31.33 ($CH_2$), 32.11 ($CH_2$), 55.61 (NCH), 80.13 (OCH), 160.14 (C=O). Anal. Calcd for $C_9H_{17}NO_2$: C, 63.11; H, 10.03; N, 8.18. Found: C, 63.45; H, 10.20; N, 8.10. The configuration was assigned on the basis of $^1H$ NMR to be cis because the chemical shifts and coupling constants of the two methine protons were of the same magnitude as those reported for *cis*-4,5-diethyl-2-oxazolidinone:[16] 3.70 (dt, $J_1$ = 5.5 Hz, $J_2$ = 7.5 Hz, NCH), 4.52 (dt, $J_1$ = 5.5 Hz, $J_2$ = 7.5 Hz, OCH).

***cis*-4,5-Trimethylene-2-oxazolidone (37)**: colorless needles from hexane–acetone, mp 87–88 °C; IR (KBr disk) 3025 (N—H), 1740 and 1700 (C=O); $^1H$ NMR (60 MHz) 1.1–2.3 (m, 6 H, $CH_2$), 4.1–4.4 (m, 1 H, NCH), 4.6–5.3 (m, 1 H, OCH), 6.51 (br, 1 H, NH). Anal. Calcd for $C_6H_9NO_2$: C, 56.67; H,7.15; N, 11.02. Found: C, 56.63; H, 6.97; N, 10.77.

**3-Methyl-*cis*-4,5-tetramethylene-2-oxazolidinone (39)**:[24] colorless oil; IR (liquid film) 1745 (C=O); $^1H$ NMR (60 MHz) 1.0–2.3 (m, 8 H, $CH_2$), 2.80 (s, 3 H, $CH_3$), 3.4–3.8 (m, 1 H, NCH), 4.2–4.6 (m, 1 H, OCH).

**3-Ethyl-*cis*-4,5-tetramethylene-2-oxazolidinone (40)**: colorless oil; IR (liquid film) 1740 (C=O); $^1H$ NMR (60 MHz) 1.17 (t, $J$ = 8 Hz, 3 H, $CH_3$), 1.1–2.0 (m, 8 H, $CH_2$), 3.27 (m or AB q with $J$ = 14 Hz on irradiation at $\delta$ 1.17, 2 H, $CH_2$), 3.5–3.9 (m, 1 H, NCH), 4.2–4.8 (m, 1 H, OCH); exact mass calcd for $C_9H_{15}NO_2$ 169.1104, found (high-resolution mass spectrum) 169.1086.

***cis*-4,5-Pentamethylene-2-oxazolidinone (41)**: colorless leaflets from hexane–acetone, mp 105–106 °C; IR (KBr disk) 3240 (N—H), 1730 (C=O); $^1H$ NMR (60 MHz) 0.9–2.3 (m, 10 H, $CH_2$), 3.7–4.3 (m, 1 H, NCH), 4.5–5.0 (m, 1 H, OCH), 6.68 (br, 1 H, NH). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.90; H, 8.46; N, 9.03. Found: C, 61.82; H, 8.42; N, 8.97.

***cis*-Indano[1,2-*d*]-2-oxazolidinone (42)**: brown crystals from hexane–acetone, mp 159–160 °C (lit.[18] mp 159.5–160 °C); IR (KBr disk) 3260 (N—H), 1760 and 1715 (C=O); $^1H$ NMR (60 MHz) 3.35 (d, $J$ = 4 Hz, 2 H, $CH_2$), 5.10 (d, $J$ = 7 Hz, 1 H, NCH), 5.30 (dt, $J_1$ = 7 Hz, $J_2$ = 4 Hz, 1 H, OCH), 6.73 (br, 1 H, NH), 7.23 (s, 4 H, Ar H).

***cis*-Tetralino[1,2-*d*]-2-oxazolidinone (43)**: brown needles from hexane–acetone, mp 141–142.5 °C (lit.[18] mp 140.5–142 °C); IR (KBr disk) 3250 (N—H), 1730 (C=O); $^1H$ NMR (60 MHz) 1.7–3.1 (m, 4 H, $CH_2$), 4.83 (d, $J$ = 8 Hz, 1 H, NCH), 5.06 (dt, $J_1$ = 8 Hz, $J_2$ = 3 Hz, 1 H, OCH), 6.73 (br, 1 H, NH), 7.13 (s, 4 H, Ar H).

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# Reactions of Lithium Bicyclo[1.1.0]butan-2-olates Formed by Carbenoid Type Decomposition of Lithiothioacetal Enolates. A Novel Concept for One-Pot Cyclopropanation of Enones

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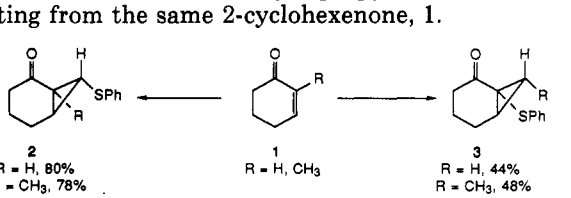
A new cyclopropanation procedure for $\alpha,\beta$-unsaturated ketones is based upon the low-temperature decomposition of enolate carbenoids generated by conjugate addition of tris(phenylthio)methyllithium to $\alpha,\beta$-unsaturated ketones followed by lithium/phenylthio exchange. Evidence suggests that the reactions employing 2-cyclohexenones as starting materials proceed through lithium bicyclo[1.1.0]butan-2-olate intermediates. The latter ordinarily lead to 7-(phenylthio)-substituted norcaranones via intermediate lithiocyclopropyl ketones which can be captured by various electrophiles or they can be modified in situ leading to other norcaranones or bridged cyclobutanes. The cyclopropyl ketones derived from 2-cyclopentenone and methyl vinyl ketone can only be obtained efficiently by the low-temperature deprotonation of the corresponding lithiocyclopropyl ketone to its enolate ion. Two of the cyclopropyl ketones derived from 2-cyclohexenone have been converted to potentially useful dianions by a deprotonation/reductive lithiation sequence.

Recent reports from this laboratory have enunciated and expanded the concept that, when positioned in a molecule with a second anionic site nearby, normally stable anions of bis(phenylthio) acetals behave as carbenoids which exhibit novel and selective behavior.[1] The wide availability of such carbenoids renders this mechanistically interesting concept of considerable potential synthetic utility. In this paper, we demonstrate that the application of this concept to enolate carbenoids results in a novel and apparently general cyclopropanation procedure for $\alpha,\beta$-unsaturated ketones. In some cases, the reactions proceed through lithium bicyclo[1.1.0]butan-2-olate derivatives, which heretofore have not been generally accessible. In a preliminary report of this work,[1g] the intermediates in the cyclopropanation procedure for various 2-cyclohexenones were shown to be such strained species. The recognition of this fact allowed the stereospecific, one-flask production of two different cyclopropyl ketones, **2** and **3**, starting from the same 2-cyclohexenone, **1**.




**2**
R = H, 80%
R = $CH_3$, 78%

**1**
R = H, $CH_3$

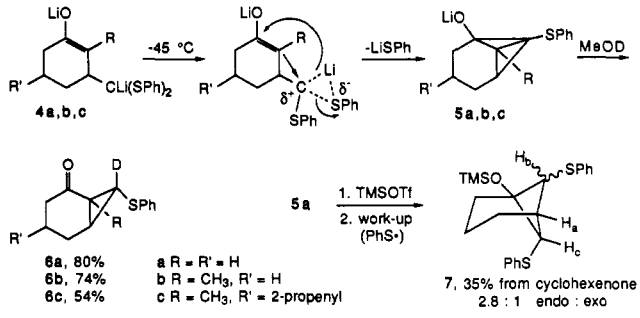
**3**
R = H, 44%
R = $CH_3$, 48%

New data presented here have shed light on the mechanistic subtleties of the new process. The resulting insight has suggested an artifice by which the procedure can be made general for a variety of $\alpha,\beta$-unsaturated ketones. For example, the efficient cyclopropanation of 2-cyclopentenone, a process which was reported in an earlier

(1) (a) Cohen, T.; Ouellette, D.; Senaratne, K. P. A.; Yu, L.-C. *Tetrahedron Lett.* **1981**, *22*, 3377. (b) Cohen, T.; Ritter, R. H.; Ouellette, D. *J. Am. Chem. Soc.* **1982**, *104*, 7142. (c) Cohen, T.; Yu, L.-C. *J. Am. Chem. Soc.* **1983**, *105*, 2811. (d) Cohen, T.; Yu, L.-C. *J. Org. Chem.* **1984**, *49*, 605. (e) Ritter, R. H.; Cohen, T. *J. Am. Chem. Soc.* **1986**, *108*, 3718. (f) Abraham, W. D.; Bhupathy, M.; Cohen, T. *Tetrahedron Lett.* **1987**, *28*, 2203. (g) Ramig, K.; Bhupathy, M.; Cohen, T. *J. Am. Chem. Soc.* **1988**, *110*, 2678.

0022-3263/89/1954-4404$01.50/0 

**Scheme I**




study[1c] to proceed in only low yield, is now possible. Furthermore, synthetic uses of the phenylthio-substituted cyclopropyl ketone products are demonstrated.

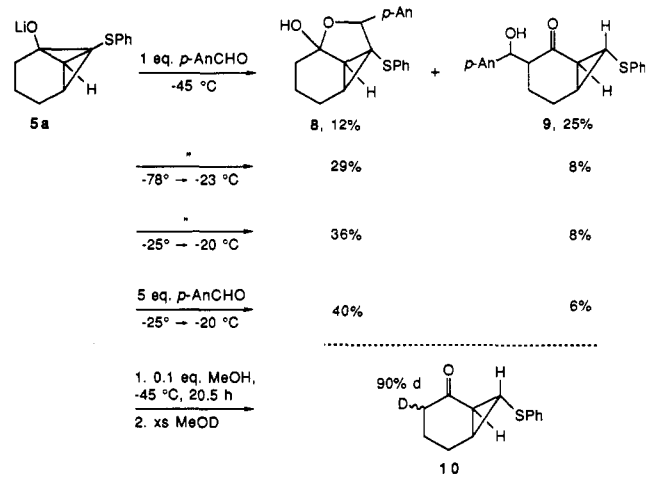
## Results and Discussion

**Detection of the Bicyclo[1.1.0]butan-2-olate Intermediates.** When the conjugate adducts of tris(phenylthio)methyllithium and 2-cyclohexenones[2] are treated with *sec*-butyllithium at −78 °C for 1–3 h, nearly quantitative[3] lithium–phenylthio exchange[1c,g] occurs to form dianions **4a–c**. When the latter are heated to −45 °C for several hours (or, more conveniently, warmed toward ambient temperature until the color of the reaction mixture changes from orange to yellow) and then the reaction mixtures are quenched with methanol-$d_1$, cyclopropyl ketones **6a–c** are isolated (Scheme I).

