a 20-hr period gave, after recrystallization from 95% ethanol, 0.48 g (85%) of 2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide: mp 187–188.5°; ir ($CHCl_3$) 1635 (m), 1325, and 1150 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.38–8.24 (m, 1, C_9 H), 7.93–7.37 (m, 3, C_6, C_7, C_8 H's), 7.05 (s, 1, C_5 H), 5.22 (t, 1, J = 5 Hz, $-SO_2C\mathbf{H}ClCH_aH_b-$), 3.83 (dd, 1, J_{C3a-C2} = 5 Hz, $J_{C3a-C3b}$ = 19 Hz, $-SOCHClC\mathbf{H}_aH_b-$), 3.33 (dd, 1, J_{C3b-C2} = 5.5 Hz, $J_{C3b-C3a}$ = 19 Hz, $-SO_2CHClCH_a\mathbf{H}_b-$).

Anal. Calcd for $C_{10}H_8Cl_2O_2S$: C, 45.64; H, 3.06; Cl, 26.95; O, 12.16. Found: C, 45.51; H, 3.18; Cl, 26.67; O, 12.21.

Registry No.—**15**, 21609-70-1; **16**, 19373-31-0; **17**, 14171-33-6; **18**, 40322-44-9; **19**, 40322-45-0; **20**, 40322-46-1; **21**, 40322-47-2; **22**, 40322-48-3; **23**, 40322-49-4; **24**, 40322-50-7; **25**, 40322-51-8; **26**, 22710-97-0; **27a**, 40322-28-9; **27b**, 40322-29-0; **28**, 40322-30-3; **29a**, 40322-33-6; **29b**, 40322-34-7; **30**, 40322-58-5; **31**, 40322-59-6; **32**, 40322-60-9; **34**, 40322-61-0; **35**, 40322-62-1; **36** (X = Cl), 40322-63-2; **36** (X = Br), 21609-67-6; **37**, 40322-65-4; **38**, 40322-66-5; **39**, 40322-67-6; **41**, 40322-68-7; **42**, 40322-69-8; **43**, 40322-70-1; **44**, 40322-71-2; **45**, 40322-72-3; **46**, 40322-73-4; dimethylamine hydrochloride, 506-59-2; paraformaldehyde, 30525-89-4; isoamyl alcohol, 123-51-3; ethanol, 64-17-5; acetic acid, 64-19-7; formalin, 50-00-0; *tert*-butyl alcohol, 75-65-0; sodium hydroxide, 1310-73-2; benzaldehyde, 100-52-7; *p*-toluenesulfonic acid, 104-15-4; ozone, 10028-15-6; benzaldehyde 2,4-dinitrophenylhydrazone, 1157-84-2; ethyl formate, 109-94-4; morpholine, 110-91-8; triethylamine, 121-44-8; *m*-chloroperbenzoic acid, 937-14-14; acetic anhydride, 108-24-7; pyridine, 110-86-1; *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide, 40322-31-4; *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5-(2*H*)-one 1,1-dioxide, 40322-32-5.

Synthesis of Thiabicyclo[2.2.2]octenes. Carbon-13 Nuclear Magnetic Resonance Spectra of Bicyclic Sulfides

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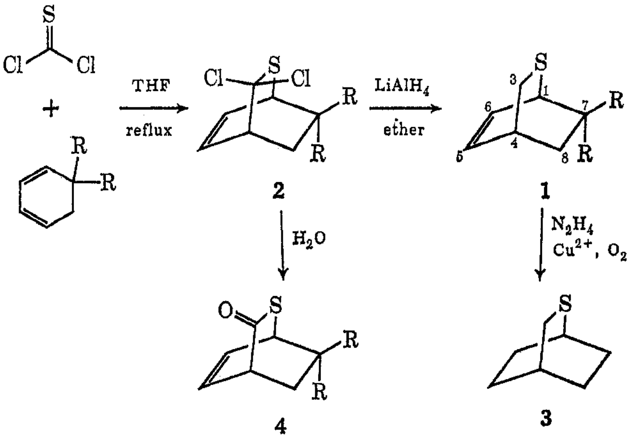
2-Thiabicyclo[2.2.2]oct-5-ene (**1a**) was synthesized by 1,4 addition of thiophosgene to 1,3-cyclohexadiene giving 3,3-dichloro-2-thiabicyclo[2.2.2]oct-5-ene (**2a**) followed by reduction with lithium aluminum hydride. 7,7-Dimethyl-2-thiabicyclo[2.2.2]oct-5-ene (**1b**) and 4,6,7,7-tetramethyl-2-thiabicyclo[2.2.2]oct-5-ene (**8**) were synthesized similarly from 5,5-dimethyl- and 1,3,5,5-tetramethyl-1,3-cyclohexadiene. Compound **1a** was characterized by diimide reduction to the known 2-thiabicyclo[2.2.2]octane which was shown not to be the photolysis product of 3-cyclohexenylmethanethiol (**5**) as previously reported. Compound **8** was characterized by oxidation to the sulfoxide **9** and sulfone **10**. Hydrolysis of the thiophosgene–cyclohexadiene adducts **2a**, **2b**, and **7** gave the corresponding δ-thiolactones **4a**, **4b**, and **12** (3-oxo-2-thiabicyclo[2.2.2]oct-5-enes). ^{13}C nmr was used to establish the structures of **1a**, **8**, **9**, **10**, and **12**.

