233.1364; found, 233.1352. In a similar experiment, except that the solution was stirred at −50° C for 6 h before being quenched with water, 62% (69% based on consumed starting material) of 1,1-bis(phenylthio)pent-3-en-2-ol, 10% of recovered starting alcohol, and 8% of 7 were produced.

Acknowledgment. We thank the National Science Foundation for general support of this work (CHE 8210245) and for providing the funds for purchase of the 300-MHz Bruker NMR instrument used in this study (CHE 7905185). We also thank Dr. Alvin Marcus for recording the mass spectra.

Registry No. 1, 4170-30-3; 2, 14572-78-2; 3, 88130-66-9; 4, 88130-67-0; 4 (conjugate acid), 88130-75-0; 5, 88130-68-1; 6, 88130-69-2; (*E*)-(*R**,*R**)-7, 88130-71-6; (*E*)-(*R**,*S**)-7, 88130-70-5; (*E*)-(*R**,*R**)-7-*1*-*d*, 88130-77-2; (*E*)-(*R**,*S**)-7-*1*-*d*, 88130-76-1; 8, 88130-72-7; 10, 88130-73-8; *sec*-BuLi, 598-30-1; *sec*-BusPh, 14905-79-4; 4,4,4-tris(phenylthio)-3-methylbutanal, 88130-74-9; thioanisole, 100-68-5.

Ring Expansion of Ketones to 1,2-Keto Thioketals. Control of Bond Migration[1]

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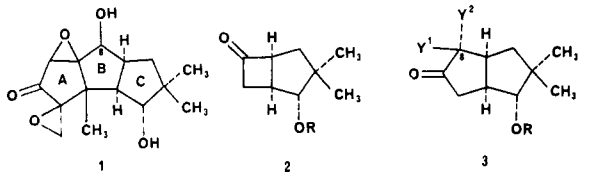
Received August 12, 1983

A practical two-step procedure for the title transformation has been developed. Treatment of cyclic ketones with $(CH_3S)_3CLi$ gave adducts **6** and **13–17**, which underwent ring expansion at 75 °C in the presence of $CuBF_4{\cdot}4CH_3CN$ to the keto thioketals **7** and **18–21**. In the cases examined the reaction was highly regioselective, giving the product resulting from migration of the more substituted carbon. The procedure has been used to prepare a key bicyclic intermediate (**33**) for a total synthesis of (±)-coriolin (**1**). An alternative synthesis of **33** suggests that where there is steric crowding in the vicinity of the tris(methylthio)methyl group of the adduct, the bond migration is controlled by the location of the obtruding group.

The bicyclo[3.3.0] carbocyclic assembly is a characteristic shared by the antitumor agent coriolin (**1**)[4] and a host of

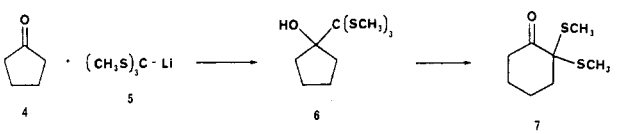


1 **2** **3**

other sesquiterpenes.[5] A number of laboratories have recently produced methods for the construction of this ring system,[6] and a variety of total syntheses have appeared.[7,8] Our own efforts at a total synthesis of **1** were founded on the belief that a ring-expansion method could be developed for the transformation **2** → **3**, wherein the unit CY^1Y^2 is inserted next to the carbonyl carbon in regioselective fashion.[9,10] Ideally Y^1 and Y^2 would be groups that block enolate formation at C-8 (coriolin numbering) and are removeable or convertible to the C-8 hydroxyl of **1**. In the preliminary report[11] we reported the ring expansion of **2** to **3** where R = $COCH_3$ and $Y^1 = Y^2 = SCH_3$ or SPh. In this paper we present our optimized conditions for ring expansion of simple ketones and describe the efficient synthesis of **3** (R = $CH_2OCH_2CH_2SiMe_3$, $Y^1 = Y^2 = SCH_3$). We have also examined, in parallel synthetic sequences, the relative importance of electronic and steric influences on bond migration during the ring-expansion reaction.

Results

Model Studies. Treatment of cyclopentanone (**4**) with 1.5 equiv of tris(methylthio)methyllithium[12] (**5**) in tetra-



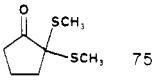
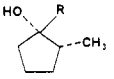
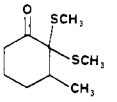
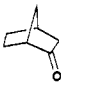
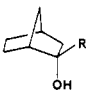
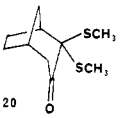
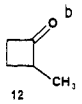
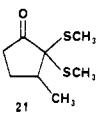
4 **5** **6** **7**

hydrofuran solution at −78 °C gave the adduct **6**, which was isolated in 83% yield after chromatography or 78% yield after bulb-to-bulb vacuum distillation at 110 °C. IR and TLC analyses indicated that the only other product

(1) This paper is dedicated to the memory of Paul D. Michna (1957–1982).
(2) Johnson and Johnson Industrial Fellow, 1982.
(3) (a) Henry Rutgers Undergraduate Scholar, 1980–1981. (b) Henry Rutgers Undergraduate Scholar, 1979–1980.
(4) (a) Takeuchi, T.; Iinuma, H.; Iwanaga, J.; Takahashi, T.; Takita, T.; Umezawa, H. *J. Antibiot.* **1969**, 22, 215. (b) Takahashi, S.; Naganawa, H.; Iinuma, H.; Takita, T.; Maeda, K.; Umezawa, H. *Tetrahedron Lett.* **1971**, 1955. (c) Nakamura, H.; Takita, T.; Umezawa, H.; Kunishima, M.; Nakayama, Y.; Iitaka, Y. *J. Antibiot.* **1974** *27*, 301.
(5) For a recent compilation of references, see: Greene, A. E.; Luche, M.-J.; Depres, J.-P. *J. Am. Chem. Soc.* **1983**, *105*, 2435.
(6) For leading references, see: Schuda, P. F.; Ammon, H. L.; Heimann, M. R.; Bhattacharjee, S. *J. Org. Chem.* **1982**, *47*, 3434.
(7) Coriolin syntheses: (a) Tatsuta, K.; Akimoto, K.; Kinoshita, M. *J. Antibiot.* **1980**, *33*, 100; *Tetrahedron* **1981**, *37*, 4365. (b) Danishefsky, S.; Zamboni, R.; Kahn, M.; Etheredge, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3460. (c) Iseki, K.; Yamazaki, M.; Shibasaki, M.; Ikegami, S. *Tetrahedron* **1981**, *37*, 4411. (d) Trost, B. M.; Curran, D. P., *J. Am. Chem. Soc.* **1981**, *103*, 7380. (e) Mehta, G.; Reddy, A. V.; Murthy, A. N.; Reddy, D. S. *J. Chem. Soc., Chem. Commun.* **1982**, 540. (f) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477.
(8) For leading references to syntheses of related sesquiterpenes, see: *Tetrahedron* **1981**, *37* and ref 5.
(9) Gutsche, C. D.; Redmore, D. "Carbocyclic Ring Expansion Reactions", Academic Press: New York, 1968.
(10) (a) Cohen, T.; Kuhn, D.; Falck, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 4749. (b) Mock, W. L.; Hartman, M. E. *J. Org. Chem.* **1977**, *42*, 459. (c) Yamashita, M.; Onozuka, J.; Tsuchihashi, G.; Ogura, K. *Tetrahedron Lett.* **1983**, *24*, 79. (d) Taguchi, H.; Yamamoto, H.; Nozaki, H. *Ibid.* **1976**, 2617. (e) Smith, R. A. J.; Keng, G. S. *Ibid.* **1978**, 675 (footnote 10).
(11) Knapp, S.; Trope, A. F.; Ornaf, R. M. *Tetrahedron Lett.* **1980**, *21*, 4301.
(12) Seebach, D. *Angew, Chem., Int. Ed. Engl.* **1967**, *6*, 442, 443.