We believe that these reactions proceed through the corresponding bicyclo[1.1.0]butan-2-olate intermediates **5a–c**, formed by metal-assisted[4] (and nucleophile-assisted) ionization of the thiophenoxide group of enolate carbenoids **4a–c**. The isolation of cyclopropyl ketones **6a–c**, which have regio- and stereospecifically incorporated a deuterium atom, is surprising considering that the only other known examples of bicyclo[1.1.0]butan-2-olate derivatives[5] were incapable of being trapped by added reagents due to rapid deprotonation of solvent by these highly basic intermediates. Apparently, the phenylthio group in **5a–c** stabilizes any negative charge that may build up at the $\alpha$-carbon atom. Indeed, the reaction mixture containing **5a** can be quenched with methanol-$d_1$ after >15 h at −45 °C with no significant loss of deuterium in cyclopropyl ketone **6a**.

In an attempt to isolate a derivative of bicyclobutoxide **5a**, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (2 equiv[6]) was added at −45 °C. TLC indicated that bicyclobutoxide **5a** had virtually disappeared after 4 h. Basic workup and radial chromatography surprisingly gave cyclobutane **7** (along with some intractable material[7]), instead

**Scheme II**




of the expected *O*-trimethylsilyl derivative of bicyclobutoxide **5a**. The formation of cyclobutane **7** can be rationalized by assuming that trimethylsilyl thiophenoxide formed during silylation[6] is hydrolyzed during workup to give thiophenol, which is then oxidized by traces of air to the phenylthio radical. The latter then reacts via a radical chain process with the *O*-trimethylsilyl derivative of bicyclobutoxide **5a** to give cyclobutane **7** in a precedented process.[9] The structural characterization of cyclobutane **7** relied heavily upon its $^1$H NMR spectrum. For the endo,endo isomer, a doublet at $\delta$ 3.57 ($J$ = 6.42 Hz) was assigned to the two equivalent protons $H_b$ and $H_c$. For the endo,exo isomer, $H_c$ was a doublet at $\delta$ 4.33 ($J$ = 6.97 Hz). A singlet at $\delta$ 3.83 was assigned to $H_b$, on the assumption, as indicated by a molecular model, that the dihedral angle between $H_a$ and $H_b$ $\cong$ 90° and therefore $J_{ab} \cong$ 0 Hz. Further confirmation of the structure came from the similarity of the $^1$H NMR spectra of the cyclobutane **7** and its destrimethylsiloxy derivative.[9]

The ambident homoenolic[10] nature of bicyclobutoxide **5a** is revealed by its C-protonation to **6a** and its O-silylation to the precursor of **7**. We are aware of only one other example[11] of a group I metal homoenolate that is capable of reaction either at oxygen or at carbon.

**Electrophilic Capture of the Bicyclobutoxide Intermediate 5a.** Because methanol is a strong enough electrophile to induce ring cleavage of bicyclobutoxide **5a**, other weak electrophiles such as carbonyl compounds were anticipated to react similarly. The synthetic method then would not only be an efficient method of cyclopropanation of an enone but would also become a method for making a third C–C bond in a one-pot process. *p*-Anisaldehyde caused ring cleavage of **5a** even at −45 °C after 6.5 h to give two new products (Scheme II) in addition to cyclopropyl ketone **2** (R = H). Hemiketal **8** was characterized by an O–H stretching frequency in the IR spectrum (3372 cm$^{-1}$) and by its $^1$H NMR spectrum, which showed a singlet for the benzylic proton at $\delta$ 5.51. In addition to an O–H stretching frequency (3389 cm$^{-1}$) in the IR spectrum of ketone **9**, an absorption was seen at 1660 cm$^{-1}$ which was assigned to the carbonyl group. The benzylic proton of ketone **9** was a doublet of doublets at $\delta$ 5.36.

(2) Manas, A. R.-B.; Smith, R. A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 216. Smith, R. A. J.; Lal, A. R. *Aust. J. Chem.* **1979**, *32*, 353. Cohen, T.; Nolan, S. M. *Tetrahedron Lett.* **1978**, 3533.

(3) For example, enolate carbenoid **4a** can be quenched at −78 °C, and the resulting ketone isolated in >90% yield.

(4) Rachon, J.; Goedken, V.; Walborsky, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 7435 and references cited therein.

(5) (a) Nilsen, N. O.; Sydnes, L. K.; Skattebøl, L. *J. Chem. Soc., Chem. Commun.* **1978**, 128. (b) Nilsen, N. O.; Skattebøl, L.; Sydnes, L. K. *Acta Chem. Scand. B* **1982**, *36*, 587. (c) Jørgensen, E.; Sydnes, L. K. *J. Org. Chem.* **1986**, *51*, 1926.

(6) In the presence of 1 equiv of TMSOTf, **5a** is not consumed (as monitored by TLC) at −45 °C after almost 20 h. When a second equivalent is added, **5a** disappears after 4 h at this temperature. This indicates that TMSOTf is more reactive toward the lithium thiophenoxide generated during carbenoid decomposition than it is toward tertiary alkoxide **5a**.

(7) It is assumed that the intractable material found in the reaction mixture containing cyclobutane **7** is a polymer[8] of the *O*-trimethylsilyl derivative of bicyclobutoxide **5a**.

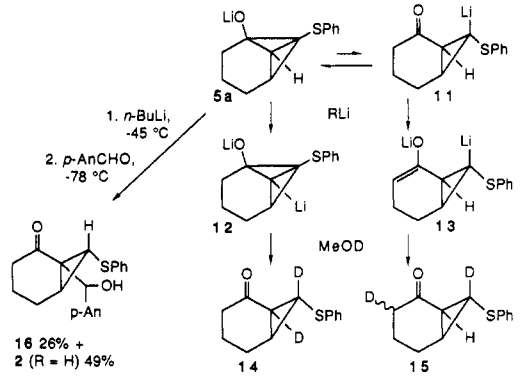
(8) Hall, H. K., Jr.; Blanchard, E. P., Jr.; Cherkofsky, S. C.; Sieja, J. B.; Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 110.

(9) An analogous addition of the phenylthiyl radical to a bicyclobutane similar to the *O*-trimethylsilyl derivative of bicyclobutoxide **5a** is known: Szeimies, G.; Schlosser, A.; Philipp, F.; Dietz, P.; Mickler, W. *Chem. Ber.* **1978**, *111*, 1922.

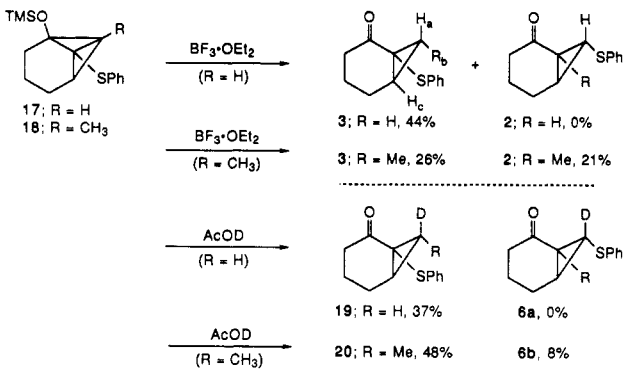
(10) Review of homoenolates: Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205.

(11) Gassman, P. G.; Mullins, M. J. *Tetrahedron Lett.* **1980**, *21*, 2219. We thank Professor Gassman for bringing this article to our attention.

**Scheme III**




**Scheme IV**




Ketone **9** is apparently the result of homoenolate to enolate equilibration. The acid catalyst for this reaction is probably the relatively acidic ketonic precursor of **8**. That such equilibration can be caused by a trace of weak acid is shown by the isolation of cyclopropyl ketone **10** (Scheme II), the enolate of which is generated when **5a** is treated with a catalytic amount of methanol but not in the absence of the latter. Furthermore, when the *p*-anisaldehyde used was not entirely free from acidic impurities, a lower ratio of hemiketal **8** to ketone **9** was found. The relative amounts of **8** and **9** were found to strongly depend on the reaction conditions. Temperatures of −25 to −20 °C maximize the yield of hemiketal **8**. When the reaction temperature is raised above −20 °C, the yield of **8** does not improve while **9** disappeared completely. Ketone **9** appears to be converted to its dehydration product at these higher temperatures. Employing an excess of *p*-anisaldehyde raised the yield slightly. This was expected to be the case, as it was assumed that raising the concentration of the electrophile would cause the rate of its reaction with bicyclobutoxide **5a** to increase relative to the rate of unwanted equilibration. Other electrophiles gave less satisfactory results.[12]

**Deprotonation of Bicyclobutoxide 5a.** Attention was turned to deprotonation of the bridgehead carbon atom of bicyclobutoxide **5a**. Bicyclobutanes in general can be deprotonated at this position with *n*-BuLi, and the resulting anion can be trapped by a variety of electrophiles.[13] It was anticipated that the alkoxide group in bicyclobutoxide **5a** might facilitate heteroatom-directed lithiation because of its proximity to the bridgehead carbon atom. Attempts at deprotonation of the bridgehead carbon atom with alkyllithiums are shown in Scheme III. A variety of conditions, including different temperatures (−78 and −45 °C) and different bases (*n*-, *sec*-, and *t*-BuLi), caused lithiation of bicyclobutoxide **5a** as evidenced by formation of cyclopropyl ketone **14**. The best conditions (*n*-BuLi, −45 °C, 12 h) gave a 2:3 ratio of **14**:**15**. Because deuterium content was also found at the $\alpha'$-position, it appeared that the open form (**11**) of bicyclobutoxide **5a** was being deprotonated to give dianion **13**.

