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Tetrathiomolybdate Assisted Epoxide Ring Opening with Masked Thiolates and Selenoates: Multistep Reactions in One Pot

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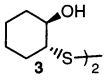
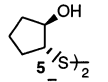
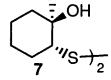
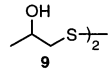
Tetrathiomolybdate provides an easy access to β-hydroxy disulfides, β-hydroxy sulfides, and selenides from epoxides in a tandem, multistep process in one pot. This strategy has been utilized effectively in the construction of thiabicylo[3.2.2]nonane derivative **24**.

Ring opening of epoxides by thiols is a widely used reaction for the synthesis of β-hydroxy thio derivatives which are useful intermediates in natural product synthesis.[1] The most common protocols employ opening of the epoxide with thiol in the presence of acid or base[2,3] and also in the presence of ZnI_2,[4] $CoCl_2$,[5] lanthanide trichlorides,[6] zinc or magnesium tartrates,[7] etc. Recent years have witnessed a large number of papers on the asymmetric version of epoxide opening by thiols assisted by chiral catalysts.[8]

The tandem reactions involving multistep, one-pot transformations of substrates to products are currently of interest because of potential applications in organic synthesis.[9] Additionally, disulfide/diselenide bond cleavage could lead to interesting products in adding nucleophilic sulfur[10]/selenium[11] species to a variety of organic substrates. The cleavage of disulfide/diselenide bonds under neutral conditions would enhance the utility of such reactions, particularly in tandem reactions.

TABLE 1. Reaction of Epoxides with Tetrathiomolybdate (1)

Entry	Substrate	Time (h)	Product[a]	Yield[b] (%)
1	 **2**	6	 **3**	84
2	 **4**	3.5	 **5**	74
3	 **6**	5	 **7**	90
4	 **8**	4	 **9**	70

Earlier we demonstrated that benzyltriethylammonium tetrathiomolybdate,[12] $[C_6H_5CH_2NEt_3]_2MoS_4$, **1**, is a useful reagent that effects a tandem sulfur transfer reduction−Michael addition in one pot.[13] In continuation of our investigation into the utility of **1** in organic synthesis,[12−14] we report herein a convenient strategy to open an epoxide ring with **1** (1 equiv; CH_3CN:EtOH, 1:1; 28 °C; under sonication) to provide β-hydroxy disulfides[15] (Table 1).

Additionally we disclose our results on the cleavage of disulfide/diselenide bonds assisted by **1** and the use of masked thiolate/selenoate for the synthesis of β-hydroxy sulfides/β-hydroxy selenides involving multistep, tandem reactions in one pot (Scheme 1).

It has earlier been shown that disulfide bonds are cleaved in the presence of **1** involving an induced redox

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(1) (a) Corey, E. J.; Clark, D. A.; Goto, G. Marfat, A.; Mioskowski, C.; Samuelsson, B.; Hammarström, S. *J. Am. Chem. Soc.* **1980**, *102*, 1436 and 3663. (b) Adams, H.; Bell, R.; Cheung, Y.; Jones, D. N.; Tomkinson, N. C. O. *Tetrahedron: Asymm.* **1999**, *10*, 4129.

(2) Peach, M. E. In *The Chemistry of the Thiol Group*; Patai, S., Ed; John Wiley & Sons: New York, 1974; Part 3, p 771.

(3) Chini, M.; Crotti, P.; Giovani, E.; Macchia, F.; Pineschi, M. *Synlett* **1992**, 303, and references therein.

(4) (a) Guindon, Y.; Young, R. N.; Frenette, R. *Synth. Commun.* **1981**, *11*, 391. (b) de Pomar, J. C. J.; Soderquist, J. A. *Tetrahedron Lett.* **1998**, *39*, 4409.

(5) Iqbal, J.; Pandey, A.; Shukla, A.; Srivastava, R. R.; Tripathi, S. *Tetrahedron* **1990**, *46*, 6423.

(6) Vougioukas, A. E.; Kagan, H. B *Tetrahedron Lett.* **1987**, *28*, 6065.

(7) Yamashita, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1213.

(8) Selected references for asymmetric version of epoxide opening by thiols: (a) Iida, T.; Yamamoto, N.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1997**, *119*, 4783. (b) Wu, M. H.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 5252.

