Lassaad Wechteti, Nejib Hussein Mekni and Moufida Romdhani-Younes*

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 eco-friendly 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].

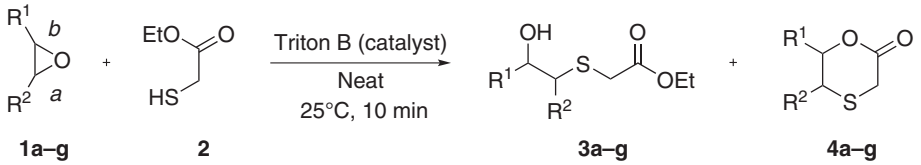
***Corresponding author: Moufida Romdhani-Younes,** Laboratory of Structural Organic Chemistry, Faculty of Sciences, University of Tunis El Manar, 2092 Tunis, Tunisia; and Department of Chemistry, Faculty of Sciences of Bizerte, University of Carthage, 7021 Jarzouna, Tunisia, e-mail: moufida.romdhani@gmail.com
Lassaad Wechteti: Laboratory of Structural Organic Chemistry, Faculty of Sciences, University of Tunis El Manar, 2092 Tunis, Tunisia; and Department of Chemistry, Faculty of Sciences of Bizerte, University of Carthage, 7021 Jarzouna, Tunisia
Nejib Hussein Mekni: Laboratory of Structural Organic Chemistry, Faculty of Sciences, University of Tunis El Manar, 2092 Tunis, Tunisia

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 S_N2 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



1a–g 2 3a–g 4a–g

	3/4 ratio
a: R^1, $R^2 = (CH_2)_4$	57/43
b: R^1 = Et; R^2 = H	76/24
c: R^1 = *n*-Bu; R^2 = H	54/46
d: R^1 = Me; R^2 = H	56/44
e: $R^1 = CH_2Cl$; R^2 = H	73/27
f: $R^1 = PhOCH_2$; R^2 = H	59/41
g: R^1 = Ph; R^2 = H	49/13
g′: R^1 = H; R^2 = Ph	29/9

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_3 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 Et_3N (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** = 57/43 and **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).

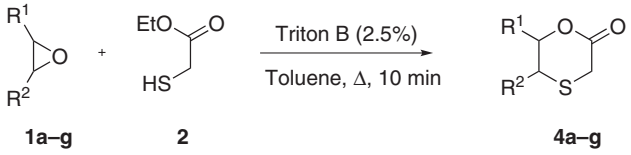
After the successful one-pot conversion of epoxide **1a** into 1,4-oxathian-2-one **4a** in the presence of triton B as catalyst at refluxing toluene (Table 1), the scope of the reaction with epoxides **1b–g** was explored (Scheme 2). Thus, the use of triton B as a catalyst allows the one-pot synthesis 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 (^{1}H NMR), carbon-13 nuclear magnetic resonance (^{13}C 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 ^{1}H NMR spectra, the protons of the S-CH_2-CO_2 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 $^2J_{HH} = 15$ Hz.

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

Entry	Base	T (°C)	Solvent	Time, min (h)	Ratio 3a/4a (%)[a]	Yield (%)
1	Et_3N (2 eq)	rt	Neat	(24)	100/0	75
2	Et_3N (2 eq)	100	Neat	(24)	100/0	67
3	Et_3N (2 eq)	110	Toluene	(18)	0/100	60
4	Triton B (2.5%)	rt	Neat	10	57/43	95[b]
5	Triton B (2.5%)	100	Neat	10	54/46	90[b]
6	Triton B (2.5%)	110	Toluene	10	0/100	97

[a]The ratios were determined by ^{1}H NMR; [b]total yield of products.



1a–g **2** **4a–g**

a: R^1, R^2 = $(CH_2)_4$
b: R^1 = Et; R^2 = H
c: R^1 = *n*-Bu; R^2 = H
d: R^1 = Me; R^2 = H
e: R^1 = CH_2Cl; R^2 = H
f: R^1 = $PhOCH_2$; R^2 = H
g: R^1 = Ph; R^2 = H
g′: R^1 = H; R^2 = Ph