Phenyllithium and lithium diisopropylamide were unsuccessfully employed in an attempt to obtain selectively the dianion **13**. It was hoped that these relatively weak bases would be unable to abstract the bridgehead proton of bicyclobutoxide **5a** and hence would remove only the $\alpha'$-proton of the open form **11**. It was then projected that the dianion **13** could be trapped with electrophiles at the carbenoid carbon atom. However, use of these two bases resulted in the formation of both dianions **12** and **13**, as ascertained by methanol-$d_1$ quenching. This method, had it been successful, might have been a general way to obtain compounds such as hemiacetal **8** without homoenolate-to-enolate equilibration. In order to trap bicyclobutoxide **5a** in the closed form and thus allow selective deprotonation of the bridgehead carbon atom, the *O*-trimethylsilyl derivative of bicyclobutoxide **5a** was prepared (vide supra). During the in situ deprotonation at −45 °C with *sec*-BuLi, it was determined, as inferred by TLC, that the trimethylsiloxy compound was converted back to bicyclobutoxide **5a**. Apparently, the alkyllithium reacted with the trimethylsilyl group in preference to causing deprotonation.

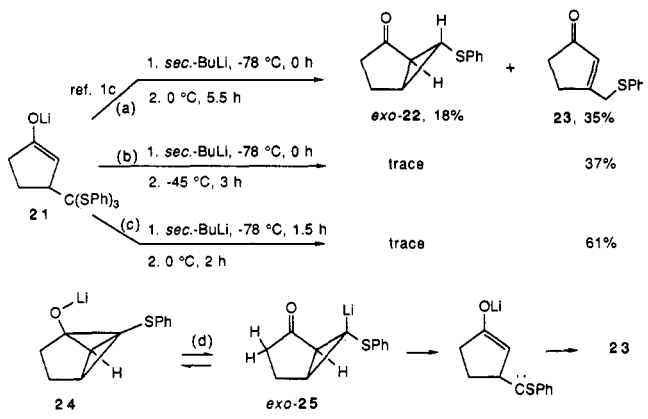
When bicyclobutoxide **5a** was treated with *n*-BuLi at −45 °C, the mixture was cooled to −78 °C, *p*-anisaldehyde was added, and ketone **16** was isolated after methanol quenching. A strong hydrogen-bonding interaction between the hydroxyl proton and the carbonyl group oxygen atom of ketone **16** was noted by examination of the $^1$H NMR and IR spectra. In the IR spectrum, the carbonyl stretching frequency was at an extremely low value (1676 cm$^{-1}$). The $^1$H NMR spectrum showed that the hydroxyl proton peak was a doublet at $\delta$ 5.21, downfield from most hydroxyl protons. Other important peaks in the $^1$H NMR spectrum were a doublet at $\delta$ 2.49, which was assigned to the proton $\alpha$ to the phenylthio group, and a doublet at $\delta$ 4.88, which was assigned to the benzylic proton. When dianion **12** was treated with *p*-anisaldehyde at −45 °C instead of −78 °C, a complex mixture resulted that contained lesser amounts of both ketone **16** and cyclopropyl ketone **2** (R = H).

**Electrophilic Cleavage of Silylated Bicyclobutoxides.** It was indicated above that bicyclobutoxides **5a–c** can be cleaved selectively when treated with electrophiles. Even though **5a–c** appear to have four nearly equivalent C–C bonds at which electrophiles can attack, the ionic character of the O–Li bond coupled with the ability of the phenylthio group to stabilize a negative charge on the $\alpha$ carbon atom causes only one bond of the bicyclobutane nucleus to be broken by electrophiles. It would be desirable to direct selectively electrophilic attack to one of the other bonds of the bicyclobutane nucleus because this could result in production of a different type of cyclopropyl ketone. A search of the literature revealed that bicyclobutanes in general are attacked electrophilically at the least substituted bridgehead carbon atom,[14,15] in contrast to bicyclobutoxide **5a**. If the

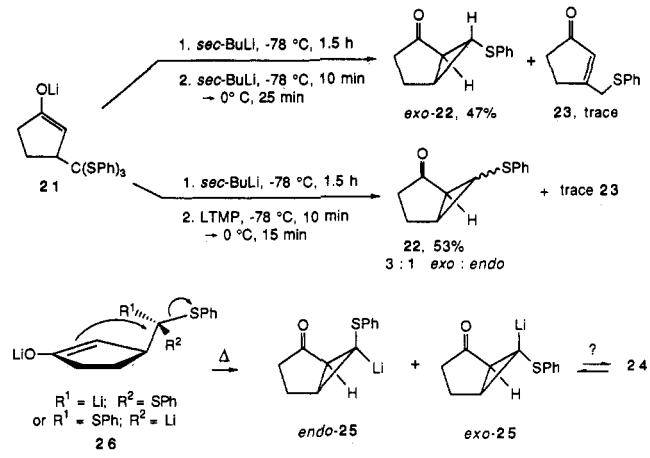
(12) Benzophenone, propionaldehyde, and 2-cyclohexenone caused equilibration of bicyclobutoxide **5a** and/or gave products analogous to ketone **9** in low yield. Methyl iodide gave a 33% yield of the $\alpha'$-methylated derivative of cyclopropyl ketone **2** (R = H). Both bromine and *N*-chlorosuccinimide gave complex mixtures.

(13) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 2022. Szeimies, G.; Philipp, F.; Baumgartel, O.; Harnisch, J. *Tetrahedron Lett.* **1977**, 2135. Schluter, A.-D.; Huber, H.; Szeimies, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 404.

**Scheme V**




**Scheme VI**




oxygen–metal bond of bicyclobutoxide **5a** were to be made more covalent, then the resulting bicyclobutane derivative would incorporate an attacking electrophile at the least substituted bridgehead carbon atom. The obvious choice for the testing of this hypothesis would be homoenolate **17**, the putative in situ silylation product of the homoenolate **5a** (Scheme IV).

When **17** was treated in situ with boron trifluoride etherate, **3** (R = H) was isolated as the sole cyclopropyl ketone. If either of the proposed mechanisms of acid-catalyzed rearrangement of bicyclobutanes[15a,16] (in this case edge protonation of the bond between the carbinol carbon atom and the hydrogen or methyl substituted carbon atom or protonation of the rear lobe of one of orbitals constituting the central C–C bond) is indeed operative, then the electrophile must be incorporated in an endo orientation. Isolation of cyclopropyl ketone **19** with the deuteron in an endo orientation after treatment of silylated homoenolate **17** with acetic acid-$d_1$ is significant because it suggests that other synthetically interesting electrophiles may also be incorporated regio- and stereospecifically. The assignment of endo orientation to the deuteron in **19** was based on an investigation of the $^1$H NMR spectrum of cyclopropyl ketones **3** (R = H) and **19**. It was found that in **3** (R = H) $H_a$ was a doublet of doublets at $\delta$ 1.79 ($J_{ac}$ = 6.05 Hz) while $H_b$ was a doublet of doublets at $\delta$ 1.53 ($J_{bc}$ = 8.41 Hz). By comparison, for *exo*-7-(phenylthio)bicyclo[4.1.0]heptane, the coupling constant of the proton $\alpha$ to the phenylthio group = 6 Hz and for *endo*-7-(phenylthio)bicyclo[4.1.0]heptane, the coupling constant of the proton $\alpha$ to the phenylthio group = 8.5 Hz.[17] In the $^1$H NMR spectrum of **19**, it was found that the doublet of doublets at $\delta$ 1.53 had collapsed into a doublet ($J$ = 8.41 Hz) while the doublet of doublets at $\delta$ 1.79 had virtually disappeared. The same set of reactions was performed in situ on putative silylated homoenolate **18** (prepared analogously to **17**). The lower selectivity of bond cleavage of **18** vs **17** may be attributed to the steric bulk of the methyl group causing electrophilic attack to be directed away from it.

The results discussed above indicate that the new cyclopropanation procedures have the ability to produce selectively different cyclopropyl ketone products starting from a given $\alpha,\beta$-unsaturated ketone (e.g. 2-cyclohexenone → **2** or **3**). It was hoped that the utility of intermediates such as silylated homoenolate **17** could be broadened by reaction with electrophilic reagents other than acids. To this end, **17** was treated with *p*-anisaldehyde under a variety of conditions either by itself or by employing magnesium bromide or boron trifluoride etherate as catalysts. In all cases, complex mixtures which contained small amounts of cyclopropyl ketones **3** (R = H) and/or **2** (R = H) were obtained as the only isolable products.

**Generalization of the Cyclopropanation Procedure.** It was previously reported[1c] that an attempt to extend this cyclopropanation procedure to cyclopentenone was rather unsatisfactory as indicated by eq a in Scheme V. We now relate a procedure for greatly improving the cyclopropanation process by suppressing the competitive formation of products such as **23**. Equation b of Scheme V shows that treatment of adduct **21** under conditions which cause conversion of the corresponding adduct in the six-membered ring series to a cyclopropyl ketone results in isolation of only a trace of cyclopropyl ketone *exo*-**22**, the major product being enone **23**. A more satisfactory yield of **23** can be obtained if lithium/phenylthio exchange is allowed to occur at −78 °C before the reaction mixture is warmed to 0 °C (eq c, Scheme V). The preliminary report[1g] noted that a product homologous to **23** was generated in the six-membered ring series by ring opening (retro-carbenoid addition) of **11** (the homologue of *exo*-**25**, thought to be present in minute amounts in equilibrium with **5a**, the homologue of **24**) followed by 1,2-hydride transfer when bicyclobutoxide **5a** (Scheme III) was warmed briefly to 0 °C. It seems likely that the greater tendency to produce hydride transfer product in the 5- than in the 6-membered ring case is a result of equilibrium d lying farther toward the open chain isomer than the analogous equilibrium (**5a** ⇌ **11**; Scheme III) in the 6-membered ring series due to the greater ring strain in the possible intermediate **24**; indeed, it is conceivable that none at all of the closed form **24** is produced.

