(Na$_2$SO$_4$), and evaporated. The remaining oil was chromatographed on 180 g of silicic acid. A mixture of hexane and AcOEt (3:1) eluted 0.86 g of recovered alcohol **16** and 2.84 g (72%, based on recovered starting material) of alcohol **20**, mp 54–56°. A sample was recrystallized from benzene–hexane to give colorless needles: mp 58–60°; $[\alpha]_D$ -124° (c 1.82); uv 234 mμ (ε 20,700); ir 3600, 3440, 2200, 1670 cm^{-1}; nmr 1.16 (d, 6, J = 6.5 Hz), 1.76 (s broad, 3), 2.0–3.5 (m, 6), 4.08 (s, 3) (1 H disappears on exchange with D$_2$O), 5.55 (m, 1), 6.8 (broad, 1) ppm.

Anal. Calcd for C$_{15}$H$_{20}$O$_2$: C, 77.55; H, 8.68. Found: C, 77.72; H, 8.79.

Bilobanone (1).—A mixture of 2.63 g of alcohol **20**, 50 ml of monoglyme, 40 ml of water, 0.5 ml of 0.1 N H$_2$SO$_4$, and 500 mg of HgSO$_4$ was stirred and refluxed under nitrogen for 8 hr. Working up as described above gave a yellow oil which was transferred to a distillation flask. Upon heating in a 150° oil bath for 5 min (2 mm), followed by distillation at 120° (0.1 mm), 1.60 g of a mixture of products was obtained. Vpc analysis indicated the presence of approximately 56% bilobanone (**1**), 23% starting material **20**, 3% ketone **23**, and 8% phenol **22**. For separation on a preparative scale the mixture was chromatographed on 60 g of silicic acid. Elution with hexane and 1% AcOEt gave 950 mg of bilobanone, containing *ca.* 5% of ketone **23**. Further purification was achieved by vpc collection, followed by distillation. Pure bilobanone (**1**) had bp 102° (0.05 mm); $[\alpha]_D$ $+32^\circ$ (c 4.85); uv 224 mμ (ε 13,600); ir 1670, 1610, 1550 cm^{-1}; nmr 0.94 (d, 6, J = 6.5 Hz), 1.75 (d, 3, J = 2 Hz), 2.8–3.3 (m, 8), 5.88 (s, 1), 6.67 (broad, 1), 7.08 (s, 1) ppm; ms 232 (parent peak), 148 (base peak). Synthetic and natural bilobanone were indistinguishable on two different vapor phase chromatographic columns and had identical R_f values on thin layer chromatography.

Anal. Calcd for C$_{15}$H$_{20}$O$_2$: C, 77.55; H, 8.68. Found: C, 77.64; H, 8.78.

The semicarbazone had mp 143–145° pure and admixed with an authentic sample.

Ketone 23.—This substance obtained from above vpc collection had ir absorptions at 1670, 1600, 1550 cm^{-1}; uv 229 mμ (ε 19,800); nmr 1.22 (d, 6, J = 6.5 Hz), 1.75 (d, 3, J = 2 Hz), 2.2–3.5 (m, 6), AB system centered at 5.78 (2 H), 6.63 (broad, 1) ppm; ms 218 (parent peak), 121 (base peak).

Phenol 22.—This compound (135 mg) was eluted with 5% AcOEt in hexane from the chromatogram described above: ir 3590, 3320, 1630, 1610, 1570 (broad), 870 cm^{-1}; uv 210 mμ (ε 41,300), 255 (8200), 292 (3600); nmr 0.92 (d, 6, J = 6.5 Hz), 1.94 (m, 1), 2.20 (s, 3), 2.46 (d, 2, J = 6.5 Hz), 5.23 (broad, 1) (disappears on exchange with D$_2$O), 6.10 (s, 1), 6.72 (s broad, 1), AB system centered at 6.94 (2 H, signals at 6.89 and 6.75 further split into doublets, J = 1.5 Hz), 7.39 (s, 1) ppm; ms 230 (parent peak), 187 (base peak). This substance is exceptionally air sensitive and its solutions in organic solvents turn green rapidly.

Registry No.—**1**, 17015-33-7; **5**, 19191-07-2; **7**, 19202-67-6; **16**, 19191-08-3; **17**, 19191-09-4; **20**, 19202-68-7; **22**, 19185-78-5; **23**, 19185-79-6.

Acknowledgment.—The authors wish to thank Firmenich et Cie, Geneva, for generous financial support.

Synthesis of 2-Thiabicyclo[2.2.1]heptane Derivatives[1a–c]

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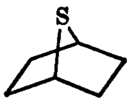
The addition of thiophosgene to cyclopentadiene provided 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene (**5**) which was converted into the more stable sulfone **7** by oxidation with *m*-chloroperbenzoic acid. Catalytic hydrogenation of the dichloro sulfone **7** resulted in the formation of the saturated monochloro sulfone **13** which was subsequently reduced to the parent sulfide **12** with lithium aluminum hydride. Reduction of sulfone **7** with chromous ion in aqueous acetone followed by lithium aluminum hydride provided 2-thiabicyclo[2.2.1]hept-5-ene (**10**). The alcohol, *exo*-5-hydroxy-2-thiabicyclo[2.2.1]heptane, was prepared by a multistep sequence from 4-hydroxycyclopentene.

