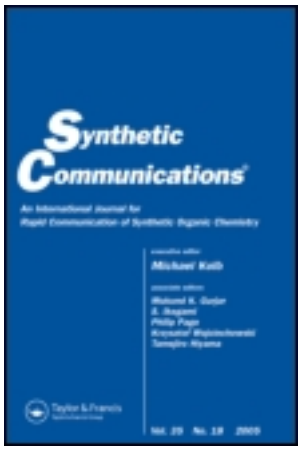

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# Conversion of Thiiranes to β-Chlorothioacetates Catalyzed with $CoCl_2$

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## ABSTRACT

Cobalt (II) chloride catalyzes the ring opening of thiiranes with acetyl chloride to produce vicinal chlorothioesters in good yields.

*Key Words:* Thiirane; β-Chlorothioacetate; Acetyl chloride; $CoCl_2$.

Due to the ready polymerization of thiiranes, ring-opening reactions of this class of compounds are rarely studied. The reaction of thiiranes are limited to the reaction with primary alcohols in the presence of highly acidic catalysts such as $BF_3$, HCl or $H_2SO_4$,[1,2] which occurs at high

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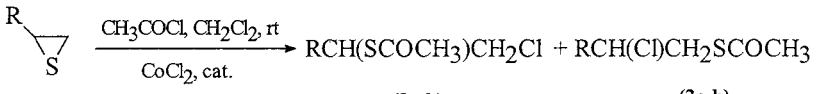



Thiirane or R= (a) Ph; (b) cyclohexene oxide;(c) $CH_2$=$CHCH_2OCH_2$; (d) n-$C_4H_9$
(e) $(CH_3)_2CHOCH_2$; (f) $ClCH_2$; (g) $PhOCH_2$; (h) CH2=$CH(CH_3)CO_2CH_2$

***Scheme 1.***

temperature with extensive Polymerization[1,3] to produce β-alkoxy mercaptans in low yields.

This reaction with boiling acetic acid is reported to produce a mixture of monomeric and dimeric acetoxy mercaptans.[4] We have also reported the use of catalysts such as Ce(IV),[5] DDQ,[6] $I_2$, and $I_2$/PVP[7] for ring opening dimmerization of thiiranes to their β,β′-dialkoxy- or diacetoxy disulfides. Although the ring opening of epoxides with acyl chlorides has been reported in the presence of different catalysts,[8,9] but to the best of our knowledge, this catalyzed reaction with thiiranes has not been studied yet.

In this work, we report on the synthesis of β-chlorothioesters from the reaction of thiiranes catalyzed with Co(II) as anhydrous $CoCl_2$ (Sch. 1).

We first studied the reactions of styrene sulfide (**1a**) and epichlorohydrine (**1f**) as examples of activated and deactivated thiiranes with acetyl chloride in the presence of different Lewis acids as catalyst and also in the absence of catalyst. The reaction of styrene episulfide (**1a**) with acetyl chloride in the absence of catalyst occured in $CH_2Cl_2$ at room temperature and after 6 h produced a mixture of **2a** and **3a** (60%) with the ratio of 88:12. However the reaction of epichlorohydrine (**1f**) with acetyl chloride did not produce any product under these conditions (Table 1).

We then studied the catalytic effect of different Lewis acids on these reactions. The results of Table 1 show that, among the studied catalysts in this work, the presence of $CoCl_2$, not only improves the yield and the regioselectivity of the reaction of styrene oxide (**1a**) with acetyl chloride, but also greatly affects the reaction's time. The role of catalyst for this transformation is also demonstrated in the reaction of epichlorohydrine (**1f**). This epoxide which does not react with acetyl chloride in the absence of catalyst, reacts in the presence of 0.05 molar equivalents of anhydrous Co(II) chloride and produces the corresponding thioacetates (**2f/3f**) in 81% yield with absolute chemoselectivity of 0/100.