A possible solution to the apparent nongenerality of this cyclopropanation procedure was derived from speculation as to the reason for the better yield of cyclopropane **22** obtained by the conditions in eq a than by those in eq c of Scheme V. In the conditions indicated in eq c, lithium/phenylthio exchange was allowed to go to completion *before* thermolysis. On the other hand, in the conditions of eq a,[1c] the reaction mixture was warmed *directly* to 0 °C after *sec*-BuLi addition and thus the *sec*-BuLi not only came in contact with adduct **21** at high temperatures, but also with intermediates **24** and *exo*-**25**. Both of the latter

(14) Moore, W. R.; Taylor, K. G.; Muller, P.; Hall, S. S.; Gaibel, Z. L. F. *Tetrahedron Lett.* **1970**, *11*, 2365. Paquette, L. A.; Wilson, S. E.; Henzel, R. P.; Allen, G. R. *J. Am. Chem. Soc.* **1972**, *94*, 7761.

(15) (a) Paquette, L. A.; Allen, G. R., Jr.; Broadhurst, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 4503. (b) Taylor, K. G.; Hobbs, W. F.; Clark, M. S.; Chaney, J. *J. Org. Chem.* **1972**, *37*, 2436.

(16) Wiberg, K. B.; Szeimies, G *J. Am. Chem. Soc.* **1970**, *92*, 571.

(17) Bhupathy, M.; Cohen, T. *Tetrahedron Lett.* **1987**, *28*, 4797. Schöllkopf, U.; Lehmann, G. J.; Paust, J.; Hartl, H.-D. *Chem. Ber.* **1964**, *97*, 1527.

**Table I. Cyclopropanation of α,β-Unsaturated Ketones**

| entry | ketone | LTMP present | product(s), yield(s), % |
|---|---|---|---|
| 1 | 2-cyclohexenone | no | **2**, R = H, 80 |
| 2 | 2-methyl-2-cyclohexenone | no | **2**, R = Me, 78 |
| 3 | 2-cyclopentenone | no | *exo*-**22**, trace; **23**, 61 |
| 4 | 2-cyclopentenone | yes | **22**, 53 (3:1 exo:endo); **23**, trace |
| 5 | 2-methyl-2-cyclopentenone | no | *exo*-**27**, ~25; **28**, 42 |
| 6 | 2-methyl-2-cyclopentenone | yes | **27**, 25 (1:1 exo:endo); **28**, 41 |
| 7 | methyl vinyl ketone | no | **29**, 9[a] |
| 8 | methyl vinyl ketone | yes | **29**, 39[a] |
| 9 | ethyl vinyl ketone | yes | **30**, 26[b] |

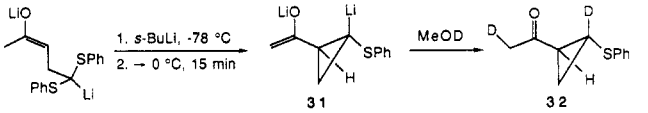
[a] The yields in the cyclopropanation step are double these since the addition step proceeds in only 50% yield. See text. [b] Unoptimized.

have acidic protons which are capable of being removed by *sec*-BuLi. If proton removal were indeed to occur, then presumably thermal unraveling would be foiled and protonation of either dianion would ultimately yield cyclopropyl ketone *exo*-**22**. In order to test this hypothesis, an extra equivalent of *sec*-BuLi was added to the reaction mixture containing dianion **26** followed by warming to 0 °C for 25 min (Scheme VI). The result, after quenching, was confirmation of the hypothesis in that a 47% yield of cyclopropyl ketone *exo*-**22** was isolated. In addition, a small amount of a product which had seemingly incorporated the *sec*-butyl group was isolated in an impure state. This product may have arisen from nucleophilic attack of the alkyllithium on the carbenoid carbon atom of the intermediates on the way to *exo*-**22**.[18]

In hope of suppressing this side reaction, *sec*-BuLi was replaced with the nonnucleophilic base lithium tetramethylpiperidide (LTMP). When LTMP was added to the mixture containing the enolate–carbenoid **26** and the mixture was warmed to 0 °C for 15 min, a 53% yield of cyclopropyl ketone **22** was obtained after quenching. Surprisingly, this product was a 3:1 mixture of *exo*- and *endo*-**22**. The assignment of endo stereochemistry to *endo*-**22** was based on the large (8.01 Hz) coupling constants between the proton on C-6 and the protons on C-1 and C-5. (The corresponding coupling constants for *exo*-**22** are 2.2 and 3.2 Hz.[1c]) These are consistent with the coupling constants found in a related system.[17] A rationalization of the difference in behavior between *sec*-BuLi and LTMP is given in the sequel.

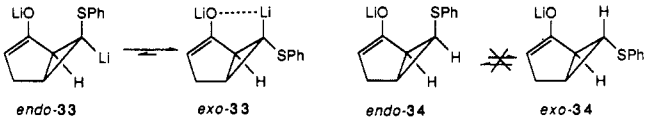
Table I shows the results of the application of the new cyclopropanation procedure to six α,β-unsaturated ketones. It is seen that the cyclopropanation procedure, and particularly the cyclopropanation step itself, is rather general as long as LTMP is added after enolate carbenoid formation in those cases in which the yield is otherwise poor. In the case of methyl vinyl ketone (entries 7 and 8), since the conjugate addition step proceeds only with 50% efficiency,[19] oligomerization presumably being a major competing process, the efficiency of ring closure is seen to improve from 18% to 78% upon the addition of LTMP. On the other hand, in the case of 2-methyl-2-cyclopentenone (entries 5 and 6), the addition of this base has no effect on the ratio of cyclopropyl ketone **27** to enone **28** but it does, as in the case of 2-cyclopentenone, cause randomization of the stereochemistry of the cyclopropane ring which is produced.

**Scheme VII**




31 32

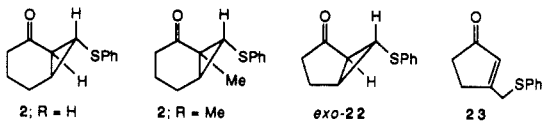
**Scheme VIII**



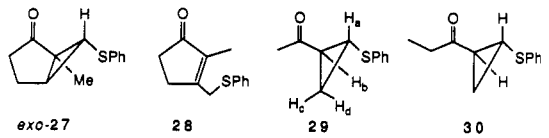

*endo*-33 *exo*-33 *endo*-34 *exo*-34

Interestingly, the methyl group foils 1,2-hydride transfer to a small extent in entry 5 (compare entry 3). This same effect was seen to operate in the six-membered ring series and a similar explanation[1c,g] is likely.

The trans stereochemistry of both **29** and **30** was confirmed by the magnitude of the coupling constants between the hydrogen atom on C-1 and the hydrogen atoms on C-2 and C-3. Taking **29**, for example, it was found that $J_{ab}$ = 3.47 Hz, $J_{ac}$ = 8.16 Hz, and $J_{ad}$ = 5.71 Hz. These numbers match well with the coupling constants found in 1-(phenylthio)-2,2-dimethylcyclopropane, where $J_{cis}$ = 8.2 Hz and $J_{trans}$ = 4.8 Hz.[17] Evidence that dianion **31** is the intermediate in the cyclopropanation of methyl vinyl ketone in the presence of added base was obtained by the method shown in Scheme VII.




2; R = H 2; R = Me




*exo*-27 28 29 30

The differences in the results with cyclohexenone vs cyclopentenone and in those with the use of *sec*-BuLi vs LTMP in the deprotonation of the intermediate can be rationalized as follows. It is likely that in the case in which cyclohexenone is the reactant the bicyclo[1.1.0]butane intermediate **5a** is formed directly by attack of the carbenoid or derived carbene on the enolate double bond. Thus, the production of a high yield of the expected product **2** (R = H) of protonation of this intermediate is explained. On the other hand, when cyclopentenone is the reactant, the analogous but more strained **24**, if produced at all as an intermediate, is generated in a two-step process (**26** → *exo*-**25** → **24**; see Scheme VI).

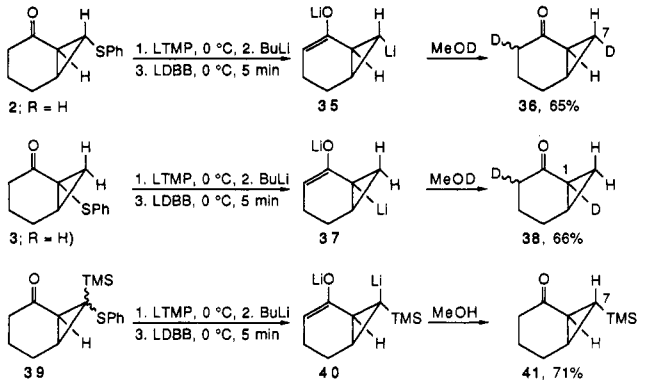
The difference in the effect of the two added bases may lie in the acidity of their conjugate acids. When *sec*-BuLi removes an α′-proton from *endo*- and *exo*-**25**, *endo*- and *exo*-**33** are produced. As the latter are being warmed to 25 °C, the cyclopropyl anions undergo stereochemical equilibration (Scheme VIII). When LTMP removes a proton, the 2,2,6,6-tetramethylpiperidine which is produced could readily donate a proton to the carbanionic sites of **33** to yield the endo and exo isomers of **34**, compounds which would undoubtedly be stereochemically stable.

If this explanation is correct, the presence of LTMP should not cause randomization of the stereochemistry of

(18) The same sort of product was isolated in an impure state when *t*-BuLi was used as the added base. For an analogous attack of a carbanion on a carbene, see: Beak, P.; Worley, J. W. *J. Am. Chem. Soc.* **1972**, *94*, 597.

(19) Mura, A. J., Jr. Ph.D. Thesis, University of Pittsburgh, 1976, p 161.

**Scheme IX**




the cyclopropyl ketone product derived from cyclohexenone since the concerted nature of the production of the bicyclo[1.1.0]butanolate **5a** precludes production of the endo isomer of homoenolate **11**. Indeed, addition of LTMP to the reaction mixture containing dianion **4a** followed by warming to 0 °C for 15 min and quenching resulted in isolation of cyclopropyl ketone **2** (R = H) which had not been stereochemically randomized at the carbon atom bearing the phenylthio group.

