Cycloaddition of 4b with 2-Bromojuglone Methyl Ether (8a). The cycloaddition was carried out according to the general procedure with 0.80 g (3.0 mmol) of **8a** and was quenched after 40 h. After treatment with fluoride, chromatography, and recrystallization, 0.38 g (31%) of **10b** and 46 mg (3.6%) of **10c** were obtained.

10b: mp 166–168 °C; R_f 0.06; ^{1}H NMR 1.08 (t, 3 H), 1.6–2.0 (m, 3 H), 2.3–2.6 (m, 2 H), 3.1–3.3 (m, 1 H), 3.97 (s, 3 H), 4.05 (s, 3 H), 7.36 (dd, 1 H), 7.71 (s, 3 H), 7.73 (t, 1 H), 7.96 (dd, 1 H), 12.76 (s, 1 H); IR 2950, 1750, 1735, 1660, 1630, 1580 cm^{-1}; UV λ_{max} (relative absorbance) 229 (1.00), 257 (0.68), 285 (0.24), 414 (0.28); HRMS, m/e calcd for $C_{23}H_{20}O_7$ 408.1209, found 408.1205.

10c: mp 197–199 °C; ^{1}H NMR δ 1.08 (t, 3 H), 1.6–2.0 (m, 3 H), 2.3–2.7 (m, 2 H), 3.2–3.4 (m, 1 H), 3.88 (s, 3 H), 3.98 (s, 3 H), 4.04 (s, 3 H), 7.30 (dd, 1 H), 7.72 (t, 3 H), 7.90 (dd, 1 H), 8.40 (s, 1 H); IR 2940, 1750, 1730, 1665, 1580 cm^{-1}; UV λ_{max} (relative absorbance) 221 (1.00), 260 (0.93), 387 (0.21); HRMS, m/e calcd for $C_{24}H_{22}O_7$ 422.1366, found 422.1383.

Cycloaddition of 4b with 3-Bromojuglone (7b). The cycloaddition reaction was carried out according to the general procedure with 0.51 g (2.0 mmol) of **7b** and was quenched after 2 h. After treatment with fluoride, chromatography, and recrystallization, 0.48 g (61%) of **9e** and 0.01 g (1%) of **9f** were obtained.

9e: mp 224–226 °C (lit.[1] mp 221–224 °C, lit.[3] mp 229–230 °C); R_f 0.22; ^{1}H NMR δ 1.13 (t, 3 H), 1.65–2.05 (m, 3 H), 2.35–2.60 (m, 2 H), 3.15–3.3 (m, 1 H), 4.00 (s, 3 H), 7.28 (dd, 1 H), 7.68 (t, 1 H), 7.71 (s, 1 H), 7.79 (dd, 1 H), 11.99 (s, 1 H), 12.37 (s, 1 H); IR 2990, 1730, 1665, 1620, 1590 cm^{-1}; UV λ_{max} ($\epsilon \times 10^{-4}$) 230 (3.9), 258 (2.5), 293 (0.81), 434 (1.2).

9f: mp 175–176 °C; R_f 0.16; ^{1}H NMR δ 1.10 (t, 3 H), 1.5–2.1 (m, 3 H), 2.2–2.8 (m, 2 H), 3.1–3.5 (m, 1 H), 3.88 (s, 3 H), 3.98 (s, 3 H), 7.29 (dd, 1 H), 7.61 (t, 1 H), 7.74 (dd, 1 H), 8.04 (s, 1 H), 12.08 (s, 1 H); IR 2960, 1720, 1660, 1630, 1580 cm^{-1}; UV λ_{max} (relative absorbance) 223 (1.00), 260 (0.94), 283 (0.29), 392 (0.20), 410 (0.21); HRMS, m/e calcd for $C_{23}H_{20}O_7$ 408.1209, found 408.1198.

Cycloaddition of 4b with 2-Bromojuglone Acetate (8c). The cycloaddition was carried out as above with 0.89 g (3.0 mmol) of **8c** and was quenched after 24 h. When the reaction with fluoride was complete, 10 mL of methanol and 1.5 g of K_2CO_3 were added to the THF solution and stirring was continued. After 2 h at room temperature, the solution was decanted from the remaining K_2CO_3, poured into 100 mL of benzene, and neutralized with 1 M HCl. The benzene solution was washed sequentially with bicarbonate (2 × 50 mL) and brine (50 mL), dried, and filtered. The benzene was evaporated, the residue was dissolved in 15 mL of glacial acetic acid and 1 mL of water, and this mixture was stirred overnight and then poured into 100 mL of benzene. The benzene solution was washed sequentially with water (3 × 50 mL), bicarbonate (2 × 50 mL), and brine (50 mL) and dried. Chromatography and recrystallization provided 0.66 g (56%) of **10e**, 0.01 g (1%) of **9e**, and 0.01 g (1%) of **10f**.

10e: mp 160–161 °C; R_f 0.31; ^{1}H NMR δ 1.14 (t, 3 H), 1.65–2.05 (m, 3 H), 2.35–2.6 (m, 2 H), 3.15–3.3 (m, 1 H), 4.01 (s, 3 H), 7.30 (dd, 1 H), 7.66 (t, 1 H), 7.71 (s, 1 H), 7.80 (dd, 1 H), 12.58 (s, 1 H), 12.93 (s, 1 H); IR 2960, 1750, 1630, 1600, 1570 cm^{-1}; UV λ_{max} ($\epsilon \times 10^{-4}$) 231 (4.2), 259 (3.0), 295 (1.0), 436 (1.3).