***Table 1.*** Effect of 0.05 molar equivalents of different catalysts in the reaction of styrene sulfide (**1a**) and epichlorohydrine (**1f**) with acetyl chloride in $CH_2Cl_2$ at room temperature.

| Entry | Thiirane | Catalyst | Time (min) | Product | Ratio of **3/2**[a] | % Yield[b] |
|---|---|---|---|---|---|---|
| 1 | **1a** | Non | 600 | **3a + 2a** | 90/10 | 60 |
| 2 | **1a** | $AlCl_3$[c] | 5 | **3a + 2a** | 90/10 | 40 |
| 3 | **1a** | $FeCl_3$[c] | 5 | **3a + 2a** | 90/10 | 20 |
| 4 | **1a** | $ZnCl_2$[c] | 5 | **3a + 2a** | 88/12 | 35 |
| 5 | **1a** | $CoCl_2$ | 10 | **3a + 2a** | 98/2 | 85 |
| 6 | **1f** | Non | 600 | No reaction | | |
| 7 | **1f** | $CoCl_2$ | 240 | **3f + 2f** | 0/100 | 81 |
| 8 | **1f** | $AlCl_3$[c] | 2 | **3e + 2e** | 10/90 | 37 |

[a]Isomeric ratio was determined by GC and NMR analysis. [b]Isolated yield of the mixture of isomers. The reaction completes quickly and produces an unidentified polymeric material as major product.

The use of other Lewis acids in this study such as $AICl_3$, $FeCl_3$, and $ZnCl_2$ do not show the pronounced effect of anhydrous $CoCl_2$ on the progress of the reaction. We therefore studied the ring opening reaction of different thiiranes with acetyl chloride in the presence of anhydrous $CoCl_2$ in $CH_2Cl_2$ at room temperature (Table 2).

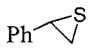
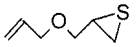
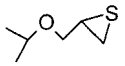
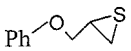
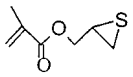
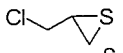
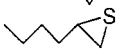
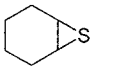
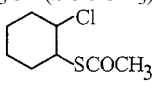
The reactions were occurred smoothly and furnished the corresponding β-chloroacetates in good yields. The regioselectivity of the reaction is controlled mainly by the electronic nature of the substituents on the thiirane ring.

In the case of styrene sulfide, the presence of phenyl group as an electron-releasing substituent favored the attack of chloride ion on the benzylic carbon of the ring, however, in the case of electron-withdrawing substituted thiiranes, the opposite attack is responsible for production of the major isomer. The mechanism of the reaction is not clear, but the activation of acetyl chloride with $COCl_2$ followed by the attack of thiirane sulfur atom can be suggested (Sch. 2).

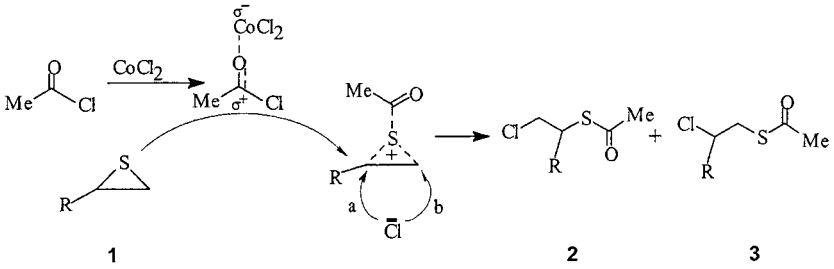
The interaction of Co(II) with the oxygen of acetyl chloride could both accelerate the reaction rate, and also affect the regioselectivity as it was shown in Table 2.

In conclusion, the presence of Co(II) as catalyst, provides the possibility of praparing β-chlorothioacetates from different thiiranes. The role of this catalyst is well shown in the possiblity of reacting thiiranes having electron-withdrawing substituents. The good to excellent chemoselectivities and high yields of the reactions are also considerable.

***Table 2.*** Reaction of thiiranes with acetyl chloride in the presence of 0.05 mmol of anhydrous $CoCl_2$ as a catalyst.

| Entry | Thiiranes | Product (isomeric ratio)[a] | Time, min (Yield %)[b] |
|---|---|---|---|
| 1 |  | i) $PhCHClCH_2(SCOCH_3)$ (98%)<br>ii) $PhCH(SCOCH_3)CH_2Cl$ (2%) | 10 (85) |
| 2 |  | i) $CH_2{=}CHCH_2OCH_2CHClCH_2(SCOCH_3)$ (29%)<br>ii) $CH_2{=}CHCH_2OCH_2CH(SCOCH_3)CH_2Cl$ (71%) | 135 (94) |
| 3 |  | i) $(CH_3)_2CHOCH_2CHClCH_2(SCOCH_3)$ (30%)<br>ii) $(CH_3)_2CHOCH_2CH(SCOCH_3)CH_2Cl$ (70%) | 110 (77) |
| 4 |  | i) $PhOCH_2CHClCH_2(SCOCH_3)$ (24%)<br>ii) $PHOCH_2CH(SCOCH_3)CH_2Cl$ (76%) | 210 (86) |
| 5 |  | i) $CH_2{=}CH(CH_3)CO_2CHClCH_2(SCOCH_3)$ (25%)<br>ii) $CH_2{=}CH(CH_3)CO_2CH_2CH(SCOCH_3)CH_2Cl$ (75%) | 180 (89) |
| 6 |  | i) $ClCH_2CH(SCOCH_3)CH_2Cl$ (100%) | 240 (81) |
| 7 |  | i) $CH_3(CH_2)_3CHClCH_2(SCOCH_3)$ (55%)<br>ii) $CH_3(CH_2)_3CH(SCOCH_3)CH_2Cl$ (45%) | 30 (75) |
| 8 |  |  | 8 (87) |