**Reductive Lithiation of Cyclopropyl Ketone Enolates.** Now that a novel route to phenylthio-substituted cyclopropyl ketones such as **2** (R = H) and **3** (R = H) is at hand, synthetic uses of these products focusing on the great versatility of the phenylthio group suggest themselves. It was thought after conversion of the ketones to their enolates by deprotonation,[20] the phenylthio group could be reductively lithiated,[21] and the resulting dianions **35** and **37** could be trapped with electrophiles (Scheme IX).

To this end, cyclopropyl ketone **2** (R = H) was treated with LTMP at 0 °C followed by *n*-BuLi to deprotonate the tetramethylpiperidine produced. The enolate was then added to a solution of lithium 4,4′-di-*tert*-butylbiphenylide (LDBB).[22] The result, after quenching with methanol-$d_1$, was isolation of **36** (75% d at C-7) in 65% yield.[23] The exo orientation of the deuterium atom at C-7 was determined by inspection of the $^1$H NMR spectrum of bicyclo[4.1.0]heptan-2-one (**36$_h$**).[24] For the fully protiated cyclopropyl ketone, it was found that HC-7exo was a doublet of doublet of doublets at $\delta$ 0.45. The two large (9.85, 8.04 Hz) vicinal coupling constants were in line with the exo assignment.[17] HC-7endo was a doublet of doublet of doublets at $\delta$ 0.60. The two small (5.14, 5.14 Hz) vicinal coupling constants for this proton were also in line with this assignment.[17] For cyclopropyl ketone **36**, HC-7endo had collapsed into a doublet of doublets and HC-7exo integrated 75% less than the corresponding proton in bicyclo[4.1.0]heptan-2-one. The 25% exo protium at C-7 of cyclopropyl ketone **36** may have arisen from abstraction of solvent protons by the dianion intermediate.

Cyclopropyl ketone **3** (R = H) was treated under the same conditions to give a 66% yield of **38** (91% d at C-1). Cyclopropyl ketone **39**, which was obtained by a different cyclopropanation procedure,[25] was reductively lithiated similarly to achieve a 71% yield of **41** after quenching with methanol. The endo orientation of HC-7 was indicated by the small 6.41 Hz vicinal coupling constants.[17] The dianion **40** derived from cyclopropyl ketone **39** is particularly interesting because of the possibility of its use in the Peterson olefination reaction.[26]

In summary, a new and versatile cyclopropanation procedure for enones, which allows for regio- and stereospecific construction of various phenylthio-substituted cyclopropanes, has been revealed. Some of the cyclopropanation reactions proceed through bicyclo[1.1.0]butan-2-olate derivatives which can be modified in situ, yielding highly functionalized products in which several new C–C bonds have been formed. The cyclopropanation procedure shows signs of being general; we are confident that any enone to which tris(phenylthio)methyllithium adds in a conjugate fashion can be cyclopropanated by the new procedure. Synthetic uses of the (phenylthio)cyclopropyl ketone products are suggested by the conversion of two of these products to dianions by means of reductive lithiation using aromatic radical anions; this process should be general for these types of cyclopropyl ketones.

## Experimental Section

**7-*exo*-(Phenylthio)bicyclo[4.1.0]heptan-2-one (2 (R = H)). Procedure A.** *n*-BuLi (7.2 mL, 1.6 M in hexane, 12 mmol) was added to a solution of tris(phenylthio)methane in 70 mL of dry THF at −78 °C under argon. After the solution had been stirred for 0.5 h, 2-cyclohexenone (1.1 mL, 11 mmol) was added, and the stirring was continued for 2.3 h. *sec*-BuLi (9.0 mL, 1.4 M in cyclohexane, 13 mmol) was added dropwise, resulting in an orange solution. The mixture was stirred at −45 °C for 5 h, followed by quenching with water. The mixture was extracted twice with ether, and the combined ether layer was washed with brine. Drying ($MgSO_4$) and removal of the ether under reduced pressure gave a dark yellow oil, which was subjected to flash chromatography (1000 mL 5%, 1000 mL 20%, 500 mL 40% EtOAc/hexanes); 2.02 g (82%) of **2** (R = H)[27] was isolated (mp 56–59 °C), along with 3-[(phenylthio)methyl]-2-cyclohexenone[1c] (4%). **2** (R = H): $^1$H NMR ($C_6D_6$) $\delta$ 0.70–1.45 (m, 5 H, $H_2C$-4, $H_2C$-5, HC-6), 1.57 (ddd, $J$ = 17.63, 11.56, 6.08 Hz, 1 H, HC-3 axial), 1.83 (ddd, $J$ = 17.63, 4.68, 4.68 Hz, 1 H, HC-3 equatorial), 1.95 (dd, $J$ = 8.01, 3.75 Hz, 1 H, HC-6), 2.34 (dd, $J$ = 3.75, 3.75 Hz, 1 H, HCSPh), 6.89–7.36 (m, 5 H, aromatic). **Procedure B.** *n*-BuLi (0.900 mL, 1.29 M in hexane, 1.16 mmol) was added to a solution of tris(phenylthio)methane (395 mg, 1.16 mmol) in 7 mL of dry THF at −78 °C under argon. After the solution had been stirred for 0.5 h, 2-cyclohexenone (0.112 mL, 1.16 mmol) was added, and stirring was continued for 1 h. *sec*-BuLi (0.911 mL, 1.35 M in cyclohexane, 1.23 mmol) was added dropwise, resulting in an orange solution which was stirred for 1.5 h. The mixture was removed from the cold bath until a complete orange to yellow color change was noted (approx. 7 min). The mixture was then returned to the cold bath and quenched with 0.5 mL of MeOH. Extraction with ether (3 × 20 mL) was performed after addition of the mixture to 20 mL of brine. Drying ($MgSO_4$) and removal of the ether under reduced pressure gave yellow oil, which was subjected to radial chromatography (4 mm rotor; 10%, 30% EtOAc/hexanes); 196 mg (77%) of **2** (R = H) was isolated, along with 3-[(phenylthio)methyl]-2-cyclohexenone[1c] (4%). Recrystallization of **2** (R = H) from hexanes gave white crystals with mp 61–62 °C (lit.[27] mp 62–63 °C).

**1-Methyl-7-*exo*-(phenylthio)bicyclo[4.1.0]heptan-2-one (2 (R = Me)).** *n*-BuLi (0.610 mL, 1.64 M in hexane, 1.00 mmol) was added to a solution of tris(phenylthio)methane (341 mg, 1.00 mmol) in 7 mL of THF at −78 °C under argon. After 0.5 h, 2-methyl-2-cyclohexenone (114 $\mu$L, 1.00 mmol) was added, and the solution was stirred for 11 h. *sec*-BuLi (0.71 mL, 1.4 M in

(20) Unpublished results of M. Bhupathy indicate that reductive lithiation of cyclopropyl ketone **2** (R = H) with 2 equiv of lithium 1-(dimethylamino)naphthalenide results in ring cleavage of the cyclopropyl group to create a dianion. The dianion then unavoidably abstracts a proton from the starting material.

(21) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.*, submitted for publication.

(22) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1983**, *48*, 4705.

(23) The yields of cyclopropyl ketones **36**, **38**, and **41** are unoptimized.

(24) This compound was obtained by quenching of dianion **35** with methanol (see the Experimental Section).

(25) Cohen, T.; Myers, M. *J. Org. Chem.* **1988**, *53*, 457.

(26) Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245.

(27) Cohen, T.; Yu, L.-C. *J. Org. Chem.* **1985**, *50*, 3266.

cyclohexane, 1.0 mmol) was added, resulting in a cloudy orange mixture (the mixture became biphasic and nonstirrable after 1 h), which was kept at −78 °C for 2 h. The reaction was placed in an ice water bath for 15 min, affording a light yellow homogeneous solution which was poured into 20 mL of brine. Extraction with ether (3 × 20 mL), drying ($MgSO_4$), and removal of the ether under reduced pressure gave yellow oil, which was radially chromatographed (4 mm rotor; 10% EtOAc/hexanes). Isolated was 182 mg (78%) of **2** (R = Me) as a colorless oil ($R_f$ in 20% EtOAc/hexanes = 0.38): IR (film) 1683 (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.37 (s, 3 H, Me), 1.60–1.90 (m, 3 H, cyclohexyl), 2.00–2.10 (m, 2 H, cyclohexyl), 2.18 (ddd, $J$ = 17.53, 10.29, 6.77 Hz, 1 H, HC-3 axial), 2.39 (ddd, $J$ = 17.53, 5.27, 5.27 Hz, 1 H, HC-3 equatorial), 2.82 (d, $J$ = 5.33 Hz, 1 H, HCSPh), 7.10–7.32 (m, 5 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 232 (100) ($M^+$), 176 (50), 110 (46), 99 (91), 95 (80); exact mass calcd for $C_{14}H_{16}OS$ 232.0922, found 232.0922.

**1-(Phenylthio)bicyclo[4.1.0]heptan-2-one (3 (R = H)).** To a solution of tricyclic homoenolate **5a** (prepared by procedure B using 1.00 mmol of tris(phenylthio)methane) at −78 °C was added TMSCl (254 μL, 2.00 mmol). The mixture was placed in an ice water bath for 1 h, affording a faintly yellow solution. Boron trifluoride etherate (246 μL, 2.00 mmol) was added all at once, and the mixture was poured into 20 mL of 10% $NaHCO_3$ after 15 min. Extraction with ether (3 × 20 mL), drying ($MgSO_4$), and removal of the ether under reduced pressure gave yellow oil, which was radially chromatographed (4 mm rotor; 15%, 40% EtOAc/hexanes). Isolated was 97 mg (44%) of **3** (R = H) as a yellow oil ($R_f$ in 20% EtOAc/hexanes = 0.30): IR (film) 1695.6 (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.53 (dd, $J$ = 8.41, 6.05 Hz, 1 H, HC-7 exo), 1.60–1.75 (m, 2 H, cyclohexyl), 1.79 (dd, $J$ = 6.05, 6.05 Hz, 1 H, HC-7 endo), 2.05–2.25 (m, 4 H, cyclohexyl), 2.48 (ddd, $J$ = 18.20, 5.34, 3.78 Hz, 1 H, HC-3 equatorial), 7.10–7.30 (m, 5 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 218 (100) ($M^+$), 110 (30), 91 (45), 81 (65), 41 (38); exact mass calcd for $C_{13}H_{14}OS$ 218.0765, found 218.0763.