10f: mp 167–169 °C; R_f 0.16; ^{1}H NMR δ 1.10 (t, 3 H), 1.5–2.1 (m, 3 H), 2.2–2.8 (m, 2 H), 3.1–3.5 (m, 1 H), 3.87 (s, 3 H), 3.99 (s, 3 H), 7.22 (dd, 1 H), 7.63 (t, 1 H), 7.76 (dd, 1 H), 8.06 (s, 1 H), 12.40 (s, 1 H); IR 2950, 1735, 1670, 1635, 1580 cm^{-1}; UV λ_{max} (relative absorbance) 222 (0.97), 259 (1.000), 286 (0.28), 391 (0.21), 404 (0.21); HRMS, m/e calcd for $C_{23}H_{20}O_7$ 408.1209, found 408.1198.

Registry No. (±)-**1a**, 78821-97-3; (±)-**1b**, 80173-04-2; (±)-**1c**, 78821-96-2; (±)-**3**, 95935-63-0; (±)-**4b**, 95935-64-1; **7a**, 69833-10-9; **7b**, 52431-65-9; **7c**, 77197-58-1; **8a**, 69833-09-6; **8c**, 77189-69-6; (±)-**9a**, 95935-65-2; (±)-**9b**, 95935-66-3; (±)-**9c**, 95935-67-4; (±)-**9d**, 95935-68-5; (±)-**9e**, 95374-66-6; (±)-**9f**, 95935-69-6; (±)-**10a**, 95935-70-9; (±)-**10b**, 95935-71-0; (±)-**10c**, 95935-72-1; (±)-**10e**, 95935-73-2; (±)-**10f**, 95935-74-3; (±)-**10g**, 95935-75-4; (±)-**11**, 95935-76-5.

Copper(I)-Induced Reactions of the Adducts Formed from Cyclopropyl Ketones and [Tris(methylthio)methyl]lithium

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Received October 5, 1984

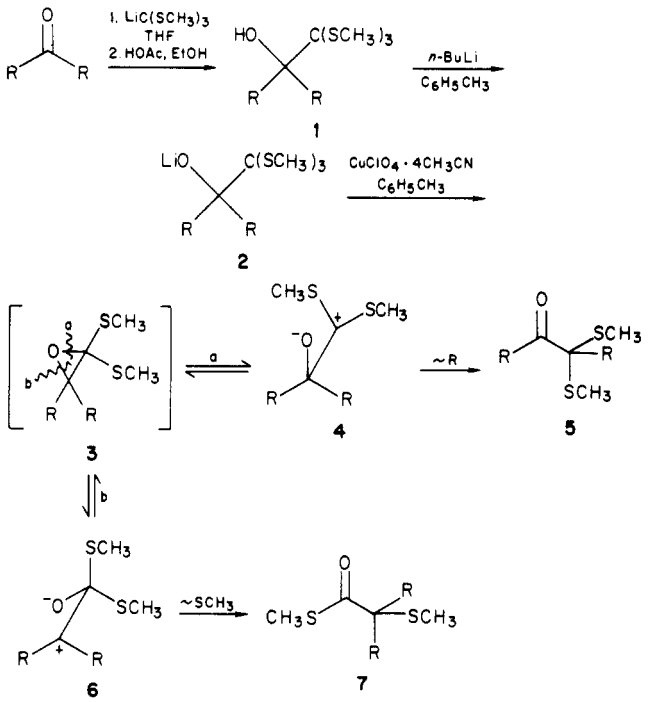
The products obtained from the reaction of $CuClO_4 \cdot 4CH_3CN$ with the adducts formed from acyclic and cyclic cyclopropyl ketones and [tris(methylthio)methyl]lithium can be rationalized via the intervention of epoxide intermediates. Under the reaction conditions, cleavage of the C–O bond in the epoxide occurs in the direction that leads to a cyclopropylcarbinyl carbocation. This bond scission is accompanied by the migration of a thiomethyl group. For example, treatment of the lithium salt of 2-cyclopropyl-2-hydroxy-1,1,1-tris(methylthio)propane with $CuClO_4 \cdot 4CH_3CN$ in toluene gave only *S*-methyl 2-cyclopropyl-2-(methylthio)propanethioate. If geometric restrictions hinder the cyclopropyl substituent from effectively stabilizing an adjacent electron-deficient center, then cleavage of the alternative C–O bond in the epoxide becomes competitive. For example, reaction of $CuClO_4 \cdot 4CH_3CN$ with the adduct formed from nortricyclanone and [tris(methylthio)methyl]lithium provided 4,4-bis(methylthio)tricyclo[3.2.1.0^{2,7}]octan-3-one and *S*-methyl 3-(methylthio)tricyclo[2.2.1.0^{2,6}]heptane-3-carbothioate in yields of 72 and 27%, respectively.

