Acid-Catalyzed Rearrangement of Cyclic Allylic Monothioketals to Exocyclic Enol Ethers

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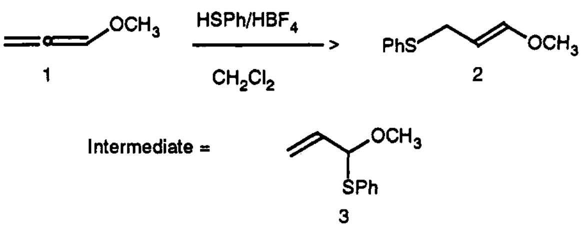
In previous work we have shown that the acid-catalyzed addition of thiols to methoxypropadiene (1) reported by Hoffmann[1] proceeds, at least in part, by rearrangement of the intermediate monothioacetal 3.[2]

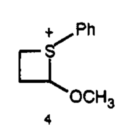


We report here additional experiments intended to assess the generality of the rearrangement and to probe its mechanism.

Results and Discussion

Rearrangement must be rapid, possibly even occurring in the solvent cage, since attempted trapping of the intermediate cation with 1,3-cyclohexadiene, as Gassman has done with the related acrolein diethyl acetal,[3] failed. Only 2 was found.

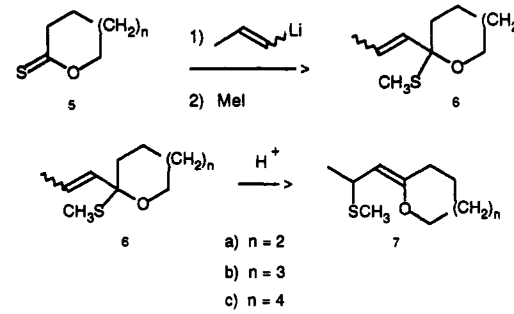
We have also considered the possibility of intramolecular rearrangement via sulfonium ion 4. Formation of 4



requires unlikely protonation at C-2 of propene 3. Furthermore, rearrangement in deuterated triflic acid showed no evidence of deuterium incorporation. Thus, in this simple system 4 was not apparently an intermediate.

We have extended this rearrangement to cyclic monothioketals since these systems have recently attracted attention in natural product syntheses. For example, the transformation of thionolactones into cyclic ethers via monothioketals has been reported.[4] This methodology gave the desired cyclic alkenyl monothioketals 6. Addition of vinyllithium has been reported by Nicolaou.[4a]

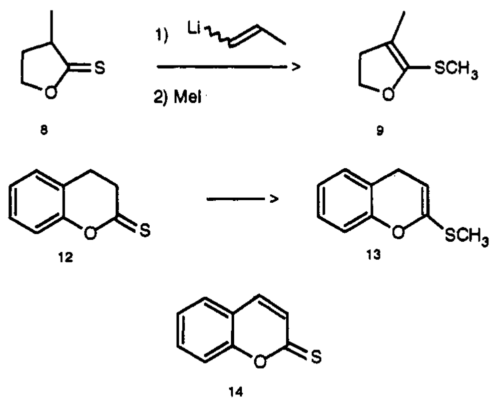
We found that the rearrangement proceeded smoothly in the following cases. These cases also demonstrated that the phenylthio group is not unique in the ability to migrate.



Surprisingly, only one geometrical isomer of 7 was formed,[5] although the starting material 6 was a cis/trans mixture with the cis isomer apparently predominating.

We have observed no tendency for alkoxy substituents to migrate to the other terminus of the allylic system. Sulfur is unique in this behavior. Thus, a two carbon ring expansion did not occur.

Attempts to observe the rearrangement in smaller rings failed. Five-membered thionolactones undergo enolization. For example, 8 gave 9. The thionolactones required were prepared by treatment of the corresponding lactone with Lawesson's reagent. Monocyclic six-membered lactones did not give useful yields with this reagent.[6] Benzofused six-membered lactones (coumarins) underwent smooth thionation but did not give the desired addition product; 12 undergoing enolization to give 13, and 14 giving an uncharacterized mixture.