0022-3263/84/1949-0608$01.50/0

Table I. Ring Expansions of Ketones[a]

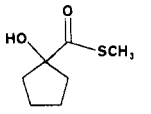
ketone	adduct [R = C(SCH$_3$)$_3$]	yield, %	keto thioketal	yield, %
 8	 13	78	 18	75
 9	 14	85	 19	58
 10	 15	95	 20	61
 11	 16	72	c	c
 12	 17	73	 21	87

[a] See general procedures in Experimental Section. [b] van Leusen, D.; van Leusen, A. M. *Synthesis* **1980**, 325. [c] No keto thioketal was isolated. The products included the hydroxy thio ester **26** (28%), **16** (15%), and **5** (13%).

was recovered **4**, probably due to enolization by **5**.[12] The lithium salt of **6** is stable at −78 °C but reverts to **4** at room temperature with decomposition of **5** to tetrakis(methylthio)ethene.[12] Conducting the reaction at −100 °C did not improve the yield of **6** significantly, and the use of a less polar solvent, such as toluene or hexane, resulted in little or no condensation.

Table I shows the results of condensation of **5** with several other simple ketones. In none of these cases was enolization a serious problem,[13] and the yields are all satisfactory. Where diasteriomeric adducts might have resulted (**14**, **15**, and **17**), only one was obtained, presumably reflecting attack by **5** on the less-hindered face of the ketone.

The ring expansion of **6** to **7** was studied by using a variety of thiophilic reagents, bases, and reaction conditions. The highest and most consistent yield (66%) was obtained when **6** was first converted to its lithium salt (*n*-butyllithium, −78 °C) in toluene solution and then treated with 2.2 equiv of $CuBF_4 \cdot 4CH_3CN$ and warmed at 75 °C for 4 h. Very little **7** was obtained by substituting copper(I) triflate, mercury(II) chloride, or mercury(II) trifluoroacetate as the thiophile, and the reaction failed completely when tetrahydrofuran was used instead of toluene, ruling out a one-pot conversion of **4** to **7**. A 42% yield of **7** was obtained when *i*-Pr_2EtN replaced *n*-butyllithium, but many other combinations of reagents (for example, mercury(II) trifluoroacetate, *i*-Pr_2EtN, dichloromethane, 0 °C; or copper(I) triflate, *i*-Pr_2EtN, toluene, 75 °C) gave after aqueous quench the hydroxy thio ester **22**. Hence ring expansion did not accompany carbon–sulfur bond cleavage in these cases. When the lithium salt of **6** was treated with $CuClO_4 \cdot 4CH_3CN$[14] in toluene solution for 45 min at 55 °C, partial conversion to **7** occurred, and after quenching with aqueous sodium bicarbonate only **7** and unreacted **6** were obtained. Neither **22** nor the epoxide **23** was observed. Since the fate of **23** upon hydrolysis would be conversion to **22**, it seems unlikely that **23** accumulates during the transformation of **6** to **7** under these conditions, although it may form as a short-lived intermediate.


22

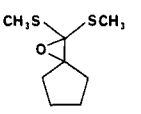
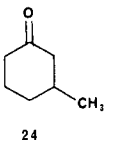
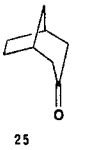
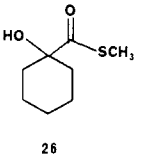

23

Table I shows the results of ring expansion of the adducts **13**–**17** using the optimized conditions. The structures of ring-expanded products **19** and **20** were established by reductive desulfurization to 2-methylcyclohexanone (**24**) and bicyclo[3.2.1]octan-3-one (**25**), respectively. Gas chromatographic analysis revealed that **24** was contaminated with no more than 5% of 2-methylcyclohexanone and **25** with no more than 0.5% of bicyclo[3.2.1]octan-2-one. Thus in those cases (**14**, **15**, and **17**) where either a methine or methylene may migrate, the product is the one resulting from migration of the more substituted carbon.

Unlike the adducts from the smaller ring ketones, the adduct from cyclohexanone **16** did not undergo ring expansion but instead gave the hydroxy thio ester **26**. It

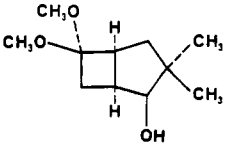

24


25


26

therefore seems that relief of angle strain and torsional strain provides an important driving force for this ring-expansion reaction.

Coriolin Synthesis. The synthesis of the coriolin BC-ring system using the optimized conditions for ring expansion is shown in Scheme I. The photoadduct **28**[15] was twice methylated at C-11 (coriolin numbering) without competition from C-2, and the resulting ketone was reduced by using lithium–ammonia–ethanol to a 5:1 mixture of epimeric alcohols **29** and **36**. The major product was


36

assigned structure **29** on the basis of literature precedent[16] and R_f.[17] The hydroxyl group of **29** was protected as its

(13) Tris(phenylthio)methyllithium adds to unhindered ketones that are not easily enolized, such as cyclobutanones,[11] but the condensation is not generally successful with five- and six-membered cyclic ketones because of competing proton transfer.[12]

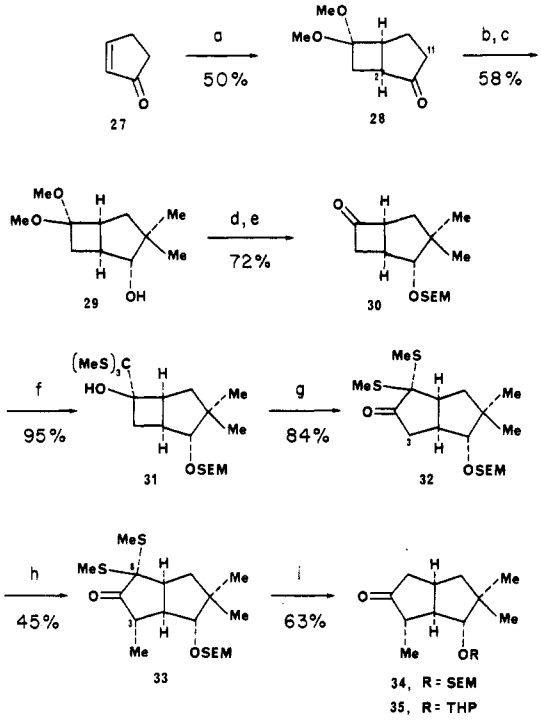
(14) In many early experiments,[11] $CuClO_4 \cdot 4CH_3CN$ was used instead of $CuBF_4 \cdot 4CH_3CN$. The two reagents gave comparable yields of **7**.