Scheme 2

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

^{1}H and ^{13}C 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; ^{1}H NMR: δ 1.21 (t, *J* = 7.2 Hz, 3H, CH_3), 1.24–2.11 [m, 8H, $(-CH_2)_4$-], 2.05 (s, 1H, OH), 2.38–2.51 (m, 1H, CHS), 3.40 (s, 2H, SCH_2CO), 3.34–3.37 (m, 1H, CHOH), 4.11 (q, *J* = 7.2 Hz, 2H, CH_2O); ^{13}C 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 $C_{10}H_{18}O_3S$: 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; ^{1}H NMR: δ 0.90 (t, *J* = 7.4 Hz, 3H, CH_3), 1.22 (t, *J* = 7.1 Hz, 3H, CH_3), 1.41–1.55 (m, 2H, CH_2), 3.34 (s, 1H, OH), 2.55–2.85 (m, 2H, CH_2S), 3.32 (s, 2H, SCH_2), 3.62–3.67 (m, 1H, CH), 4.13 (q, *J* = 7.1 Hz, 2H, CH_2O); ^{13}C NMR: δ 9.4, 14.1, 29.0, 33.9, 40.0, 61.6, 71.0, 170.9. Anal. Calcd for $C_8H_{16}O_3S$: 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; ^{1}H NMR: δ: 0.88 (t, *J* = 5.9 Hz, 3H, CH_3), 1.30 (t, *J* = 7.1 Hz, 3H, CH_3), 1.33–1.78 [m, 6H, $(CH_2)_3$], 2.16 (s, 1H, OH), 2.48–2.92 (m, 2H, CH_2S), 3.26 (s, 2H, SCH_2CO), 3.60–3.68 (m, 1H, CH), 4.21 (q, *J* = 7.1 Hz, 2H, CH_2); ^{13}C 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; ^{1}H NMR: δ 1.23–1.31 (m, 6H, $2CH_3$), 2.58–2.80 (m, 2H, CH_2S), 3.04 (s, 1H, OH), 3.28 (s, 2H, SCH_2CO), 3.90–3.93 (m, 1H, CH), 4.19 (q, *J* = 7.1 Hz, 2H, CH_2-O); ^{13}C NMR: δ 13.9, 21.9, 34.1, 41.8, 61.2, 66.1, 170.6. Anal. Calcd for $C_7H_{14}O_3S$: C, 47.17; H, 7.92; S, 17.99. Found: C, 47.22; H, 7.98; S, 18.02.

Ethyl 2-(3-chloro-2-hydroxypropylthio)acetate (3e) Colorless viscous oil; yield 75%; ^{1}H NMR: δ 1.29 (t, *J* = 7.1 Hz, 3H, CH_3), 2.78–2.94 (m, 2H, CH_2S), 3.31 (s, 2H, CH_2CO), 3.56 (s, 1H, OH), 3.61–3.69 (m, 2H, CH_2Cl), 3.97–4.03 (m, 1H, CH), 4.20 (q, *J* = 7.1 Hz, 2H, CH_2); ^{13}C NMR: δ 14.1, 34.3, 37.1, 47.8, 61.8, 70.3, 171.0. Anal. Calcd for $C_7H_{13}ClO_3S$: 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%; ^{1}H NMR: δ 1.31 (t, *J* = 7.2 Hz, 3H, CH_3), 2.82–3.04 (m, 2H, CH_2S), 3.16 (s, 1H, OH), 3.33 (s, 2H, CH_2CO), 4.03–4.17 (m, 3H, CH, CH_2OPh), 4.21 (q, *J* = 7.2 Hz, 2H, CH_2O), 6.90–7.32 (m, 5H, H_{ar}); ^{13}C 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; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.27 (t, *J* = 7.1 Hz, 3H, CH_3), 2.28 (s, 1H, OH), 2.80–3.01 (m, 2H, CH_2S), 3.24 (s, 2H, SCH_2CO), 4.19 (q, *J* = 7.1 Hz, 2H, CH_2O), 4.77–4.82 (m, 1H, CH), 7.27–7.35 (m, 5H, H_{ar}); ^{13}C 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 $C_{12}H_{16}O_3S$: 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; ^{1}H NMR: δ 1.18 (t, *J* = 7.1 Hz, 3H, CH_3), 1.87 (s, 1H, OH), 2.97–3.15 (m, 2H, CH_2OH), 3.59 (s, 2H, SCH_2), 4.02–4.10 (m, 1H, CH), 4.09 (q, *J* = 7.1 Hz, 2H, CH_2O), 7.19–7.28 (m, 5H, H_{ar}); ^{13}C 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%; ^{1}H NMR: δ 1.22–2.24 [m, 8H, $(CH_2)_4$], 3.00 (ddd, *J* = 12.2, 12.0, 4.2 Hz, 1H, CHS), 3.22 (d, *J* = 15.0 Hz, 1H, CH_2CO), 3.68 (d, *J* = 15.0 Hz, 1H, CH_2CO), 4.17 (ddd, *J* = 12.2, 12.0, 4.2 Hz, 1H, CHO), ^{13}C 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 $C_8H_{12}O_2S$: 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%; ^{1}H NMR: δ 1.04 (t, *J* = 7.5 Hz, 3H, CH_3), 1.70–1.90 (m, 2H, $MeCH_2$), 2.74–2.97 (m, 2H, SCH_2), 3.17 (d, *J* = 15.0 Hz, 1H, CH_2CO), 3.58 (d, *J* = 15.0 Hz, 1H, CH_2CO), 4.35–4.43 (m, 1H, CH-O); ^{13}C NMR: δ 9.5, 25.8, 28.0, 29.0, 80.3, 168.3. HRMS. Calcd for $C_6H_{10}O_2S$: *m/z* 146.04015. Found: *m/z* 146.03957.

