over a 10 min period to a stirred mixture of epoxide **1a–g** (15 mmol) and 2.5 mol% of Triton B at room temperature. The consumption of the epoxide was monitored using thin layer chromatography (TLC). The crude products were purified by distillation excepting **2f** and **2e** which were isolated by column chromatography on silica gel eluting with hexane/ethyl acetate, 60:40.

Ethyl 2-(2-hydroxycyclohexylthio)acetate (3a) Colorless viscous oil; yield 95%; bp 88°C/0.1 mm Hg; ¹H NMR: δ 1.21 (t, *J* = 7.2 Hz, 3H, CH₃), 1.24–2.11 [m, 8H, (-CH₂)₄-], 2.05 (s, 1H, OH), 2.38–2.51 (m, 1H, CHS), 3.40 (s, 2H, SCH₂CO), 3.34–3.37 (m, 1H, CHOH), 4.11 (q, *J* = 7.2 Hz, 2H, CH₂O); ¹³C NMR: δ 14.0, 24.4, 26.2, 32.2, 32.4, 34.3, 54.1, 61.6, 73.1, 171.5. Anal. Calcd for C₁₀H₁₈O₃S: C, 55.02; H, 8.31; S, 14.69. Found: C, 55.08; H, 8.36; S, 14.72.

Ethyl 2-(2-hydroxybutylthio)acetate (3b) Colorless viscous oil; yield 83%; bp 104°C/0.02 mm Hg; [']H NMR: δ 0.90 (t, J=7.4 Hz, 3H, CH₃), 1.22 (t, J=7.1 Hz, 3H, CH₃), 1.41–1.55 (m, 2H, CH₂), 3.34 (s, 1H,

OH), 2.55–2.85 (m, 2H, CH₂S), 3.32 (s, 2H, SCH₂), 3.62–3.67 (m, 1H, CH), 4.13 (q, J = 7.1 Hz, 2H, CH₂O); ¹³C NMR: δ 9.4, 14.1, 29.0, 33.9, 40.0, 61.6, 71.0, 170.9. Anal. Calcd for C₈H₁₆O₃S: C, 49.97; H, 8.39; S, 16.68. Found: C, 49.99; H, 8.41; S, 16.72.

Ethyl 2-(2-hydroxyhexylthio)acetate (3c) Colorless viscous oil; yield 88%; bp 110°C/0.02 mm Hg; ¹H NMR: δ: 0.88 (t, *J*=5.9 Hz, 3H, CH₃), 1.30 (t, *J*=7.1 Hz, 3H, CH₃), 1.33–1.78 [m, 6H, (CH₂)₃], 2.16 (s, 1H, OH), 2.48–2.92 (m, 2H, CH₂S), 3.26 (s, 2H, SCH₂CO), 3.60–3.68 (m, 1H, CH), 4.21 (q, *J*=7.1 Hz, 2H, CH₂); ¹³C NMR: δ 13.9, 14.1, 22.6, 27.8, 33.8, 34.7, 40.7, 60.6, 69.7, 169.4. Anal. Calcd for $C_{10}H_{20}O_3S$: C, 54.51; H, 9.15; S, 14.55. Found: C, 54.58; H, 9.19; S, 14.59.

Ethyl 2-(2-hydroxypropylthio)acetate (3d) Colorless viscous oil; yield 80%; bp 80°C/0.01 mm Hg; ¹H NMR: δ 1.23–1.31 (m, 6H, 2CH₃), 2.58–2.80 (m, 2H, CH₂S), 3.04 (s, 1H, OH), 3.28 (s, 2H, SCH₂CO), 3.90–3.93 (m, 1H, CH), 4.19 (q, J=7.1 Hz, 2H, CH₂-O); ¹³C NMR: δ 13.9, 21.9, 34.1, 41.8, 61.2, 66.1, 170.6. Anal. Calcd for C₇H₁₄O₃S: C, 47.17; H, 7.92; S, 17.99. Found: C, 47.22; H, 798; S, 18.02.

Ethyl 2-(3-chloro-2-hydroxypropylthio)acetate (3e) Colorless viscous oil; yield 75%; ¹H NMR: δ 1.29 (t, J=7.1 Hz, 3H, CH₃), 2.78–2.94 (m, 2H, CH₂S), 3.31 (s, 2H, CH₂CO), 3.56 (s, 1H, OH), 3.61–3.69 (m, 2H, CH₂Cl), 3.97–4.03 (m, 1H, CH), 4.20 (q, J=7.1 Hz, 2H, CH₂); ¹³C NMR: δ 14.1, 34.3, 37.1, 47.8, 61.8, 70.3, 171.0. Anal. Calcd for C₇H₁₃ClO₃S: C, 39.53; H, 6.16; S, 15.08. Found: C, 39.58; H, 6.21; S, 15.12.