(9) (a) Ikeda, S. *Acc. Chem. Res.* **2000**, *33*, 511, and references therein. (b) Son, S. U.; Park, K. H.; Seo, H.; Chung, Y. K.; Lee, S.-G. *Chem. Commun.* **2001**, 2440, and references therein.

(10) Kondo, T.; Uenoyama, S.; Fujita, K.; Mitsudo, T. *J. Am. Chem. Soc.* **1999**, *121*, 482.

(11) (a) Sakakibara, M.; Katsumata, K.; Watanabe, Y.; Toru, T.; Ueno, Y. *Synthesis* **1992**, 377. (b) Engman, L.; Gupta, V. *J. Org. Chem.* **1997**, *62*, 157, and references therein.

(12) (a) Ramesha, A. R.; Chandrasekaran, S. *Synth. Commun.* **1992**, *22*, 3277. (b) Ramesha, A. R.; Chandrasekaran, S. *J. Org. Chem.* **1994**, *59*, 1354.

(13) Prabhu, K. R.; Sivanand, P.; Chandrasekaran, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4316.

(14) Prabhu, K. R.; Chandrasekaran, S. *Chem. Commun.* **1997**, 1021.

(15) Reactions were performed under sonochemical conditions (ultrasonic cleaning bath, 25 kHz). Without sonication it took a longer time (22−70 h) to produce a lower yield (30−60%) of the products.

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SCHEME 1

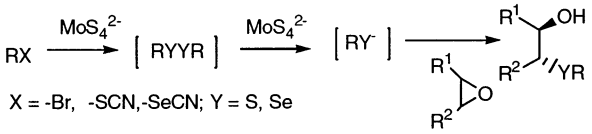
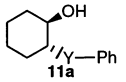
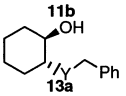
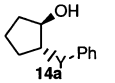
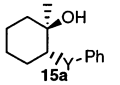
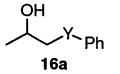


TABLE 2. Disulfide/Diselenide Bond Cleavage−Epoxide Opening Assisted by Tetrathiomolybdate (1)

Entry		Substrate	Time (h)	Product[a]	Yield[b] (%)
1	**2**	PhYYPh			
		Y=S, **10a**	4	**11a**	87
		Y=Se, **10b**	5	**11b**	82
2	**2**	$PhCH_2YYCH_2Ph$			
		Y=S, **12a**	4	**13a**	80
		Y=Se, **12b**	4	**13b**	60
3	**4**				
		10a	6	**14a**	90
		10b	5	**14b**	80
5	**6**				
		10a	7	**15a**	88
		10b	7	**15b**	78
6	**8**	**10a**	7	 **16a**	48
		10b	4	**16b**	73

[a] All compounds exhibited expected spectral and analytical data. [b] Isolated yields.

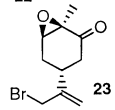
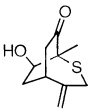
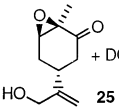
reaction.[13,16] The results of tandem cleavage of disulfide bonds assisted by **1** followed by epoxide ring opening to provide β-hydroxy sulfides are summarized in Table 2. Thus, in the reaction of disulfide **10a** or **12a** with **1** (1 equiv) followed by the addition of epoxide **2** (CH_3CN:EtOH, 1:1; 28 °C; 4 h) the corresponding β-hydroxy sulfide **11a** or **13a** was obtained as the only product in very good yield. Treatment of epoxide **4**, **6**, or **8** and diphenyl disulfide **10a** with **1** under similar conditions gave the β-hydroxy sulfides **14a**, **15a**, and **16a**, respectively.

The fact that **1** cleaves the disulfide bond under appropriate reaction conditions[13,16] prompted us to explore the possibility of cleavage of diselenides in situ, which can be taken advantage of in the ring opening of epoxides. Accordingly, epoxide **2** was treated with diphenyl diselenide **10b** in the presence of **1** (1 equiv; CH_3CN:EtOH, 1:1; 28 °C; 5 h), and the β-hydroxy selenide **11b** was obtained in 82% yield. The reaction of **10b** with epoxides **4**, **6**, and **8** in the presence of **1** also gave the corresponding **14b**, **15b**, and **16b**, respectively, in very good yield. Under similar reaction conditions **2** and **12b** in the presence of **1** afforded **13b** (Table 2).