Conclusion

Acid-catalyzed rearrangement of allylic monothioacetals to 3-thio-substituted enol ethers seems to be a general process for acyclic and large ring substrates. The reaction

(1) Hoffmann, R. W.; Kemper, B.; Metternich, R.; Lehmeier, T. *Liebigs Ann. Chem.* 1985, 2246.

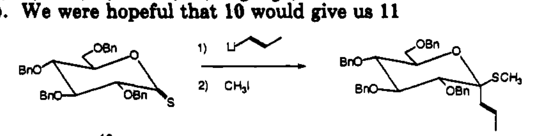
(2) Hagen, J. P.; Harris, J. J.; Lakin, D. *J. Org. Chem.* 1987, *52*, 782.

(3) Gassman, P. G.; Singleton, D. A.; Wilwerding, J. J.; Chavan, S. P. *J. Am. Chem. Soc.* 1987, *109*, 2182.

(4) (a) Nicolaou, K. C.; McGarry, D. G.; Somers, P. K.; Kim, B. H.; Ogilvie, W. W.; Yiannikouros, G.; Prasad, C. V. C.; Veale, C. A.; Hark, R. R. *J. Am. Chem. Soc.* 1990, *112*, 6263. (b) Nicolaou, K. C.; McGarry, D. G.; Somers, P. K.; Veale, C. A.; Furst, G. T. *J. Am. Chem. Soc.* 1987, *109*, 2504.

(5) The *Z* geometry was assigned by NOE. Irradiation of 7a at δ 2.34 (CH_2CO) gave a 16% enhancement at δ 4.18 (HC=) and a 0.56% enhancement at δ 3.9–4.0 (CH_2O). No enhancement was seen at δ 3.8–3.9 (HCS). Irradiation at δ 4.18 gave a 3.6% enhancement at δ 2.34. Since the chemical shifts and coupling constants for 7b and 7c are very like 7a, they were assigned the same geometry.

(6) Scheibye, Kristensen, and Lawesson have reported that tetrahydro-2-pyranone does not give an isolable thionoester with Lawesson's reagent.[10] The glucose thionolactone 10 has been reported by Kahne (Kahne, D.; Yang, D.; Lim, J.; Miller, R.; Paguaga, E. *J. Am. Chem. Soc.* 1988, *110*, 8716). We were hopeful that 10 would give us 11



which could serve as a useful substrate to probe the stereochemistry of the rearrangement. Unfortunately, the preparation of 10 by thionation of the corresponding glucolactone gave very low yields in our hands.

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shows stereoselectivity in both cases, although the reasons for this are unclear in the cyclic examples. The reaction is so fast at low temperature that the putative carbocation intermediate cannot be trapped.

This rearrangement is related to the question of C–S versus C–O cleavage in the hydrolysis of *O,S*-acetals. Hydrolysis of benzaldehyde *O*-ethyl *S*-phenyl acetal is thought to occur by C–S cleavage. In most other cases such as benzaldehyde *O*-ethyl *S*-ethyl acetal the C–O bond cleaves. The rate differences have been attributed to sulfur's lower basicity.[7] The results of these and other workers imply that in our cyclic system O–C cleavage may occur many times before irreversible C–S cleavage/rearrangement, a process which could be detected by changes in the relative stereochemistry of ring substituents in recovered monothioketal.

Experimental Section

NMR spectra were obtained at 200 MHz using TMS as internal standard and $CDCl_3$ as solvent unless specified otherwise. ^{13}C NMR spectra were obtained on the same samples at 50 MHz. Melting and boiling points were obtained with uncalibrated partial-immersion thermometers. THF and ether were distilled from sodium and benzophenone; CH_2Cl_2 was distilled from P_2O_5 and stored over 4A sieves. All strong base reactions were done under a positive pressure of nitrogen. Kugelrohr distillations employed the apparatus available from Aldrich Chemical Co. Organic reagents were purchased from Aldrich. Ratios of geometric and regioisomers formed were determined by ^1H NMR analysis. Spectral and physical data were not necessarily obtained from the experimental run described.