Ethyl 2-(2-hydroxy-3-phenoxypropylthio)acetate (3f) Colorless viscous oil; yield 92%; ¹H NMR: δ 1.31 (t, *J* = 7.2 Hz, 3H, CH₃), 2.82–3.04 (m, 2H, CH₂S), 3.16 (s, 1H, OH), 3.33 (s, 2H, CH₂CO), 4.03–4.17 (m, 3H, CH, CH₂OPh), 4.21 (q, *J* = 7.2 Hz, 2H, CH₂O), 6.90–7.32 (m, 5H, H_{ar}); ¹³C NMR: δ 14.1, 34.1, 36.5, 61.7, 69.2, 70.3, 114.6, 121.2, 129.6, 158.5, 171.1. Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71; S, 11.86. Found: C, 57.81; H, 6.76; S, 11.89.

Ethyl 2-(2-hydroxy-2-phenylethylthio)acetate (3g) Colorless viscous oil; yield 76%; bp 150/0.1°C/mm Hg; ¹H NMR (300 MHz, CDCl₃), δ: 1.27 (t, *J* = 7.1 Hz, 3H, CH₃), 2.28 (s, 1H, OH), 2.80–3.01 (m, 2H, CH₂S), 3.24 (s, 2H, SCH₂CO), 4.19 (q, *J* = 7.1 Hz, 2H, CH₂O), 4.77–4.82 (m, 1H, CH), 7.27–7.35 (m, 5H, H_{ar}); ¹³C NMR: δ 14.1, 34.0, 42.1, 61.6, 72.4, 125.8, 127.8, 128.5, 142.6, 170.9. Anal. Calcd for C₁₂H₁₆O₃S: C, 59.97; H, 6.71; S, 13.34. Found: C, 60.01; H, 6.76; S, 13.38.

Ethyl 2-(2-hydroxy-1-phenylethylthio)acetate (3g') Colorless viscous oil; yield 76%; bp 150°C/0.1 mm Hg; ¹H NMR: δ 1.18 (t, *J* = 7.1 Hz, 3H, CH₃), 1.87 (s, 1H, OH), 2.97–3.15 (m, 2H, CH₂OH), 3.59 (s, 2H, SCH₂), 4.02–4.10 (m, 1H, CH), 4.09 (q, *J* = 7.1 Hz, 2H, CH₂O), 7.19–7.28 (m, 5H, H_a); ¹³C NMR: δ 14.1, 32.7, 53.1, 61.6, 65.4, 127.9, 128.2, 128.8, 138.6, 170.8.

Synthesis of 1,4-oxathian-2-ones 4

A mixture of epoxide 1 (15 mmol), ethyl 2-mercaptoacetate 2 (1.80 g, 15 mmol) and Triton B (2.5 mol%), in toluene (50 mL) was heated to 110° C in a two-neck flask equipped with a condenser to remove ethanol. After completion of the reaction, as indicated by TLC analysis, the mixture was cooled, and the toluene was removed. The residue was subjected to column chromatography on silica gel eluting with hexane/ethyl acetate (60:40) to give pure 1,4-oxathian-2-one 4.

Hexahydrobenzo[*b*][1,4]-oxathiin-2(3*H*)-one (4a) White solid; mp 88–89°C (lit. [26] mp 87–88°C); yield 97%; ¹H NMR: δ 1.22–2.24 [m, 8H, (CH₂)₄], 3.00 (ddd, *J*=12.2, 12.0, 4.2 Hz, 1H, CHS), 3.22 (d, *J*=15.0 Hz, 1H, CH₂CO), 3.68 (d, *J*=15.0 Hz, 1H, CH₂CO), 4.17 (ddd, *J*=12.2, 12.0, 4.2 Hz, 1H, CHO), ¹³C NMR: δ 23.8, 25.1, 26.8, 32.2, 32.6, 43.1, 81.7, 168.1; MS: *m/z* 172.245 (M⁺). Anal. Calcd for C₈H₁₂O₂S: C, 55.78; H, 7.02. Found: C, 55.65; H, 7.22.

6-Ethyl-1,4-oxathian-2-one (4b) Colorless viscous oil; yield 90%; ¹H NMR: δ 1.04 (t, *J*=7.5 Hz, 3H, CH₃), 1.70–1.90 (m, 2H, MeCH₂), 2.74– 2.97 (m, 2H, SCH₂), 3.17 (d, *J*=15.0 Hz, 1H, CH₂CO), 3.58 (d, *J*=15.0 Hz, 1H, CH₂CO), 4.35–4.43 (m, 1H, CH-O); ¹³C NMR: δ 9.5, 25.8, 28.0, 29.0, 80.3, 168.3. HRMS. Calcd for C₆H₁₀O₂S: *m/z* 146.04015. Found: *m/z* 146.03957.