The preparation of conformationally rigid molecules which include heteroatoms in the skeleton is of value for a variety of reasons including stereochemical studies and studies of intramolecular interactions.[2,3] Polycyclic compounds provide examples of conformationally fixed systems; however, only a few such simple compounds which incorporate sulfur in the skeleton are known. The most recent examples are certain caged ketosulfides synthesized by Paquette and Wise.[3] Thiabicycloheptanes would be of interest for stereochemical studies, but only a few such compounds (*e.g.*, **1** and **2**) are known.[4]



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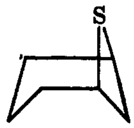

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We wish to report convenient syntheses of 2-thiabicyclo[2.2.1]heptane (**12**) and 2-thiabicyclo[2.2.1]hept-5-ene (**10**) and certain of their derivatives *via* the reaction sequences outline in Scheme I. The Diels–Alder reaction between cyclopentadiene and thiophosgene, first reported by Middleton,[5] was found to proceed readily to furnish dichlorosulfide **5** in very good yield. This compound is quite unstable; it decomposes to a black tar unless stored at Dry Ice temperatures and solvolyzes rapidly in hydroxylic solvents. The extreme reactivity of **5** places severe restrictions on the conditions which can be employed to effect synthetic transformations on the molecule; *i.e.*, moderate temperatures and nonhydroxylic solvents must be

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(1) (a) Part XIII in the series Chemistry of Sulfoxides and Related Compounds. (b) Part XII: C. R. Johnson and J. J. Rigau, *J. Org. Chem.*, **33**, 4340 (1968). (c) We gratefully acknowledge support of this work by the National Science Foundation (GP 5944). (d) Alfred P. Sloan Reasearch Fellow, 1965–1968.

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

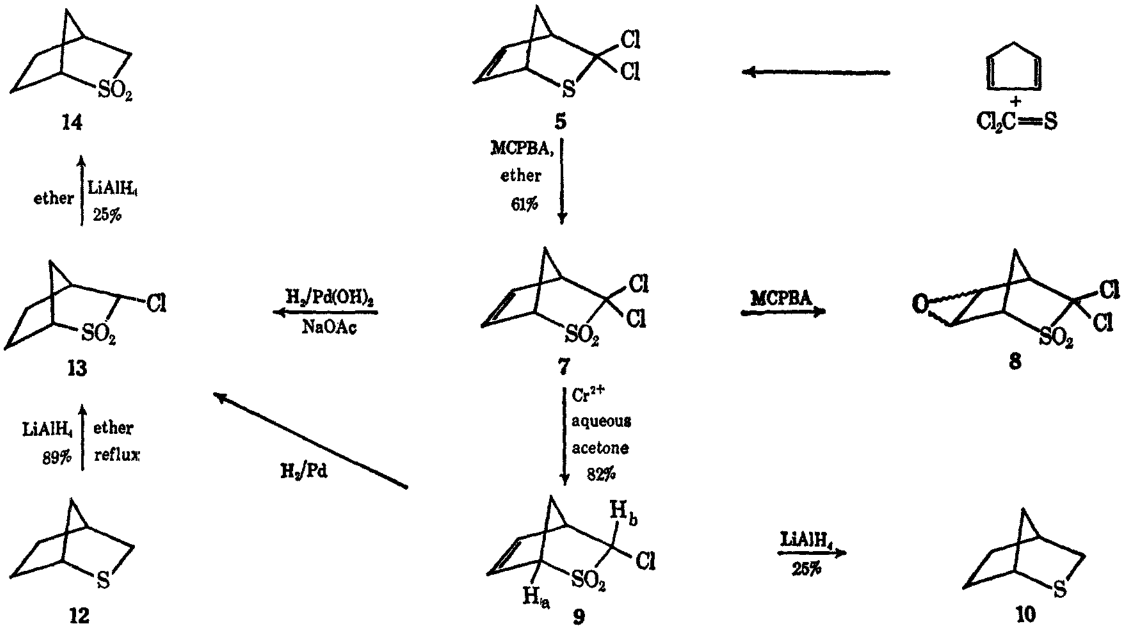
(3) L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, **89**, 6659 (1967).

(4) (a) S. F Birch, R. A. Dean and N. J. Hunter, *J. Org. Chem.*, **23**, 1026 (1958); (b) E. J. Corey and E. Block, *ibid.*, **31**, 1663 (1966).

(5) W. J. Middleton, *ibid.*, **30**, 1390 (1965).