Knapp and his co-workers have reported recently a sequence of reactions for the ring expansion of cyclobutanones and cyclopentanones to the corresponding 1-keto 2-thioketals.[1] According to this procedure, a solution of the ketone in tetrahydrofuran is treated initially with [tris(methylthio)methyl]lithium at −78 °C, and the resulting adduct **1** is isolated (Scheme I). In a subsequent step, a solution of the lithium salt **2** in toluene is prepared from **1** by reacting **1** with *n*-butyllithium at −78 °C. At this point, an excess of tetrakis(acetonitrile)copper(I) perchlorate or tetrafluoroborate is added. Heating this reaction mixture at 75 °C for 2–4 h provides 1-keto 2-thioketal **5**. Knapp has suggested that **2** → **5** may take place via epoxide **3**.[1] Cleavage of bond a in **3** would give **4** and 1,2-alkyl migration in **4** would afford **5**. However,

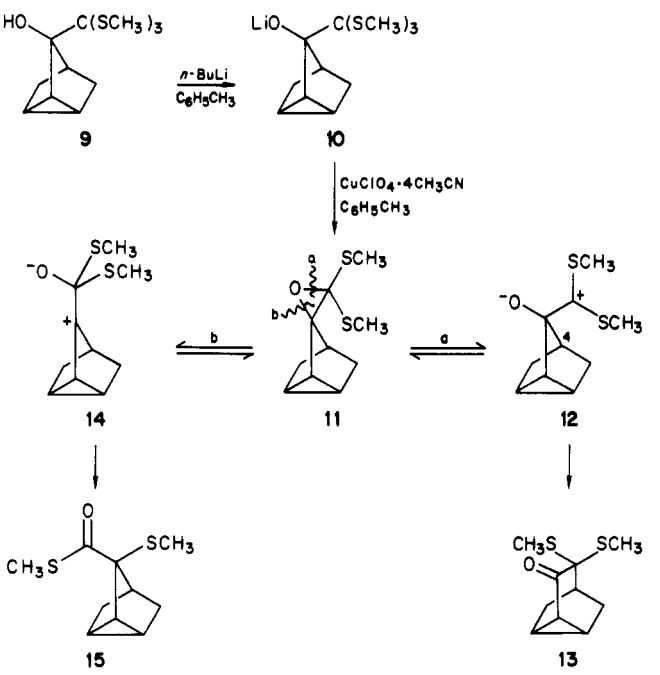
(1) Knapp, S.; Trope, A. F.; Theodore, M. S.; Hirata, N.; Barchi, J. J. *J. Org. Chem.* **1984**, *49*, 608–614.

0022-3263/85/1950-1573$01.50/0

Scheme I



Scheme II

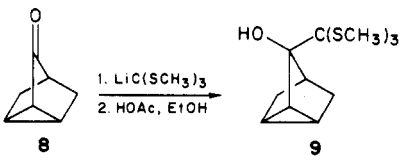


Knapp has pointed out that "the timing of the carbon–sulfur bond cleavage, the formation and collapse of intermediates, and the carbon–carbon migration in this reaction is very much open to question and may differ among various substrates".[1]

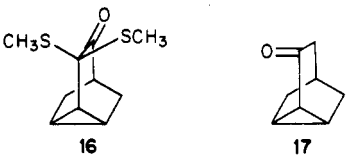
If epoxide **3** does intervene in **2** → **5**, then it is interesting to note that all of the products isolated by the Rutgers group result from exclusive cleavage of bond a in **3**. Of course, this is the expected pathway when both of the R groups are simple alkyl substituents. Scission of bond a in **3** would give zwitterion **4** in which the electron-deficient center would be highly stabilized by the two thiomethyl groups. On the other hand, rupture of bond b in **3** would provide zwitterion **6** in which the carbocation would not be nearly as well stabilized. However, in principle, it should be possible to make the cleavage of bond b in **3** competitive with the scission of bond a by employing an R group which is effective at stabilizing an adjacent electron-deficient center. We now wish to report our observations on the reaction of **2** with $CuClO_4 \cdot 4CH_3CN$ when one of the R groups is cyclopropyl.

Results and Discussion

Since Knapp had reported that his procedure for ring expansion failed for cyclic ketones larger than cyclopentanone,[7] and in order to minimize potential stereochemical complications, the first cyclopropyl ketone that we subjected to the Knapp sequence was nortricyclanone[2] (**8**). Addition of a solution of **8** in tetrahydrofuran to [tris(methylthio)methyl]lithium at −78 °C provided **9** in 74% yield. Sequential treatment of a solution of **9** in



toluene at −78 °C with 1 equiv of *n*-butyllithium and then with 2.2 equiv of $CuClO_4 \cdot 4CH_3CN$, followed by heating the reaction mixture for 1.5 h at room temperature and 2 h at 78 °C, gave 4,4-bis(methylthio)tricyclo[3.2.1.$0^{2,7}$]octan-3-one (**13**) and *S*-methyl 3-(methylthio)tricyclo[2.2.1.$0^{2,6}$]heptane-3-carbothioate (**15**) in yields of 72 and 27%, respectively (Scheme II). The structural assignments for **13** and **15** were straightforward. Due to the presence of a plane of symmetry in **13** and the accidental coincidence of the resonances for the C-2 methine and the enantiotopic C-6 and C-8 methylenes, the ^{13}C NMR spectrum of **13** contains only six signals. In principle, this spectrum also would be reasonable for 3,3-bis(methylthio)tricyclo[3.2.1.$0^{2,7}$]octan-4-one (**16**). However, the



carbonyl absorption of the product occurs at 1692 cm^{-1} and this is more indicative of a conjugated cyclopropyl ketone, i.e., **13**. The structure of **13** was firmly established by reductive desulfurization of **13** with Raney nickel in methanol to give only tricyclo[3.2.1.$0^{2,7}$]octan-3-one[3] (**17**). The structure of **15** follows from its spectroscopic properties. Particularly informative is the carbonyl absorption at 1671 cm^{-1} in **15** which is characteristic of carbothioates.[4] Moreover, the parent ion in the 70 eV-electron-impact mass spectrum of **15** corresponds to the loss of the *S*-methyl carbothioate moiety from **15**. The ^1H and ^{13}C NMR spectra of **15** are completely consistent with the assigned structure.