6-Butyl-1,4-oxathian-2-one (4c) Colorless viscous oil; yield 92%; ¹H NMR: δ 0.89 (t, *J* = 7.0 Hz, 3H, CH₃), 1.23–1.88 (m, 6H, (CH₂)₃), 2.75– 2.94 (m, 2H, SCH₂); 2.90 (d, *J* = 15.0 Hz, 1H, CH₂CO), 3.72 (d, *J* = 15.0 Hz, 1H, CH₂CO), 4.35–4.48 (m, 1H, CH); ¹³C NMR: δ 13.8, 22.3, 25.8, 27.1, 29.3, 34.7, 79.2, 168.4. HRMS. Calcd for C₈H₁₄O₂S: *m/z* 174.262. Found: *m/z* 174.261. Anal. Calcd for C₈H₁₄O₂S: C, 55.14; H, 8.10. Found: C, 55.01; H, 8.18.

6-Methyl-1,4-oxathian-2-one (4d) [27] Colorless viscous oil; yield 88%; ¹H NMR: δ 1.48 (d, *J*=6.0 Hz, 3H, CH₃), 2.78–2.97 (m, 2H, SCH₂), 3.18 (d, *J*=15.0 Hz, 1H, CH₂CO), 3.58 (d, *J*=15.0 Hz, 1H, CH₂CO), 4.61–4.68 (m, 1H, CH); ¹³C NMR: δ 20.9, 25.7, 30.7, 75.5, 168.3. HRMS. Calcd for C₅H₈O₅S: *m/z* 132.02450. Found: *m/z* 132.02465.

6-(Chloromethyl)-1,4-oxathian-2-one (4e) Oil; yield 70%; ¹H NMR: δ 2.04–2.29 (m, 2H, SCH₂), 3.37–3.51 (m, 2H, CH₂CO), 3.74–3.78 (m, 2H, CH₂Cl), 5.21 (m, 1H, CH); ¹³C NMR: δ 33.3, 33.9, 44.1, 72.5, 170.0. HRMS. Calcd for C₅H₂O₅SCl: *m/z* 165.98553. Found: *m/z* 165.98635.

6-(Phenoxymethyl)-1,4-oxathian-2-one (4f) Oil; yield 85%; ¹H NMR: δ 2.51–2.69 (m, 2H, CH₂S), 3.30 (d, *J*=15.0 Hz, 1H, CH₂CO), 3.62 (d, *J*=15.0 Hz, 1H, CH₂CO), 4.00–4.03 (m, 2H, CH₂O); 5.13–5.23 (m, 1H, CH), 6.89–7.30 (m, 5H_{ar}); ¹³C NMR: δ 27.7, 28.9, 69.7, 79.1, 114.9, 121.5, 129.6, 159.7, 167.7. HRMS. Calcd for C₁₁H₁₂O₂S: *m/z* 208.55800. Found: *m/z* 208.55812.

6-Phenyl-1,4-oxathian-2-one (4g) White solid; mp 116–117°C (lit. [27] mp 117°C); yield 55%; ¹H NMR: δ 3.08–3.10 (m, 2H, CH₂S), 3.25 (d, *J*=15.0 Hz, 1H, CH₂CO), 3.68 (d, *J*=15.0 Hz, 1H, CH₂CO), 5.47–5.51 (m, 1H, CH); 7.26–7.41 (5H, CH_ar); ¹³C NMR: δ 25.9, 31.2, 80.3, 125.7, 128.5, 128.9, 137.1, 167.5. HRMS. Calcd for C₁₀H₁₀O₂S: *m/z* 194.04015. Found: *m/z* 194.03963.

5-Phenyl-1,4-oxathian-2-one (4g') White solid; mp 90°C (lit. [27] mp 90–91°C); yield 45%; ¹H NMR: δ 3.32 (d, *J*=15.0 Hz, 1H, CH₂S); 3.43 (d, *J*=15.0 Hz, 1H, CH₂S); 4.49–4.59 (m, 3H, SCH, CH₂O); 7.32–7.38 (m, 5H, CH_a); ¹³C NMR: δ 26.7, 43.9, 72.5, 125.9, 127.9, 128.4, 137.7, 167.4. HRMS. Calcd for C₁₀H₁₀O₂S: *m/z* 194.04015. Found: *m/z* 194.03963.

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