5-Methyl-1,3-oxathiole 3-Oxide (28).—A solution of 0.5 g (3.06 mmol) of the acetyl-stabilized ylide **7** was stirred with 0.98 g (6 mmol) of anhydrous copper sulfate at 70° for 36 hr. The insoluble salts were filtered off and washed with methylene chloride to give 300 mg (80%) of **28**: ir (film) 1620, 1050–1030 cm^{-1}; nmr ($CDCl_3$) δ 6.05 (s, 1, vinyl), 5.35 (d, 1, J = 12 Hz, CHSO), 4.9 (d, 1, J = 12 Hz, CHSO), 2.2 (s, 3, CH_3). This product displayed a mass spectrum in accord with the assigned structure.

Registry No.—**1**, 38709-75-0; **2**, 38421-38-4; **3**, 38709-77-2; **4**, 38709-78-3; **5**, 38709-79-4; **6**, 38709-80-7; **7**, 38709-81-8; **8**, 38709-82-9; **9**, 38709-83-0; **10**, 38709-84-1; **11**, 38709-85-2; **12**, 38709-87-4; **13**, 38709-88-5; **14**, 38709-89-6; **15-*Z***, 38708-52-0; **15-*E***, 38708-53-1; **16-*Z***, 38708-54-2; **16-*E***, 38708-55-3; **17-*Z***, 38780-33-5; **17-*E***, 38708-56-4; **17-*Z*** tetraphenylborate salt, 38811-40-4; **17-*E*** tetraphenylborate salt, 38704-60-8; **18-*Z***, 38708-57-5; **18-*E***, 38708-58-6; **18-*Z*** tetraphenylborate salt, 38704-61-9; **18-*E*** tetraphenylborate salt, 38704-62-0; **19**, 38709-90-9; **20**, 38709-91-0; **25**, 38709-92-1; **26**, 38709-93-2; **27**, 38709-94-3; **28**, 38709-95-4; **29**, 38709-96-5; phenyl isocyanate, 103-71-9; benzoic anhydride, 93-97-0; benzoyl chloride, 98-88-4; acetic anhydride, 108-24-7; acetyl chloride, 75-36-5; *p*-chlorobenzoyl chloride, 122-01-0; trifluoroacetic anhydride, 407-25-0; phenylacetyl chloride, 103-80-0; methanesulfonyl chloride, 124-63-0; ethyl phenylpropiolate, 2216-94-6; triethyloxonium tetrafluoroborate, 368-39-8; trimethyloxonium tetrafluoroborate, 420-37-1; sodium tetraphenylborate, 143-66-8; (dimethylamino)methyloxosulfonium (3-cyano-3-carbomethoxy-2-phenyl)allylide, 38709-99-8.

Conformationally Rigid Organosulfur Molecules. Derivatives of 4-Thiatricyclo[4.2.1.$0^{3,7}$]nonane and 4-Thiatricyclo[4.3.1.$0^{3,7}$]decane[1]

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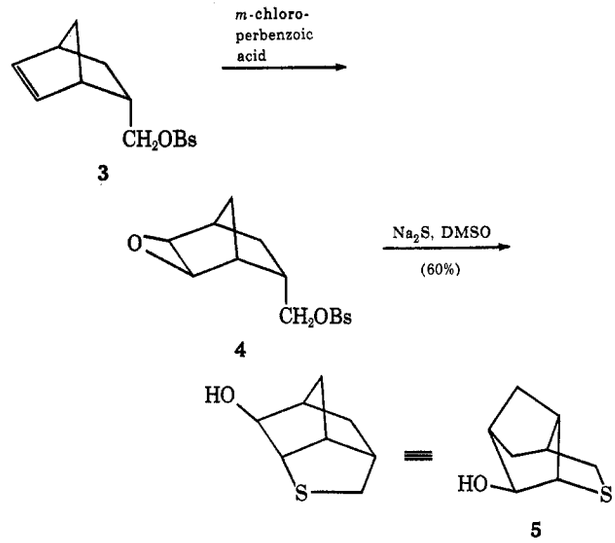
The reaction of sodium sulfide with the epoxy brosylates **4** and **12** provided *exo*-2-hydroxy-4-thiatricyclo[4.2.1.$0^{3,7}$]nonane (**5**) and *exo*-2-hydroxy-4-thiatricyclo[4.3.1.$0^{3,7}$]decane (**13**), respectively. Compound **5** has been oxidized to the corresponding hydroxy sulfone **14**, to sulfoxides **15a** and **15b**, and to keto sulfide **17**. Reduction of the latter compound with sodium borohydride gave the endo hydroxy sulfide **16**. Reduction of **17** by hydrazine and base yielded sulfide **18**. Compound **13** was converted to the keto sulfide **19**, which upon reduction with sodium borohydride gave the epimeric alcohol **20**.