Treatment of Methyl (1-Methoxyallyl)thiosalicylate with d_1-Triflic Acid. Deuterated triflic acid was prepared by addition of D_2O (0.45 mL, 24.5 mmol) to triflic anhydride (7.69 g, 27.3 mmol).[8] To the thioacetal[2] (0.25 g, 1.05 mmol) at -70 °C was added d_1-triflic acid (93 μL, 1.5 mmol). The solution was stirred for 30 min and then quenched with *N,N*-diisopropylethylamine (0.26 mL). The mixture was diluted with pentane and then filtered. Rotatory evaporation of solvent gave an oil. The NMR spectrum showed no deuterium incorporation in the rearranged product: ^1H NMR (60 MHz) δ 8.07 (m, 1 H, Ph), 7.60–7.00 (m, 3 H, Ph), 6.67 (d, *J* = 12 Hz, 1 H, OC*H*=C), 4.93 (dt, *J* = 12, 7 Hz, 1 H, OCH=C*H*CH$_2$), 4.00 (s, 3 H, CO$_2$C*H*$_3$), 3.65 (d, *J* = 7 Hz, 2 H, C*H*$_2$CH=C), 3.63 (s, 3 H, OC*H*$_3$).

General Procedure for Preparation of Lactones. To *m*-chloroperoxybenzoic acid (80%, 10.44 g, 48.4 mmol) in CH_2Cl_2 or $CHCl_3$ (60 mL) was added the ketone (44.0 mmol) in 10 mL of solvent. The solution was refluxed until TLC apparently showed complete reaction. The solvent was concentrated by rotatory evaporation and then ether (70 mL) was added. The organic layer was washed with 25% $Na_2S_2O_5$ (20 mL), then with saturated $NaHCO_3$ (70 mL), and finally with brine. The solution was dried over $MgSO_4$ and then filtered. Removal of solvent with rotatory evaporation gave the crude product.

2-Oxooxocane. Reflux in CH_2Cl_2 for 3 days and workup gave an oil which upon Kugelrohr distillation (41–58 °C, 0.15 mm) gave the lactone (4.29 g, 76%): IR (neat) 1725 cm^{-1}; ^1H NMR (60 MHz) δ 4.37 (t, *J* = 5.5 Hz, 2 H, C*H*$_2$O), 2.57 (t, *J* = 6 Hz, 2 H, C*H*$_2$C=O), 2.20–1.50 (m, 8 H, 4-C*H*$_2$). Huisgen[9] and Nicolaou[4a] have prepared this compound previously.

2-Oxooxonane. Reflux in $CHCl_3$ for 2 days gave an oil which upon Kugelrohr distillation (39–50 °C, 0.05 mm) gave a mixture of product and ketone. The ketone was removed using Huisgen's procedure[9] to give the lactone (1.96 g, 33%): IR (neat) 1746 cm^{-1}; ^1H NMR (60 MHz) δ 4.30 (t, *J* = 5.5 Hz, 2 H, OC*H*$_2$), 2.57–2.03 (m, 2 H, C*H*$_2$C=O), 2.03–1.17 (m, 10 H, 5-C*H*$_2$). Huisgen[9] and Nicolaou[4a] have prepared this compound previously.

Preparation of Thionolactones. Thionation of lactones was done according to literature procedures.[10]

2-Oxepanethione (5a, *n* = 2). A mixture of 2-oxooxepane (3.53 g, 30.9 mmol) and Lawesson's reagent (9.72 g, 23.3 mmol) in toluene (25 mL) was stirred at reflux 2 h to give **5a** (1.92 g, 48%, n^{25}_D 1.5522) after chromatography and Kugelrohr distillation (80–87 °C, 0.08 mm). The spectral data agreed with that in ref 4a. In another run, Kugelrohr distillation (144–160 °C, 19 mm) of chromatographed **5a** gave a mixture (n^{25}_D 1.5480). ^1H NMR (60 MHz) showed new absorptions at δ 4.40–4.10 (bs, 2 H, OCH$_2$) and 2.83–2.47 (bs, 2 H) which appeared similar to the lactone starting material. Combustion analysis of this distillate suggested an isomeric mixture. Anal. Calcd for $C_6H_{10}OS$: C, 55.35; H, 7.74. Found: C, 55.50; H, 7.72.