Epoxide ring opening reactions using disulfides or diselenides assisted by **1** present an opportunity to explore tandem, multistep reactions with **1** in one pot. Therefore, it was of interest to study the reaction of epoxides with **1** and precursors of disulfides or diselenides (for example, alkyl halides or tosylates; Scheme 1).

(16) Coyle, C. L.; Harmer, M. A.; George, G. N.; Daage, M.; Stiefel, E. I. *Inorg. Chem.* **1990**, *29*, 14, and references therein.

TABLE 3. Multistep Reactions with Tetrathiomolybdate (1) in One Pot

Entry		Substrate	Time (h)	Product[a]	Yield[b] (%)
1	**2**	**17**	2	**13a**	81
2	**2**	**18**	2.5	**13a**	87
3	**2**	**17** + KSCN	6	**13a**	73
4	**2**	$PhCH_2OH$ (**19**) + DCC/CuCl	10.5	**13a**	73
5	**2**	**17** + KSeCN	6.5	**13b**	60
6	**2**	**19** + DCC/CuCl +KSeCN	14	**13b**	56
7	 **20**		3	 **21**	90
8	 **22**	DCC/CuCl	10	**21**	73
9	 **23**		7	 **24**	90
10	 **25**	+ DCC/CuCl	12	**24**	72

[a] All compounds exhibited expected spectral and analytical data. [b] Isolated yields.

Reaction of benzyl bromide **17** with **2** and **1** (2 equiv; CH_3-CN:EtOH, 1:1; 28 °C; 2 h) proceeded smoothly to furnish the corresponding **13a** in good yield (81%, entry 1, Table 3). As expected, under identical experimental conditions, **1** reacted with benzyl thiocyanate **18** and **2** to produce the corresponding **13a** (87%, entry 2, Table 3). The reaction of **1** with benzyl thiocyanate generated in situ (from **17** and potassium thiocyanate) and **2**, afforded the **13a** (73%, Table 3). When benzyl alcohol **19** was activated with DCC/CuCl[17] and treated with **1** followed by the addition of **2**, **13a** was obtained (73%, Table 3).

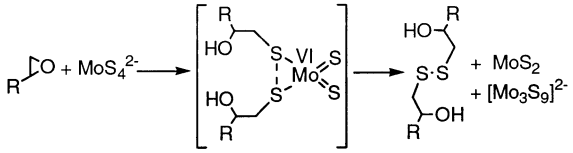
Employing a similar strategy, **13b** was obtained from the corresponding bromide or alcohol precursor in a four-/five-step tandem reaction in one pot. Thus, **17** on treatment with KSeCN followed by the addition of **1** (2 equiv) and **2** furnished the corresponding **13b** in 60% yield (entry 5, Table 3). In the reaction of benzyl alcohol, activation of alcohol (DCC/CuCl) followed by treatment with KSeCN, **1** (2 equiv), and **2** resulted in the formation of **13b** in 56% yield (entry 6, Table 3). The noteworthy feature of this methodology is the five-step reactions (activation of alcohol, formation of selenocyanate, diselenide formation, cleavage of diselenide bond, and epoxide ring opening) are performed in tandem in one pot using tetrathiomolybdate as the key reagent.[18]

The one-pot intramolecular reactions of ω-halo-epoxides and ω-hydroxy epoxides with **1** are presented in Table 3 (entries 7−10). When epichlorohydrin **20** was treated with **1** (2 equiv; CH_3CN:EtOH, 1:1; 28 °C; 3 h), the four membered β-hydroxy sufide **21** was isolated in excellent yield. Hydroxy epoxide **22** on activation with DCC/CuCl followed by treatment with excess **1** underwent a tandem reaction to produce the same four

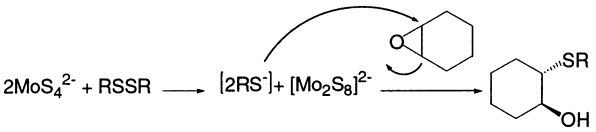
(17) Sinha, S.; Ilankumaran, P.; Chandrasekaran, S. *Tetrahedron* **1999**, *55*, 14769.

(18) In an incomplete reaction dibenzyl diselenide can be isolated (10−15%), indicating its intermediacy in the reaction.