Conformationally rigid organosulfur molecules provide substrates which are useful in studies pertaining to stereochemistry and intramolecular interactions.[2,3] Examples of systems presently available for such studies are sulfides **1**[4] and **2**.[5] We now report several additions, namely *exo*-2-hydroxy-4-thiatricyclo[4.2.1.$0^{3,7}$]nonane (**5**) and *exo*-2-hydroxy-4-thiatricyclo[4.3.1.$0^{3,7}$]decane (**13**) along with several derivatives.

1 **2**

The synthesis of compound **5** is outlined in Scheme I. The reaction of sodium sulfide with epoxy brosylate **4** is thought to lead to intermediate **6** by initial displacement of the brosyl group. This postulate is supported by experiments of Gray and Heitmeier,[6] which demonstrated that exo norbornyl epoxides are resistant to opening on treatment with lithium aluminum hydride. From intermediate **6** C–O cleavage could occur at either C_2 or C_4, leading to either sulfide alcohol **5** or **7**, respectively. Studies of Dreiding models indicated that attack at C_2 would involve more strain than attack at C_4; therefore, *a priori*, sulfide alcohol **5** was expected to be the product of this reaction. In fact, a stable, waxy solid was obtained in 60% yield, which, upon acetylation followed by desulfurization, afforded *exo*-2-acetoxy-5-*endo*-methylbicyclo[2.2.1]heptane (**8**). Sulfide alcohol **7** would have led to *exo*-2-acetoxy-*endo*-6-methylbicyclo[2.2.1]heptane (**9**).

SCHEME I
SYNTHESIS OF *exo*-2-HYDROXY-4-THIATRICYCLO[4.2.1.$0^{3,7}$]NONANE (**5**)[a]



[a] Bs = *p*-bromobenzenesulfonyl.

(1) Part XLI in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

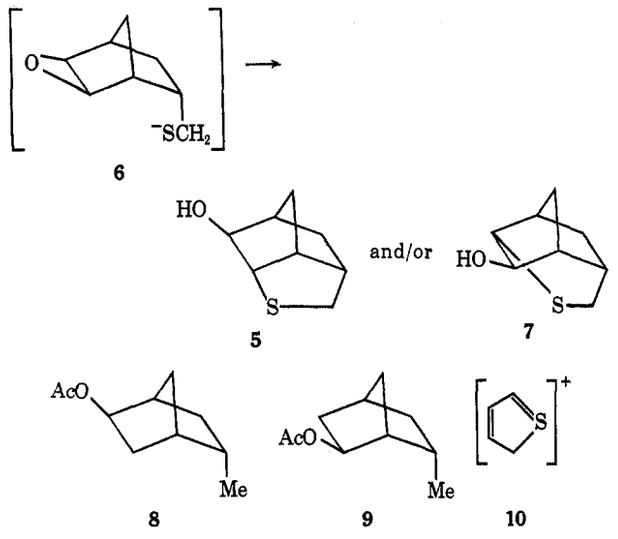
(2) For reviews of this subject, see N. J. Leonard, *Rec. Chem. Progr.*, **17**, 24, (1956); L. N. Ferguson and J. C. Nadi, *J. Chem. Educ.*, **42**, 529 (1965).