SCHEME I

SYNTHESIS OF 2-THIABICYCLO[2.2.1]HEPTANES[a]

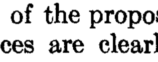


[a] MCPBA refers to *m*-chloroperbenzoic acid.

used. Accordingly, it was oxidized to the corresponding sulfone (**7**), a stable crystalline solid. This sulfone is inert; it was recovered unchanged from treatment with lithium aluminum hydride in refluxing tetrahydrofuran. The olefinic linkage is resistant to attack by electrophiles. The compound was recovered from treatment with bromine and iron in refluxing carbon tetrachloride and from treatment with trifluoroacetic acid. In order to prepare epoxide **8** with *m*-chloroperbenzoic acid, it was necessary to use refluxing benzene instead of the milder conditions more commonly employed for internal olefins.[6]

A solution of chromous ion[7] in aqueous acetone converted the dichloro sulfone into a white crystalline solid to which we have assigned the structure *endo*-3-chloro-2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide (**9**). The assignment of structure was based on the following nmr data. The 60-MHz spectrum of sulfone **7** shows broad, unresolved multiplets centered at δ 3.55 and 4.26, attributed to the bridgehead protons, and absorptions at 6.45 (vinyl H) and 2.52 (bridge H). Treatment of **7** with potassium hydroxide in dioxane–deuterium oxide led to a marked decrease in the intensity of the absorption centered at δ 4.26 which is therefore assigned to the bridgehead proton α to the sulfone function. Sulfone **9** shows a broad multiplet centered at δ 4.08 (H_a in Scheme I), a doublet at δ 4.71 (J = 4.0 Hz, assigned to H_b), another multiplet at 3.61 (H_c) and absorption resulting from the bridge and vinyl hydrogens. This assignment was confirmed by deuterium exchange. Consideration of reported[8,9] analyses of the nmr spectra of similar carbocyclic systems leads to the conclusions that (a) if H_b is *exo*, the doublet pattern results from coupling with the bridgehead proton, H_c, and (b) if H_b is *endo*, it is coupled with the *anti* bridge proton. The stereochemical question was resolved through the use of nuclear magnetic double resonance.[10] Irradiation of the multiplet at δ 3.61 (H_c) causes the doublet at δ 4.71 to collapse to a singlet. Irradiation of the bridge protons caused no change in the pattern at δ 4.71. The proton α to chlorine is thus clearly established as being coupled to the bridgehead proton and is therefore *exo*.

Attempts to reduce **9** to the chlorine-free sulfone **11** using the chromium (II)–ethanolamine method of Kochi[7] were unsuccessful. Reduction of sulfone **9** with a large excess of lithium aluminum hydride in ether produced a waxy, odoriferous, volatile solid which was identified by infrared, mass and nmr spectroscopy as well as elemental analysis as 2-thiabicyclo[2.2.1]hept-5-ene (**10**). The nmr spectrum provided particularly convincing evidence of the proposed structure. All of the proton resonances are clearly separated and the bridgehead and bridge hydrogens are readily identified by their shape and peak integrations. The well-known phenomenon of *exo*-H resonance occurring at lower field than *endo* H[8,9] lead to the assignment of a four-peak multiplet centered at δ 3.11 to the *exo* H α to sulfur and a doublet centered at δ 2.13 to the *endo* H. The doublet arises from geminal coupling with the *exo* H and is of the usual magnitude (*ca.* 9 Hz) for such systems.



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[6] Such expoxidations are usually conducted in chlorinated hydrocarbons at room temperature or below. For example, see A. P. Gray and D. E. Heitmeier, *J. Org. Chem.*, **30**, 1226 (1965).

[7] J. K. Kochi and P. E. Macadlo, *J. Amer. Chem. Soc.*, **88**, 4094 (1966), and references therein. Use of the reagent was stimulated by a discussion with Professor Kochi for which we thank him.

[8] P. M. Subramanian, M. R. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965)

[9] P. Laszlo and P. R. von Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

[10] We wish to thank Professor Daniel Pasto of the University of Notre Dame for the double resonance spectra.

Coupling with the *anti* bridge proton is so small as to be barely observable. The *exo* H α to sulfur is coupled to both the bridgehead hydrogen and the *endo* H.

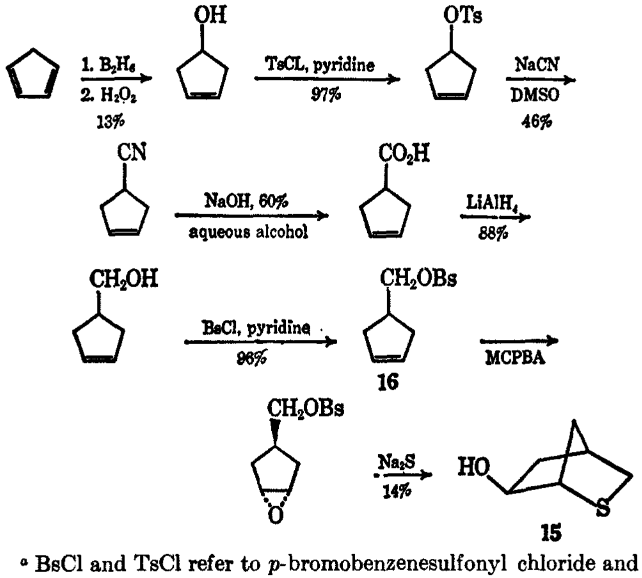
Sulfide **10** was found to be unstable. Purified samples (preparative vpc) polymerize within several days when stored at 10°. Attempts at alkylation on sulfur with trimethyloxonium tetrafluoroborate as well as attempts to prepare a mercuric chloride adduct led to black tars.