(15) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

(16) Lithium–ammonia reduction of a C-ring ketone in any of several coriolin precursors gives the exo alcohol preferentially.[6,7bc]

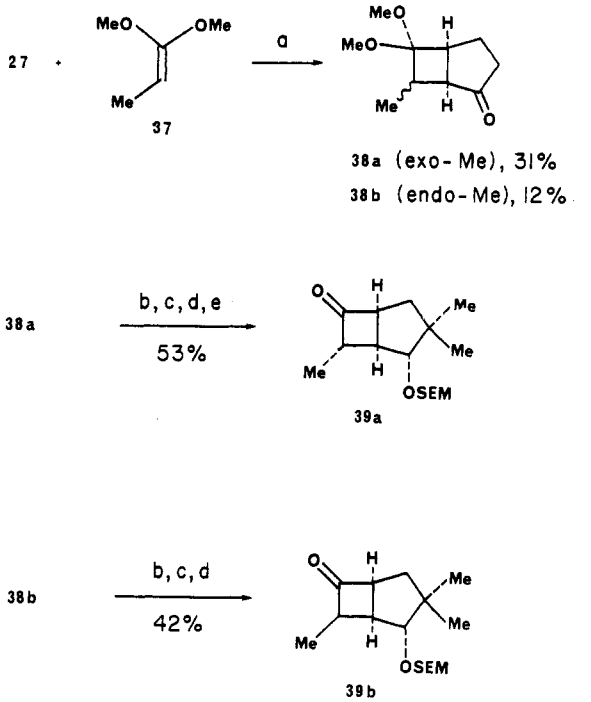
(17) For the bicyclo[3.2.0]heptane and bicyclo[3.3.0]octane ring systems, the R_fs of a pair of epimers may be used to assign stereochemistry. In this work, without exception, the epimer with a polar group endo (e.g., **36**) or a nonpolar group exo (e.g., **38a**) had the higher R_f when chromatographed on silica gel by using a nonpolar eluant.

Scheme I. Synthesis of the Coriolin BC Rings[a]



[a] (a) $CH_2=C(OCH_3)_2$, $h\nu$, pentane; (b) CH_3I, NaH, THF; (c) Li, NH_3, EtOH; (d) SEMCl, *i*-$PrEt_2N$; (e) HOAc, H_2O, THF; (f) $(CH_3S)_3CLi$, THF; (g) *n*-BuLi, $CuBF_4 \cdot 4CH_3CN$, toluene; (h) LDA, THF, CH_3I, HMPA; (i) Ra Ni, EtOH.

Scheme II. Synthesis of Methylated Substrates for Ring Expansion[a]



[a] (a) $h\nu$, ether; (b) CH_3I, NaH, THF; (c) Li, NH_3, EtOH; (d) SEMCl, *i*-$PrEt_2N$; (e) HOAc, H_2O, THF.

[β-(trimethylsilyl)ethoxy]methyl (SEM) ether,[18] and the ketal was hydrolyzed to give the fused cyclobutanone **30**.

Application of the ring-expansion procedure to **30** gave a very gratifying result. Condensation of **30** with **5** led to a single adduct (**31**), which was smoothly expanded to the keto thioketal **32** without formation of its regioisomer. The ring expansion of **30** is thus more efficient (80% overall) than any other we have attempted.

Monoalkylation of **32** at C-3 was achieved, although in modest yield, by treatment of the lithium enolate with iodomethane in tetrahydrofuran containing 1.1 equiv of hexamethylphosphoramide. The structure of the product **33** was assigned by assuming exo approach of the alkylating agent and later confirmed by independent synthesis (see below).

Keto thioketal **33** has the requisite features for elaboration of the coriolin A ring: an enolizable hydrogen at C-3 where exo alkylation with an annulation reagent might be performed and a thioketal at C-8, which may be reductively removed or retained for eventual conversion to a ketone or hydroxyl group. The appearance of Ikegami's coriolin synthesis in 1981[7c] rendered these transformations considerably less compelling, however, since his BC-ring intermediate **35** (prepared by a lengthy but efficient route) had been converted to (±)-**1** by an annulation sequence. We therefore exercised the formality of converting **33** to **34**, thus reaching a comparable point in only nine steps and completing our efforts toward coriolin.

Bond Migration Studies. Since the methyl group (C-14) of coriolin had to be introduced by a separate alkylation step (**32** → **33**, Scheme I), we pondered the feasibility of carrying it through the sequence from the beginning. To explore this possibility, we carried out the photocycloaddition of cyclopentenone (**27**) and 1,1-dimethoxypropene (**37**), and two adducts, tentatively assigned structures **38a** and **38b** on the basis of R_f[17] and known regiochemical preferences,[19] were isolated by chromatography. Scheme II shows the separate conversion of these to fused cyclobutanone substrates (**39a** and **39b**) for ring expansion.

While methine migration occurs in preference to methylene migration in the ring expansions we had studied, there is no evidence for predicting the outcome when the choice is between two different methine groups. Certainly new steric effects might become manifest in the case of **39a** or **39b**. In fact, there are few detailed studies of any sort that address the relative importance of steric and electronic influences on bond migration to electron-deficient centers,[20] since (a) the substrates must have enough stereochemical complexity to reveal subtle effects, (b) the proper control substrates must be available, and (c) the structures of all compounds must be proven. We found ourselves in possession of a series of substrates (**12**, **30**, **39a**, and **39b**) for which these criteria could be met.

Scheme III shows the results of ring expansion of the methylated BC-ring substrates. *exo*-Methylcyclobutanone **39a** reacted with **5** to give two adducts (**40a** and **41a**), resulting from both exo and endo attack. The exo methyl group at C-3 evidently provides about as much steric hindrance as the concave face of the bicyclo[3.2.0]heptane framework, but the condensation still occurs in high combined yield. Conversely, the formation of two adducts demonstrates that the methyl group of **39a** has in fact the exo configuration, since the comparison substrates **9**, **12**, and **30** each gave only a single adduct. The stereochemistry of **40a** and **41a** was assigned on the basis of the

(18) Lipshutz, B. H.; Pegram, J. J. *Tetrahedron Lett.* **1980**, *21*, 3343.