(3) L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, **89**, 6659 (1967); L. A. Paquette, G. V. Meehan, and L. D. Wise, *ibid.*, **91**, 3231 (1969).

(4) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1662 (1966).

(5) C. R. Johnson, J. E. Keiser, and J. C. Sharp, *ibid.*, **34**, 860 (1969).

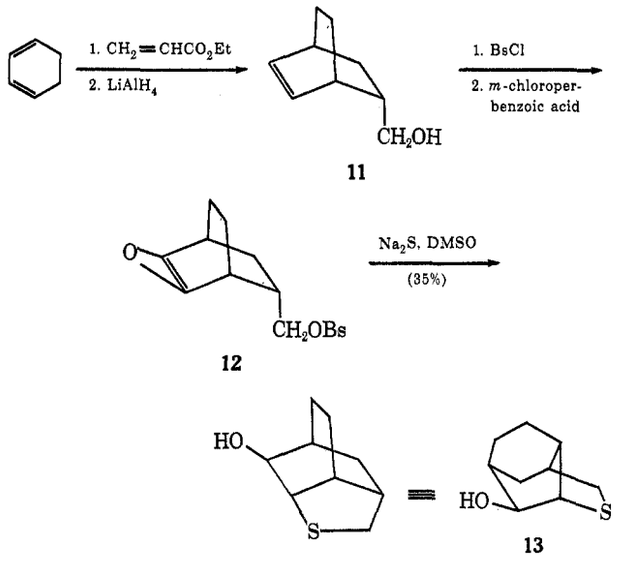
(6) A. Gray and D. Heitmeier, *ibid.*, **34**, 3253 (1969).



Further evidence supporting structure **5** was furnished by mass spectral data. A strong ion (52%) at *m/e* 85 assumed to be **10** indicates that the sulfur is bound in a five-membered ring, whereas the sulfur atom is contained in a six-membered ring, and would not be expected to fragment in such a way that would produce the *m/e* 85 ion.[7]

The preparation of compound **13** is outlined in Scheme II. Treatment of epoxy brosylate **12** with

SCHEME II
PREPARATION OF
exo-2-HYDROXY-4-THIATRICYCLO[4.3.1.0^{3,7}]DECANE (13)



sodium sulfide also furnished a waxy, crystalline solid (35%). The ir and nmr spectra were very similar to those of **5** and the mass spectrum displayed an intense ion (51%) at *m/e* 85. Similar ring closures involving nucleophilic attack by carbon,[8] oxygen,[9a] or nitrogen[9b] produced products corresponding to "frontal" closure.

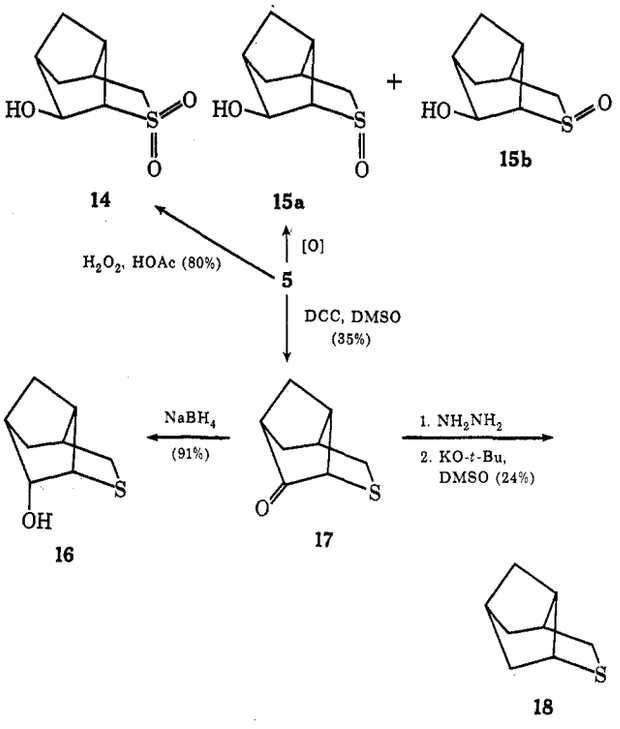
(7) For another example see C. R. Johnson and F. Billman, *J. Org. Chem.*, **36**, 855 (1971).