The saturated sulfide, 2-thiabicyclo[2.2.1]heptane (**12**), was prepared from **7** *via* a two-step sequence. Catalytic hydrogenation using 20% palladium hydroxide on carbon produced monochloro sulfone **13**. The stereochemistry of the chlorine was assigned as *endo*, since **13** could also be prepared by hydrogenation of **9**. Brief treatment of **13** with lithium aluminum hydride in ether produced 2-thiabicyclo[2.2.1]heptane 2,2-dioxide (**14**). Sulfone **14** could also be prepared by treatment of **13** with excess lithium dispersion in hexane followed by hydrolysis. Extended treatment with lithium aluminum hydride in refluxing ether provided sulfide **12** in 89% yield. Sulfide **12** was easily converted into a sulfonium salt using methyl iodide in ether.

An earlier investigation of alternate synthetic routes to 2-thiabicyclo[2.2.1]heptane resulted in the preparation of other interesting members of this series. *exo*-6-Hydroxy-2-thiabicyclo[2.2.1]heptane (**15**) was obtained *via* the route shown in Scheme II.

Scheme II

Synthesis of *exo*-6-Hydroxy-2-thiabicyclo[2.2.1]heptane[a]



[a] BsCl and TsCl refer to *p*-bromobenzenesulfonyl chloride and *p*-toluenesulfonyl chloride, respectively.

Hydroboration of cyclopentadiene on a small scale followed by hydrogen peroxide oxidation of the alkyl borane produces 4-hydroxycyclopentene in 30% yield.[11] The reaction was scaled up to consistently produce 1 mol of alcohol in 12–13% yield based on starting diene. The alcohol was converted into the *p*-toluenesulfonate *via* the standard pyridine–tosyl chloride method. Sodium cyanide in dimethyl sulfoxide displaced the sulfonic ester to form 4-cyanocyclopentene which was hydrolyzed to the corresponding acid. Reduction of the acid to the corresponding alcohol was found to give a higher yield in tetrahydrofuran (82%) than in ether (63%).

Conversion of 4-hydroxymethylcyclopentene into its *p*-bromobenzenesulfonate (**16**) was found to proceed in 96% yield. The expoxidation of **16** was accomplished with *m*-chloroperbenzoic acid in methylene chloride, conditions expected to give more *trans*- than *cis*-expoxide[12] (only the *trans* can cyclize to the desired poduct). The product was a white solid, mp 50–80°, which slowly discolored on standing at room temperature. Attempts to separate the isomers by thin layer chromatography were unsuccessful. The crude solid, presumably a stereoisomeric mixture, was heated under reflux with sodium sulfide in aqueous alcohol to produce *exo*-5-hydroxy-2-thiabicyclo[2.2.1]heptane in 14% yield as a gummy semisolid which crystallized readily on cooling in ice. The alcohol was characterized as its phenylurethan.

Reactions with particular emphasis on stereochemical aspects of the compounds herein reported will be discussed in future papers.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary apparatus and are 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 except for the double resonance studies which were conducted on a DP-60 spectrometer. Analytical vapor phase chromatogaphy was performed on an F & M 720. Preparative vpc was conducted on an F & M 776 Prepmaster Jr.

3,3-Dichloro-2-thiabicyclo[2.2.1]hept-5-ene (5).—The procedure was that of Middleton.[5] To 21.0 g (0.319 mol) of freshly distilled cyclopentadiene stirring in a Dry Ice–isopropyl alcohol bath was added 33.4 g (0.290 mol) of thiophosgene. After about three-fourths addition, a white solid formed and the mixture was warmed to 0° and addition completed. Evacuation to 0.1 mm yielded a yellow oil which was dissolved in pentane, treated with decolorizing carbon, filtered and cooled in Dry Ice to yield 44.4 g (0.245 mol, 84%) of white solid, mp 47–51° (sealed capillary) (lit.[5] mp 50–52°).