Published synthetic approaches to the thiabicyclo[2.2.2]octene system have usually involved either cyclization of substituted cyclohexanes[1] or the cycloaddition of cyclohexadienes with thiocarbonyl compounds.[2] None of the reported syntheses is easily modified for the preparation of 2-thiabicyclo[2.2.2]octene (**1a**) which we required for photochemical studies. In particular, reported examples of the latter method have involved substituted thiocarbonyl compounds (cyanothioformyl halides,[2a] perfluorinated thioketones,[2b] thiofluorenone,[2c] and thiobenzophenone[2d]) such that substituents are not easily replaced by hydrogen, and in any event have often proceeded in synthetically unattractive yields.

Middleton[2b] reported the cycloaddition of thiophosgene with cyclopentadiene to give 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene, and Johnson, Keiser, and Sharp[3] subsequently accomplished the reductive removal of the chlorine substituents, although only with difficulty and in low yield. The *S*-oxide of thiophosgene also undergoes cycloaddition with cyclopentadiene.[4] We have examined the reaction of thiophosgene with several cyclohexadienes and would like to report that this is a general route to the desired ring system, as well as to the saturated analog.

The reaction of cyclohexadiene with thiophosgene proceeded exothermically to give 3,3-dichloro-2-thiabicyclo[2.2.2]oct-5-ene (**2a**). Since the dichloride is moisture sensitive, reduction with lithium aluminum



a, R = H
b, R = CH_3

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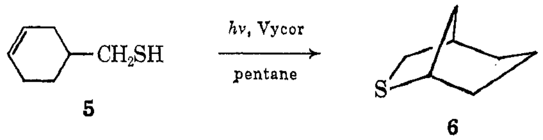
hydride[5] to give **1a** was best carried out on the crude product, and resulted in 45% yield overall from cyclohexadiene. The spectral data for **1a** and **2a** were as anticipated, with the possible exception of the $\mathrm{CH_2}$–S geminal coupling constant of 7.5 Hz in **1a**. Geminal coupling for such protons in thiabicyclo[2.2.1]heptanes of 9 Hz has been reported,[3] and Liberatore, *et al.*, have reported a 9.5-Hz geminal coupling in a complex 2-azabicyclo[2.2.2]octene.[6]

Compound **1a** was further characterized by diimide reduction to the known saturated sulfide **3**, which had identical melting point and ir spectrum with those given by Birch, *et al.*[1a] Our nmr spectrum of **3** did not match that reported for the product of photocyclization of 3-cyclohexenylmethanethiol (**5**) to which Surzur, *et al.*,[1d] also had assigned structure **3**. Unambiguous proof of the correctness of our structural assignment for the reduction product of **1a** was provided by the ^{13}C nmr spectrum, which gave only five peaks [δ^{TMS} ($\mathrm{CDCl_3}$)[7] 23.2, d; 24.5, t; 29.3, t; 30.33; 30.37] in a 1:2:2:1:1 ratio as required for the symmetric structure. We have repeated the photolysis of **5** and find that it leads to a compound with the nmr spectrum reported,[1d] but with the ir and melting point identical with those of 6-thiabicyclo[3.2.1]octane[1a] (**6**). The ^{13}C nmr spectrum has seven resonances [δ^{TMS} ($\mathrm{CDCl_3}$)[7] 18.5, t; 32.0, t; 33.5, t; 35.7, t; 36.9, d; 42.9, t; 45.7, d] supporting this assignment and conclusively ruling out structure **3**. The photolysis of **5** leads to no detectable formation of **3** (2% would have been observed).

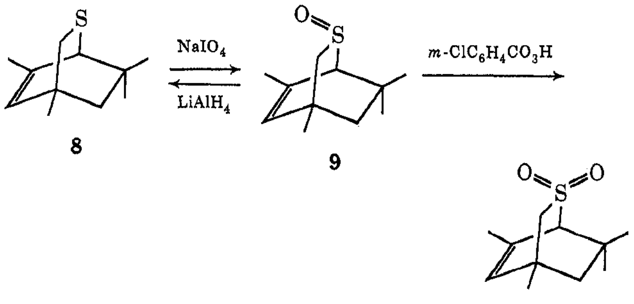


5
6

Chromatography on silica gel converted **2a** into the thiolactone **4a**, which was characterized by the nmr spectrum and ir carbonyl frequency of 1680 cm^{-1},[8] as well as by a major mass spectral fragmentation involving loss of COS (*m/e* 80, base peak).