(8) R. R. Sauers, R. A. Parrent, and S. B. Demale, *J. Amer. Chem. Soc.*, **88**, 2257 (1966); R. R. Sauers, R. M. Hawthorne, and B. I. Dentz, *J. Org. Chem.*, **32**, 4071 (1967).

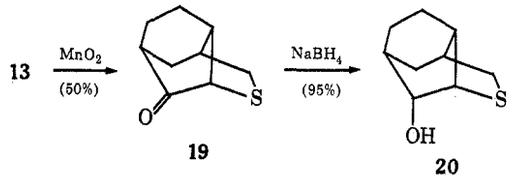
(9) (a) P. O. Hoch, G. Stratton, and J. Coulson, *ibid.*, **34**, 1912 (1969); (b) R. E. Banks, L. E. Birks, and R. N. Haszeldine, *J. Chem. Soc. C*, 201 (1970).

Summaries of chemical transformations achieved starting with the target compounds **5** and **13** are found in Schemes III and IV, respectively.

SCHEME III
TRANSFORMATIONS OF COMPOUND 5



SCHEME IV
TRANSFORMATIONS OF COMPOUND 13



The oxidation of **5** to sulfone **14** was found to proceed readily with hydrogen peroxide in acetic acid. The use of other reagents, such as *m*-chloroperbenzoic acid, ozone, or hydrogen peroxide in acetone, resulted in incomplete oxidation, yielding mixtures of sulfoxides and sulfone. Sulfide alcohol **5** was oxidized to an isomeric mixture of sulfoxide alcohols **15** by treatment with a variety of oxidizing agents (see Experimental Section). Separation of this isomeric mixture into the endo (**15a**) and exo (**15b**) isomers was accomplished by preparative gas chromatography after prior silyation[10] of the hydroxyl group; all attempts to separate these isomers by tlc or elution chromatography failed. The stereochemical assignments were made on the basis of the syn-axial effect,[11] which summarily states that, if a pair of isomeric sulfoxides exists in which a proton is syn-axial with the electron pair in one isomer and with the SO bond in the other isomer, the proton that is syn

(10) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Amer. Chem. Soc.*, **85**, 2497 (1963).

(11) K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 759 (1966); A. B. Foster, J. M. Duxbury, T. D. Inch, and J. M. Webber, *ibid.*, 881 (1967); A. B. Foster, T. D. Inch, H. M. Qadir, and J. M. Webber, *ibid.*, 1086 (1968); C. R. Johnson and W. O. Siegl, *Tetrahedron Lett.*, 1879 (1969).

axial with the SO bond is invariably downfield. Hence, the assignment of stereochemistry of isomeric sulfoxides **15a** and **15b** is possible by observing the chemical shift of the CHOH proton.

The first isomer eluted from glpc, after hydrolysis back to the alcohol sulfoxide, displayed a broadened singlet at δ 4.60 for the CHOH proton. This peak was not affected by sample dilution, eliminating the possible absorption of the hydroxyl proton at this position. The second isomer eluted was found to have the CHOH absorption more upfield and contained under the envelope of ring protons. The chemical shift of the CHOH proton in **5** is δ 3.64. Thus, the first isomer to be eluted is assigned the structure **15a** and the second **15b**. This result could be rationalized by assuming that the exo sulfoxide **15b** would bind to the column more strongly than would **15a** owing to diminished steric hindrance of the exo sulfoxide isomer.[12]

Sulfide ketone **19** was prepared from **13** in moderate yield by treatment with "activated" manganese dioxide[13] in hexane–pentane (1:1, v/v). Conversely, sulfide alcohol **5** was resistant to oxidation by these conditions for reaction times of up to 3 weeks. The problem became one of selective oxidation of the hydroxyl group without concomitant oxidation at sulfur. Jones' reagent and chromium trioxide in pyridine were found to be unsatisfactory. Keto sulfide **17** was prepared in moderate yield (35%), however, by oxidation *via* the Pfitzner–Moffatt method.[14]