2-Oxocanethione (5b, *n* = 3). A mixture of 2-oxooxocane (1.84 g, 12.9 mmol) and Lawesson's reagent (9.72 g, 23.3 mmol) in toluene (25 mL) was stirred at reflux 4 h to give **5b** (1.07 g, 24%) as yellow crystals from hexane (mp 48.0–48.5 °C), not an oil as reported in ref 4a: IR (KBr pellet) 1440, 1385, 1314, 1294, 1280, 1230, 1193, 1134, 1083 cm^{-1}; ^1H NMR (60 MHz) δ 4.63 (t, 2 H, *J* = 5.5 Hz), 3.12 (t, 2 H, *J* = 6.0 Hz), 2.20–1.40 (m, 8 H). Anal. Calcd for $C_7H_{12}OS$: C, 58.29; H, 8.39. Found: C, 58.01; H, 8.43.

2-Oxonanethione (5c, *n* = 4). A mixture of 2-oxooxonane (1.84 g, 12.9 mmol) and Lawesson's reagent (4.06 g, 9.7 mmol) in toluene (14.5 mL) was stirred at reflux to give **5c** (0.88 g, 43%) after chromatography. The spectral data agreed with that in ref 4a. Anal. Calcd for $C_8H_{14}OS$: C, 60.72; H, 8.92. Found: C, 60.54; H, 9.10.

3-Methyloxolane-2-thione (8). A mixture of 3-methyl-2-oxooxolane (3.06 g, 30.0 mmol) and Lawesson's reagent (6.88 g, 16.5 mmol) in toluene (17 mL) was stirred at reflux 4 h to give **8** (2.47 g, 71%) after chromatography and Kugelrohr distillation (95–97 °C, 8 mm): IR (neat) 1450, 1371, 1295, 1235, 1170, 1110, 1030, 994, 932, 899 cm^{-1}; ^1H NMR (60 MHz) δ 4.90–4.30 (m, 2 H) 3.17–1.57 (m, 3 H), 1.42 (d, *J* = 7.0 Hz, 3 H). Anal. Calcd for C_5H_8OS: C, 51.69; H, 6.94. Found: C, 51.30; H, 6.88.

3,4-Dihydro-2*H*-1-benzopyran-2-thione (12). A mixture of dihydrocoumarin (2.5 g, 16.9 mmol) and Lawesson's reagent (5.28 g, 12.7 mmol) in toluene (13 mL) was stirred at reflux 6 h to give **12** (1.7 g, 62%) as a yellow solid (mp 45–46 °C) after chromatography: IR (KBr pellet) 1360, 1327, 1287, 1259, 1180, 1163, 1127 cm^{-1}; ^1H NMR δ 7.30–7.06 (m, 4 H), 3.23–3.16 (m, 2 H, ArC*H*$_2$), 2.90–2.83 (m, 2 H, C*H*$_2$C=O); ^{13}C NMR δ 215.2 (*C*=S), 152.5, 128.1, 128.0, 124.8, 122.9, 116.2, 40.12 (*C*H$_2$C=S), 22.85 (Ar*C*H$_2$). Anal. Calcd for C_9H_8OS: C, 65.82; H, 4.91. Found: C, 66.08; H, 4.90.

