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A facile method for the synthesis of 1,3-oxathiolan-2-ones by reaction of oxiranes, sulfur, and carbon monoxide

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Abstract—A new method for the synthesis of 1,3-oxathiolan-2-ones has been developed. When oxiranes were allowed to react with sulfur in the presence of a catalytic amount of sodium hydride under pressurized carbon monoxide, the three-component coupling of oxiranes, sulfur, and carbon monoxide smoothly proceeded to give the 1,3-oxathiolan-2-ones in moderate to good yields. The reaction proceeded with a high regioselectivity and stereospecificity. For the reaction of oxiranes possessing an aromatic ring, the yields of the 1,3-oxathiolan-2-ones were lower than that of the oxiranes possessing no aromatic ring due to the formation of alkenes and thiiranes as byproducts. However, the product yields were improved by the addition of a catalytic amount of selenium.

1. Introduction

The development of the process to replace the use of phosgene as a carbonylating reagent has received considerable attention in recent years due to environmental and industrial concerns. Carbon monoxide is one of the promising agents to replace phosgene; the development of new methods for the carbonylation of various organic compounds with carbon monoxide could have a significant impact on organic and industrial chemistries.[1]

Since 1,3-oxathiolan-2-one is an important synthetic intermediate in organic[2] and polymer sciences,[3] considerable attention has been devoted to the development of a convenient method for the synthesis of 1,3-oxathiolan-2-one. Although various synthetic methods of 1,3-oxathiolan-2-one, such as the carbonylation of β-hydroxy thiol with phosgene, the treatment of oxirane with carbonyl sulfide in the presence of triethylamine, the base-catalyzed cyclization of the imidazolide derivative prepared by the treatment of epoxy alcohol with thiocarbonyl diimidazole, the oxidation of 2-alkoxy-1,3-oxathiolane, and the acid-assisted cyclization of 2-hydroxyethyl thiocarbonate have been reported,[2–6] these methods have the following disadvantages: (i) the use of poisonous phosgene and carbonyl sulfide, (ii) the use of intolerable and odorous thiol, (iii) the harsh reaction conditions for the preparation of carbonyl sulfide, and (iv) limitation of starting materials. Furthermore, the decarboxylation of 1,3-oxathiolan-2-one sometimes occurred under these reaction conditions, and thiirane was formed as a byproduct.[7]

We have now developed a facile method for the synthesis of 1,3-oxathiolan-2-ones by the reaction of oxiranes with sulfur and carbon monoxide in the presence of a catalytic amount of sodium hydride under mild reaction conditions.[8,9] Furthermore, it was confirmed that the yields of the 1,3-oxathiolan-2-ones possessing an aromatic ring were improved by the addition of a selenium catalyst.

2. Results and discussion

In order to determine the optimized reaction conditions, 2-decyloxirane (**1a**) was allowed to react with sulfur and carbon monoxide under various reaction conditions and the results are shown in Table 1. When **1a** was treated with sulfur (5 equiv) in the presence of sodium hydride under pressurized carbon monoxide (10 kg cm^{-2}) in THF solvent at 60 °C for 3 h, 5-decyl-1,3-oxothiolan-2-one (**2a**) was obtained in 96% yield (entry 5). The yield of **2a** decreased when the reaction was carried out at lower reaction temperatures and carbon monoxide pressures (entries 5 and 13–16). The product yield was also affected by the amount of sulfur used (entries 1–5). Although **1a** was coupled with sulfur and carbon monoxide, even using 1,4-dioxane, DMSO, DMF, and acetonitrile instead of THF as the solvent, the best yield was observed in the THF solvent (entries 5 and 7–10). In the case of hydrocarbon solvents, such as toluene and hexane, the reaction did not proceed

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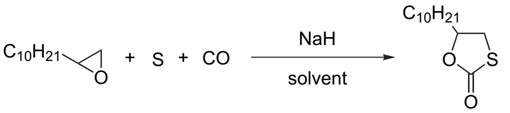
Table 1. The reaction of 2-decyloxirane with carbon monoxide and sulfur under various reaction conditions[a]



Entry	Sulfur (mmol)	Solvent	Temp (°C)	CO (kg cm^{-2})	Yield (%)[b]
1	2	THF	60	10	28
2	4	THF	60	10	67
3	6	THF	60	10	76
4	8	THF	60	10	85
5	10	THF	60	10	96 (92)
6[c]	10	THF	60	10	95
7	10	1,4-Dioxane	60	10	22
8	10	DMSO	60	10	56
9	10	DMF	60	10	82
10	10	Acetonitrile	60	10	60
11	10	Toluene	60	10	0
12	10	Hexane	60	10	0
13	10	THF	50	10	72
14	10	THF	40	10	29
15	10	THF	60	5	37
16	10	THF	60	1	0

[a] Reaction conditions: 2-decyloxirane (2 mmol), NaH (2 mmol), and solvent (2 mL) for 3 h.