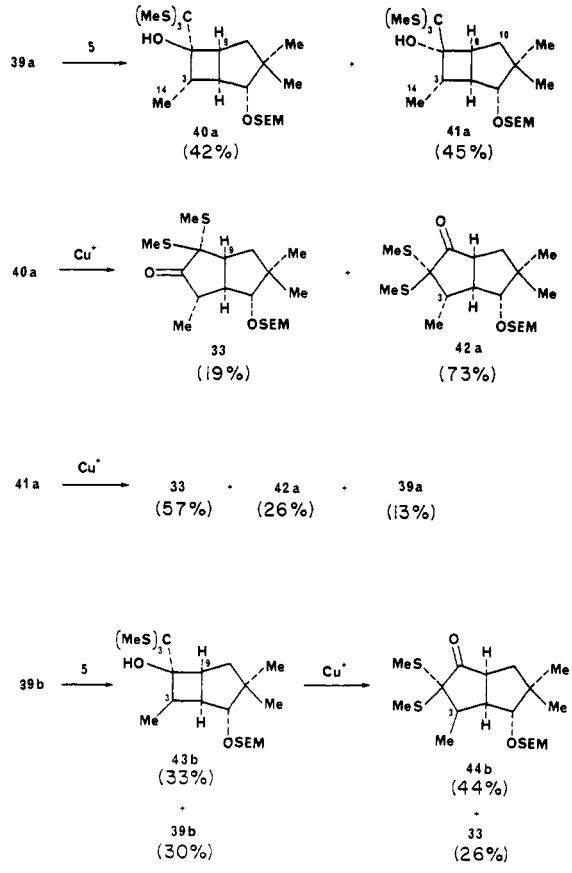
(19) Hill, E. A.; Theissen, R. J.; Cannon, C. E.; Miller, R.; Guthrie, R. B.; Chen, A. T. *J. Org. Chem.* **1976**, *41*, 1191.

(20) For early examples and discussion, see ref 9. Two exemplary studies are those of Sauers[21] and Ramirez.[22]

(21) Sauers, R. R.; Beisler, J. A. *J. Org. Chem.* **1964**, *29*, 210.

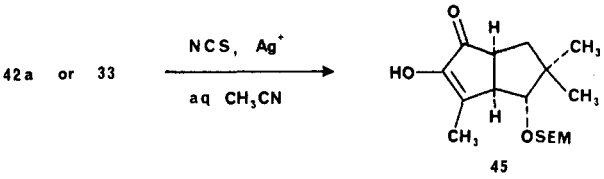
(22) Ramirez, F.; Stafiej, S. *J. Am. Chem. Soc.* **1956**, *78*, 644.

Scheme III. Ring Expansion of Methylated Substrates



relative R_fs[17] and the chemical shifts of the C-14 methyl doublet in the ^{1}H NMR spectra. Whereas adducts **14**, **17**, and **41a** show normal values for this resonance (δ 1.12, 1.10, and 1.14, respectively), adduct **40a**, in which the tris(methylthio)methyl group and C-14 are cis and unavoidably eclipsed, shows a doublet at δ 1.49. This pronounced deshielding effect is due to the proximity of the methyl group and the sulfur atoms.[23]

Ring expansion of **40a** occurred with migration of C-9 to give **33** *and* migration of C-3 to give the regioisomer **42a** in a ratio of 1:3.8.[24] In contrast, **41a** gave **33** and **42a** in a ratio of 2.2:1.[24] This shows not only that both methines migrate but also that the preferred product depends upon the stereochemistry of the adduct. The structure of **42a**

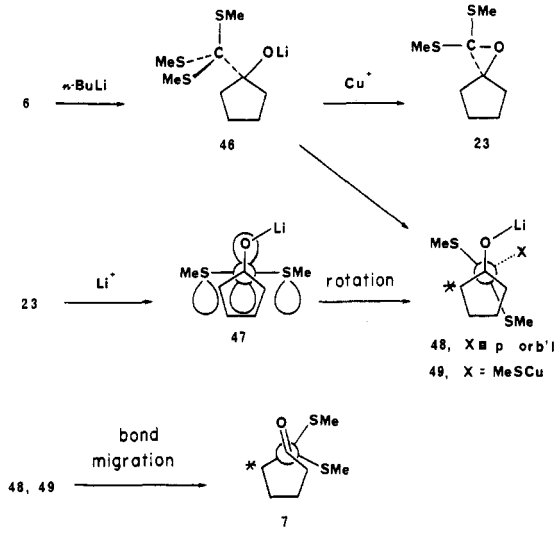


was secured by its hydrolysis[25] to the diketone **45** (λ_{max} 260 nm, calcd[26] 261). Compound **33**, which had first been prepared as in Scheme I, also gave **45** upon hydrolysis.

Condensation of **39b** (the endo-methyl isomer) with **5** gave a single adduct (**43b**), as expected, although the conversion was low. Ring expansion of **43b** gave two products, the ketone from C-9 migration, which epimerized upon standing[17] to **33**, and the isomeric ketone **44b** (from C-3 migration). The ratio of **33** to **44b** was 1:1.7.

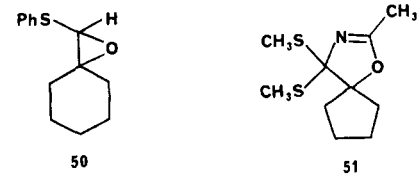
The total amount of **33** produced by this route does not exceed that from Scheme I, so this is not a competitive route to **1**.[27] Nevertheless, the information in Scheme III is very useful for understanding the factors that control regiochemistry in the ring-expansion step (see below).

Scheme IV. Proposed Mechanisms for Ring Expansion (* = Migrating Carbon)



Discussion

The mechanism of the ring-expansion step, to the extent that it may be inferred from the information here and from other ring-expansion studies, is shown in Scheme IV by using the cyclopentanone adduct **6** as the example. Proton exchange between **6** and *n*-butyllithium in toluene at −78 °C gives the alkoxide **46**, which is treated with solid $CuBF_4 \cdot 4CH_3CN$ at that temperature and slowly warmed to 75 °C. The lithium cation may exchange with copper(I) during the warming,[28] but the identity of the cation is not crucial to the events that follow. Complexation of a sulfur lone pair with Cu^+ leads to rupture of a carbon–sulfur bond with assistance by (a) the nearby alkoxide to give epoxide **23**, (b) the aligned[29] sulfur lone pairs to give the cation (e.g., **47** or **48**), or (c) the migrating carbon–carbon bond to give the product (**49** → **7**). The intervention of epoxide **23** is supported by the observation that the ring expansions examined proceed at about the same rate at 70 °C, by the isolation (after aqueous quench) of a hydroxy thio ester (**22**, **26**) in cases where expansion did not accompany carbon–sulfur bond cleavage, and by the isolation by Cohen, Kuhn, and Falck[10a] of α-epoxy thioether intermediates (e.g., **50**) from the copper(I)-promoted ring expansion of



bis(phenylthio)methyllithium adducts. Yet **23** is by no

(23) Lambert, J. B.; Shurvel, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. "Organic Structural Analysis"; MacMillan Press: New York, 1976, p 33.

(24) The ratio is based on our best isolated yields. In earlier experiments using $CuClO_4 \cdot 4CH_3CN$ under unoptimized conditions, we obtained smaller **33**:**42a** ratios from **40a** and larger **33**:**42a** ratios from **41a** but lower combined yields.

(25) Corey, E. J.; Crouse, D. *J. Org. Chem.* **1968**, *33*, 298.

(26) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1974; p 245.

(27) Since all ring-expanded products can be converted to **45**, this compound might represent an interesting coriolin precursor.

(28) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658.