Reduction of keto sulfides **17** and **19** furnished exclusively endo-hydroxyl derivatives **16** and **20**. The ir (CCl_4) showed hydroxyl absorption at 3400 cm^{-1} which was not shifted to higher frequency upon dilution. The exo alcohols **5** and **13** each possess two absorptions appearing at 3600 and 3450 cm^{-1}. The 3450-cm^{-1} absorption is found to decrease upon dilution relative to the 3600-cm^{-1} absorption. The alcohol sulfides **16** and **20** are, therefore, assumed to contain fairly strong intramolecular hydrogen bonding to sulfur.

Conversion of the sulfide ketone **17** to sulfide **18** was achieved by reduction *via* the Cram modification of the Wolff–Kishner reduction.[15]

Experimental Section

Melting points were determined with a Thomas-Hoover capillary apparatus and were uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 21 grating spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer. Analytical vapor phase chromatography was performed on an F & M 5750 using 0.25-in. columns. Preparative glpc was conducted on an F & M 776 Prepmaster Jr. Microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind. The mass spectra were measured on Atlas CH4 or AEI MS9 mass spectrometers.

5-(*p*-Bromobenzenesulfonoxymethyl)bicyclo[2.2.1]hept-2-ene (3).—To 50 g (0.40 mol) of a mixture of exo and endo alcohols[16] of 5-(hydroxymethyl)norbornene in an ice bath was added 110 g (0.43 mol) of brosyl chloride. After the solution was stirred at 0° for 0.5 hr the temperature was allowed to rise to room temperature; stirring was continued for 17 hr. The solution was then poured into 2 l. of water previously cooled to 0° and the heterogeneous mixture was stirred for 5 hr. The resulting mixture was extracted with ethyl ether (3 × 250 ml), and the extracts were combined and washed with a 10% aqueous solution of hydrochloric acid (3 × 100 ml) and a saturated sodium bicarbonate solution (3 × 100 ml) and dried ($MgSO_4$). Evaporation of the ether gave a clear oil which crystallized on standing to produce 100 g (73%) of a white solid, mp 62–68°.

Anal. Calcd for $C_{14}H_{15}BrO_3S$: C, 48.98; H, 4.40. Found: C, 49.13; H, 4.62.

6-(*p*-Bromobenzenesulfonoxymethyl)-3-oxatricyclo[3.2.1.0^{2,4}]-octane (4).—A solution of 20 g (0.059 mol) of **3** dissolved in 50 ml of benzene was added dropwise over a 20-min period to 14 g (0.07 mol) of *m*-chloroperbenzoic acid dissolved in 500 ml of benzene and cooled to 0°. The reaction mixture was stirred for 14 hr, during which time the mixture was allowed to warm to room temperature. The reaction mixture was washed with a 10% sodium hydroxide solution and water, and after drying ($MgSO_4$) the solvent was evaporated to give 19.9 g (95.6%) of a white, crystalline solid, mp 89–90°. This material was used without further purification in the following reaction.

***exo*-2-Hydroxy-4-thiatricyclo[4.2.1.0^{3,7}]nonane (5).**—A 2-l. three-necked flask was equipped with a mechanical stirrer and a Y joint to which was connected a condenser and an addition funnel; the remaining neck was fitted with a second addition funnel. Gas inlet–outlet equipment was assembled and the system was purged with nitrogen. Dimethyl sulfoxide (200 ml) was added to the reaction vessel and the solution was heated to 60°. Then 19 g (0.053 mol) of **4** dissolved in 200 ml of dimethyl sulfoxide and 16.8 g (0.07 mol) of sodium sulfide nonahydrate dissolved in dimethyl sulfoxide–water (500:30 ml, v/v) were simultaneously added over a 3-hr period. The reaction was allowed to stir for 24 hr at a temperature between 60 and 70°, after which time the reaction mixture was concentrated to 100 ml, diluted with 500 ml of water, and extracted with methylene chloride (5 × 200 ml), and the combined extracts were washed with water (5 × 200 ml) and dried ($MgSO_4$). Evaporation of the methylene chloride yielded an oily gum which was purified by chromatography over silica gel (0.05–0.20 mm, E. Merck, Darmstadt) using ethyl ether as the eluent. The yield was 4.9 g (60%) of a waxy solid, mp 136–137°. The mass spectrum showed a parent ion at the calculated molecular weight of 156.