[b] GC yield. The number in parenthesis shows the isolated yield.

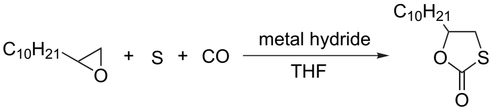
[c] NaH (0.5 mmol) was used.

and **1a** (92 and 95%, respectively) was recovered (entries 11 and 12). In this reaction, it is possible to still further reduce the amount of sodium hydride (25 mol %) and form **2a** in 95% yield (entry 6).

The reaction of **1a** with sulfur and carbon monoxide was next examined in the presence of various metal hydrides, and these results are shown in Table 2.[10] Although the other metal hydrides, lithium, potassium, and calcium hydrides and sodium borohydride also functioned as a base, the yields of **2a** were distinctly decreased (entries 2, 3, 5, and 6). For the reaction in the presence of potassium hydride, it is interesting to note that the yield of **2a** was dramatically increased by the addition of dibenzo-18-crown-6, which strongly binds with the potassium cation (entry 4).

To determine the scope and limitation of the synthesis of the 1,3-oxathiolan-2-ones, various oxiranes were reacted with sulfur and carbon monoxide in the presence of a catalytic amount of sodium hydride, and these results are shown in Table 3. The yields of the products were influenced by the structure of the oxiranes. For the 2-alkyl and 2,2-dialkyl substituted oxiranes, 5-alkyl and 5,5-dialkyl substituted 1,3-oxathiolane-2-ones were obtained in 95, 87, and 99% yields, respectively, (entries 1–3). The treatment of 7-oxabicyclo[4.1.0]heptane with sulfur and carbon monoxide produced 4,5-tetramethylene-1,3-oxathiolan-2-one in a 61% yield (entry 4). For the sterically hindered oxirane, such as 2,2,3-trimethyloxirane, the product yield was low (entry 5). For the reaction of the oxiranes possessing an aromatic ring, such as 2-phenyl-, 2-(4-methylphenyl)-, 2-(4-bromophenyl)-, 2-benzyl-, and 2-phenoxymethyl oxirane, the yields of the 1,3-oxathiolan-2-ones were low compared to those of the oxiranes possessing no aromatic ring due to the formation of alkene, thiirane, and oligomers of oxirane as byproducts (entries 6–10).

Table 2. The reaction of 2-decyloxirane with carbon monoxide and sulfur in the presence of metal hydride[a]



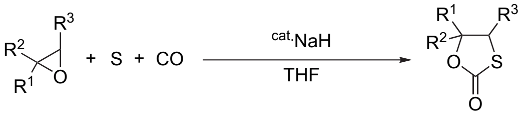
Entry	Metal hydride	Yield (%)[b]
1	LiH	0
2	NaH	95
3	KH	28
4[c]	KH	82
5	CaH$_2$	61
6	NaBH$_4$	7

[a] Reaction conditions: 2-decyloxirane (2 mmol), S (10 mmol), CO (10 kg cm^{-2}), metal hydride (0.5 mmol), and THF (2 mL) at 60 °C for 3 h.

[b] GC yield.

[c] Dibenzo-18-crown-6 (0.5 mmol) was added.

Table 3. The reaction of various oxiranes with carbon monoxide and sulfur[a]