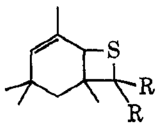
Substituted cyclohexadienes are also accessible by this route. 5,5-Dimethylcyclohexadiene[9] forms with thiophosgene the adduct **2b**. This compound could be reduced to **1b** or hydrolyzed to the thiolactone **4b**. The orientation of the cycloaddition is shown by the nmr spectra of the thiolactone and of the sulfoxide prepared by sodium metaperiodate oxidation of **1b**. The bridgehead protons of both compounds appear as a broad triplet [$\mathrm{H_4}$, for **4b**: δ ($\mathrm{CCl_4}$) 3.44; decoupling experiments showed $J_{4,5}$ = 6 Hz, $J_{4,6}$ = 1.5 Hz, $J_{4,8}$ = 4 Hz, and $J_{4,8'}$ = 2 Hz] and a broad doublet [$\mathrm{H_1}$, for **4b**: δ ($\mathrm{CCl_4}$) 3.59, $J_{1,6}$ = 6 Hz, $J_{1,5}$ = 2 Hz] which must be the bridgehead proton next to the *gem*-dimethyl group. In the presence of shift reagent [Eu(fod)$_3$] the broad triplet resonance is shifted downfield about three times as far as the doublet resonance in the thiolactone, whereas the reverse is true for the sulfoxide. Since complexation occurs at carbonyl oxygen in the thiolactone[10] and at sulfoxide oxygen in the sulfoxide, the cycloadducts of 5,5-dimethylcyclohexadiene must have the orientation shown.

1,3,5,5-Tetramethylcyclohexadiene[11] reacted with thiophosgene to give the cycloadduct **7**, which could be reduced to **8**. Apart from the allylic and vinyl protons, all of the pmr absorptions of **8** fall in the region δ 0.8–1.3, including the methylene group next to sulfur, which is normally found near 2.5. The $\mathrm{CH_2}$–S protons are shifted to lower field in the corresponding sulfoxide **9** (which gives a broadened AB quartet at δ 1.69 and 2.98) and the sulfone **10** (singlet at δ 2.58), although these shifts are still at somewhat higher field than normal. We have no rationale for the unusual $\mathrm{CH_2}$–S chemical shift of **8**, particularly in view of the fact that **1a** (2.42, H-syn; 2.91, H-anti) and **1b** (2.34, H-syn; 2.81, H-anti) show normal shifts for these protons. We have been unable to devise another structure to better fit the spectroscopic and chemical data. The only reasonable grouping which could be expected to give upfield shifts of this magnitude is a thiirane. Thiiranes are reduced by lithium aluminum hydride[12] and the ability to prepare **8** from **7** or the sulfoxide **9** rules out the presence of such a function in these compounds. Furthermore, the sulfone **10** is stable to at least 190°, whereas thiirane *S,S*-dioxides usually decompose near room temperature.[13]

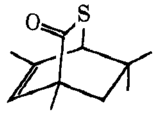


8
9
10

A thietane structure for **7** and **8** (*e.g.*, **11**, the product of a [$2_\pi + 2_\pi$] cycloaddition) can be ruled out by considering the hydrolysis product **12**, which is formed from **7** under both basic (aqueous pyridine) and acidic (chromatography on silica gel) conditions. The compound has a carbonyl frequency (1680 cm^{-1}) identical with that of **4a** and **4b**, for which there is little doubt



11, R = H or Cl



12

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(5) Other reducing agents such as $\mathrm{NaBH_4}$ in ethylene glycol [H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962)], diglyme, and dimethyl sulfoxide did not give the desired product.

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(8) Monocyclic δ-thiolactones absorb near 1665 cm^{-1}: F. Korte and H. Christoph, *Chem. Ber.*, **94**, 1966 (1961).

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(13) F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Amer. Chem. Soc.*, **90**, 429 (1968).

about the structure. β-Thiolactones are reported to have carbonyl frequencies near 1775 cm^{-1}.[14]

The ^{13}C nmr spectra (Table I) clearly require the presence of two carbons bonded to sulfur, since these are shifted strongly downfield as the sulfur is oxidized. The downfield shifted carbons in **8**, **9**, and **10** were shown to be a methyne and methylene by single frequency off-resonance decoupling,[7] thus demonstrating that the orientation of the cycloaddition must be as depicted. This is supported by the δ-thiolactone (**12**) ^{13}C shifts, where a quaternary carbon (C-4) is shifted downfield.