(29) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463.

means a necessary intermediate for ring expansion to occur; almost any route to **48** or **49** will suffice. For instance, an intermediate containing acetonitrile (e.g., **51**) is also possible. In fact, the timing of the carbon–sulfur bond cleavage, the formation and collapse of intermediates, and the carbon–carbon bond migration are very much open to question and may differ among the various substrates. If **23** does form, it would be expected to lead rapidly to **7** via **47** and **48** under these conditions, by analogy to the LiClO_4-catalyzed epoxide rearrangements studied by Rickborn and Gerkin.[30]

The high regioselectivity of the ring expansion in cases where either a methylene or methine carbon may migrate (**14**, **15**, **17**, and **31**) is attributable to the formation of a highly stabilized cation (or developing cation, **49**), followed by a transition state in which there is substantial charge delocalization onto the migrating carbon. Conformational and steric effects do not seem to be important here, since there are no groups that can affect the appropriate trans–anti alignment of orbitals[9] for bond migration involving either the methylene or methine carbon. In literature examples of ring expansions where a less-stabilized cation is involved, the regioselectivity is reduced,[10a] or even reversed,[10b] because the difference in electron-donating ability of the migrating carbons is not so important a factor.

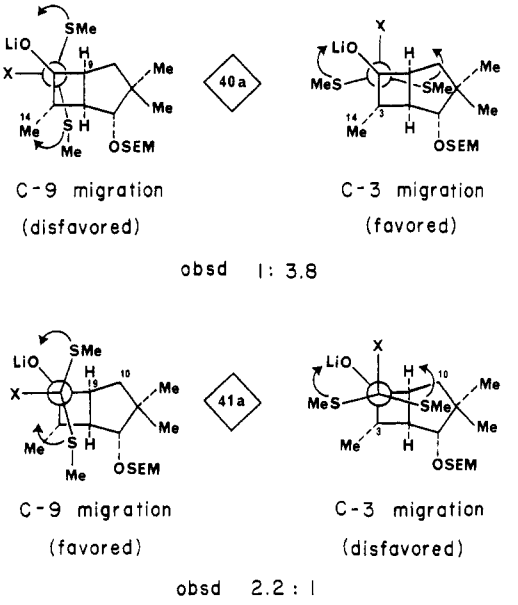
Compound **43b** offers a case where either of two *methines* (C-9 and C-3) may migrate without apparent complication by steric effects. The product ratio (C-9:C-3 = 1:1.7) may reflect a small difference in the abilities of these two like-substituted carbons to share the positive charge.

In the two examples (**40a** and **41a**) where the choice is between two methines (C-9 and C-3) *and* there is a difference in the steric influences upon the respective transition states for bond migration, the situation is more complex. In ring-expansion reactions involving diazoalkanes, steric effects control the conformer population of the diazo–alcohol intermediate, which in turn determines the products.[9,10b,22] While this may be a factor here, it is probably less important, since a more stable cation could achieve both reactive conformations, and rearrangement might occur preferentially from the higher energy one. We offer an alternative rationale for the ring-expansion results with **40a** and **41a** that depends on the presumed movement of the CH_3S- groups as the transition state is approached. In Scheme IV, the two remaining CH_3S- groups of **46** move into the plane of the developing sp^2 carbon (**48**) and then continue the Walden inversion motion toward **7** as the bond migration proceeds. If a steric interaction exist between one of these CH_3S- groups and a group on the migrating (starred) carbon, then relief of this interaction occurs as the transition state is approached.[31]

The relevant conformations of **40a** and **41a** are displayed in Scheme V. The methyl group (C-14) of **40a** is positioned very close to the tris(methylthio)methyl group, as its chemical shift demonstrates. Migration of C-9 exacerbates this interaction as a CH_3S- group moves toward C-14, whereas C-3 migration relieves the same interaction. For **41a** a similar, though perhaps less severe, situation exists with respect to the C-10 methylene group. Here C-9 (but not C-3) migration would be accompanied by relief of strain.

If this "steric acceleration" effect operates in the case of **40a** and **41a**, it is still not quite so decisive in controlling regiochemistry as the electronic effect found for **14**, **15**, **17**, and **31**. But since the former effect will rarely oppose the latter, the results described herein form an empirical basis for predicting the regiochemical outcome of most ketone to 1,2-keto thioketal ring expansions.

Scheme V. Steric Effects on Bond Migration (X = Empty p Orbital or Developing p Orbital)



Experimental Section

Apparatus and Reagents. Melting points were determined on an Electrothermal apparatus and are uncorrected. Infrared spectra were recorded by using a Perkin-Elmer Model 727B spectrophotometer. Proton nuclear magnetic resonance spectra were obtained on a Varian Associates T-60 or CFT-20 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Coupling constants are in hertz. Mass spectra were obtained from Cornell University MS Services and elemental analyses from Robertson Laboratories (Florham Park, NJ) or Galbraith Laboratories (Knoxville, TN). Ultraviolet spectra were recorded on a Cary 17D spectrophotometer.

Precoated silica gel plates (E. Merck 5765) were used for analytical thin-layer chromatography. Silica gel 60 from E. Merck (70–230 or 230–400 mesh) was employed for column chromatography. Analytical gas chromatography was done on a Hewlett Packard 5790A chromatograph (thermal conductivity detector, 10% Carbowax 20M TPA on Chromosorb WAW column).

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Acetonitrile, dichloromethane, pentane, hexamethylphosphoramide, and toluene were distilled from calcium hydride. Organic solutions were dried over anhydrous magnesium sulfate. All reactions were run under argon atmosphere.

Tetrakis(acetonitrile)copper(I) Tetrafluoroborate. A slurry of 35 g of copper(II) tetrafluoroborate in 1 L of acetonitrile was warmed near the boiling point and filtered. Copper wool was added to the hot filtrate until the blue color disappeared. Cooling to 0 °C gave colorless crystals, which were collected by vacuum filtration and freed of traces of acetonitrile in vacuo. The resulting salt (70 g) was stored at room temperature in a Pyrex flask under argon and was used over a period of 2 years. The reagent was routinely transferred and weighed in the open laboratory without decomposition, although samples allowed to stand in contact with air for several hours turned blue.

General Procedure for Ring Expansions. Condensation Reaction. A solution of tris(methylthio)methane (1.5 equiv) in THF was stirred at −78 °C. *n*-Butyllithium (1.5 equiv of a 1.7 M solution in hexane) was added dropwise, resulting in a white precipitate. A 1 M solution of the ketone (1 equiv) in THF was added by drops, and the homogeneous solution was stirred for an additional 1.5 h. The reaction was quenched at −78 °C with ethanolic acetic acid (1.5 equiv) and allowed to warm to room temperature. The THF was removed by rotary evaporator,

(30) Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 1693.
(31) To explain the regiochemistry in the Baeyer–Villager oxidation of fenchone, relief of torsional strain was invoked.[21]

saturated aqueous sodium bicarbonate was added, and the aqueous solution was extracted three times with dichloromethane. The combined organic extract was dried and concentrated, giving a residue which was chromatographed on silica gel (30 g per 1 g of crude product) to afford the pure adduct.