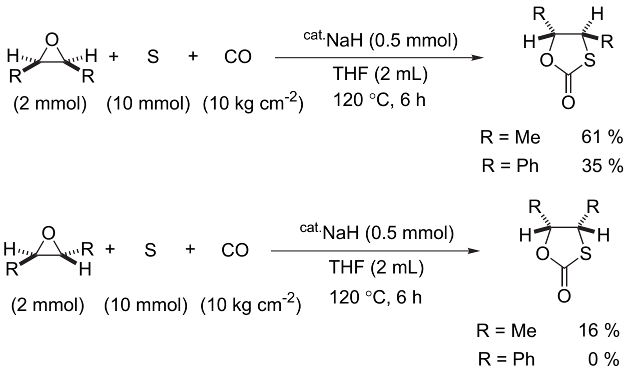
Entry	R^1	R^2	R^3	Yield (%)[b]
1	n-C$_{10}$H$_{21}$	H	H	95
2	C$_2$H$_5$	H	H	87
3	CH$_3$	CH$_3$	H	99
4	H	—(CH$_2$)$_4$—		61
5[c]	CH$_3$	CH$_3$	CH$_3$	4
6	Ph	H	H	39
7	4-Tol	H	H	32
8	4-BrC$_6$H$_5$	H	H	4
9	PhCH$_2$	H	H	53
10	PhOCH$_2$	H	H	24

[a] Reaction conditions: oxirane (2 mmol), S (10 mmol), CO (10 kg cm^{-2}), NaH (0.5 mmol), and THF (2 mL) at 60 °C for 3 h.

[b] GC yield.

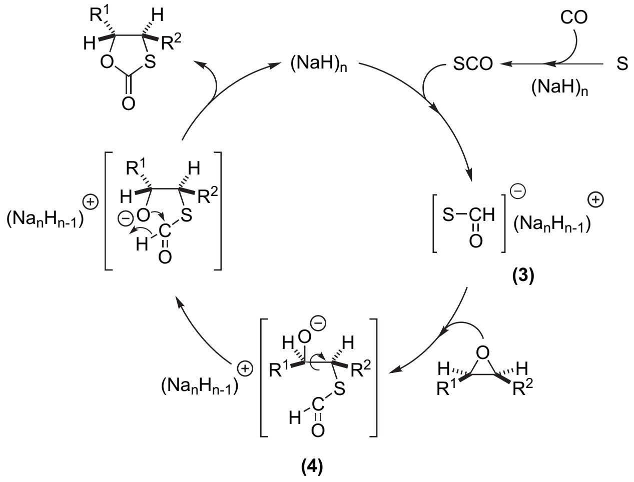
[c] The reaction was carried out at 150 °C for 8 h.

The reaction of *cis*-2,3-disubstituted oxiranes, such as *cis*-2,3-dimethyl- and 2,3-diphenyloxiranes, stereospecifically proceeded and formed the *trans*-4,5-disubstituted 1,3-oxathiolan-2-ones in moderate yields (Scheme 1). Similarly, *trans*-2,3-dimethyloxirane produced the *cis*-4,5-dimethyl-1,3-oxothiolan-2-one, however, for *trans*-2,3-diphenyloxirane, *cis*-4,5-diphenyl-1,3-oxathiolan-2-one was not confirmed and the oxirane (86%) was recovered.



Scheme 1.

Although the reaction pathway for the formation of 1,3-oxathiolan-2-one has not been fully clarified, one of the plausible reaction pathways is shown in Scheme 2. It was suggested that the preparation of carbonyl sulfide by the reaction of sulfur and carbon monoxide was the first step in the reaction. The hydride anion attacked the carbonyl sulfide to give the corresponding thioformate anion (**3**).[11] The attack of **3** on the oxirane from the less hindered side then formed an intermediate (**4**). Rotation of the carbon–carbon bond followed by intramolecular cyclization gave the corresponding 1,3-oxathiolan-2-one and regenerated the hydride anion. For the reaction of the *trans*-2,3-dimethyl or *trans*-2,3-diphenyl substituted oxiranes, it was suggested that the rotation of the carbon–carbon bond of **4** was strongly suppressed by the steric effect and the oxygen anion attacked the β-carbon to regenerate the oxirane.

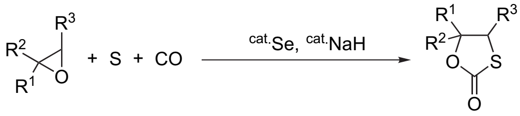


Scheme 2. A plausible reaction pathway.