3,3-Dichloro-2-thiabicyclo[2.2.1]hept-5-ene 2,2-Dioxide (7).—The crude dichlorosulfide prepared from 70 g of cyclopentadiene and 115 g of thiophosgene was dissolved in 1 l. of anhydrous ether, and to this solution, at −10 to 0°, was added slowly over a 4-hr period 425 g of *m*-chloroperbenzoic acid dissolved in 2 l. of anhydrous ether. The mixture was stirred overnight at 0°. The excess peracid was destroyed with sodium bisulfite and the *m*-chlorobenzoic acid removed with sodium carbonate solution. The ether layers were washed twice with water. Then all washings, sodium carbonate and water, were extracted with methylene chloride. After the methylene chloride extracts were back washed with fresh sodium carbonate and water, the extracts were concentrated. The brownish solid obtained was dissolved in a minimum amount of dimethylformamide. The resulting solution was poured into water to precipitate a light tan solid which was washed several times with sodium carbonate solution followed by water. A total yield of 190 g (89.3%) was obtained. One recrystallization afforded a tan solid, 164 g (78%), mp 165–175°. Recrystallization from carbon tetrachloride and chloroform several times afforded a white solid: yield 140 g (66%); mp 175.5–176.5°; $\nu_{max}^{CHCl_3}$ 1330 (s), 1140

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[11] E L. Allred, J. Sonnenberg, and S. Winstein *J. Org. Chem.*, **25**, 26 (1960). An improvement of this reaction using diisopinocamphenylborane has recently been reported: H. M. Hess and H. C. Brown, *ibid.*, **32**, 4138 (1967).

[12] For a discussion of the factors influencing stereochemistry in the epoxidation of 4-substituted cyclopentenes, see H. B. Henbest, Special Publication No. 19, The Chemical Society, London, 1965 p 83; N. S. Crossley, A. C. Darby, H. B. Hembest, J. J. McCullough, B. Nicholls, and M. F. Stewart, *Tetrahedron Lett.*, 398 (1961), and H. B. Henbest, *Proc. Chem. Soc.*, 159 (1963).

cm^{-1} (s). An analytical sample was again recrystallized and vacuum sublimed, mp 177–179°.

Anal. Calcd for $C_6H_6Cl_2O_2S$: C, 33.83; H, 2.87; Cl, 33.28. Found: C, 33.89; H, 2.86; Cl, 33.22.

Epoxidation of Sulfone 7.—To 0.81 g (4.0 mmol) of *m*-chloroperbenzoic acid in 25 ml of dry benzene was added 0.50 g (2.34 mmol) of sulfone **7** and the solution was heated under reflux for 10 hr. The brown solution then was cooled and washed twice with saturated sodium hydrogen carbonate solution and once with saturated sodium chloride solution. After drying over sodium sulfate and evaporation of the solvent a yellow solid was obtained. This was recrystallized from carbon tetrachloride to give 0.25 g (1.1 mmol, 28%) of epoxide **8**, mp 191–196°. Two more recrystallizations gave an analytical sample, mp 201.5–203.0°.

Anal. Calcd for $C_6H_6Cl_2O_3S$: C, 31.46; H, 2.66. Found: C, 31.67; H, 2.50.

***endo*-3-Chloro-2-thiabicyclo[2.2.1]hept-5-ene 2,2-Dioxide (9).**—In a 1-l. flask fitted with a mechanical stirrer, a pressure-equalizing addition funnel, a nitrogen outlet and a gas dispersion tube (reaching nearly to the bottom of the flask) was placed 65.37 g (1 g-atom) of zinc powder. The flask was flushed thoroughly with nitrogen. A solution of 266 g (1 mol) of chromium(III) chloride hexahydrate in 500 ml of 5% hydrochloric acid was added (mildly exothermic) and the solution was stirred for 12 hr.

The nitrogen flow was reversed and the deep blue solution forced through the gas dispersion tube into a nitrogen-flushed 2-l. flask fitted with a pressure-equalizing addition funnel and mechanical stirrer. A solution of 42.6 g (0.20 mol) of sulfone **8** in 500 ml of acetone was added over a 35-min period (moderately exothermic) and stirring was continued for 20 hr.

The solution was extracted with three 500-ml portions of methylene chloride. (The organic layer is the upper one on the first two extractions, the lower one on the third. The aqueous layer is readily identified by its intense green color.) The combined organic phases were washed with three 500-ml portions of saturated sodium chloride solution and then were dried over sodium sulfate. Removal of the solvent on a rotary evaporator at reduced pressure gave 29.1 g (0.164 mol, 82%) of an off-white solid, mp 86–93°. Recrystallization from *ca.* 900 ml of carbon tetrachloride gave 23.0 g of white crystals: mp 93–95°; $\nu_{max}^{CHCl_3}$ 1310 (s), 1130 cm^{-1} (s). An analytical sample was recrystallized from carbon tetrachloride, mp 93.5–95.5°.

Anal. Calcd for $C_6H_7ClO_2S$: C, 40.34; H, 3.95. Found: C, 40.12; H, 4.02.

3,3-Dichloro-2-thiabicyclo[2.2.1]hept-5-ene-1-*d* 2,2-Dioxide.—To 0.71 g (3.3 mmol) of sulfone **7** in 8 ml of dioxane was added a solution of 4.0 g (68 mmol) of potassium hydroxide in 8 ml of water and the solution was refluxed for 6 days. It was then cooled in an ice bath while 6.1 ml of 12 *M* hydrochloric acid was added dropwise with stirring. The resulting solid was filtered and recrystallized from carbon tetrachloride to give 0.52 g, mp 175–178°. A mixture melting point with starting sulfone was not depressed. An nmr spectrum revealed the multiplet centered at δ 4.26 to be greatly decreased in intensity.