Expansion Reaction. A mixture of *n*-butyllithium (1.1 equiv of a 1.7 M solution in hexane) and toluene was treated with a solution of the adduct (1.0 equiv) in toluene at −78 °C, giving a clear, colorless solution (about 0.1 M solution of adduct). After 10 min, solid $CuBF_4 \cdot 4CH_3CN$ (2.2 equiv) was added all at once, and the reaction mixture was allowed to warm slowly to room temperature with stirring, resulting in an olive colored solid and pale green supernatant. The flask was placed in an oil bath at 75 °C and heated for 4 h, during which time the solid became dark brown and the supernatant tan. After being cooled to room temperature, the reaction was quenched with saturated aqueous ammonium chloride–ammonium hydroxide (pH 8.2) and stirred overnight. The resulting precipitate was removed by filtration through Celite, and the filtrate was extracted three times with ethyl ether. The combined organic extract was dried, concentrated, and chromatographed on silica gel to afford the pure ring-expanded ketone.

Following the general procedure on a 1–3 mmol scale, the adducts of Table I were prepared. **6**: NMR ($CDCl_3$) δ 1.44–2.54 (m, 8 H), 2.27 (s, 9 H), 2.68 (s, 1 H); IR (film) 3479 cm^{-1}. **13**: NMR ($CDCl_3$) δ 1.5–3.0 (m, 6 H), 2.23 (s, 9 H), 3.29 (br s, 1 H); IR (film) 3485 cm^{-1}. **14**: NMR ($CDCl_3$) δ 1.12 (d, J = 7, 3 H), 1.35–2.65 (m, 7 H), 2.27 (s, 9 H), 2.72 (br s, 1 H); IR (film) 3515 cm^{-1}. **15**: NMR ($CDCl_3$) δ 1.09–2.86 (m, 10 H), 2.30 (s, 9 H), 2.97 (br s, 1 H); IR (film) 3500 cm^{-1}. **16**: NMR ($CDCl_3$) δ 1.34–2.30 (m, 11 H), 2.25 (s, 9 H); IR (film) 3505 cm^{-1}. **17**: NMR ($CDCl_3$) δ 1.12 (d, J = 7, 3 H), 1.42–2.88 (m, 5 H), 2.22 (s, 9 H), 3.05 (br s, 1 H); IR (film) 3507 cm^{-1}.

Ring expansion of these adducts using the general procedure gave the 1,2-keto thioketals in Table I. **7**: NMR ($CDCl_3$) δ 1.5–2.94 (m, 8 H), 1.98 (s, 9 H); IR (film) 1715 cm^{-1}; mass spectrum, calcd for $C_8H_{14}OS_2$ m/e 190.0486, found 190.0476. **18**: NMR ($CDCl_3$) δ 1.73–2.77 (m, 6 H), 2.07 (s, 6 H); IR (film) 1727 cm^{-1}; mass spectrum calcd for $C_7H_{12}OS_2$ m/e 176.0330, found 176.0330. **19**: NMR ($CDCl_3$) δ 1.20 (d, J = 7, 3 H), 1.38–3.33 (m, 7 H), 1.90 (s, 3 H), 1.93 (s, 3 H); IR (film) 1709 cm^{-1}; mass spectrum calcd for $C_9H_{16}OS_2$ m/e 204.0643, found 204.0632. **20**: NMR ($CDCl_3$) δ 1.51–3.13 (m, 10 H), 1.94 (s, 6 H); IR (film) 1697 cm^{-1}; mass spectrum calcd for $C_{10}H_{16}OS_2$ m/e 216.0643, found 216.0637. **21**: NMR ($CDCl_3$) δ 1.12 (d, J = 7, 3 H), 1.54–2.60 (m, 5 H), 1.93 (s, 6 H); IR (film) 1720 cm^{-1}; mass spectrum calcd for $C_8H_{14}OS_2$ m/e 190.0486, found 190.0476.

Attempted ring expansion of **16** gave a mixture of products but no 2,2-bis(methylthio)cycloheptanone (NMR analysis). Chromatography using 9:1 petroleum ether–ether as eluant gave recovered **5** and **6** and a new product, (*S*)-methyl 1-hydroxy-1-cyclohexanethiocarboxylate (**26**): NMR ($CDCl_3$) δ 1.5–2.2 (m, 10 H), 2.27 (s, 3 H), 2.8 (br s, 1 H); IR (film) 3458, 1655 cm^{-1}; mass spectrum (no M^+ at m/e 174), m/e (relative intensity) 146 (6, -CO), 99 (100, $-CH_3SCO$), 81 (68, $-CH_3SCO$, $-H_2O$). Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.04, S, 18.39. Found: C, 55.79, H, 8.16; S, 17.49.

Reductive Desulfurization of 3-Methyl-2,2-bis(methylthio)cyclohexanone (19) and 2,2-Bis(methylthio)bicyclo[3.2.1]octan-3-one (20). A mixture of thioketal **19** (50 mg, 0.25 mmol), zinc dust (327 mg, 5 mmol), and acetic acid (1.4 mL) was warmed on a steam bath for 15 min. TLC indicated the disappearance of UV-active (sulfur-containing) intermediates. Ether and water were added, and the mixture was filtered through Celite and made basic to litmus with 1 M aqueous sodium hydroxide. The aqueous layer was washed twice with ether, and the combined extracts were dried and concentrated, giving 26 mg of an oil whose NMR and IR spectra matched those of authentic 3-methylcyclohexanone (**24**). Gas chromatographic analysis of the product showed several very minor contaminants, and the peak at the retention time of authentic 2-methylcyclohexanone amounted to no more than 5% of the major product.

In the same way 61 mg of **20** was desulfurized, giving 30 mg of bicyclo[3.2.1]octan-3-one (**25**). Gas chromatographic analysis showed no peak at the retention time of authentic bicyclo[3.2.1]octan-2-one. We estimate its presence at less than 0.5%, which amount would have been detected.

Attempted Ring Expansion Using Mercury(II) Chloride. A mixture of **6** (120 mg, 0.5 mmol), mercury(II) chloride (270 mg, 1.0 mmol), diisopropylethylamine (0.098 mL, 0.5 mmol), and 2 mL of dimethylformamide was stirred for 3 days at 23 °C. The solvent was removed in vacuo and the residue dissolved in ether, filtered to remove insoluble mercury salts, and concentrated. Chromatography using 9:1 petroleum ether–ether as eluant gave 16 mg (20%) of (*S*)-methyl 1-hydroxy-1-cyclopentanethiocarboxylate (**22**): NMR ($CDCl_3$) δ 1.46–2.07 (m, 8 H), 2.30 (s, 3 H), 2.7 (br s, 1 H); IR (film) 3445, 1687 cm^{-1}; mass spectrum (no M^+ at m/e 160), m/e (relative intensity) 132 (4, -CO), 85 (100, $-CH_3SCO$), 67 (55, $-CH_3SCO$, $-H_2O$).