An epoxide intermediate is especially appealing to account for the formation of both **13** and **15** from **9**. Thus, treatment of **9** with *n*-butyllithium gives **10** (Scheme II). Addition of $CuClO_4 \cdot 4CH_3CN$ to **10** should lead to scission of a carbon–sulfur bond. Intramolecular assistance by the neighboring alkoxide ion in this process would provide

(2) Meinwald, J.; Crandall, J.; Hymans, W. E. *Org. Synth.* **1965**, *45*, 77–79.

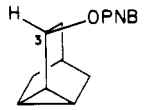
(3) Moore, W. R.; Moser, W. F.; LaPrade, J. E. *J. Org. Chem.* **1963**, *28*, 2200–2205.

(4) Wladislaw, B.; Viertier, H.; Demant, E. B. *J. Chem. Soc. B* **1971**, 565–566.

epoxide 11. Formal cleavage of bond a in 11 would give zwitterion 12 which could ring expand to 13 by migration of C-4. Formal cleavage of bond b in 11 would afford zwitterion 14, and a 1,2-shift of a thiomethyl group in 14 would provide 15. Presumably, zwitterions 12 and 14 also could close to regenerate epoxide 11.

Ketone 13 is the only ring expansion product that is obtained in the Cu(I)-induced reaction of 10. The formation of 13 from 10 shows that migration of the "alkyl" substituent in the reactive species derived from 10 has occurred in marked preference to migration of the cyclopropyl group. This observation stands in striking contrast to reports that homologation of nortricyclanone with diazomethane[5] or by the Tiffeneau–Demjanov procedure[6] proceeds by preferential migration of the cyclopropyl substituent.

According to the general analysis presented in the introduction, the more effective a substituent is in stabilizing an adjacent positive charge, the more competitive the cleavage of bond b in 3 should be when compared with the scission of bond a. This proposal can be tested quite readily for a cyclopropyl group since it is now well established that the stabilization afforded to a carbocation by a cyclopropyl substituent is dependent on geometric factors.[7] Indeed, Grob and his co-workers have shown that the solvolysis of the *p*-nitrobenzoate of 3-homonortricyclanol[8] (18) takes place considerably faster than the



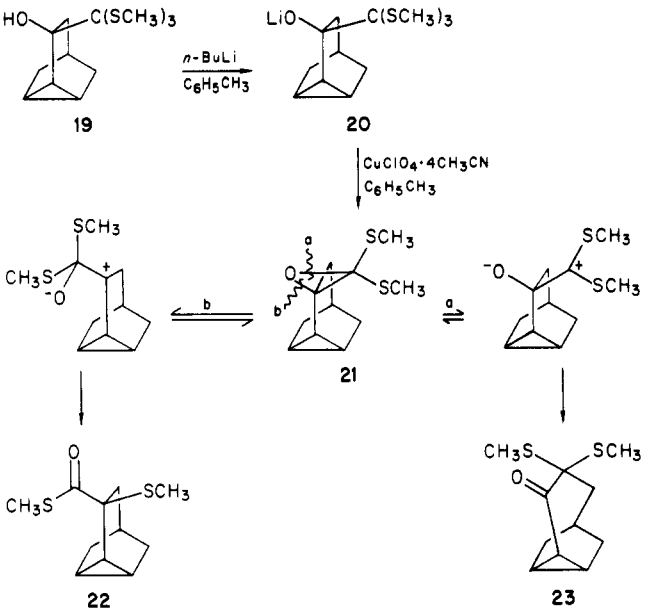
18

corresponding 3-nortricyclyl derivative[9] under comparable conditions. This suggests that the cyclopropyl moiety in homonortricyclane is much better at stabilizing a developing electron-deficient center at C-3 than is the cyclopropyl group in nortricyclane. Consequently, we would predict that if epoxide 21 results from the reaction of 20 with $CuClO_4 \cdot 4CH_3CN$ (Scheme III), then the cleavage of bond b in 21 should be more competitive with the scission of bond a in 21 than was observed for 11. This has proved to be the case.

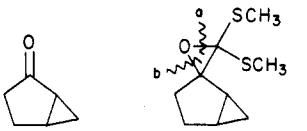
Reaction of 3-homonortricyclanone (17) with [tris(methylthio)methyl]lithium at −78 °C in tetrahydrofuran gave 19 in 70% yield. Subsequent treatment of the lithium salt of 19 with $CuClO_4 \cdot 4CH_3CN$ in toluene provided *S*-methyl 3-(methylthio)tricyclo[3.2.1.$0^{2,7}$]octane-3-carbothioate (22) in 68% yield as the only isolated product. This is the compound that is predicted to result from cleavage of bond b in epoxide 21. It is to be emphasized that ketone 23, the ring homologation product that would be expected to result from scission of bond a in epoxide 21, was not isolated from this reaction nor was it detected in the crude reaction mixture.