**1-(Phenylthio)-7-*exo*-methylbicyclo[4.1.0]heptan-2-one (3 (R = Me)).** $BF_3$ etherate (246 μL, 2.00 mmol) was added all at once to a solution of silylated homoenolate **18** (prepared analogously to **17**). After stirring for 11 min, the mixture was poured into 20 mL of 10% $NaHCO_3$ and shaken vigorously. Extraction with ether (3 × 20 mL), drying ($MgSO_4$), and removal of the ether under reduced pressure gave a yellow oil, which was radially chromatographed (4 mm rotor; 10%, 30% EtOAc/hexanes). Isolated were 48 mg (21%) of **2** (R = Me) and 61 mg (26%) of **3** (R = Me) as colorless oils ($R_f$ in 20% EtOAc/hexanes = 0.31). **3** (R = Me): IR (film) 1696.1 (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.37 (d, $J$ = 6.20 Hz, 3 H, Me), 1.68–1.85 (m, 3 H, cyclohexyl), 1.98 (qd, $J$ = 6.20, 6.20 Hz, 1 H, HC-7), 2.05–2.11 (m, 2 H, cyclohexyl), 2.20 (ddd, $J$ = 17.82, 10.51, 7.06 Hz, 1 H, HC-3 axial), 2.47 (ddd, $J$ = 17.82, 5.06, 5.06 Hz, 1 H, HC-3 equatorial), 7.10–7.31 (m, 5 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 232 (70) ($M^+$), 123 (39), 105 (100), 95 (40), 67 (40); exact mass calcd for $C_{14}H_{16}OS$ 232.0922, found 232.0921.

**7-*exo*-(Phenylthio)-7-deuteriobicyclo[4.1.0]heptan-2-one (6a).** To a solution of tricyclic homoenolate **5a** (prepared by procedure A (vide infra) using 2.00 mmol tris(phenylthio)methane) at −45 °C was added MeOD (12-fold excess). Compound **6a** was isolated with 94% $d$ by $^1H$ NMR analysis. The $^1H$ NMR spectrum ($C_6D_6$) was identical with that of **2** (R = H), except that the dd at $\delta$ 2.34 had virtually disappeared and the dd at $\delta$ 1.95 had collapsed into a d ($J$ = 8.01 Hz).

**1-Methyl-7-*exo*-(phenylthio)-7-deuteriobicyclo[4.1.0]heptan-2-one (6b).** 2-Methyl-2-cyclohexenone was subjected to the same conditions as were used to obtain cyclopropyl ketone **2** (R = Me) except quenching was with 0.5 mL of MeOD at −78 °C. Isolated was 172 mg (74%) of **6b**. $^1H$ NMR analysis indicated 94% $d$ at C-7. For full characterization, see preparation of cyclopropyl ketone **2** (R = Me).

**7-*exo*-(Phenylthio)-7-deuterio-1-methyl-4-isopropenylbicyclo[4.1.0]heptan-2-one (6c).** $n$-BuLi (0.610 mL, 1.64 M in hexane 1.00 mmol) was added to a solution of tris(phenylthio)-methane (341 g, 1.00 mmol) in 7 mL of THF at −78 °C under argon. After 0.5 h, (−)-carvone (156 μL, 1.00 mmol) was added dropwise. After 2 h, *sec*-BuLi (0.71 mL, 1.4 M in cyclohexane, 0.99 mmol) was added, and the resulting orange solution was stirred for 2 h. The reaction mixture was placed in an ice water bath for 2 h and quenched with 0.5 mL of MeOD added all at once. The mixture was poured into 20 mL of brine and extracted with ether (3 × 20 mL). Drying ($MgSO_4$) and removal of the ether under reduced pressure gave crude product, which was radially chromatographed (4 mm rotor; 7% EtOAc/hexanes). Isolated was 146 mg (54%) of the title compound as a 4:1 mixture of isomers. The mixture was dissolved in 5 mL of boiling hexanes, and the solution was cooled to room temperature. After several hours, the solution was filtered and the crystals were washed with cold hexanes. The major isomer of compound **6c** (cis relationship between the methyl and isopropenyl groups[27]) (62 mg) was obtained as white crystals (mp 122–3 °C). $^1H$ NMR analysis indicated 77% $d$ at C-7. The mother liquor contained a mixture of major and minor isomers. The minor isomer showed 87% $d$ at C-7.

**6-(*endo* and *exo*),7-*endo*-Bis(phenylthio)-1-(trimethylsiloxy)norpinane (7).** To a solution of tricyclic homoenolate **5a** (prepared by procedure B (vide infra) using 1.50 mmol of tris(phenylthio)methane) at −78 °C was added trimethylsilyl trifluoromethanesulfonate (0.580 mL, 3.00 mmol) dropwise. The resulting orange solution was stirred for 15 min and then warmed to −45 °C for 5 h. At this point, the pale yellow solution was added to 20 mL of 10% aqueous $NaHCO_3$, and the mixture was shaken vigorously followed by ether extraction (3 × 30 mL). During extraction, a white solid was found which was partially soluble in ether but which could not be filtered. Drying ($MgSO_4$) and removal of the ether under reduced pressure gave a yellow oil, which was subjected to radial chromatography (2 mm rotor; 1% EtOAc/hexanes). Isolated was a 210 mg (35%) of 2.8:1 mixture of *endo*- and *exo*-**7** as a yellow oil. Small amounts of isomerically pure *endo*-**7** and *exo*-**7** could be isolated. *endo*-**7**: IR (film) 1167 $cm^{-1}$ (C–O); $^1H$ NMR ($CDCl_3$) $\delta$ 0.17 (s, 9 H, TMS), 1.75–1.95 (m, 4 H, methylene), 2.00–2.10 (m, 2 H, methylene), 2.20–2.80 (m, 1 H, methine), 3.57 (d, $J$ = 6.42 Hz, 2 H, HCSPh), 7.10–7.55 (m, 10 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 400 (7) ($M^+$), 291 (60), 182 (40), 169 (30), 73 (100); exact mass calcd for $C_{22}H_{28}OSiS_2$ 400.1351, found 400.1345. *exo*-**7**: IR (film) 1163 $cm^{-1}$ (C–O); $^1H$ NMR ($CDCl_3$) $\delta$ 0.17 (s, 9 H, TMS), 1.70–2.11 (m, 5 H, methylene), 2.23–2.35 (m, 1 H, methylene), 2.43–2.52 (m, 1 H, methine), 3.83 (s, 1 H, *endo*-HCSPh), 4.33 (d, $J$ = 6.97 Hz, 1 H, *exo*-HCSPh), 7.10–7.42 (m, 10 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 400 (12) ($M^+$), 291 (40), 182 (30), 169 (30), 73 (100); exact mass calcd for $C_{22}H_{28}OSiS_2$ 400.1351, found 400.1350.

**7-(Phenylthio)-8-(hydroxy-*p*-anisylmethyl)-9-oxatricyclo[4.3.0$^{5,7}$]nonan-1-ol (8) and 7-*exo*-(Phenylthio)-3-(hydroxy-*p*-anisylmethyl)bicyclo[4.1.0]heptan-2-one (9).** A solution of tricyclic homoenolate **5a** (prepared by procedure B using 2.00 mmol of tris(phenylthio)methane), at −78 °C, was placed in a −20 °C bath. When the reaction temperature reached −25 °C, *p*-anisaldehyde (0.250 mL, 2.05 mmol) was injected all at once. The solution immediately decolorized, and after 15 min, 1 mL of MeOH was added. The mixture was poured into 50 mL of brine and extracted with ether. Washing of the combined ether layers with brine, drying ($MgSO_4$), and removal of the ether under reduced pressure gave a yellow oil, which was subjected to radial chromatography (4 mm rotor; 20%, 40% EtOAc/hexanes). Isolated was a mixture of cyclopropyl ketone **2** (R = H), *p*-anisaldehyde, others, and a mixture of 3-[(phenylthio)-methyl]-2-cyclohexenone, hemiketal **8**, and alcohol **9** ($R_f$ in 30% EtOAc/hexanes = 0.33). Also isolated was a small amount of what might have been very impure **9** (another diastereomer). The mixture of 3-[(phenylthio)methyl]-2-cyclohexenone, **8**, and **9** was subjected to further radial chromatography (2 mm rotor; 5% EtOAc/50% $CHCl_3$/hexanes) to give 36 mg of impure 3-[(phenylthio)methyl]-2-cyclohexenone, 60 mg (8%) of **9** ($R_f$ in 10% EtOAc/$CHCl_3$ = 0.51), and 255 mg (36%) of **8** ($R_f$ in 10% EtOAc/$CHCl_3$ = 0.40) as a 4:1 mixture of diastereomers. Alcohol **9** was recrystallized from 80% EtOH to give a white solid (mp 145–147 °C). **9**: IR (KBr disk) 3389 (O—H), 1660 (C=O), 1250 (aryl C—O—C) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.35–2.20, (m, 4 H, cyclohexyl), 2.09 (dd, $J$ = 8.01, 3.62 Hz, 1 H, cyclopropyl H $\alpha$ to C=O), 2.11–2.22 (m, 1 H, cyclohexyl), 2.25–2.60 (m, 1 H, cyclohexyl $\alpha$ to C=O), 2.88 (d, $J$ = 5.22 Hz, 1 H, HO), 3.00 (dd, $J$ = 3.62, 3.62 Hz, 1 H, HCSPh), 3.78 (s, 3 H, MeO), 5.36 (dd, $J$ = 5.22, 3.22 Hz, 1 H, *H*COH), 6.82 (m, 9 H, aromatic); MS (70 eV) $m/e$

(rel intensity) 336 (2) ($M^+ - H_2O$), 218 (60), 162 (50), 135 (100), 85 (70); exact mass calcd for $C_{21}H_{20}O_2S$ 336.1184, found 336.1187. Hemiketal **8** was recrystallized from 50% EtOAc/hexanes to give the major diastereomer as a white solid (mp 126–128 °C). **8**: IR ($CCl_4$ slurry) 3372 (O–H), 1250 (aryl C–O–C) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.50–1.95 (m, 7 H, cyclohexyl), 2.13 (d, $J$ = 9.23 Hz, 1 H, cyclopropyl H $\alpha$ to hemiketal), 2.76 (s, 1 H, HO), 3.79 (s, 3 H, MeO), 5.51 (s, 1 H, benzylic), 6.82–7.49 (m, 9 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 354 (30) ($M^+$), 218 (2), 185 (15), 135 (100), 100 (20); exact mass calcd for $C_{21}H_{22}O_3S$ 354.1290, found 354.1290. $^1H$ NMR analysis of **8** indicated the presence of 15% of the open form of the hemiketal: $\delta$ 2.54 (d, $J$ = 8.23 Hz, 1 H, HO), 3.76 (s, 3 H, MeO), 4.94 (d, $J$ = 8.23 Hz, 1 H, benzylic).