6,6-Dimethoxy-7-methylbicyclo[3.2.0]heptan-2-ones (38a and 38b). A solution of 2.0 g (24.4 mmol) of cyclopentenone (**27**), 1,1-dimethoxypropene[32] **37**, 5.18 g, 50.8 mmol), 50 mL of diethyl ether, and three drops of diisopropylethylamine was irradiated at −78 °C in a quartz vessel equipped with a Corex filter and a Hanovia 250-W medium-pressure mercury arc lamp. After disappearance of **27** (NMR analysis), the solvents were removed by rotary evaporater and the remaining liquid was distilled at 1 mm. The distillate collected below 100 °C was chromatographed on 50 g of silica gel by using 4:1 petroleum ether–ethyl ether as eluant. The exo isomer **38a** (1.4 g, 31%) was collected and then the endo isomer **38b** (0.54 g, 12%). **38a**: NMR ($CDCl_3$) δ 1.18 (d, 3 H, J = 7), 1.66–3.03 (m, 7 H), 3.10 (s, 3 H), 3.16 (s, 3 H); IR (film) 1740 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.47; M, 8.61. **38b**: NMR ($CDCl_3$) δ 0.98 (d, 3 H, J = 7), 1.8–2.93 (m, 7 H), 3.20 (s, 3 H), 3.26 (s, 3 H); IR (film) 1740 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.07; H, 8.64.

Conversion of C-Ring Ketones 28, 38a, and 38b to Protected Hydroxy Ketones 30, 39a, and 39b. Sodium hydride (6.15 g of a 50% oil dispersion, 125 mmol) was triturated twice with 25-mL portions of THF, and then 350 mL of THF and 38 mL (610 mmol) of iodomethane were added and the mixture was stirred at 0 °C. A solution of **28**[15] (10.4 g, 61 mmol) in 175 mL of THF was added over 25 min, and the reaction was allowed to warm to room temperature and stir overnight. TLC analysis indicated a single product, with higher R_f than **28**. Saturated aqueous sodium bicarbonate (350 mL) was added, the THF removed by rotary evaporator, and the aqueous layer extracted with dichloromethane to give 12.6 g of dimethylated ketone of sufficient purity for the next step: NMR ($CDCl_3$) δ 1.05 (s, 3 H), 1.20 (s, 3 H), 1.8–3.1 (m, 6 H), 3.19 (s, 3 H), 3.21 (s, 3 H). A solution of the dimethylated ketone (12.6 g), 175 mL of anhydrous ethyl ether, and 372 mL of absolute ethanol was added to anhydrous ammonia (1.75 L) at −78 °C. The mixture was stirred with an overhead mechanical stirrer, and lithium metal (31 g, 448 mmol) was added by pieces over 1 h. Stirring was continued until the blue color disappeared. The solvents were evaporated at room temperature, 1.5 L of water was added, and the aqueous solution was extracted with ethyl ether to give 12 g of an oil, which solidified at 0 °C. Crystallization from pentane gave 7.07 g (58% from **28**) of **29** as colorless crystals: mp 63–64 °C; NMR ($CDCl_3$) δ 0.89 (s, 3 H), 1.17 (s, 3 H), 1.3–3.0 (m, 7 H), 3.17 (s, 3 H), 3.22 (s, 3 H), 3.74 (apparent d, 1 H, J = 6). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.06. Found: C, 66.06; H, 10.08. Chromatography of the mother liquor gave 1.4 g of the isomeric alcohol **36** as an oil (R_f = 0.28 using 3:1 petroleum ether–ether; compare **29**, R_f = 0.18): NMR δ 0.87 (s, 3 H), 1.12 (s, 3 H), 1.2–3.0 (m, 7 H), 3.17 (apparent s, 6 H), 3.6 (br s, 1 H).

A solution of 1.0 g (4.67 mmol) of **29** and 1.91 mL (11 mmol) of diisopropylethylamine in 12 mL of dichloromethane was stirred at room temperature. Neat SEM-Cl (1.74 mL, 11 mmol) was added by drops. After 1.5 h the reaction was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane, giving 2.17 of crude product. This was dissolved in 25 mL of a 3:1:1 mixture of acetic acid–THF–water and heated at 37 °C for 50 min. After cooling, the mixture was neutralized with sodium bicarbonate and extracted with dichloromethane, giving a residue, which was chromatographed on 50 g of silica gel by using 9:1 petroleum ether–ether. Pure **30** (1.02 g, 72% from **29**) was obtained as a colorless oil: NMR ($CDCl_3$) δ 0.03 (s, 9 H),

(32) Scheeren, H. W.; Aben, R. W. M.; Ooms, P. H. J.; Nivard, R. J. F. *J. Org. Chem.* **1977**, *42*, 3128.

0.93 (s, 3 H), 1.00 (br t, 2 H, J = 8), 1.06 (s, 3 H), 1.70 (apparent d, 2 H, J = 8), 2.5–4.0 (m, 7 H), 4.68 (apparent d, 2 H, J = 2); IR (film) 1786 cm^{-1}.

By the same procedure, the methylated analogues **38a** and **38b** were converted to the corresponding protected hydroxy ketones **39a** and **39b**, respectively. **39a**: NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.92 (s, 3 H), 0.98 (br t, 2 H, J = 8), 1.09 (s, 3 H), 1.26 (d, 3 H, J = 8), 1.71 (apperant d, 2 H, J = 11), 2.1–2.4 (m, 1 H), 2.83–3.28 (m, 2 H), 3.4–3.8 (m, 3 H), 4.71 (br s, 2 H); IR (film) 1780 cm^{-1}. **39b**: NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.98 (br t, 2 H, J = 8), 1.03 (s, 3 H), 1.10 (s, 3 H), 1.24 (d, 3 H, J = 10), 1.73 (apparent d, 2 H, J = 10), 2.0–3.3 (m, 3 H), 3.4–3.8 (m, 3 H), 4.69 (br s, 2 H); IR (film) 1780 cm^{-1}. Anal. Calcd for $C_{16}H_{30}O_3Si$: C, 64.38; H, 10.13; Si, 9.41. Found: C, 64.64; H, 10.25; Si, 9.50.