SCHEME 2



SCHEME 3



membered **21**[19] (73%). The application of this methodology has been demonstrated in the synthesis of the 2-thiabicyclo[3.2.2]nonane skeleton (entries 9 and 10, Table 3). Interestingly, when ω-bromo epoxide **23** was treated with an excess of tetrathiomolybdate, the only product formed in the reaction turned out to be the 2-thiabicylo[3.2.2]nonane derivative **24** in excellent yield (90%). A similar result was achieved in the reaction of ω-hydroxy epoxide **25**, which was activated by DCC/CuCl and treated with **1** (2 equiv) at room temperature to furnish the bicyclic product **24** in 72% yield (Table 3).

A plausible reaction mechanism is proposed in Scheme 2. It is believed that alkylation of the metal−sulfur bond with opening of the epoxide ring is the key step, which triggers an internal redox reaction with oxidation of the ligand to the disulfide and the concomitant reduction of the metal center, leading to the formation of dihydroxy disulfide and sulfide cluster of molybdenum.[20]

Further, the cleavage of disulfide by **1** is an induced internal redox reaction, which is thoroughly investigated by Stiefel,[16] and the thiolate generated in situ further reacts with the epoxide to generate the corresponding β-hydroxy sulfide (Scheme 3).[21]

In summary, tetrathiomolybdate **1** provides an easy access to β-hydroxy disulfides, β-hydroxy sulfides, and selenides from epoxides in a tandem, multistep process in one pot. Additionally, interesting examples of tandem reactions to construct the 2-thiabicyclo[3.2.2]nonane skeleton utilizing **1** makes this methodology attractive.

Experimental Section

General Methods. All reactions are performed in an oven-dried apparatus. Reaction mixtures were stirred magnetically unless otherwise stated. The products were characterized by NMR, IR, FTIR, and GCMS. Commercial grade solvents were distilled prior to use. Chloroform, dichloromethane, and acetonitrile were initially dried over phosphorus pentoxide and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Coupling constants are reported in hertz. Infrared (IR) spectra were measured as $CHCl_3$ solution or as thin film.

Reaction of Epoxides with Tetrathiomolybdate 1 (General Procedure). To a well-stirred solution of epoxide (1 mmol) in CH_3CN:EtOH (1:1, 2 mL) was added tetrathiomolybdate (**1**; 1.1 mmol) at once. The reaction mixture was subjected to sonication using an ultrasonic cleaning bath (20 kHz) for 3.5−6 h (Table 1). The solvent was removed under reduced pressure, and the black residue was extracted with dichloromethane:diethyl ether (1:5, 10 mL × 3) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by chromatography on silica gel using ethyl acetate:hexane (1:15). The products **3**,[22] **5**,[22] **7**,[22] and **9**[22] exhibited expected analytical and spectral data (reaction of epoxides **6** and **8** with **1** resulted in the formation of **7** and **9**, respectively, as single regioisomers).

Disulfide/Diselenide Bond Cleavage−Epoxide Ring Opening Assisted by Tetrathiomolybdate (1) (General Procedure). To a well-stirred solution of disulfide (**10a** or **12a**, 0.5 mmol) or diselenide (**10b** or **12b**, 0.5 mmol) in CH_3CN (2 mL) was added **1** (1.2 mmol). The reaction mixture was stirred at room temperature (26 °C) for 2 h, and then a solution of epoxide (**2** or **4** or **6** or **8**, 1 mmol) in EtOH (2 mL) was added and stirred at room temperature (26 °C) for the time indicated in Table 2. The solvent was removed under vacuum. The black residue was extracted with dichloromethane:diethyl ether (1:5, 10 mL × 3) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by chromatography on silica gel using ethyl acetate:hexane (1:15). The products **11a**,[4] **11b**,[23] **13a**,[7] **13b**,[23] **14a**,[4] **14b**,[24] **15a**,[4] **15b**,[23] **16a**,[5] and **16b**[23] exhibited expected analytical and spectral data.