General Procedure for Preparation of Monothioketals 6. To THF (19 mL) under nitrogen was added 1-bromo-1-propene (1.09 mL, 12.7 mmol, a mixture of isomers). The solution was cooled to −78 °C and then *tert*-butyllithium (13.6 mL, 1.7 M in pentane) was added dropwise by syringe over 10 min. The lactone (3.85 mmol) in THF (4 mL) was added dropwise over 3 min. The solution was stirred for 1 h, and then methyl iodide (264 μL, 4.24 mmol) was added. After 10 min the cold solution was poured into 30 mL of brine and diluted with 20 mL of ether. The layers were separated and then the brine was extracted three times with 20-mL portions of ether. The solution was dried over $MgSO_4$ and then filtered. The solvent was then removed under reduced pressure to give the crude product. In all cases, the crude oil contained an impurity absorbing above δ 1.00 in the ^1H NMR and at δ 32.3 and 22.0 in the ^{13}C NMR which seemed to be derived from the *tert*-butyllithium and was inert to the conditions of the subsequent rearrangement. Compounds **6** were too nonpolar for purification on silica gel.

2-(Methylthio)-2-(1-propenyl)oxepane (6a). Slow Kugelrohr distillation (40–50 °C, 0.1 mm) gave an oil (85%) as a 1.5/1 cis/trans mixture: IR (neat) 3020, 1442, 1148, 1089, 982, 968, 871, 813 cm^{-1}; major (cis) isomer ^1H NMR δ 5.56 (dq, *J* = 12.0, 7.0 Hz, 1 H, =C*H*CH$_3$), 5.15 (dq, *J* = 12.0, 1.7 Hz, 1 H, CC*H*=), 3.88 (m, 1 H, OC*H*$_2$), 3.62 (m, 1 H, OC*H*$_2$), 2.10 (m, 2 H, C*H*$_2$C(S)O), 1.97 (s, 3 H, SC*H*$_3$), 1.89 (dd, *J* = 6.9, 1.8 Hz, 3 H, C*H*$_3$CH), 2.0–1.20 (m, 6 H, 3-C*H*$_2$); minor (trans) isomer, partial ^1H NMR

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(9) Huisgen, R.; Ott, H. *Tetrahedron* **1959**, *6*, 253.

(10) Scheibye, S.; Kristensen, J.; Lawesson, S.-O. *Tetrahedron* **1979**, *35*, 1339.

δ 5.72 (dq, J = 15.1, 6.6 Hz, 1 H, =CHCH$_3$), 5.30 (dq, J = 15.2, 1.5 Hz, 1 H, CCH=), 1.88 (s, 3 H, SCH_3), 1.74 (dd, J = 6.5, 1.7 Hz, 3 H, CH_3CH), impurity δ 1.00 (s) and 0.93 (s); ^{13}C NMR isomeric shifts assigned by intensity, the major isomer assumed to be cis δ 133.4 (CCH=), 126.2 (=CHCH$_3$), 90.1 (OCS), 62.8 (OCH$_2$), 41.3 (CH$_2$C(S)O), 30.6, 29.3, 23.1 (3-CH$_2$), 14.0 (CH$_3$-CH=), 10.6 (CH$_3$S); minor (trans) isomer δ 134.7, 125.4, 93.3?, 63.0, 40.7, 30.5, 29.2, 22.3, 17.3, 11.0, impurity δ 32.3, 25.3, and 22.0; MS (no molecular ion) m/e 139.1122 (M − CH$_3$S, calcd for $C_9H_{15}O$: 139.1123), 123 (M − CH$_3$SH − CH$_3$).