Ring Expansion of 30, 39a, and 39b. Condensation of **30** with **5** following the general procedure gave **31**: NMR (CCl_4) δ 0.03 (s, 9 H), 0.79 (s, 3 H), 0.86 (br t, 2 H, J = 8), 1.06 (s, 3 H), 2.20 (s, 9 H), 1.07–3.2 (m, 6 H), 3.01 (s, 1 H), 3.2–3.8 (m, 3 H), 4.61 (br s, 2 H); IR (film) 3475 cm^{-1}. Ring expansion of **31** afforded **32**: NMR (CCl_4) δ 0.03 (s, 9 H), 0.90 (br t, 2 H, J = 8), 0.95 (s, 3 H), 1.08 (s, 3 H), 1.2–1.9 (m, 2 H), 1.96 (s, 3 H), 2.03 (s, 3 H), 2.2–3.3 (m, 4 H), 3.38 (apparent d, 1 H, J = 4), 3.58 (apparent t, 2 H, J = 8), 4.66 (br s, 2 H); IR (film) 1728 cm^{-1}; mass spectrum calcd for $C_{18}H_{34}O_3S_2Si$ m/e 390.1719, found 390.1720. Condensation of **39a** with **5** gave two adducts, **40a** and **41a**, which were separated by chromatography (R_f = 0.36 and 0.24, respectively, in 9:1 petroleum ether–ethyl ether). **40a**: NMR (CCl_4) δ 0.03 (s, 9 H), 0.85 (s, 3 H), 0.95 (br t, 2 H, J = 8), 1.11 (s, 3 H), 1.11–2.63 (m, 3 H), 1.51 (d, 3 H, J = 8), 2.30 (s, 9 H), 3.26 (br s, 1 H), 3.4–3.7 (m, 3 H), 4.66 (br s, 2 H); IR (film) 3475 cm^{-1}. **41a**: NMR (CCl_4) δ 0.03 (s, 9 H), 0.83 (s, 3 H), 0.96 (br t, 2 H, J = 8), 1.11 (s, 3 H), 1.17 (d, 3 H, J = 7), 1.2–2.8 (m, 5 H), 2.30 (s, 9 H), 3.25 (s, 1 H), 3.5–3.8 (m, 3 H), 4.71 (br s, 2 H). Ring expansion of **40a** afforded **33** and **42a**, which were separated chromatographically by using 39:1 petroleum ether–ethyl ether as eluant. The NMR and IR spectra and TLC characteristics of **33** matched those of **33** prepared as in Scheme I. **42a**: NMR (CCl_4) δ 0.03 (s, 9 H), 0.85 (br t, 2 H, J = 8), 0.96 (s, 3 H), 1.05 (s, 3 H), 1.16–2.63 (m, 5 H), 1.26 (d, 3 H, J = 7), 1.96 (apparent s, 6 H), 3.3–3.8 (m, 3 H), 4.66 (br s, 2 H); IR (Film) 1730 cm^{-1}; mass spectrum calcd for $C_{19}H_{36}O_3S_2Si$ m/e 404.1875, found 404.1893. Ring expansion of **41a** gave a mixture of **33** and **42a**, which were purified and characterized as above. A small amount of "reverse condensation" product, **39a**, was also isolated from this reaction. Condensation of **39b** with **5** gave a single adduct, **43b**, and some recovered starting material. **43b**: NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.69–2.53 (m, 7 H), 0.85 (s, 3 H), 1.12 (s, 3 H), 1.16 (d, 3 H, J = 7), 2.22 (s, 9 H), 2.99 (s, 1 H), 3.44–3.89 (m, 3 H), 4.64 (br s, 2 H); IR (film) 3460 cm^{-1}. Expansion of **43b** gave a mixture of two new ketones, which were noticeably different from **33** and **42a** (TLC analysis). Upon standing and chromatography, however, one product was converted to **33**, which was isolated and characterized as above. The other (**44b**) was isolated unchanged. **44b**: NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.88 (s, 3 H), 0.92 (br t, 2 H, J = 8), 0.95 (s, 3 H), 1.09–3.93 (m, 11 H), 4.74 (br s, 2 H); IR (film) 1730 cm^{-1}; mass spectrum calcd for $C_{14}H_{36}O_3S_2Si$ m/e 404.1875, found 404.1893.

(3aα,4α,6aα)-4,5,6,6a-Tetrahydro-2-hydroxy-3,5,5-trimethyl-4-[[2-(trimethylsilyl)ethoxy]methyl]-1(3a*H*)-pentalenone (45). A solution of silver nitrate (52.7 mg, 0.31 mmol) and *N*-chlorosuccinimide (37 mg, 0.277 mmol) in 5 mL of 30% aqueous acetonitrile was treated at 0 °C with a solution of thioketal **42a** (28 mg, 0.0693 mmol) in 1.5 mL of the same solvent. After 30 min, the reaction mixture was concentrated and applied directly to 10 g of silica gel, which was eluted with 9:1 petroleum ether–ether, giving 11 mg (48%) of **45**: NMR (CCl_4) δ 0.03 (s, 9 H), 0.89 (br t, J = 8, 2 H), 0.95 (s, 3 H), 1.00 (s, 3 H), 1.10–1.36 (m, 3 H), 2.03 (s, 3 H), 2.36–3.23 (m, 2 H), 3.3–3.8 (m, 3 H), 4.68 (br s, 2 H); IR (film) 3350, 1700, 1655 cm^{-1}; UV (CH_3CN) λ_{max} 260 nm; mass spectrum calcd for $C_{17}H_{30}O_4Si$ m/e 326.1913, found 326.1925.

Treatment of **33** in the same way gave **45** (64%).

(3aα,3aα,4α,4aα)-Hexahydro-3,5,5-trimethyl-2,2-bis(methylthio)-4-[[2-(trimethylsilyl)ethoxy]methoxy]-1(2*H*)-pentalenone (33). Butyllithium (0.728 mL of a 1.55 M solution in hexane, 1.128 mmol) was added dropwise to a solution of diisopropylamine (0.158 mL, 1.128 mmol) in 5 mL of THF at −78 °C. After 10 min a solution of ketone **32** (200 mg, 0.513 mmol) and hexamethylphosphoramide (0.089 mL, 0.51 mmol) in 8 mL of THF was added by drops. After 30 min at −78 °C and 3 h at 0 °C, the mixture was cooled back to −78 °C and 0.191 mL (3.07 mmol) of iodomethane was added all at once. The reaction was kept at −78 °C for 30 min, −40 °C for 30 min, and 0 °C for 30 min, quenched with saturated aqueous sodium bicarbonate, and extracted with two 75-mL portions of 1:1 ether–petroleum ether. The combined organic layers were washed with water, dried, concentrated, and chromatographed by using 19:1 petroleum ether–ether as eluant, giving 98 mg (45%) of **33** as a colorless oil: NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.92 (br t, J = 8, 2 H), 0.98 (s, 3 H), 1.13 (s, 3 H), 1.21–2.95 (m, 5 H), 1.38 (d, J = 7, 3 H), 1.96 (s, 3 H), 2.05 (s, 3 H), 3.65 (t, J = 8, 3 H), 4.70 (br s, 2 H); IR (film) 1730 cm^{-1}; mass spectrum calcd for $C_{19}H_{36}O_3S_2Si$ m/e 404.1875, found 404.1878.

(1α,3aα,6α,6aα)-Hexahydro-1,5,5-trimethyl-6-[[2-(trimethylsilyl)ethoxy]methoxy]-2(1*H*)-pentalenone (34). A solution of thioketal **33** (27 mg, 0.067 mmol) in 1 mL of absolute ethanol was heated in an oil bath at 75 °C. Small portions of Raney nickel[33] were added over a period of 2 days until TLC analysis indicated no more sulfur-containing intermediates. The reaction mixture was cooled, filtered through Celite, and chromatographed on 3 g of silica by using 9:1 petroleum ether–ether as eluant, giving 13 mg (63%) of **34** as a colorless oil: NMR (80 MHz, $CDCl_3$) δ 0.03 (s, 9 H), 0.92 (br t, J = 8, 2 H), 0.98 (s, 3 H), 1.08 (s, 3 H), 1.18 (d, J = 8, 3 H), 1.5–3.7 (M, 10 H), 4.65 (br s, 2 H); IR (film) 1729 cm^{-1}. Anal. Calcd for $C_{17}H_{32}O_3Si$: C, 65.38; H, 10.26; Si, 9.00. Found: C, 65.30; H, 10.36, Si, 8.99.

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