It might be argued that it is not fair to expect the ring expansion pathway for 21 to be competitive with the cleavage of bond b in 21 because cyclohexanone cannot be

Scheme III

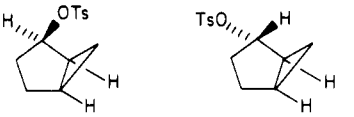


ring expanded by the Knapp procedure.[1] Consequently, we have examined the behavior of the corresponding adduct prepared from bicyclo[3.1.0]hexan-2-one (24). In this



24 25

case, reaction would be expected to occur via epoxide 25. Since cyclopentanone undergoes only ring expansion by the Knapp reaction sequence,[10] the cleavage of bond a in 25 should be possible. However, previous studies on the solvolysis of the tosylates of 2-*endo*- and 2-*exo*-bicyclo[3.1.0]hexanol (26 and 27, respectively) have shown that



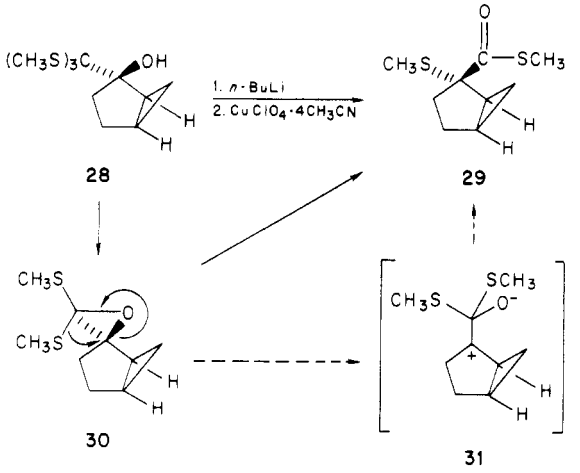
26 27

both of these compounds react approximately 1.7×10^4 times faster than the corresponding nortricyclyl derivative under the same reaction conditions.[11] Thus, in light of the arguments presented in this paper and the observed behavior of 20, it is to be expected that there would be a strong preference for the cleavage of bond b in 25. This pathway would lead to the *S*-methyl carbothioate product.

Treatment of ketone 24[12] with [tris(methylthio)methyl]lithium in tetrahydrofuran at −78 °C provided 28 in 82% yield. The stereochemistry assigned to the substituents in 28 follows from the report that reduction of

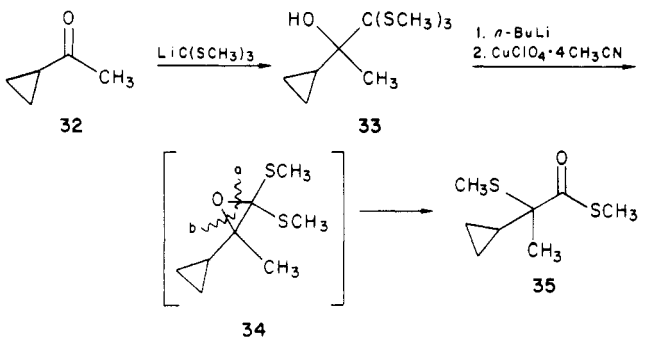
(5) Sauers, R. R.; Beisler, J. A.; Feilich H. *J. Org. Chem.* **1967**, *32*, 569–575.
(6) Lumb, J. T.; Whitham, G. H. *Tetrahedron* **1965**, *21*, 499–501.
(7) (a) de Meijere, A.; Scallner, O.; Weitemeyer, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *84*, 56–57. (b) Rhodes, Y. E.; DiFate, V. G. *J. Am. Chem. Soc.* **1972**, *94*, 7582–7583. (c) Andersen, B.; Schallner, O.; de Meijere, A. *Ibid.* **1975**, *97*, 3521–3522. (d) de Meijere, A.; Schallner, O.; Weitemeyer, C.; Spielmann, W. *Chem. Ber.* **1979**, *112*, 908–935. (e) Harris, J. M.; Moffatt, J. R.; Case, M. G.; Clarke, F. W.; Polley, J. S.; Morgan, T. K., Jr.; Ford, T. M.; Murray, R. K., Jr. *J. Org. Chem.* **1982**, *47*, 2740–2744.
(8) Geisel, M.; Grob, C. A.; Traber, R. P.; Tschudi, W. *Helv. Chim. Acta* **1976**, *59*, 2808–2820.
(9) (a) Roberts, J. D.; Bennett, W.; Armstrong, R. *J. Am. Chem. Soc.* **1950**, *72*, 3329–3333. (b) Winstein, S.; Walborsky, H. M.; Schreiber, K. *Ibid.* **1950**, *72*, 5795. (c) Richey, H. G., Jr.; Buckley, N. C. *Ibid.* **1963**, *85*, 3057–3058.
(10) Knapp, S.; Trope, A. F.; Ornaf, R. M. *Tetrahedron Lett.* **1980**, *21*, 4301–4304.
(11) Private communication of S. Winstein and E. C. Friedrich reported in: Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III "Carbonium Ions", Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26. Also see: Friedrich, E. C.; Saleh, M. A. *Tetrahedron Lett.* **1971**, 1373–1376.
(12) Dauben, W. G.; Berezin, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3449–3452.

24 with lithium aluminum hydride gives a 90:10 mixture of the 2-*syn*- and 2-*anti*-bicyclo[3.1.0]hexanols, respectively.[13] In each case, nucleophilic attack on the syn face of the carbonyl carbon is hindered by the syn hydrogen of the one-carbon bridge. Reaction of the lithium salt of **28** with $CuClO_4 \cdot 4CH_3CN$ in toluene afforded **29** in 78% yield. Both the exclusive formation of the *S*-methyl



carbothioate product in this reaction and the formation of a single stereoisomer can be readily accounted for by the reaction proceeding via epoxide **30**. The migration of the thiomethyl group may take place in concert with the cleavage of the C–O bond in **30**. Consequently, zwitterion **31** may not be a discrete intermediate in **30** → **29**. However, it is apparent that sufficient electron deficiency must develop at C-2 in **30** so that the cyclopropyl group can exert its stabilizing influence.