Anal. Calcd for $C_8H_{12}OS$: C, 61.49; H, 7.74. Found: C, 61.34; H, 7.64.

***exo*-2-Hydroxy-4-thiatricyclo[4.2.1.0^{3,7}]nonane 4-Oxides (15).**—Oxidation of sulfide **5** with *tert*-butyl hypochlorite[17] in anhydrous methanol at −78° gave a 62% yield of a mixture, mp 182–195°, composed of **15a** (15%) and **15b** (85%). A sample of the mixture was purified for analysis by vacuum sublimation at 110° (0.1 Torr).

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02. Found: C, 56.04; H, 7.23.

Oxidation of **5** with sodium metaperiodate[18] in aqueous methanol at 0° gave 44% of a mixture, mp 188–194°, which contained 34% of **15a** and 66% of **15b**. Oxidation of **5** with 1-chlorobenzotriazole[19] in anhydrous methanol at −78° gave 66% of a solid, mp 188–194°, composed of 33% **15a** and 67% **15b**.

Separation of Sulfoxide Isomers 15a and 15b.—The silyl ethers were prepared according to the method of Sweeley, Bentley, Makita, and Wells.[10] Thus, 0.10 g of isomeric sulfoxide mixture **15** was dissolved in 2 ml of dry pyridine to which was added 0.4 ml of hexamethyldisilazane followed by 0.2 ml of trimethylsilyl chloride. A white precipitate immediately formed and was allowed to settle. Injections were made on an F & M Prepmaster Jr. 776 using a 6 ft × 0.75 in. 15% FFAP column operating at 210° with a nitrogen flow rate of 300 ml/min. The first isomer, the trimethylsilyl ether of **15a**, had a retention time of 9 min; the retention time of the second isomer, the trimethylsilyl ether of **15b**, was 16 min. The compound were washed from their traps with methanol and stirred overnight in an aqueous methanolic solution. Extraction with methylene chloride, drying ($MgSO_4$), and evaporation produced 0.01 g of **15a**, mp 205–208°, and 0.04 g of **15b**, mp 198–200°. The ir spectra of each isomer was undistinguishable from the ir spectrum of the isomeric mixture **15**.

***exo*-2-Hydroxy-4-thiatricyclo[4.2.1.0^{3,7}]nonane 4,4-Dioxide (14).**—To 0.312 g (2 mmol) of **5** dissolved in 25 ml of glacial acetic acid was added 1.36 g (12 mmol) of hydrogen peroxide (30%).

(12) W. O. Siegl and C. R. Johnson, *J. Org. Chem.*, **35**, 3657 (1970).
(13) J. Attenburrow, A. F. B. Camerson, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jones, and T. Walker, *J. Chem. Soc.*, 1094 (1952).
(14) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661 (1965).
(15) D. J. Cram, M. Sayhun, and G. Knox, *ibid.*, **84**, 1734 (1962).
(16) K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).
(17) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).
(18) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).
(19) W. D. Kingsbury and C. R. Johnson, *Chem. Commun.*, 365 (1969).

The reaction mixture was stirred for 12 hr, then diluted with 40 ml of water and extracted with methylene chloride. Evaporation afforded 0.30 g (80%) of a white solid: mp 190–192°; ir ($CHCl_3$) 1300, 1120 cm^{-1} (SO_2).

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.05; H, 6.43. Found: C, 50.85; H, 6.67.