[a]Determined by GC and NMR analysis. [b]Total yield of the isomeric products.




***Scheme 2.***

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## EXPERIMENTAL

Infra red spectra were recorded on a Perkin Elmer IR-157 G and a Perkin Elmer 781 spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance DPX-250.

**General procedure for preparation of β-chlorothioacetates.** To a solution of thiirane (1 mmol) in $CH_2Cl_2$ (2 mL), acetyl chloride (1.2–2 mmol) was added followed by the addition of anhydrous $CoCl_2$ (0.05 mmol, 6.5 mg). The reaction mixture was stirred at room temperature for 0.1–4 h and monitored with GC or TLC analysis. After completion of the reaction, diethyl ether (35 mL) was added. The organic layer was separated and washed with water (20 mL) and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent followed by chromatography on a short column of silica-gel using petroleum ether/ethyl acetate (8:2) afforded the pure β-chlorothioacetates in 77–94% yield. The ratio of each isomer was determined by both GC and NMR analysis.

**Thioacetate acid *S*-(2-chloro-2-phenyl-ethyl) ester (3a).** IR (neat) $\nu$ 3095, 3060, 2850, 1705, 1505, 1469, 1369, 1250, 1150. $^{1}H$ NMR ($CDCl_3$) $\delta$: 7.2–7.4 (5H, m), 4.9 (IH, t), 3.5 (2H, dd), 2.2 (3H, s). $^{13}C$ NMR ($CDCl_3$) $\delta$: 194.8, 140.4, 129.2, 128.6, 127.6, 62.3, 38.4, 30.9. MS (70 eV): (M, 1.7%), (M + 2, 0.6%), (M-Cl, 3.7%), (M-HCl, 0.8%), (M-$C_2H_2OS$, 8.7%), (M-$C_2H_3OS$, 5.1%), (M-$C_2H_4OS$, 26.8%), (M-$C_2H_5OSCl$, 10%), (M-$C_2H_4OCl$, 13.3%).

**Thioacetate acid *S*-(2-chloro-cyclohexyl-ethyl) ester (3b).** Colorless oil. IR (neat) $\nu$ 2925, 2870, 1700, 1450, 1360, 1270, 1238, 1225, 1215, 1130, 1010. $^{1}H$ NMR ($CDCl_3$) $\delta$: 3.95 (1H, m), 3.7 (IH, m), 2.3 (3H, s), 2.15–2.34 (2H, m), 1.75–1.82 (2H, m), 1.41–1.55 (4H, m). $^{13}C$ NMR ($CDCl_3$) $\delta$: 194.4, 61.6, 48.95, 34.9, 31.5, 31.1, 24.7, 23.6. MS (70 eV); (M, 2.8%), (M + 2, 1%), (M-Cl, 1.2%), (M-HCl, 3.4%), (M-$C_2H_4O_5$, 12.3%), (M-$C_2H_3OCl$, 2.3%), (M-$C_3H_4OSCl$, 2.3%), (M-$C_3H_5OSCl$, 29.6%), (M-$C_3H_6OSCl$, 14.6%).

**Thioacetate acid *S*-(2-chloro-hexyl) ester (3d).** Colorless oil. IR (neat) $\nu$ 2970, 2945, 2890, 2875, 1750, 1710, 1475, 1362, 1240, 1140. $^{1}H$ NMR ($CDCl_3$) $\delta$: 3.7 (2H, m), 3.25 (IH, m), 2.3 (3H, s), 1.8–1.3 (6H, m), 0.9 (3H, t). $^{13}C$ NMR ($CDCl_3$) $\delta$: 195.4, 61.8, 48.1, 37.2, 30.9, 29.1, 22.7, 14.3. MS (70 eV): (M, 0.1%), (M-HCl, 0.1%), (M-$C_2H_3OS$, 0.3%), (M-$C_2H_4OS$, 0.3%), (M-$C_2H_4OSCl$, 0.9%).