We have recently reported that selenium acts as a catalyst for the reaction of sulfur and carbon monoxide producing carbonyl sulfide in the presence of an amine.[12] During the continuing study of the selenium-catalyzed reaction of sulfur and carbon monoxide, it was found that various organosulfur compounds having a thiolester (–C(=O)S–) group were synthesized in moderate to good yields using this catalytic reaction system under mild conditions.[13] Based on these results, we next investigated the application of the selenium-catalyzed reaction system on the preparation of 1,3-oxathiolan-2-ones. Various oxiranes were allowed to react with sulfur and carbon monoxide in the presence of a catalytic amount of sodium hydride and selenium, and these results are shown in Table 4. It is interesting to note that the yields of the 1,3-oxathiolan-2-ones having an aromatic ring were improved using the selenium-catalyzed reaction system.[14,15]

In summary, we found that the reaction of oxiranes with sulfur and carbon monoxide in the presence of a catalytic amount of sodium hydride produced the corresponding 1,3-oxathiolan-2-ones. In addition, for the reaction of oxiranes having an aromatic ring, the yields of the 1,3-oxathiolan-2-ones were improved by the addition of the selenium catalyst. From the viewpoint of a simple operation, mild reaction conditions, and good yields, the present reaction provides a useful method for the synthesis of the 1,3-oxathiolan-2-ones.

Table 4. Selenium-catalyzed synthesis of 1,3-oxathiolan-2-ones[a]



Entry	R^1	R^2	R^3	Yield (%)[b]
1[b]	Ph	H	H	79
2	*p*-Tol	H	H	50
3	*p*-BrC_6H_5	H	H	22
4	$PhCH_2$	H	H	97
5	$PhOCH_2$	H	H	66
6	H	—$(CH_2)_4$—		16
7[c]	H	CH_3	CH_3	31
8[c]	CH_3	H	CH_3	7
9[c,d]	H	Ph	Ph	10
10[e]	CH_3	CH_3	CH_3	4

[a] Reaction conditions: epoxide (2 mmol), S (10 mmol), CO (10 atm), Se (0.05 mmol), NaH (0.5 mmol), and THF (2 mL) at 60 °C for 3 h.

[b] GC yield.

[c] The reaction was carried out at 120 °C for 6 h.

[d] *cis*-Stillbene (24%) was formed as byproduct.

[e] The reaction was carried out at 150 °C for 8 h.

3. Experimental

3.1. General procedure

The ^1H and ^{13}C NMR spectra were recorded by 400 or 270 and 99.5 or 67.8 MHz spectrometers using $CDCl_3$ as a solvent with tetramethylsilane as an internal standard. IR spectra were obtained using a FT-IR spectrophotometer. The mass spectra were measured by GC–MS. Gas chromatography (GC) was carried out using a spectrometer with flame-ionizing detector and a capillary column. 2-(4-Methylphenyl) oxirane was synthesized by the oxidation of 4-methylstyrene with MCPBA. Powdered sulfur, sodium hydride, and elemental selenium were commercially available and used without purification. The solvents oxiranes and amines were distilled before use.

3.2. General procedure for the synthesis of 1,3-oxathiolan-2-ones

In a 50 mL stainless steel autoclave were placed powdered sulfur (10 mmol, 0.321 g), THF (2 mL), oxirane (2 mmol), and NaH (0.5 mmol, 0.024 g in mineral oil). The apparatus was flushed several times with carbon monoxide and then charged with carbon monoxide at 10 kg cm^{-2}. The mixture was heated with stirring at 60 °C for 3 h. After the reaction was complete, H_2O was added to the resulting solution and extracted with diisopropyl ether (15×3 mL). The combined organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure. Purification by column chromatography (hexane/AcOEt=3/1) on silica gel and HPLC ($CHCl_3$) gave the corresponding 1,3-oxathiolan-2-ones. The product was characterized by comparison of its spectral data with those of authentic samples (5-decyl-1,3-oxathiolan-2-one,[16] 5-ethyl-1,3-oxathiolan-2-one,[17,18] 4,5-tetramethylene-1,3-oxathiolan-2-one,[19] *trans*-4,5-dimethyl-1,3-oxathiolan-2-one,[20] and 2-phenylthiirane[21]).

3.3. General procedure for the selenium-catalyzed synthesis of 1,3-oxathiolan-2-ones

In a 50 mL stainless steel autoclave were placed powdered sulfur (10 mmol, 0.321 g), elemental selenium (0.05 mmol, 0.004 g), THF (2 mL), oxirane (2 mmol), and NaH (0.5 mmol, 0.024 g in mineral oil). The apparatus was flushed several times with carbon monoxide and charged with carbon monoxide at 10 kg cm^{-2}. The mixture was then heated with stirring at 60 °C for 3 h. After the reaction was complete, H_2O was added to the resulting solution and extracted with diisopropyl ether (15×3 mL). The combined organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure. Purification by column chromatography (hexane/AcOEt=3/1) on silica gel and HPLC ($CHCl_3$) gave the corresponding 1,3-oxathiolan-2-ones.