Finally, it should be noted that the adducts formed from acyclic cyclopropyl ketones and [tris(thiomethyl)-methyl]lithium react with Cu(I) salts in a parallel manner to their more strained counterparts. For example, treatment of cyclopropyl methyl ketone (**32**) with [tris(methylthio)methyl]lithium provided **33** in 78% yield. Subsequent reaction of the lithium salt of **33** with $CuClO_4 \cdot 4CH_3CN$ in toluene gave **35** in 71% yield. Of course, this



is now the "expected" product since the cyclopropyl substituent in epoxide **34** is free to rotate and thus it is able to adopt the geometry that is best suited for the stabilization of the developing carbocation resulting from cleavage of bond b in **34**.

Experimental Section

Infrared spectra were recorded with Perkin-Elmer 180 or Unicam SP1100 spectrophotometers. Proton magnetic resonance spectra were obtained with a Bruker AM 250-MHz spectrometer. Apparent splittings are reported in all cases. Carbon magnetic resonance spectra were recorded with the Bruker instrument at 62.9 MHz. Both the ^1H and ^{13}C NMR spectra were obtained with $CDCl_3$ as the solvent and are referenced to an internal standard of tetramethylsilane. Electron-impact mass spectra were recorded with a Du Pont 21-492B mass spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE.

Tetrakis(acetonitrile)copper(I) Perchlorate (36).[14] Copper(II) perchlorate hexahydrate (34.0 g, 0.11 mol) was dissolved in acetonitrile (150 mL), and the resulting solution was filtered. Purified copper turnings (8.0 g, 0.13 mol) were added to the solution, and the mixture was refluxed for 1.5 h. The resulting mixture was filtered while it was still hot and then concentrated until a white precipitate was observed. After the mixture was cooled, the white crystalline product was collected via suction filtration and dried under nitrogen to give 34.5 g (95% yield) of **36**.

3-[Tris(methylthio)methyl]nortricyclan-3-ol (9). Dropwise addition of *n*-butyllithium (10.25 mL of a 1.36 M solution in hexane, 13.9 mmol) to a stirred solution of tris(methylthio)-methane (2.14 g, 13.9 mmol) in anhydrous tetrahydrofuran (THF, 15 mL) which was maintained at −78 °C under nitrogen resulted in the formation of a white precipitate. After the addition was complete, the reaction mixture was stirred at −78 °C for 0.5 h. At this point, a solution of **8**[2] (1.0 g, 9.26 mmol) in anhydrous THF (5 mL) was added dropwise and the resulting reaction mixture was stirred at −78 °C for 1.5 h. The reaction was quenched then at −78 °C with 1.0 equiv of acetic acid in ethanol (5 mL), and the reaction mixture was allowed to warm to room temperature. The resulting solution was diluted with methylene chloride (50 mL), washed with saturated aqueous ammonium chloride, and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a yellow oil which was Kugelrohr distilled (65–70 °C at 0.3–0.5 mm) to remove the excess tris-(methylthio)methane that was present. The oily residue that was obtained was column chromatographed on silica gel. Elution with 9:1 petroleum ether/ether gave 1.80 g (74% yield) of **9** as an oil: ^1H NMR δ 3.63 (s, 1 H), 2.64 (dd, J = 10.9 and 1.5 Hz, 1 H), 2.29 (s, 9 H), 2.19 (dd, J = 10.2 and 1.5 Hz, 1 H), 2.11 (br s, 1 H), 1.42 (td, J = 5.2 and 1.0 Hz, 1 H), 1.38–1.23 (m, 3 H), 1.13 (td, J = 5.2 and 1.0 Hz, 1 H); ^{13}C NMR δ 91.1 (C-3), 77.0 [$C(SCH_3)_3$], 40.8 (C-4), 33.6 (C-5 or C-7), 32.2 (C-5 or C-7), 20.6 (C-2), 16.3 (C-1 or C-6), 15.2 (SCH_3), 14.5 (C-1 or C-6); IR ν (CCl_4) 3440 (br), 3065, 2985, 2950, 2920, 2875, 1475, 1440, 1420, 1360, 1330, 1295, 1285 cm^{-1}.

4,4-Bis(methylthio)tricyclo[3.2.1.0^{2,7}]octan-3-one (13) and *S*-Methyl 3-(Methylthio)tricyclo[2.2.1.0^{2,6}]heptane-3-carbothioate (15). *n*-Butyllithium (0.59 mL of a 1.36 M solution in hexane, 0.80 mmol) was added slowly to a stirred solution of **9** (200 mg, 0.764 mmol) in anhydrous toluene (40 mL) which was maintained at −78 °C under nitrogen. After the addition was complete, the solution was stirred at −78 °C for 0.5 h, and then **36** (550 mg, 1.68 mmol) was added. At this point, the cooling bath was removed and the resulting mixture was stirred at room temperature for 1.5 h. The mixture was then warmed to 78 °C and stirred an additional 2.0 h. The reaction was then quenched by the addition of aqueous ammonium chloride/ammonium hydroxide (pH ca. 8.0) and cooled to room temperature. The reaction mixture was suction filtered and the filter cake was washed with ether (3 × 20 mL). The combined ether washings were added to the filtrate, and the layers were separated. The organic phase was then washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a yellow oil which was Kugelrohr distilled to give 162 mg (99% yield) of an oil. Analysis of this material by quantitative ^{13}C NMR spectroscopy showed that it consisted of a mixture of **13** and **15** in a ratio of 2.7:1.0, respectively. The products were separated and purified by GLC (10 ft × 0.25 in, QF-1 column, 220 °C) to give **13** [^1H NMR δ 2.50 (d, J = 12.8 Hz, 2 H), 2.20 (t, J = 5.3 Hz, 1 H), 2.07 (s, 6 H), 2.01 (d, J = 7.3 Hz, 2 H), 1.82 (dd, J = 12.7 and 5.1 Hz, 2 H), 1.75 (t, J = 7.5 Hz, 1 H); ^{13}C NMR δ 201.3 (C-3), 66.1 (C-4), 36.2 (C-5), 28.5 (C-2), 28.5 (C-6 and C-8), 23.0 (C-1 and C-7), 11.0 (SCH_3); IR ν (CCl_4) 3050, 2965, 2920, 2870, 1690, 1325, 1285, 1235, 1190 cm^{-1}; exact mass calcd for $C_{10}H_{14}OS_2$