**Reaction of 5a with Bases.** To a solution of tricyclic homoenolate **5a** (prepared by either procedure A or B) was added 1 equiv of the base. After stirring for the prescribed time at the prescribed temperature, at least a 20-fold excess of MeOD was added. The mixture was poured into brine and extracted with ether. Drying ($MgSO_4$) followed by removal of the ether under reduced pressure gave crude product, which was subjected to radial chromatography. The extent of deuteration of the cyclopropyl ketone isolated (the yield was usually 10–15% lower than normal) was determined by $^1H$ NMR analysis, assuming a mixture of **14** and **15**.

**7-*exo*-(Phenylthio)-1-(hydroxy-*p*-anisylmethyl)bicyclo[4.1.0]heptan-2-one (16).** To a solution of tricyclic homoenolate **5a** (prepared by procedure B using 1.50 mmol tris(phenylthio)methane) was added *n*-BuLi (0.915 mL, 1.64 M in hexane, 1.50 mmol), followed by stirring at −45 °C for 12 h. The solution was then cooled to −78 °C and *p*-anisaldehyde (0.183 mL, 1.50 mmol) was added. After 15 min, 1 mL of MeOH was added, and the mixture was poured into 20 mL of brine and extracted with ether (3 × 25 mL). Drying ($MgSO_4$) and removal of the ether under reduced pressure gave a yellow oil, which was subjected to radial chromatography (4 mm rotor; 15%, 30% EtOAc/hexanes) to give a fraction which contained cyclopropyl ketone **2** (R = H) and a new compound. This fraction was radially chromatographed (2 mm rotor; 5% EtOAc/30% $CH_2Cl_2$/hexanes) to give 159 mg (49%) of **2** (R = H) and 141 mg (26%) of alcohol **16** (1:1 mixture of diastereomers) as a colorless oil. A small amount of one of the diastereomers ($R_f$ in 20% EtOAc/hexanes = 0.21) could be isolated from the mixture. **16**: IR (film) 3489.7 (O—H), 1676 (C=O), 1248 (C—O—C) $cm^{-1}$; $^1H$ NMR ($C_6D_6$) $\delta$ 0.60–1.45 (m, 6 H, cyclohexyl), 1.72 (ddd, $J$ = 17.60, 4.26, 4.26 Hz, 1 H, $\alpha$ to C=O (equatorial)), 2.49 (d, $J$ = 4.95 Hz, 1 H, HCSPh), 3.31 (s, 3 H, MeO), 4.88 (d, $J$ = 10.45 Hz, 1 H, benzylic), 5.21 (d, $J$ = 10.45 Hz, 1 H, HO), 6.75–7.58 (m, 9 H, aromatic) (addition of $D_2O$ to the sample caused the d at $\delta$ 4.88 to collapse to a s, while the d at $\delta$ 5.21 apparently collapsed into a very broad s); MS (70 eV) $m/e$ (rel intensity) 354 (2) ($M^+$), 336 (2), 229 (100), 216 (80), 137 (90), 77 (70); exact mass calcd for $C_{21}H_{22}O_3S$ 354.1290, found 354.1281. The other diastereomer of **16** showed the following important peaks in the $^1H$ NMR spectrum ($CDCl_3$): $\delta$ 2.75 (d, $J$ = 5.63 Hz, 1 H, HCSPh), 3.77 (s, 3 H, MeO), 5.32 (d, $J$ = 2.81 Hz, 1 H, benzylic).

**1-(Phenylthio)-7-*endo*-deuteriobicyclo[4.1.0]heptan-2-one (19).** To a solution of the silylated tricyclic homoenolate **17** (prepared as above) at 0 °C was added AcOD (1.0 mL, 17 mmol) all at once. The mixture was brought to room temperature for 2 h and was poured into 20 mL of 10% $NaHCO_3$. Workup and chromatography as above gave a 37% yield of **19**. The $^1H$ NMR spectrum ($CDCl_3$) was identical with that of **3** (R = H) except the dd at 1.53 ppm had collapsed into a d ($J$ = 8.41 Hz) and the dd at 1.79 ppm had virtually disappeared.

**1-(Phenylthio)-7-*exo*-methyl-7-deuteriobicyclo[4.1.0]heptan-2-one (20).** The above procedure was followed to obtain the silylated tricyclic homoenolate **18**. At 0 °C, 1 mL of AcOD was added all at once, and the solution was stirred for 2.25 h. Workup proceeded as above to yield 111 mg (48%) of **20** as a colorless oil and a 8% yield of **6b**. $^1H$ NMR analysis showed 80% d at C-7 of **20**.

**6-*exo*-(Phenylthio)bicyclo[3.1.0]hexan-2-one (*exo*-22).** *n*-BuLi (0.667 mL, 1.50 M in hexane, 1.00 mmol) was added to a solution of tris(phenylthio)methane (341 mg, 1.00 mmol) in 7 mL of THF at −78 °C under argon. After 0.5 h, 2-cyclopentenone (84 $\mu$L, 1.0 mmol) was added dropwise. After 1 h, *sec*-BuLi (0.775 mL, 1.29 M in cyclohexane, 1.00 mmol) was added, and the solution was stirred for 1.5 h. *sec*-BuLi (0.775 mL, 1.29 M in cyclohexane, 1.00 mmol) was added, and the solution was stirred for 10 min. The orange solution was raised from the bath for 6.5 min (until the orange color had changed to yellow) and then was placed in a 0 °C bath for 25 min. The light orange reaction mixture was quenched with 1 mL of MeOH and poured into 20 mL of brine. Extraction with ether (3 × 20 mL), drying ($MgSO_4$), and removal of the ether under reduced pressure gave yellow oil, which was radially chromatographed (4 mm rotor; 15%, 50% EtOAc/hexanes). Isolated was 96 mg (47%) of *exo*-**22**,[1c] contaminated with a trace of 3-[bis(phenylthio)methyl]cyclopentanone.

**6-*endo*-(Phenylthio)bicyclo[3.1.0]hexan-2-one (*endo*-22).** 2-Cyclopentenone was subjected to the same conditions as above, except LTMP was used instead of the second equivalent of *sec*-BuLi, the reaction flask was placed directly into a 0 °C bath 10 min after addition of LTMP, and the reaction was quenched 15 min after placement in the 0 °C bath. Isolated were 82 mg (40%; contaminated with a trace of 3-[bis(phenylthio)methyl]-cyclopentanone) of cyclopropyl ketone *exo*-**22** ($R_f$ in 20% EtOAc/hexanes = 0.30) and 27 mg (13%) of *endo*-**22** as a yellow oil ($R_f$ = 0.22). *endo*-**22**: IR (film) 1726 (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.95–2.65 (m, 6 H, cyclopentyl), 2.98 (dd, $J$ = 8.01, 8.01 Hz, 1 H, HCSPh), 7.15–7.60 (m, 5 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 204 (37) ($M^+$), 162 (100), 110 (40), 85 (66), 67 (70); exact mass calcd for $C_{12}H_{12}OS$ 204.0609, found 204.0608.

**3-[(Phenylthio)methyl]-2-cyclopentenone (23).** *n*-BuLi (0.625 mL, 1.6 M in hexane, 1.00 mmol) was added to a solution of tris(phenylthio)methane (341 mg, 1.00 mmol) in 7 mL of dry THF at −78 °C under argon. The solution was stirred for 0.5 h followed by addition of 2-cyclopentenone (86 $\mu$L, 1.0 mmol). After stirring for 1.5 h, *sec*-BuLi (0.714 mL, 1.4 M in cyclohexane, 1.0 mmol) was added dropwise to give an orange solution, which was brought to −45 °C for 3 h; 1 mL of MeOH was added, and the mixture was extracted with ether (3 × 20 mL). The combined ether layer was washed with brine and water. Drying ($MgSO_4$) and removal of the ether under reduced pressure gave a yellow oil, which was subjected to radial chromatography (2 mm rotor; 20% EtOAc/hexanes). Isolated were a trace of *exo*-**22** and 124 mg (61%) of **23**.[1c]