**Thioacetate acid *S*-(1-allyloxymethyl-2-chloro-ethyl) ester (2c).** Colorless oil. IR (neat) $\nu$ 3090, 2995, 2885, 1700, 1435, 1360, 1240, 1130. $^{1}H$ NMR ($CDCl_3$) $\delta$: 5.87 (1H, m), 5.21 (2H, dd), 4 (3H, m), 3.75 (2H), 3.6 (2H, m), 2.3 (3H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 194.5, 134.6, 117.8, 72.6, 68.4, 45.4, 44.4, 30.9. MS (70 eV): (M, 1%), (M + 2, 0.4%), (M-HCl,

0.1%), (M-$C_2H_3OS$, 0.3%), (M-$C_2H_4O$, 1.9%), (M-$C_3H_6O$, 5.6%), (M-$C_3H_5O$, 0.7%).

**Thioacetate acid *S*-(2-chloro-l-isopropoxymethyl-ethyl) ester (2e).** Colorless oil. IR (neat) $\nu$ 2980, 2940, 2880, 1705, 1475, 1435, 1385, 1375, 1360, 13420, 1290, 1180, 1135, 1020. $^1$H NMR ($CDCl_3$) $\delta$: 3.5–3.7 (2H + 3H, complex), 2.3 (3H, s), 1.15 (6H, d). $^{13}$C NMR ($CDCl_3$) $\delta$: 194.7, 72.6, 66.4, 45.7, 44.5, 30.8, 22.3. MS (70 eV): (M, 0.5%), (M + 2, 0.2%), (M-HCl, 0.2%), (M-$C_3H_8O$, 1.4%), (M$C_5H_{11}OCl$, 13.3%).

**Thioacetate acid *S*-(2-chloro-l-chloromethyl-ethyl) ester (2f).** Colorless oil. IR (neat) $\nu$ 2960, 2892, 1700, 1435, 1365, 1275, 1115. $^1$H NMR ($CDCl_3$) $\delta$: 4 (1H, m), 3.9 (2H, m), 3.75 (2H), 2.3 (3H). $^{13}$C NMR ($CDCl_3$) $\delta$: 198, 46.7, 44, 30.6. MS (70 eV): (M, 1.6%), (M-Cl, 0.3%), (M-HCl, 0.6%), (M-$C_2H_3OS$, 0.7%), (M-$C_2H_4OS$, 1.3%), (M-$C_2H_3OCl$, 3.1%).

**Thioacetate acid *S*-(2-chloro-1-phenoxymethyl-ethyl) ester (2g).** Colorless oil. IR (neat) $\nu$ 3063, 3042, 1930, 1880, 1695, 1600, 1590, 1495, 1460, 1430, 1385, 1355, 1300, 1290, 1240, 1175, 1130, 1080, 1055, 1035. $^1$H NMR ($CDCl_3$) $\delta$: 7.22–7.57 (2H, m), 6.87–6.97 (3H, m), 4.3 (2H, m), 4.1 (1H, m), 3.8 (2H), 2.3 (3H). $^{13}$C NMR ($CDCl_3$) $\delta$: 194.1, 158.5, 130, 121.9, 115.1, 66.5, 45, 44.2, 31. MS (70 eV): (M, 3.1%), (M + 2, 1.2%), (M-Cl, 0.5%), (M-HCl, 0.3%), (M-$C_6H_5O$, 12.2%), (M-$C_8H_8O_2$, 0.6%), (M-$C_2H_3O_5$, 0.6%), (M-$C_5H_7OSCl$, 42.8%).

**2-Methyl-acrylic acid 2-acetylsulfanyl-3-chloro-propyl ester (2h).** 2965, 2940, 1730, 1705, 1635, 1460, 1440, 1410, 1380, 1360, 1325, 1300, 1150, 1020. $^1$H NMR ($CDCl_3$) $\delta$: 6.15 (1H, dd), 5.5 (IH, dd), 4.3 (3H, m), 3.7 (2H, m), 2.3 (3H, s), 1.9 (3H, s). $^{13}$C NMR ($CDCl_3$) $\delta$: 192.4, 166, 136.1, 126.1, 63, 44.4, 44, 30.7, 18.7. MS (70 eV): (M, 0.5%), (M + 2, 0.2%), (M-Cl, 0.1%), (M-HCl, 0.3%), (M-$C_2H_4OS$, 0.5%), (M-$C_4H_6O_2$, 4%), (M-$C_2H_5OSCl$, 0.7%).



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