***endo*-3-Chloro-2-thiabicyclo[2.2.1]hept-5-ene-1,3-d_2 2,2-Dioxide.**—A solution of 4.0 g (71 mmol) of potassium hydroxide in 8 ml of deuterium oxide was added to a solution of 0.63 g (3.5 mmol) of sulfone **9** in 8 ml of dioxane and the solution was stirred at room temperature for 6 days. The solution then was cooled in ice (some precipitation) and a solution of 6.0 ml of concentrated hydrochloric acid in 10 ml of water was added slowly. Suction filtration gave 0.125 g of white solid, mp 92–95°. A mixture melting point with starting material was undepressed. The mother liquor was stored at −10° for several days to give 0.18 g, mp 93–95°. An nmr spectrum revealed the resonances centered at δ 4.08 and 4.71 to be reduced to less than half intensity.

2-Thiabicyclo[2.2.1]hept-5-ene (10).—A solution of 18.05 g (0.1 mol) of monochloro sulfone **5** in 750 ml of anhydrous ether was added slowly with stirring to 37.94 g (1 mol) of lithium aluminum hydride and the mixture refluxed for 4 hr. The excess hydride was destroyed by slow addition of saturated sodium sulfate solution to the cooled reaction mixture. The ether solution was decanted and then concentrated to *ca.* 25 ml with a stream of dry nitrogen. The crude sulfide was purified by vapor phase chromatography using a 6.5 ft × 0.75 in. column packed with 15% Carbowax on Chromosorb W to give 2.8 g (25%) of a white, waxy odoriferous solid. Sublimation at atmospheric pressure onto a 0° condenser gave an analytical sample, mp 60–63°. The nmr spectrum is discussed in the text.

Anal. Calcd for C_6H_8S: C, 64.73; H, 7.19. Found: C, 63.96; H, 7.28.

***endo*-3-Chloro-2-thiabicyclo[2.2.1]heptane 2,2-Dioxide (13).**—To 2.00 g (9.45 mmol) of sulfone **7** in 150 ml of ethanol was added 1.64 g (20 mmol) of sodium acetate and 0.50 g of 20% palladium hydroxide on carbon. The mixture was hydrogenated in a Parr apparatus at 50 psi and 60° for 13 hr. Recrystallization of the crude product from hexane–chloroform gave 0.48 g of **13**, mp 150–151°, and a second crop, 0.66 g, mp 148–150°, for a combined yield of 69%: $\nu_{max}^{CHCl_3}$ 1320, 1150 cm^{-1} (SO_2).

Anal. Calcd for $C_6H_9ClO_2S$: C, 39.89; H, 5.02; Cl, 19.63. Found: C, 39.98; H, 5.07; Cl, 19.65.

2-Thiabicyclo[2.2.1]heptane 2,2-Dioxide (14). **A.**—A tenfold excess of lithium dispersion in heptane was placed in a flame-dried flask containing a magnetic stirring bar under nitrogen. A solution of 0.60 g (3.3 mmol) of sulfone **13** in 30 ml of dry tetrahydrofuran[13] was added *via* a nitrogen flushed syringe and the solution stirred for 6 hr at room temperature. The brown reaction mixture was cooled to 0° and slowly hydrolyzed by the slow addition of 3 ml of water through a hypodermic needle. The resulting solution was thoroughly extracted with methylene chloride and the combined extracts were dried over sodium sulfate. Evaporation of solvent gave a brown gum which was vacuum sublimed and twice recrystallized from carbon tetrachloride to give 0.112 g (12%) of a white solid: mp 203–205°; $\nu_{max}^{CHCl_3}$ 1300 (s), 1130 (s, shoulder), 1105 cm^{-1}.

Anal. Calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89. Found: C, 49.03; H, 7.08.

B.—A solution of 0.38 g (100 mmol) of lithium aluminum hydride in 50 ml of dry ether was stirred in an ice bath while a solution of 1.7 g (9.5 mmol) of sulfone **13** in 200 ml of ether was added. After addition was completed the mixture was allowed to room temperature and stirring continued for 2.5 hr. The reaction mixture than was cooled and hydrolyzed with saturated sodium potassium tartrate solution. The ether solution was washed once with water and dried over sodium sulfate. Evaporation of the ether at reduced pressure gave a gummy solid which was washed with pentane to give 0.39 g (2.1 mmol, 22%) of white solid, mp 200–204°. A mixture melting point with material prepared by A was undepressed and the two samples had superimposable infrared spectra.