2-(Methylthio)-2-(1-propenyl)oxocane (6b). Rapid Kugelrohr distillation (90–100 °C, 0.05 mm) gave a colorless oil (61%) as a 9/1 cis/trans mixture of isomers. In some runs a trace of rearrangement to the enol ether **8b** was detected: IR (neat) 3020, 1480, 1445, 1129, 1085, 993, 966, 952, 840, 831, 754 cm^{-1}; major (cis) isomer ^{1}H NMR δ 5.56 (dq, J = 12.0, 7.1 Hz, 1 H, =CHCH$_3$), 5.14 (dq, J = 12.0, 1.7 Hz, 1 H, CCH=), 3.87 (dt, J = 12.2, 3.2 Hz, 1 H, OCH_2), 3.60 (m, 1 H, OCH_2), 2.14 (m, 2 H, CH_2(S)O), 1.95 (s, 3 H, SCH_3), 1.89 (dd, J = 7.2, 1.8 Hz, 3 H, CH_3CH), 2.00–1.20 (m, 8 H, 4-CH_2); minor (trans) isomer, partial ^{1}H NMR δ 5.78 (dq, J = 15.6, 7.2 Hz, 1 H, =CHCH$_3$), 5.30 (dq, J = 15.6, 1.6 Hz, 1 H, CCH=), 1.83 (s, 3 H, SCH_3), 1.76 (dd, J = 6.6, 1.6 Hz, 3 H, CH_3CH), impurity δ 0.99 (s), 0.92 (s); ^{13}C NMR cis isomer, assigned by intensity, δ 131.5 (CCH=), 125.9 (=CHCH$_3$), 93.3 (OCS), 62.3 (OCH$_2$), 33.5 (CH$_2$C(S)O), 30.5, 25.8, 24.6, 24.5 (4-CH$_2$), 14.0 (CH$_3$CH), 10.9 (CH$_3$S); Presumed trans isomer, partial ^{13}C NMR δ 132.8, 125.0, 62.6, 30.4, 25.8, 24.4, 17.4, 10.8, impurity δ 32.3, 22.0; MS (LRFAB) calcd for $C_{11}H_{21}OS$ (M + H) 201.1314, found 201.1322, m/e 153 (M − SCH$_3$).

2-(Methylthio)-2-(1-propenyl)oxonane (6c). Crude yield 100%, obtained as a 10/1 cis/trans mixture, used without further purification. An additional impurity is formed in this case which is not affected by the subsequent rearrangement conditions. A small sample of crude product was subjected to flash chromatography[11] on silica gel (Aldrich/Merck 60) using 20% ether/hexane as eluant. The first fraction obtained was enriched in **6c**; the second fraction was enriched in the impurity. Difference NMR spectra were obtained which served as the basis for the following NMR assignments: IR (neat) 3010, 1735 (w), 1655 (w), 1625 (w), 1485, 1441, 1141, 1127, 1080, 1023, 956, 930, 880, 845, cm^{-1}; major (cis) isomer ^{1}H NMR δ 5.56 (dq, J = 12.0, 7.1 Hz, 1 H, =CHCH$_3$), 5.15 (dq, J = 12.0, 1.6 Hz, 1 H, CCH=), 3.89 (dt, J = 11.5, 2.7 Hz, 1 H, OCH_2), 3.55 (dt, J = 12.0, 3.6 Hz, 1 H, OCH_2), 2.20–1.95 (m, 2 H, CH_2(S)O), 1.94 (s, 3 H, SCH_3), 1.89 (dd, J = 7.1, 1.8 Hz, 3 H, CH_3CH), 1.80–1.50 (m, 10 H, 5-CH_2), trans isomer, partial ^{1}H NMR δ 5.76 (dq, J = 15.1, 6.8 Hz, 1 H, =CHCH$_3$), 5.30 (dq, J = 15.1, 2.0 Hz, 1 H, CCH=), 1.82 (s, 3 H, SCH_3), impurity δ 5.21 (t, J = 7.2 Hz, 1 H), 4.82 (dd, J = 5.5 Hz, 0.5 H), 4.00 (t, J = 5.2 Hz, 2 H), 2.83 (dd, J = 6 Hz, 0.5 H), 2.14 (s, 6 H, 1.80–1.62 (m, 3 H) 1.62–1.50 (m, 7 H); ^{13}C NMR cis isomer, assigned by intensity, δ 131.6 (CCH=), 125.6 (=CHCH$_3$), 93.3 (OCS), 62.0 (OCH$_2$), 33.9 (CH$_2$C(S)O), 28.9, 25.5, 25.1, 23.7, 22.8 (5-CH$_2$), 14.1 (CH$_3$CH), 11.2 (CH$_3$S), presumed trans isomer, partial ^{13}C NMR δ 132.7, 124.8, 90.1, 62.3, 17.4, 10.7, impurity δ 149.6, 117.3, 72.4, 69.0, 48.6, 27.2, 26.2, 26.0, 25.6, 24.6, 14.7. MS calcd for $C_{12}H_{22}OS$: 214.13926, found 214.1386, m/e 167 (M − CH$_3$S), 123 (M − CH$_3$SH − C$_3$H$_7$).