Synthesis of 2*R*,3*R*-Epoxy-5*R*-(1-(bromomethyl)vinyl)-2-methylcyclohexanone (23).[25] 9-Bromocarvone **1** (1 g, 4.34 mmol) was dissolved in methanol (1 mL), and the solution was cooled to 0 °C. Hydrogen peroxide (30%, 1.4 mL) was added slowly with stirring to the cooled solution (0.5 h) followed by the addition of 6 M NaOH (0.37 mL), ensuring that internal temperature was always <0 °C. The reaction mixture was allowed to stir at 0 °C for an additional 16 h, then poured into water (10 mL), and saturated NaCl. The reaction mixture was extracted with Et_2O (4 × 10 mL), and the combined organic extract was washed with brine and then dried ($MgSO_4$). After filtration, the solvent was evaporated and the crude residue was purified by column chromatography on silica gel using 3% EtOAc:hexane as solvent to afford **23** as a colorless liquid. Yield: 0.651 g (62%). IR: 1709, 1639, 1051 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.26 (s, 1H), 4.98 (s, 1H), 3.94 (s, 2H), 3.44 (dd, J = 0.9 Hz, J = 3 Hz, 1H), 2.97−3.02 (m, 1H), 2.65 (ddd, J = 1.5 Hz, J = 4.8 Hz, J = 17.7 Hz, 1H), 2.41−2.49 (m, 1H), 2.03 (dd, J = 11.7 Hz, J = 17.7 Hz, 1H), 1.94 (ddd, J = 1.2 Hz, J = 11.4 Hz, J = 14.7 Hz, 1H), 1.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.1, 148.5, 117.2, 62.5, 60.3, 43.6, 36.5, 33.0, 30.7, 16.7. Low-resolution MS: *m*/*z*: 245 (M^+). Anal. Calcd for $C_{10}H_{13}BrO_2$: C, 49.00; H, 5.35. Found: C, 49.18; H, 5.49.

Tandem Reaction of 2*R*,3*R*-Epoxy-5*R*-(1-(bromomethyl)vinyl)-2-methylcyclohexanone (23) with Tetrathiomolybdate (1). To a well-stirred solution of 2*R*,3*R*-epoxy-5*R*-(1-(bromomethyl)vinyl)-2-methylcyclohexanone (**23**) (0.15 g, 0.61 mmol) in acetonitrile and ethanol mixture (1:1, 5 mL) was added benzyltriethylammonium tetrathiomolybdate (**1**) (0.77 g, 1.27 mmol) and stirred at room temperature (28 °C) for 7 h under argon atmosphere. The solvent was evaporated under reduced pressure, and the black residue was extracted with dichloromethane:diethyl ether (1:5, 10 mL × 3) and filtered through a Celite pad. The filtrate was concentrated and the residue purified by chromatography on silica gel eluting with ethyl acetate:hexane, (1:15) to obtain pure compound **24** as a colorless liquid (0.11 g, 90%). IR (neat): 3392, 1706,1639 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.80 (s, 1H), 4.78 (s, 1H), 4.27

(19) (a) Dittmer, D. C.; Christy, M. E.; Takashina, N.; Henion, R. S.; Balquist, J. M. *J. Org. Chem.* **1971**, *36*, 1324. (b) Searles, S.; Hays, H. R.; Lutz, E. F. *J. Org. Chem.* **1962**, *27*, 2828.

(20) Boorman, P. M.; Wang, M.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1995**, 999.

(21) It is important to recognize that free thiol/selenol are not generated in the cleavage of disulfides/diselenides mediated by **1**.

(22) (a) Kolar, A. J.; Olsen, R. K. *J. Org. Chem.* **1971**, *36*, 591. (b) Mousseron, M. *Bull. Soc. Chim. Fr.* **1948**, 84.

(23) Posner, G. H.; Rogers, D. Z. *J. Am. Chem. Soc.* **1977**, *99*, 8208.

(24) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9.

(25) Srikrishna, A.; Hemamalini, P. *Indian J. Chem., Sect. B* **1990**, *29*, 201.

(d, 1H, J = 6.6 Hz), 3.47 (d, 1H, J = 15.1 Hz), 3.26 (d, 1H, J = 15.1 Hz), 3.05−2.95 (m, 1H), 2.75 (dd, 1H, J = 18.3, 5.5 Hz), 2.52 (dd, 1H, J = 15.4, 7 Hz), 2.41 (d, 1H, J = 18.4 Hz), 2.20 (dd, 1H, J = 15.4 Hz, 8.8 Hz), 2.04 (bs, OH), 1.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.2, 150.0, 110.8, 75.6, 53.9, 41.9, 37.3, 36.4, 33.9, 19.7. Low-resolution MS (EI): m/z: 198 (M^+), 180, 165, 151. HRMS (EI). m/z: Calcd for $C_{10}H_{14}O_2S$: 198.0714. Found: 198.0708.