**1-Methyl-6-(phenylthio)bicyclo[3.1.0]hexan-2-one (27) and 2-Methyl-3-[(phenylthio)methyl]-2-cyclopentenone (28).** *n*-BuLi (0.725 mL, 1.38 M in hexane, 1.00 mmol) was added to a solution of tris(phenylthio)methane (341 mg, 1.00 mmol) in 7 mL of THF at −78 °C under argon. After 0.5 h, 2-methyl-2-cyclopentenone (99 $\mu$L, 1.0 mmol) was added dropwise, and the resulting light yellow solution was stirred for 1 h. *sec*-BuLi (0.715 mL, 1.40 M in cyclohexane, 1.00 mmol) was added, and the orange solution was stirred for 3 h. LTMP [prepared by reaction of TMP (169 $\mu$L, 1.00 mmol) with *n*-BuLi (0.725 mL, 1.38 M in hexane, 1.00 mmol) in 2 mL of THF at 0 °C under argon for 0.5 h] was added, and the solution was stirred for 10 min. The reaction was placed in an ice water bath for 15 min and quenched with 1 mL of MeOH. The mixture was poured into 20 mL of brine and extracted with ether (3 × 20 mL). Drying ($MgSO_4$) and removal of the ether under reduced pressure gave a yellow oil, which was radially chromatographed (4 mm rotor; 15% EtOAc/hexanes). Isolated was a mixture of **27** and 2-methyl-3-tris(phenylthio)-methylcyclpentanone and 90 mg (41%) of **28** as a solid (mp 32–34 °C, $R_f$ in 20% EtOAc/hexanes = 0.23). The first fraction was purified by radial chromatography (1 mm rotor; 2% EtOAc/benzene) to afford 55 mg (25%) of **27** (1:1 endo:exo) as a yellow oil ($R_f$ in 20% EtOAc/hexanes = 0.39). **27**: IR (film) 1722 (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.36 (s, 3 H, Me), 1.41 (s, 3 H, Me), 1.87–2.50 (m, 10 H, cyclopentyl), 2.53 (d, $J$ = 3.49 Hz, 1 H, HC-6 endo), 2.80 (d, $J$ = 7.30 Hz, 1 H, HC-6 exo), 7.10–7.35 (m, 10 H, aromatic); MS (70 eV) $m/e$ (rel intensity) (218) ($M^+$), 176 (51), 110 (100), 99 (60), 81 (82); exact mass calcd for $C_{13}H_{14}OS$ 218.0765, found 218.0766. **28**: IR (film) 1699.5 (C=O), 1647 (C=C) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.43 (t, $J$ = 1.93 Hz, 3 H, Me), 2.38 (m, 2 H, $COCH_2CH_2$), 2.62 (m, 2 H, $COCH_2$), 3.80 (s, 3 H, $CH_2SPh$), 7.23–7.39 (m, 5 H, aromatic); MS (70 eV) $m/e$ (rel intensity) 218 (95) ($M^+$), 110 (100), 81 (63), 65 (38), 53 (31); exact mass calcd for $C_{13}H_{14}OS$ 218.0765, found 218.0766.

***trans*-1-(Phenylthio)-2-acetylcyclopropane (29).** *n*-BuLi (0.614 mL, 1.63 M in hexane, 1.00 mmol) was added to a solution

of tris(phenylthio)methane (341 mg, 1.00 mmol) in 7 mL of THF at −78 °C under argon. After 0.5 h, MVK (84 μL, 1.0 mmol) was added, and the solution was stirred for 1 h. *sec*-BuLi (1.35 mL, 1.04 M in cyclohexane, 1.40 mmol) was added, and the solution was stirred for 4 h. LTMP [prepared by reaction of *n*-BuLi (0.614 mL, 1.63 M in hexane, 1.00 mmol) with TMP (169 μL, 1.00 mmol) in 2 mL THF at room temperature under argon for 20 min] was added, and the solution was stirred for 10 min. The reaction was warmed to 0 °C for 15 min and quenched with 1 mL of MeOH followed by addition to 20 mL of brine. Extraction with ether (3 × 20 mL), drying ($MgSO_4$), and removal of the ether under reduced pressure gave a yellow oil, which was radially chromatographed (4 mm rotor; 10% EtOAc/hexanes). Isolated was 75 mg (39%) of **29** as a yellow oil ($R_f$ in 1% EtOAc/$CH_2Cl_2$ = 0.44): IR (film) 1701 (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.29 (ddd, *J* = 8.51, 5.71, 4.66 Hz, 1 H, HC-3 cis), 1.70 (ddd, *J* = 8.16, 5.00, 4.66 Hz, 1 H, HC-3 trans), 2.18 (ddd, *J* = 8.51, 5.00, 3.47 Hz, 1 H, HC-2), 2.30 (s, 3 H, Me), 2.78 (ddd, *J* = 8.16, 5.71, 3.47 Hz, 1 H, HCSPh), 7.15–7.35 (m, 5 H, aromatic); MS (70 eV) *m/e* (rel intensity) 192 (4) ($M^+$), 110 (68), 83 (100), 82 (78), 43 (35); exact mass calcd for $C_{11}H_{12}OS$ 192.0609, found 192.0608.

***trans*-1-(Phenylthio)-2-propionylcyclopropane (30).** Ethyl vinyl ketone was subjected to the same conditions as MVK (see above) to give a 26% yield of **30** as yellowish oily crystals (mp 34–36 °C; $R_f$ in 75% $CH_2Cl_2$/hexanes = 0.45): IR (film) 1699 (C=O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.37 Hz, 3 H, Me), 1.27 (ddd, *J* = 8.45, 5.58, 4.63 Hz, 1 H, HC-3 cis), 1.69 (ddd, *J* = 8.18, 5.02, 4.63 Hz, 1 H, HC-3 trans), 2.17 (ddd, *J* = 8.45, 5.02, 3.44 Hz, 1 H, HC-2), 2.61 (q, *J* = 7.37 Hz, 2 H, $CH_2CO$), 2.77 (ddd, *J* = 8.18, 5.58, 3.44 Hz, 1 H, HCSPh), 7.15–7.35 (m, 5 H, aromatic); MS (70 eV) *m/e* (rel intensity) 206 (4) ($M^+$), 110 (30), 97 (90), 96 (100), 57 (28); exact mass calcd for $C_{12}H_{14}OS$ 206.0765, found 206.0766.4.15.

***trans*-1-(Phenylthio)-1-deuterio-2-(α-deuterioacetyl)-cyclopropane (32).** A solution of the dianion **31** (prepared as above using *sec*-BuLi in place of LTMP) was quenched with 4 equiv of MeOD at −78 °C. Isolated was a 27% yield of **32**. $^1H$ NMR analysis showed 95% D at C-1 and 1.8 protons α′ to the carbonyl group.

**Bicyclo[4.1.0]heptan-2-one ($36_h$).** Cyclopropyl ketone **2** (R = H) (218 mg, 1.00 mmol; solution in 2 mL of THF) was added to a solution of lithium tetramethylpiperidide (LTMP) [prepared by reaction of TMP (177 μL, 1.05 mmol) with *n*-BuLi (0.709 mL, 1.48 M in hexane, 1.05 mmol) at 0 °C under argon for 0.5 h] slowly dropwise at 0 °C under argon. After 0.5 h, *n*-BuLi (0.709 mL, 1.48 M in hexane, 1.05 mmol) was added dropwise, and the solution was stirred for 0.5 h. The yellowish solution was transferred dropwise via syringe to a solution of LDBB [prepared by reaction of Li (13.8 mg, 2.00 mmol) with a solution of 4,4′-di-*tert*-butylbiphenyl (591 mg, 2.21 mmol) in 6 mL of THF at 0 °C under argon for 4 h]. When 3.4 mL out of a total of 4.8 mL had been added to the reducing agent, the LDBB solution changed abruptly from blue-green to reddish-brown. After 5 min, the solution was poured into 20 mL of brine. Extraction with ether (3 × 20 mL), drying ($MgSO_4$), and removal of the ether under reduced pressure gave a yellow oil, which was radially chromatographed (4 mm rotor; 25% EtOAc/hexanes). Isolated was 47 mg (60% based on amount of enolate added) of $\mathbf{36_h}$[28] as a yellow oil ($R_f$ in 20% EtOAc/hexanes = 0.25): $^1H$ NMR ($C_6D_6$) δ 0.45 (ddd, *J* = 9.85, 8.04, 5.17 Hz, 1 H, HC-7 exo), 0.60 (ddd, *J* = 5.14, 5.14, 5.14 Hz, 1 H, HC-7 endo), 0.90–1.15 (m, 3 H, cyclohexyl), 1.20–1.45 (m, 2 H, cyclohexyl), 1.48–1.62 (m, 1 H, HC-1), 1.71 (ddd, *J* = 17.97, 11.11, 6.95 Hz, 1 H, HC-3 axial), 1.95 (ddd, *J* = 17.97, 4.58, 4.58 Hz, 1 H, HC-3 equatorial).

**3,7-*exo*-Dideuteriobicyclo[4.1.0]heptan-2-one (36).** A solution of dianion **35** (prepared as above) was quenched at −78 °C with 0.5 mL of MeOD added all at once. Isolated was a 65% yield of **36**. The $^1H$ NMR spectrum ($C_6D_6$) showed 75% *d* exo at C-7 and 93% *d* at C-3 (4:1 axial–equatorial).

**1,3-Dideuteriobicyclo[4.1.0]heptan-2-one (38).** Cyclopropyl ketone **3** (R = H) was subjected to the same deprotonation/reductive lithiation conditions as **2** (R = H) (see above). Isolated was a 66% yield of **38**. The $^1H$ NMR spectrum ($C_6D_6$) showed 91% *d* at C-1 and virtually complete monodeuteration at C-3.

**7-*exo*-(Trimethylsilyl)bicyclo[4.1.0]heptan-2-one (41).** Cyclopropyl ketone **39** (mixture of exo and endo isomers) was subjected to the same deprotonation/reductive lithiation conditions as **2** (R = H). Isolated was a 71% yield of cyclopropyl ketone **41** as a yellow oil ($R_f$ in 20% EtOAc/hexanes = 0.42): IR (film) 1692 (C=O) $cm^{-1}$; $^1H$ NMR ($C_6D_6$) δ −0.13 (s, 9 H, trimethylsilyl), 0.26 (dd, *J* = 6.41, 6.41 Hz, 1 H, HC-7), 1.05–1.30 (m, 3 H, cyclohexyl), 1.35–1.55 (m, 2 H, cyclohexyl), 1.63 (dd, *J* = 6.41, 6.41 Hz, 1 H, HC-1), 1.76 (ddd, *J* = 17.96, 9.06, 9.06 Hz, 1 H, HC-3 axial), 2.08 (ddd, *J* = 17.96, 4.41, 4.41 Hz, 1 H, HC-3 equatorial); MS (70 eV) *m/e* (rel intensity) 182 (25) ($M^+$), 167 (60), 75 (100), 73 (90), 57 (35); exact mass calcd for $C_{10}H_{18}OSi$ 182.1127, found 182.1127.

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