Attempted Addition of 1-Lithio-1-propene to 3-Methyloxolane-2-thione (8). Formation of 2,3-Dihydro-4-methyl-5-methylthiofuran (9). Thionolactone **8** (232 mg, 2 mmol) was treated with 1-lithio-1-propene (6.6 mmol) as above to give a red oil (0.38 g). Kugelrohr distillation (30–40 °C, 0.1 mm) gave 221 mg of a yellow oil which rapidly darkens: IR (neat) 1649 (w), 1475, 1440, 1375, 1297, 1245, 1178, 1106, 1060, cm^{-1}. Upon storage, absorptions at 3450 (OH) and 1762 (C=O) cm^{-1} appear suggesting hydrolysis: ^{1}H NMR (60 MHz) δ 4.30 (t, J = 9.5 Hz, 2 H, OCH_2, 2.63 (t, J = 9.5 Hz, 2 H, CH_2), 2.26 (s, 3 H, SCH_3), 1.77 (t, J = 1.5 Hz, 3 H, CH_3C=); MS (no molecular ion) 147.0481 (**9** + HO, calcd for $C_6H_{11}O_2S$: 147.0480), 131.0532 (**9** + H, calcd for C_6H_{11}-OS: 121.0531), 100 (**9** + H$_2$O − CH$_3$SH). These fragments are consistent with partial hydrolysis of **9** upon storage.

Attempted Addition of 1-Lithio-1-propene to 3,4-Dihydro-2*H*-1-benzopyran-2-thione (12). Formation of 2-(Methylthio)-4*H*-1-benzopyran (13). Thionolactone **12** (328 mg, 2.00 mmol) was treated with 1-lithio-1-propene (6.6 mmol) as above to give **13** (0.38 g, 86% crude): IR (neat) 3040, 1731, 1645, 1580, 1484, 1445, 1434, 1285, 1225, 1183, 1115, 1065, 756 cm^{-1}; ^{1}H NMR (60 MHz) δ 7.40–6.73 (m, 4 H), 5.17 (t, J = 4.0 Hz, 1 H), 3.47 (d, J = 4.0 Hz, 2 H), 2.33 (s, 3 H), impurity δ 0.99 (s), 0.98–0.83 (m).

General Procedure for Rearrangement of Monothioketals to Enol Ethers 7. The thioketal **6** (0.33 mmol) was dissolved in CH$_2$Cl$_2$ (4 mL), cooled to −78 °C under a nitrogen atmosphere, and then treated with HBF$_4$·Et$_2$O (2 μL) for 15 min. Triethylamine (6 μL) was then added. The solvent was removed under reduced pressure, and the residue was triturated with pentane and then filtered. The pentane was removed under reduced pressure to give the crude product. Compounds **7** were too nonpolar for purification on silica gel.

2-[2-(Methylthio)propylidene]oxepane (7a). Rapid Kugelrohr distillation (135–150 °C, 0.06 mm) gave a colorless oil (76%): IR (neat) 1658, 1445, 1345, 1332, 1192, 1180, 1101, 1079, 989, 952, 913, 794, 738 cm^{-1}; ^{1}H NMR (300 MHz) δ 4.17 (d, J = 9.9 Hz, 1 H, CH=C), 3.96 (t, J = 4.7 Hz, 2 H, OCH_2), 3.86 (dq, J = 9.9, 6.8, 1 H, CHCH$_3$), 2.32 (m, 2 H, CH_2C=CH), 2.04 (s, 3 H, SCH_3), 1.80–1.55 (m, 6 H, 3-CH_2), 1.24 (d, J = 6.9 Hz, 3 H, CH_3CH); ^{13}C NMR (75 MHz) δ 156.4 (OC=CH), 106.0 (OC=CH), 68.0 (OCH$_2$), 35.5 (HCS), 32.3 CH$_2$C=CH), 30.4, 28.6, 28.2 (3-CH$_2$), 20.7 (CH$_3$CH), 13.5 (CH$_3$S). A small amount of olefinic impurity was present by PMR and CMR (δ 134.1, 124.9, 62.6, 40.2, 31.8, 30.0, 28.8, 21.9, 16.8, 10.2). This does not seem to be an isomeric enol ether. MS calcd for $C_{10}H_{18}OS$: 186.1079, found 186.1069, m/e 139 (M − CH$_3$S), 123 (M − CH$_3$SH − CH$_3$).