3.3.1. 5,5-Dimethyl-1,3-oxathiolan-2-one. ^1H NMR (400 MHz, $CDCl_3$) δ 3.377 (s, 2H), 1.584 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.663, 85.381, 42.426, 26.447; IR (neat) 2981, 2937, 1732 cm^{-1}; MS 132 (M^+); yellow oil. Anal. Calcd for $C_5H_8O_2S$: C, 45.43; H, 6.10; S, 24.26. Found: C, 45.27; H, 6.21; S, 24.35.

3.3.2. 4,5,5-Trimethyl-1,3-oxathiolan-2-one. ^1H NMR (270 MHz, $CDCl_3$) δ 3.876 (q, J=6.8 Hz, 1H), 1.552–1.384 (m, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 171.280, 88.165, 51.963, 25.997, 21.102, 16.075; IR (neat) 2996, 1730 cm^{-1}; MS 146 (M^+); yellow oil. Anal. Calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89; S, 21.93. Found: C, 49.51; H, 6.72; S, 21.88.

3.3.3. 5-Phenyl-1,3-oxathiolan-2-one. ^1H NMR (400 MHz, $CDCl_3$) δ 7.313–7.360 (m, 5H), 5.560 (dd, J=6.8 and 9.4 Hz, 1H), 3.660 (dd, J=6.8 and 10.8 Hz, 1H), 3.463 (dd, J=9.4 and 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.001, 136.206, 128.889, 128.559, 125.367, 81.686, 38.318; IR (neat) 1740, 770, 697 cm^{-1}; MS 180 (M^+); yellow oil. Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47; S, 17.79. Found: C, 60.21; H, 4.32; S, 17.67.

3.3.4. 5-(4-Toly)-1,3-oxathiolan-2-one. ^1H NMR (270 MHz, $CDCl_3$) δ 7.244–7.139 (m, 4H), 5.516 (dd, J=6.5 and 9.5 Hz, 1H), 3.628 (dd, J=6.6 and 11.1 Hz, 1H) 3.450 (t, 1H), 2.307 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 171.864, 138.658, 133.046, 129.040, 125.321, 81.747, 38.174, 20.822; IR (neat) 3030, 2923, 1738 cm^{-1}; MS 194 (M^+); yellow oil. Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19; S, 16.51. Found: C, 61.71; H, 5.18; S, 16.28.

3.3.5. 5-(4-Bromophenyl)-1,3-oxathiolan-2-one. ^1H NMR (270 MHz, $CDCl_3$) δ 7.529–7.249 (m, 4H), 5.601 (dd, J=6.5 and 9.5 Hz, 1H), 3.761 (dd, J=6.5 and 11.2 Hz, 1H), 3.507 (dd, J=9.5 and 11.2 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 171.749, 135.276, 131.738, 127.123, 122.935, 80.925, 38.314; IR (KBr) 1719 cm^{-1}; MS 260 (M^+); colorless crystals. Anal. Calcd for $C_9H_7BrO_2S$: C, 41.72; H, 2.72; S, 12.37. Found: C, 41.85; H, 2.68; S, 12.35.

3.3.6. 5-Benzyl-1,3-oxathiolan-2-one. ^1H NMR (400 MHz, $CDCl_3$) δ 7.358–7.218 (m, 5H), 4.863 (quintet, J=6.9 Hz, 1H), 3.416–2.990 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.331, 134.771, 129.236, 128.765, 127.272, 81.257, 39.795, 35.687; IR (neat) 2923, 1716, 764, 703 cm^{-1}; MS 194 (M^+); yellow oil. Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19; S, 16.51. Found: C, 62.04; H, 5.02; S, 16.53.

3.3.7. 5-(Phenoxymethyl)-1,3-oxathiolan-2-one. ^1H NMR (270 MHz, $CDCl_3$) δ 7.334–6.892 (m, 5H), 5.052–4.961 (m, 1H), 4.197 (d, J=4.9 Hz, 2H), 3.641 (d, J=7.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.103, 157.548, 129.517, 121.643, 114.353, 77.749, 66.674, 33.130; IR (neat) 1736, 1244, 1077, 755 cm^{-1}; MS 210 (M^+); yellow oil. Anal. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79; S, 15.25. Found: C, 57.32; H, 4.76; S, 15.21.

Acknowledgements

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