6-Butyl-1,4-oxathian-2-one (4c) Colorless viscous oil; yield 92%; ^{1}H NMR: δ 0.89 (t, *J* = 7.0 Hz, 3H, CH_3), 1.23–1.88 (m, 6H, $(CH_2)_3$), 2.75–2.94 (m, 2H, SCH_2); 2.90 (d, *J* = 15.0 Hz, 1H, CH_2CO), 3.72 (d, *J* = 15.0 Hz, 1H, CH_2CO), 4.35–4.48 (m, 1H, CH); ^{13}C NMR: δ 13.8, 22.3, 25.8, 27.1, 29.3, 34.7, 79.2, 168.4. HRMS. Calcd for $C_8H_{14}O_2S$: *m/z* 174.262. Found: *m/z* 174.261. Anal. Calcd for $C_8H_{14}O_2S$: 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%; ^{1}H NMR: δ 1.48 (d, *J* = 6.0 Hz, 3H, CH_3), 2.78–2.97 (m, 2H, SCH_2), 3.18 (d, *J* = 15.0 Hz, 1H, CH_2CO), 3.58 (d, *J* = 15.0 Hz, 1H, CH_2CO), 4.61–4.68 (m, 1H, CH); ^{13}C NMR: δ 20.9, 25.7, 30.7, 75.5, 168.3. HRMS. Calcd for $C_5H_8O_2S$: *m/z* 132.02450. Found: *m/z* 132.02465.

6-(Chloromethyl)-1,4-oxathian-2-one (4e) Oil; yield 70%; ^{1}H NMR: δ 2.04–2.29 (m, 2H, SCH_2), 3.37–3.51 (m, 2H, CH_2CO), 3.74–3.78 (m, 2H, CH_2Cl), 5.21 (m, 1H, CH); ^{13}C NMR: δ 33.3, 33.9, 44.1, 72.5, 170.0. HRMS. Calcd for $C_5H_7O_2SCl$: *m/z* 165.98553. Found: *m/z* 165.98635.

6-(Phenoxymethyl)-1,4-oxathian-2-one (4f) Oil; yield 85%; ^{1}H NMR: δ 2.51–2.69 (m, 2H, CH_2S), 3.30 (d, *J* = 15.0 Hz, 1H, CH_2CO), 3.62 (d, *J* = 15.0 Hz, 1H, CH_2CO), 4.00–4.03 (m, 2H, CH_2O); 5.13–5.23 (m, 1H, CH), 6.89–7.30 (m, 5H_{ar}); ^{13}C NMR: δ 27.7, 28.9, 69.7, 79.1, 114.9, 121.5, 129.6, 159.7, 167.7. HRMS. Calcd for $C_{11}H_{12}O_2S$: *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%; ^{1}H NMR: δ 3.08–3.10 (m, 2H, CH_2S), 3.25 (d, *J* = 15.0 Hz, 1H, CH_2CO), 3.68 (d, *J* = 15.0 Hz, 1H, CH_2CO), 5.47–5.51 (m, 1H, CH); 7.26–7.41 (5H, CH_{ar}); ^{13}C NMR: δ 25.9, 31.2, 80.3, 125.7, 128.5, 128.9, 137.1, 167.5. HRMS. Calcd for $C_{10}H_{10}O_2S$: *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%; ^{1}H NMR: δ 3.32 (d, *J* = 15.0 Hz, 1H, CH_2S); 3.43 (d, *J* = 15.0 Hz, 1H, CH_2S); 4.49–4.59 (m, 3H, SCH, CH_2O); 7.32–7.38 (m, 5H, CH_{ar}); ^{13}C NMR: δ 26.7, 43.9, 72.5, 125.9, 127.9, 128.4, 137.7, 167.4. HRMS. Calcd for $C_{10}H_{10}O_2S$: *m/z* 194.04015. Found: *m/z* 194.03963.

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