2-[2-(Methylthio)propylidene]oxocane (7b): Crude oil (97%); IR (neat) 1658, 1479, 1445, 1371, 1352, 1137, 1102, 1086, 994, 962, 800, 734 cm^{-1}; ^{1}H NMR δ 4.23 (d, J = 9.9 Hz, 1 H, CH=C), 3.98 (m, 2 H, OCH_2), 3.90 (dq, J = 9.9, 6.8, 1 H, CHCH$_3$), 2.30 (m, 2 H, CH_2C=CH), 2.04 (s, 3 H, SCH_3), 1.70–1.50 (m, 8 H, 4-CH_2), 1.24 (d, J = 6.8 Hz, 3 H, CH_3CH); ^{13}C NMR δ 155.9 (OC=CH), 108.3 (OC=CH), 66.0 (OCH$_2$), 36.0 (HCS), 31.1 (CH$_2$C=CH), 30.7, 29.0, 25.5, 24.4 (4-CH$_2$), 21.1 (CH$_3$CH), 14.0 (CH$_3$S). A small quantity of the starting thioketal was present which was enriched in the trans isomer. PMR and CMR show additional olefinic impurities. This system was less stable than **7a** upon storage. MS calcd for $C_{11}H_{20}OS$ 200.1236, found 200.1238, m/e 185 (M − CH$_3$), 152 (M − CH$_3$SH), 137 (M − CH$_3$SH − CH$_3$).

2-[2-(Methylthio)propylidene]oxonane (7c). Results are complicated due to impurities formed in the preparation of **6c** from the thionolactone; assignments were made by comparison to **7a** and **7b**: crude oil (88%); ^{1}H NMR δ 4.53 (d, J = 10.3 Hz, 1 H, CH=C), 4.00 (m, 2 H, OCH_2, overlaps impurity), 3.50 (m, 1 H, CHCH$_3$), 2.46 (m, 2 H, CH_2C=CH), 2.04 (s, 3 H, SCH_3), 1.80–1.40 (m, 10 H, 5-CH_2), 1.34–1.29 (m, 3 H, CH_3CH); ^{13}C NMR δ 158.3 (OC=CH), 107.4 (OC=CH), 70.0 (OCH$_2$), 39.0 (HCS), 29.2–24.3 (CH$_2$C=CH, 5-CH$_2$), 22.3 (CH$_3$CH), 14.6 (CH$_3$S); minor impurity ^{1}H NMR δ 6.84, 6.12 (vinyl), 4.29 (t, J = 5.6 Hz), 4.21 (d, J = 10 Hz), 2.30–2.15 (m), 2.09 (s, SCH_3), 2.02 (s, CH_3), 1.90 (dd, J = 6.8, 1.6 Hz, allylic CH_3CH=CH, trace of **6c**?), 1.8–1.2 (overlapping **7c** absorptions). The impurity in **6c** was also observed; ^{13}C NMR δ 117.4, 69.1, 62.8, 32.2, 14.2, 29.2–24.3 (at least seven carbons overlapping **7c** CH$_2$ resonances); MS (no molecular ion) m/e 215.1472 (M + H, calcd for $C_{12}H_{23}OS$ 215.1471), 167 (M − SCH$_3$), 125 (M − HSCH$_3$ − C$_3$H$_5$).

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Supplementary Material Available: ^{1}H NMR spectra of compounds for which analyses were not obtained (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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