(13) Hanack, M.; Allmendinger, H. *Chem. Ber.* **1964**, *97*, 1669–1672.

(14) We are grateful to Professor H. J. Schugar of Rutgers University for this streamlined procedure for the preparation of $CuClO_4 \cdot 4CH_3CN$.

214.049, found 214.048] and **15** [^{1}H NMR δ 2.32 (s, 3 H, $COSCH_3$), 2.29 (br s, 1 H), 2.17–2.09 (m, 1 H), 2.08 (s, 3 H, SCH_3), 1.55–1.33 (m, 6 H); ^{13}C NMR δ 212.7 (C=O), 68.9 (C-3), 36.3 (C-4), 32.0 (C-5 or C-7), 31.3 (C-5 or C-7), 17.3 (C-2), 13.2 (C-1 or C-6), 12.8 (C-1 or C-6), 12.8 ($COSCH_3$), 11.4 (SCH_3); IR ν (CCl_4) 3060, 2940, 2920, 2870, 1671, 1440, 1295, 1130 cm^{-1}; exact mass calcd for $C_{10}H_{14}OS_2$ 214.049, found 214.049].

Tricyclo[3.2.1.0^{2,7}]octan-3-one (17). A solution of **13** (116 mg, 0.542 mmol) in methanol (5 mL) was added to a suspension of Raney nickel [7.6 g, washed with water until neutral and then washed with methanol (20 × 50 mL)] in methanol (60 mL). The reaction mixture was mechanically stirred and refluxed for 16 h. The reaction mixture was then cooled, filtered, and concentrated at reduced pressure. The resulting residue was dissolved in ether (20 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which was Kugelrohr distilled (50–55 °C at 0.65 mm) to give 58.8 mg (89% yield) of **17**: ^{13}C NMR δ 209.0 (C-3), 44.6 (C-4), 32.0 (C-5), 31.4 (C-6 and C-8), 27.2 (C-2), 23.0 (C-1 and C-7). The ^{13}C NMR spectrum of this material was identical with that of an authentic sample of **17**.[3]

3-[Tris(methylthio)methyl]tricyclo[3.2.1.0^{2,7}]octan-3-ol (19). Treatment of a solution of **17**[3] (200 mg, 1.64 mmol) in anhydrous THF (5 mL) with a solution of [tris(methylthio)-methyl]lithium (2.46 mmol) in anhydrous THF (10 mL) according to the procedure described for **8** → **9** gave 316 mg (70% yield) of **19** as an oil: ^{13}C NMR δ 81.8 (C-3), 81.0 [*C*(SCH_3)$_3$], 41.1 (C-4), 30.1 (C-6 or C-8), 29.1 (C-6 or C-8), 28.0 (C-5), 22.3 (C-2), 19.4 (C-1 or C-7), 16.4 (C-1 or C-7), 15.4 (SCH_3).

***S*-Methyl 3-(Methylthio)tricyclo[3.2.1.0^{2,7}]octane-3-carbothioate (22).** Reaction of a solution of **19** (316 mg, 1.14 mmol) in anhydrous toluene (50 mL) with *n*-butyllithium (1.14 mmol) and then with **36** (820 mg, 2.51 mmol) according to the procedure described for **9** → **13** + **15** provided 177 mg (68% yield) of **22**: ^{1}H NMR δ 2.30 (s, 3 H, $COSCH_3$), 2.27–2.21 (m, 1 H), 2.24 (s, 3 H, SCH_3), 2.02–1.94 (m, 1 H), 1.91 (d, J = 11.8 Hz, 1 H), 1.71–1.52 (m, 6 H), 1.27 (t, J = 7.4 Hz, 1 H); ^{13}C NMR δ 206.6 (C=O), 55.8 (C-3), 38.4 (C-4), 30.1 (C-6 or C-8), 29.7 (C-6 or C-8), 28.7 (C-5), 19.6 (C-2), 18.7 (C-1 or C-7), 17.4 (C-1 or C-7), 12.7 ($COSCH_3$), 12.3 (SCH_3); IR ν (CCl_4) 2980, 2935, 2865, 1675, 1120, 1100 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}OS_2$: C, 57.85; H, 7.06. Found: C, 57.83; H, 7.08.