Preparation of 9-Hydroxycarvone.[26] A solution of 9-bromocarvone (1.15 g, 5 mmol) and 15% aqueous HMPA (25 mL) was refluxed at 120 °C for 30 min. The reaction mixture was cooled to room temperature, diluted with water, extracted with diethyl ether (3 × 20 mL), and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel to furnish 9-hydroxycarvone as a colorless liquid. Yield: 0.747 g, (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74−6.78 (m, 1H), 5.15 (s, 1H), 4.95 (s. 1H), 4.15 (s, 2H), 2.90−2.2 (m, 5H), 2.0 (bs, 1H), 1.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.6, 150.2, 144.6, 135.4, 110.3, 64.7, 43.2, 38.2, 31.5, 15.6. Low-resolution MS (EI): m/z: 166 (M^+).

Preparation of 2*R*,3*R*-Epoxy-5*R*-(1-(hydroxymethyl)-vinyl)-2-methylcyclohexanone (25). 9-Hydroxycarvone (0.5 g, 3 mmol) was dissolved in methanol (0.5 mL), and the solution was cooled to 0 °C. Hydrogen peroxide (30%, 1 mL) was added slowly with stirring to the cooled solution (0.5 h). A solution of 6 M NaOH (0.26 mL) was added ensuring that the internal temperature was always <0 °C. The reaction mixture was allowed to stir at 0 °C for an additional 16 h and then poured into water (5 mL) and saturated NaCl. The reaction mixture was extracted with EtOAc (4 × 5 mL), and the combined organic extract was washed with brine and then dried ($MgSO_4$). After filtration, the solvent was evaporated and the crude residue was purified by column chromatography on silica gel using 1% MeOH/$CHCl_3$ as solvent to afford **25** as a colorless liquid. Yield: 0.256 g (47%). IR: 3340, 1706, 1639 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.16 (s, 1H), 5.01 (s, 1H), 4.42 (s, 2H), 3.44 (dd, 1H, J = 0.9 Hz, J = 2.1 Hz), 2.84−2.90 (m, 1H), 2.65 (ddd, 1H, J = 0.9 Hz, J = 3.6 Hz, J = 12.9 Hz, 1H), 2.38−2.42 (m, 1H), 2.07 (dd, 1H, J = 8.7 Hz, J = 13.2 Hz), 1.93 (ddd, 1H, J = 0.9 Hz, J = 8.1 Hz, J = 11.1 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.35, 146.96, 116.91, 80.52, 62.93, 60.46, 43.34, 33,37, 30.26, 16.61. Low-resolution MS (CI): m/z: 183 ($M^+ + 1$). Since this compound is unstable, CHN analysis or HRMS data could not be collected.

Tandem Reaction of 2*R*,3*R*-Epoxy-5*R*-(1-(hydroxymethyl)vinyl)-2-methylcyclohexanone (25) with Tetrathiomolybdate (1). A solution of 2*R*,3*R*-epoxy-5*R*−(1-(hydroxymethyl)vinyl)-2-methylcyclohexanone (**25**) (0.100 g, 0.55 mmol), DCC (0.126 g, 0.6 mmol), and CuCl (4 mg, 6 mol %) was stirred under a solvent free condition at room temperature (28 °C). After the completion of the reaction (8 h, TLC), a solution of **1** (0.67 g, 1.1 mmol) in CH_3CN/EtOH (4 mL, 1:1) was added at once at room temperature, and the reaction mixture was stirred at room temperature for 4 h. The solvent was removed under vacuum, and the black residue was extracted with dichloromethane:diethyl ether (1:5, 10 mL × 3) and filtered through a Celite pad. The filtrate was concentrated, and purification on a silica gel column (ethyl acetate: hexane, 1:15) afforded the pure compound **24** as a colorless liquid (0.078 g, 72%).

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Supporting Information Available: Characterization data (including ^{1}H and ^{13}C NMR spectra) for compounds **23**−**25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Weinges, K.; Schwarz, G. *Liebigs Ann. Chem*. **1993**, *7*, 811.