2-Thiabicyclo[2.2.1]heptane (12).—A solution of 15.0 g (0.083 mol) of sulfone **13**, mp 146–150°, in 600 ml of anhydrous ether was added to a stirring solution of 15.7 g (0.414 mol) of lithium aluminum hydride in 500 ml of dry ether at such a rate that the solution refluxed gently. Refluxing was continued for 24 hr. The solution then was cooled in an ice bath and the mixture was hydrolyzed by the slow addition of 100 ml of sodium potassium tartrate solution. The ether solution was decanted from the resulting solid salts, washed once with water and stored over sodium sulfate in a lightly stoppered flask for 10 days. The remaining ether was removed from the concentrated solution by rotary evaporation to give 8.4 g (0.074 mol, 89%) of a white, waxy solid, mp 99–107°. Sublimation of a sample at 50° onto a 0° condenser gave a solid, mp 111–113°. The infrared and nmr spectra were in agreement with the structure.

To a solution of 0.13 g (1.1 mmol) of sulfide **12** in 2 ml of ether was added 0.5 ml of methyl iodide and the mixture was allowed to stand at room temperature for 10 hr. Suction filtration gave a white solid which was recrystallized three times from methanol–ether to give a solid, **sulfonium iodide**, mp 176–179°.

Anal. Calcd for $C_7H_{13}IS$: C, 32.82; H, 5.11. Found: C, 32.62; H, 5.15.

Δ^3-Cyclopentenyl *p*-Toluenesulfonate.—4-Hydroxycyclopentene **10** (40 g, 0.477 mol) was dissolved in 500 ml of reagent grade pyridine, and 112 g (0.588 mol) of tosyl chloride added while the pyridine solution was stirred in an ice bath. After stirring 3 hr the solution was placed in a refrigerator at 4–5° for 12 hr. The pyridine solution was then slowly poured into a stirring solution prepared from 240 ml of 12 *M* hydrochloric acid and 0.8 kg of crushed ice. Filtration of the pyridine–water solution gave 112 g (99%) of white solid, mp 48–52° (lit.[11] mp 53.4–54.2° in 80% yield). The crude tosylate was used for the next step without further purification.

4-Cyanocyclopentene.—To a solution of 39.0 g (0.797 mol) of anhydrous sodium cyanide in 500 ml of reagent grade DMSO stirring at 70° was added 100 g (0.420 mol) of crude tosylate.

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(13) The tetrahydrofuran was dried by distillation from sodium dispersion in the presence of benzophenone ketyl.

The temperature rose quickly to 90° and was maintained at 85–95° for 4 hr. The cooled solution was poured into 2 l. of water and the resulting brown solution extracted with four 500-ml portions of ether. The combined ether extracts were washed with two 400-ml portions of water and dried over sodium sulfate. Distillation through a 30-cm Vigreux column gave a small forerun, 8.49 g of clear oil, bp 48–50° (7 mm), and 9.42 g, bp 50–51° (7 mm) [lit.[14] bp 58–63 (7 mm)], $n^{25}\mathrm{D}$ 1.4569, ν neat 2250 cm^{-1}. Vapor phase chromatography on the silicon gum rubber column indicated that the lower boiling fraction contained *ca.* 10% more volatile impurity. The nitrile discolored slowly at room temperature and therefore was stored under nitrogen at −10°.

3-Cyclopentenecarboxylic Acid.—To a solution of 86.0 g (0.924 mol) of the slightly impure 4-cyanocyclopentene in 270 ml 95% alcohol was added 90 ml of 40% aqueous sodium hydroxide solution and the mixture refluxed under nitrogen for 20 hr. The black solution was poured into 2 l. of water containing 90 ml of glacial acetic acid. Extraction with four 500-ml portions of ether followed by drying and removal of the solvent gave a brown oil. This was distilled through a 30-cm Vigreux column to give 66.3 g of yellow oil, bp 56–66° (0.3 mm). This material was redistilled through a 30-cm Podbielniak column to give 64.0 g (60%) of light yellow oil, bp 46–48° (0.3 mm), $n^{25}\mathrm{D}$ 1.4669 [lit.[15] bp 83–84° (2 mm), $n^{23}\mathrm{D}$ 1.4673]. The anilide was prepared according to the published[16] procedure, mp 138–140° (lit.[16] mp 139–140°).

4-Hydroxymethylcyclopentene.—To a stirring suspension of 4.15 g (0.113 mol) of lithium aluminum hydride in 100 ml of dry tetrahydrofuran[13] was added a solution of 11.6 g (0.110 mol) of 3-cyclopentenecarboxylic acid in 55 ml of dry tetrahydrofuran. The mixture refluxed vigorously during the course of the addition. Heating under reflux was continued for 20 hr. The reaction was worked up by the addition of 50 ml of saturated sodium potassium tartrate solution. Extraction with solid with ether, followed by drying over sodium sulfate and removal of the solvent, yielded 11.0 g of a yellow oil. The oil was distilled through a Vigreux column to give 8.00 g (82%) of a clear oil, $n^{20}\mathrm{D}$ 1.4665, bp 82–85° (30 mm) [lit.[16] bp 98–99° (57 mm), $n^{22}\mathrm{D}$ 1.4670].