4-Thiatricyclo[4.2.1.0^{3,7}]nonan-2-one (17).—To 0.93 g (4.3 mmol) of dicyclohexylcarbodiimide in a 25-ml round-bottom flask was added a solution of **5** prepared as follows. A 0.174-g (1.1 mmol) portion of 5 was dissolved in 3 ml of dimethyl sulfoxide and added to another solution containing 3 ml of benzene, 0.14 ml of dry pyridine, and 0.06 ml of trifluoroacetic acid. The reaction mixture was stirred for 3 days, after which time 15 ml of benzene was added and the salts were filtered. The benzene solution was thoroughly washed with water and dried ($MgSO_4$). Evaporation of the benzene produced an oil which was purified by chromatography over silica gel (0.05–0.20 mm, E. Merck, Darmstadt) using methylene chloride as the eluent. The resulting white solid, 0.061 g (35%), had mp 128–129°; ir ($CHCl_3$) 1745 cm^{-1} (CO); mass spectrum parent ion at *m/e* 154 (calcd, 154). An analytical sample was prepared by sublimation at 35° (0.05 Torr).

Anal. Calcd for $C_8H_{10}OS$: C, 62.30; H, 6.54. Found: C, 62.21; H, 6.63.

4-Thiatricyclo[4.2.1.0^{3,7}]nonane (18).—To 0.57 g (3.7 mmol) of sulfide ketone **17** was added 10 ml of 85% hydrazine hydrate and the resulting solution was refluxed for 20 hr. Extraction with ethyl ether, drying ($MgSO_4$), and evaporation of the solvent afforded 0.38 g (61.5%) of the hydrazone as a white solid, mp 84–86°. The ir indicated that all of the ketone had reacted. Without further purification this solid was added to a solution of 1.14 g (7.6 mmol) of potassium *tert*-butoxide in 3 ml of dimethyl sulfoxide over a period of 2 hr.[15] Nitrogen gas was evolved immediately and the solution turned reddish orange. After addition was complete the reaction mixture was allowed to stir for an additional 1 hr; 20 ml of water was added; and the resulting solution was extracted with ethyl ether and dried ($MgSO_4$). Evaporation of the ethyl ether produced a yellow oil from which 0.20 g (39%) of a white solid, mp 109–111°, could be isolated by sublimation (40°, 0.5 mm). High-resolution mass spectroscopy showed the molecular weight to be 140.063736 compared to the calculated molecular weight of 140.065957.

6-(*p*-Bromobenzenesulfonoxymethyl)-3-oxatricyclo[3.2.1.0^{2,4}]nonane (12).—To 54 g (0.389 mol) of the alcohol **11**[20,21] dissolved in 200 ml of pyridine and cooled to 0° was added 110 g (0.43 mol) of brosyl chloride. After the solution was stirred at 0° for 30 min the temperature was allowed to reach room temperature and the reaction mixture was stirred for 17 hr. The solution was then poured into 2 l. of water at 0° and stirred for 5 hr. The resulting heterogeneous mixture was extracted with ethyl ether (3 × 250 ml), and the ether extracts were combined and washed with a 10% hydrochloric acid solution (3 × 100 ml) and a saturated sodium bicarbonate solution (3 × 100 ml), and dried ($MgSO_4$). Evaporation of the ethyl ether afforded 124 g (88.5%) of the brosylate as a white solid, mp 76–77°.

This product was epoxidized using the identical conditions as previously outlined for the epoxidation of **3**. Thus from 20 g (0.056 mol) of the starting brosylate **12**, 20.7 g (97%) of a white solid was isolated, mp 85–90°. This product was used in the following reaction without further purification.

***exo*-2-Hydroxy-4-thiatricyclo[4.3.1.0^{3,7}]decane (13).**—The apparatus was arranged as described in the preparation of **5**. Thus 20.7 g (0.0554 mol) of epoxy brosylate **12** dissolved in 150 ml of dimethyl sulfoxide was treated with 18.0 g (0.075 mol) of sodium sulfide nonahydrate dissolved in dimethyl sulfoxide–water (200:50, v/v) to give 3.0 g (31.6%) of a white solid, mp 165–168°. Sublimation at 110° (0.1 mm) produced an analytical sample. The mass spectrum had a parent ion at *m/e* 170 which corresponds to the calculated molecular weight.