2-*exo*-[Tris(methylthio)methyl]bicyclo[3.1.0]hexan-2-*endo*-ol (28). Treatment of a solution of **24**[12] (323 mg, 3.36 mmol) in anhydrous THF (5 mL) with a solution of [tris(methylthio)-methyl]lithium (5.04 mmol) in anhydrous THF (10 mL) according to the procedure described for **8** → **9** gave 690 mg (82% yield) of **28** as an oil: ^{13}C NMR δ 92.5 (C-2), 77.7 [*C*(SCH_3)$_3$], 34.9 (C-3), 28.5 (C-4), 26.4 (C-1), 20.1 (C-5), 15.2 (SCH_3), 8.3 (C-6).

***S*-Methyl 2-*exo*-(Methylthio)bicyclo[3.1.0]hexane-2-*endo*-carbothioate (29).** Reaction of a solution of **28** (690 mg, 2.76 mmol) in anhydrous toluene (50 mL) with *n*-butyllithium (2.76 mmol) and then with **36** (1.67 g, 6.0 mmol) according to the procedure described for **9** → **13** + **15** provided 432 mg (78% yield) of **29**: ^{1}H NMR δ 2.31 (s, 3 H, $COSCH_3$), 2.14–2.05 (m, 1 H), 2.07 (s, 3 H, SCH_3), 1.87–1.71 (m, 3 H), 1.58–1.41 (m, 2 H), 0.63–0.39 (m, 2 H); ^{13}C NMR δ 200.8 (C=O), 66.1 (C-2), 27.3 (C-3), 25.0 (C-4), 24.2 (C-1), 17.2 (C-5), 13.0 ($COSCH_3$), 12.1 (SCH_3), 7.2 (C-6); IR ν (CCl_4) 3000, 2935, 2870, 1670 cm^{-1}.

Anal. Calcd for $C_9H_{14}OS_2$: C, 53.43; H, 6.97. Found: C, 53.78; H, 6.95.

2-Cyclopropyl-2-hydroxy-1,1,1-tris(methylthio)propane (33). Treatment of a solution of cyclopropyl methyl ketone (750 mg, 8.93 mmol) in anhydrous THF (5 mL) with a solution of [tris(methylthio)methyl]lithium (13.4 mmol) in anhydrous THF (15 mL) according to the procedure described for **8** → **9** gave 1.67 g (78% yield) of **33** as an oil: ^{13}C NMR δ 80.6 (COH), 80.4 [*C*(SCH_3)$_3$], 24.4 (CH_3), 18.2 (CH), 15.5 (SCH_3), 3.5 (CH_2), 1.5 (CH_2).

***S*-Methyl 2-Cyclopropyl-2-(methylthio)propanethioate (35).** Reaction of a solution of **33** (200 mg, 0.84 mmol) in anhydrous toluene (35 mL) with *n*-butyllithium (0.84 mmol) and then with **36** (640 mg, 1.85 mmol) according to the procedure described for **9** → **13** + **15** provided 114 mg (71% yield) of **35**: ^{1}H NMR δ 2.28 (s, 3 H, $COSCH_3$), 2.08 (s, 3 H, SCH_3), 1.37 – 1.28 (m, 1 H), 1.27 (s, 3 H, CH_3), 0.62–0.55 (m, 4 H); ^{13}C NMR δ 202.3 (C=O), 57.9 (*C*CH_3), 19.3 (CH_3), 18.1 (CH), 12.5 ($COSCH_3$), 12.2 (SCH_3), 2.7 (CH_2), 2.3 (CH_2); IR ν (CCl_4) 3090, 3010, 2990, 2930, 1675 cm^{-1}.

Anal. Calcd for $C_8H_{14}OS_2$: C, 50.48; H, 7.42. Found: C, 50.58; H, 7.43.

Acknowledgment. This work was supported by a grant from the University of Delaware Research Foundation.

Registry No. **8**, 695-05-6; **9**, 95864-09-8; **13**, 95841-59-1; **15**, 95841-60-4; **17**, 39163-38-7; **19**, 95864-10-1; **22**, 95841-61-5; **24**, 4160-49-0; **28**, 95841-62-6; **29**, 95841-63-7; **32**, 765-43-5; **33**, 81123-02-6; **35**, 95841-64-8; **36**, 14057-91-1; copper(II) perchlorate hexahydrate, 15333-31-0; acetonitrile, 75-05-8; tris(methylthio)-methane, 5418-86-0; $LiC(SCH_3)_3$, 39090-54-5.

Organoboranes. 38. A Facile and Highly Efficient Addition of *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes to Aldehydes and Ketones: An Exceptionally Chemoselective Synthesis of Propargylic Alcohols

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Received September 10, 1984

B-1-Alkynyl-9-borabicyclo[3.3.1]nonanes (*B*-1-alkynyl-9-BBN) readily undergo addition to aldehydes and ketones and afford the propargylic alcohols in very high isolated yields. Unlike many other alkynyl metals (RC≡CM, M = Li, Na, K, Mg, Zn, and Al), which are highly reactive toward various functional groups, *B*-alkynyl-9-BBN compounds are exceptionally mild and react with unhindered aldehydes in the presence of ketones with a remarkable selectivity. In addition, *B*-alkynyl-9-BBN compounds can distinguish between less and more sterically hindered aldehydes or ketones. The extraordinary chemospecificity and chemoselectivity of *B*-alkynyl-9-BBN compounds should be valuable in the alkynylation of complex organic molecules containing sensitive functional groups.

The addition of alkynylmetals to aldehydes and ketones to obtain the propargylic alcohols is a highly useful procedure in organic synthesis (eq 1).

Propargylic alcohols are key intermediates in the syn-

0022-3263/85/1950-1577$01.50/0