Δ^3-Cyclopentenylmethyl *p*-Bromobenzenesulfonate.—To 5.00 g (51.0 mmol) of 4-hydroxymethylcyclopentene in 100 ml of pyridine stirring in an ice bath was added 15.0 g (58.5 mmol) of *p*-bromobenzenesulfoxyl chloride which had been dried at 40° (50 mm) overnight. After stirring in the ice bath for 1 hr, the solution was placed in a refrigerator at 4–5° for 10 hr. The yellow solution then was poured slowly into a rapidly stirring solution of ice water containing 80 ml of 12 *M* hydrochloric acid. Suction filtration and thorough washing of the filter cake with water gave 16.7 g of white solid, mp 39.5–46.0°. The material was recrystallized from pentane to give 12.5 g (96%) of white solid, mp 39.5–42.0°. An analytical sample was again recrystallized, mp 40.5–42.0°.

Anal. Calcd for $C_{12}C_{13}BrO_3S$: C, 45.44; H, 4.13. Found: C, 45.50; H, 3.97.

3,4-Epoxycyclopentylmethyl *p*-Bromobenzenesulfonate.—To a stirring solution of 6.50 g of 88% *m*-chloroperbenzoic acid in 80 ml of methylene chloride was added 8.50 g (26.7 mmol) of Δ^3-cyclopentenylmethyl brosylate in small portions and the solution stirred for 25 min. A small amount of 10% sodium hydrogen sulfite solution was then added and the solution was suction filtered. The filter cake was washed thoroughly with methylene chloride and the layers were separated. The organic layer was washed with two portions of saturated sodium hydrogen carbonate solution and once with 1 *M* sodium hydroxide. After drying over sodium sulfate and evaporation of solvent a clear oil was obtained which slowly crystallized on standing, mp 50–80°. Thin layer chromatography failed to resolve the isomeric epoxides but did indicate the presence of a small amount of starting olefin.

***exo*-6-Hydroxy-2-thiabicyclo[2.2.1]heptane (15).**—A 6.65-g sample of the crude epoxide prepared above, dissolved in 50 ml of methanol, was added to 10.2 g (42 mmol) of sodium sulfide nonahydrate in 250 ml of methanol and the solution was refluxed for 44 hr. The majority of the methanol was removed by distillation, the residue diluted with 200 ml of water and the resulting slurry extracted with two 200-ml portions of ether. After drying over sodium sulfate and evaporation of the ether a brown oil was obtained; short-path vacuum distillation gave 0.51 g (14%) of a water white semisolid.

Addition of phenyl isocyanate to a sample of the alcohol gave a solid **urethan** which was twice recrystallized from methylene chloride–pentane, mp 123–124°.

Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.48. Found: C, 62.62; H, 6.28.

Registry No.—**7**, 18593-28-7; **8**, 18593-29-8; **9**, 18598-83-9; **10**, 6841-59-4; **12**, 279-26-5; **12** (sulfonium iodide), 18593-32-3; **13**, 18598-84-0; **14**, 18593-37-8; 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene-1-*d*, 18593-38-9; *endo*-3-chloro-2-thiabicyclo[2.2.1]-hept-5-ene-1,3-d_2, 18621-11-9; Δ^3-cyclopentylmethyl *p*-bromobenzenesulfonate, 18593-39-0; **15** (urethan), 18598-85-1; 3,4-epoxycyclopentylmethyl *p*-bromobenzenesulfonate, 18593-40-3.

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The Peroxide-Initiated Addition of Some Polyfluorochloro- and Polyfluorobromoalkanes to Some Hydrocarbon Olefins

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Both $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ have been found to give reasonable yields of simple addition products with olefins in the presence of benzoyl peroxide. The products of dehydrohalogenations of the adducts are described. The preferred reaction of $CCl_3CF_2CF_2Br$ is by cleavage of the C–Br bond rather than the C–Cl bond. Other telogens such as CF_2BrCF_2Br, $CF_3CFBrCF_2Br$ and $CFClBrClCFClBr$ react with ethylene to give 1:1 adducts. Certain polyhaloalkanes such as $CF_3CFBrCFBrCF_3$ and particularly $CF_3CClBrCFBrCF_3$ lose bromine readily in the presence of peroxide.

The peroxide-initiated reaction of polyfluorobromoalkanes such as CF_2Br_2 and $CF_2BrCFClBr$ with a variety of olefins[1,2] and fluoro olefins[3,4] gives 1:1 addition products which are useful in the synthesis of reactive fluorine-containing molecules. For example, 1,1,2-trifluorobutadiene can be made relatively easily by the following series of reactions.

$$CF_2BrCFClBr + CH_2{=}CH_2 \xrightarrow{Bz_2O_2}$$

$$CF_2BrCFClCH_2CH_2Br \xrightarrow[2.\ Zn]{1.\ KOH} CF_2{=}CFCH{=}CH_2$$

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