Anal. Calcd for $C_9H_{14}OS$: C, 63.48; H, 8.29. Found: C, 63.30; H, 8.30.

4-Thiatricyclo[4.3.1.0^{3,7}]decan-2-one (19).—To 0.3 g (1.75 mmol) of **13** dissolved in 100 ml of a 1:1 (v/v) pentane–hexane solution was added 6.0 g "active" manganese dioxide[18] and this mixture was allowed to stir for 1 week. The manganese dioxide was then filtered and the hexane–pentane was evaporated, leaving 0.14 g (50%) of a white solid, mp 110–112°, ir ($CHCl_3$) 1710 cm^{-1} (CO). Sublimation (110°, 0.5 Torr) produced an analytical sample. The mass spectrum showed a parent ion at *m/e* 168 (calcd 168).

Anal. Calcd for $C_9H_{12}OS$: C, 64.35; H, 7.19. Found: C, 64.53; H, 7.36.

Sodium Borohydride Reductions of Ketones 17 and 19.—To 1.0 mmol of ketone dissolved in 20 ml of anhydrous methanol cooled to 0° was added 0.038 g (1.0 mmol) of sodium borohydride. Stirring for 12 hr followed by evaporation of the methanol gave a solid which was stirred in methylene chloride for 1 hr and filtered. Evaporation of the methylene chloride afforded a white solid in each case. Compound **16**, mp 181–184°, was produced in 91% yield; compound **20**, mp 171–173°, was obtained in 95% yield.

***exo*-2-Acetoxy-4-thiatricyclo[4.2.1.0^{3,7}]nonane.**—To 0.312 g (2.0 mmol) of **5** dissolved in 6 ml of benzene, 4 ml of hexane, and 0.2 ml of pyridine at 0° was added 0.180 ml (2.7 mmol) of acetyl chloride. This solution was stirred at 0° for 5 hr and then placed in the refrigerator (−5°) overnight. The mixture was then poured over ice–water and stirred for 2 hr. The aqueous solution was extracted with ethyl ether (3 × 50 ml), and the ether extracts were combined and washed with a 10% aqueous hydrochloric acid solution (3 × 20 ml), a saturated aqueous sodium hydrogen carbonate solution (3 × 50 ml), and water (3 × 50 ml) and dried ($MgSO_4$). Evaporation of the ether furnished 0.28 g (90%) of a clear liquid, ir (film) 1740, 1240–1220, 1020, 1000 cm^{-1}. The acetate was used without further purification in the next step.

Desulfurization of Acetate of 5.—To the acetate prepared above was added 10 ml of absolute ethyl alcohol and *ca.* 3 g (one teaspoon) of 5-day-old Raney nickel (W-2). This mixture was stirred for 15 hr and filtered. Evaporation of the ethanol gave 0.12 g (43% based on crude acetate) of a clear liquid. The ir of this liquid is identical with that of authentic *exo*-2-acetoxy-*endo*-5-methylbicyclo[2.2.1]heptane (**8**).[22]

Registry No.—**3**, 4802-32-8; **4**, 38858-17-2; **5**, 38906-64-8; **5** acetate, 38974-09-3; **11**, 15181-03-0; **12**, 38858-19-4; **13**, 38858-20-7; **14**, 38858-21-8; **15a**, 38858-22-9; **15b**, 38858-23-0; **16**, 38858-24-1; **17**, 38868-12-1; **18**, 29625-41-0; **19**, 38868-14-3; **20**, 38858-25-2; *exo*-5-(hydroxymethyl)-2-norbornene, 13360-81-1; *endo*-5-(hydroxymethyl)-2-norbornene, 15507-06-9; *m*-chloroperbenzoic acid, 937-14-4.

(20) N. Nomura, P. v. R. Schleyer, and A. A. Arz, *J. Amer. Chem. Soc.*, **89**, 3657 (1967).

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