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A new method for the synthesis of 1,3-oxathiolan-2-ones by the reaction of epoxides with sulfur and carbon monoxide

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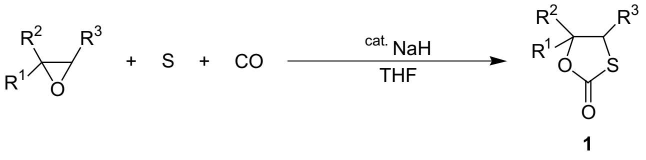
Abstract—The convenient method for the synthesis of 1,3-oxathiolan-2-ones by the reaction of epoxides with elemental sulfur and carbon monoxide in the presence of catalytic amount of sodium hydride has been developed.

Since 1,3-oxathiolan-2-one is an important synthetic intermediate in polymer science,[1] considerable attention has been devoted to the development of a convenient method for the synthesis of 1,3-oxathiolan-2-one.[2] For instance, the carbonylation route of β-hydroxy thiol with phosgene is a simple method for the synthesis of 1,3-oxathiolan-2-one, but the use of poisonous phosgene and untolerable odorous thiol are required for the method. As another one, the treatment of epoxides with carbonyl sulfide in the presence of triethylamine gave 1,3-oxathiolan-2-ones in moderate yields, however, the use of poisonous carbonyl sulfide as a starting material is also required. Furthermore, the decarboxylation of 1,3-oxathiolan-2-one sometimes occurred under these reaction conditions, and thiirane was formed as a by-product.[3]

We found a new method for the synthesis of 1,3-oxathiolan-2-ones (**1**) by the reaction of epoxides with elemental sulfur and carbon monoxide in the presence of a catalytic amount of sodium hydride (Scheme 1).[4,5]



Scheme 1.

When 1,2-epoxydodecane (2 mmol) was allowed to react with sulfur (10 mmol) in the presence of a catalytic amount of sodium hydride (0.5 mmol) under the pressurized carbon monoxide (10 atm) in THF solvent at 60 °C for 3 h, the thiocarbonylation of epoxide proceeded regioselectively to give 5-decyl-1,3-oxathiolan-2-one in 95% yield (entry 1).[6] Although the reaction of 1,2-epoxydodecane with elemental sulfur and carbon monoxide was undertaken in the presence of a catalytic amount of potassium hydride instead of sodium hydride used as a base, no formation of 5-dodecyl-1,3-oxathiolan-2-one was confirmed. However, the reaction was accelerated by the addition of dibenzo-18-crown-6, and 5-decyl-1,3-oxathiolan-2-one was obtained in 82% yield. The results of the reaction of various epoxides with elemental sulfur and carbon monoxide in the presence of a catalytic amount of sodium hydride were shown in Table 1. 5-Alkyl substituted 1,3-oxathiolan-2-ones were obtained in good to excellent yields by the reaction of mono substituted epoxides (entries 1 and 2). In the case of 1,1-dialkyl substituted epoxide such as isobutylene oxide, the same reaction occurred efficiently to give 5,5-dialkyl-1,3-oxathiolan-2-one in excellent yield, however, for trialkyl substituted epoxide, the yield was very low (entry 4). When epoxides possessing aromatic ring were allowed to react with sulfur and carbon monoxide, the yields of 1,3-oxathiolan-2-ones were slightly decreased owing to the preparation of olefins and 5-phenylthiiranes as by-products (entry 5).

We have already shown that the carbonyl sulfide was easily prepared by a facile exchange reaction of elemental sulfur with carbonyl selenide, generated in situ by the reaction of elemental selenium with carbon monoxide in

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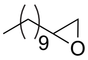
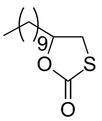
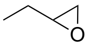
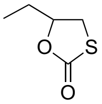
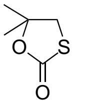
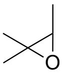
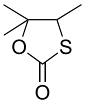
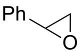
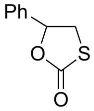
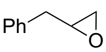
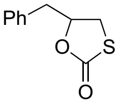
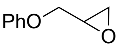
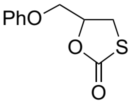
Table 1. Synthesis of 1,3-oxathiolan-2-ones[a,b]

Entry	Epoxide	Product	Yield (%)[c]
1			95
2			87
3			98
4[d]			4
5			39 (79)
6			53 (97)
7			24 (66)

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

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

[c] GC yield. The numbers in parentheses show the yield of product in the presence of selenium catalyst.

[d] At 150°C for 8h.

the presence of triethylamine under mild conditions.[7] Furthermore, this exchange reaction has been widely applicable to a synthesis of various organosulfur compounds such as *S*-alkyl thiocarbamates and *S*-alkyl carbonothiolates.[8] Then, the catalytic use of selenium in the synthesis of 1,3-oxothiolan-2-ones by the reaction of epoxide with sulfur and carbon monoxide was next investigated in order to improve the yields of 1,3-oxathiolan-2-one having aromatic ring. In fact, when styrene oxide was allowed to react with sulfur in the presence of a catalytic amount of selenium (2.5mol%) under the pressurized carbon monoxide at 60°C for 3h, the yield of 1,3-oxathiolan-2-one was improved. 1,3-Oxathionlan-2-one having aromatic ring such as 5-benzyl-[1,3]oxathiolan-2-one and 5-phenoxymethyl-[1,3]oxathiolan-2-one were also obtained in moderate to good yields by the use of selenium catalyst (entries 5–7).

Although the reaction pathway was not completely clarified at the present stage, a plausible reaction path was proposed on the reaction. Initially, carbonyl sulfide was generated in situ by the reaction of elemental sulfur with carbon monoxide in the presence sodium hydride. Carbonyl sulfide attacked to epoxide from the sterically less-hindered side in the presence of NaH and subsequent intramolecular cyclized to give 1,3-oxathiolan-2-one.

From the viewpoint of simple operation, mild reaction conditions, and good yields, the present reaction provides a useful method for synthesis of 1,3-oxathiolan-2-ones. Furthermore, application of the reaction and elucidation of the reaction pathway as well as selenium catalyst effect are now in progress.

Acknowledgement

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5. We have recently shown that the reaction of 2-alkyn-1-ols with sulfur and carbon monoxide, followed by copper(I)-catalyzed cyclization gave 4-alkylidene-2-oxo-1,3-oxathiolanes in moderate to good yields. See: Mizuno, T.; Nakamura, F.; Ishino, Y.; Nishiguchi, I.; Hirashima, T.; Ogawa, A.; Kambe, N.; Sonoda, N. *Synthesis* **1989**, 770.
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