TABLE I

CARBON-13 NMR CHEMICAL SHIFTS[a] OF 2-THIABICYCLO[2.2.2]OCTENES

Compd	C_1	C_3	C_4	C_5	C_6	C_7	C_8
1a	32.7 d[b]	33.4 t	29.1 d	131.5 d*	134.5 d*	30.3 t**	23.3 t**
8[d]	50.8 d	39.5 t	37.1 s*	127.0 d	142.7 s	36.1 s*	48.0 t
9[d]	68.3 d	61.1 dd[c]	36.3 s*	129.3 d	135.6 s	34.0 s*	47.2 t
10[d]	70.0 d	59.6 t	37.3 s*	129.0 d	138.7 s	36.1 s*	46.8 t
12[d]	59.1 d	*e*	53.2 s	126.3 d	146.5 s	37.5 s	46.4 t

[a] Chemical shifts reported downfield from TMS. Assignments for peak positions marked with an asterisk may be reversed. [b] See ref 7. [c] A doublet of doublets is observed for the C-3 methylene of **7** because of the large chemical shift difference between the geminal protons, resulting in different residual C–H couplings. [d] Methyl quartets at (**8**) 21.0, 26.6, 30.0, 30.8; (**9**) 24.8, 25.5, 28.8, 32.1; (**10**) 22.5, 25.6, 29.1, 31.9; (**12**) 19.9, 21.5, 30.1, 31.0. [e] Not observed.

Only one cycloaddition product was observed in each case, but the isolated adducts may not be the result of kinetic control. The orientation of the cycloaddition for 5,5-dimethyl- and 1,3,5,5-tetramethylcyclohexadienes can be explained as a result of steric control by the *gem*-dimethyl group, although for the latter compound electrophilic attack by sulfur also can be used to rationalize the observed mode of addition.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian XL-100, Varian A-60A, or Jeol MH-100 spectrometer. Carbon-13 (Fourier transform) nmr spectra were measured on the XL-100 system using noise modulated proton decoupling. Infrared spectra were obtained on a Beckman IR-8 spectrophotometer, and mass spectra on an AEI MS-902 spectrometer.

3,3-Dichloro-2-thiabicyclo[2.2.2]oct-5-ene (2a).—To a refluxing solution of 0.80 g (10 mmol) of 1,3-cyclohexadiene in 5 ml of pentane under nitrogen was added in one portion 0.76 ml (10 mmol) of thiophosgene. This mixture was refluxed for 2 hr and cooled to Dry Ice temperature. The orange liquid was decanted, and the pale yellow precipitate was recrystallized four times from pentane at −78° to give 0.98 g (50%) of a white, waxy, odiferous, hydrolysis-sensitive solid: mp 98–100°; nmr δ (CCl_4) 1.0–2.5 (m, 4 H), 3.4–3.9 (m, 2 H), 6.5 (td, J = 9, 2 Hz, 1 H), 6.65 (td, J = 8, 1.2 Hz, 1 H).

Anal. Calcd for $C_7H_8Cl_2S$: m/e 193.97238. Found: m/e 193.97160.

2-Thiabicyclo[2.2.2]oct-5-ene (1a).—To a solution of 5.9 g (73.5 mmol) of 1,3-cyclohexadiene in 50 ml of dry tetrahydrofuran heated to 35° was added dropwise 5.6 ml (73 mmol) of thiophosgene. The mixture was refluxed for 1 hr, and unreacted starting materials were removed by evaporating the solution to two-thirds its volume in a stream of N_2. The remaining tetrahydrofuran solution of the adduct was added dropwise with stirring to a slurry of 4 g (105 mmol) of $LiAlH_4$ in 400 ml of ether over a period of 1 hr. The reduction mixture was refluxed an additional 30 min, cooled, and quenched with saturated NH_4Cl solution. The ether layer was decanted, washed with 10% KOH solution, washed with water, and dried (Na_2SO_4). The ether was evaporated and the white solid residue was sublimed to give 4.2 g (45%) of white waxy crystals: mp 138–141° (mp 142–143° after gc purification); nmr δ (CCl_4) 1.2–1.8 (m, 3 H), 2.0 (m, 1 H), 2.42 (m, H-3-syn), 2.91 (d, J = 7.5 Hz, H-3-anti), 2.94 (m, H-4), 3.31 (m, H-1), 6.12 (td, J = 7, 1 Hz, H-5), 6.46 (td, J = 7, 1 Hz, H-6). (The spectrum of 3,3-dideuterio-**1a** (prepared by reduction of **2a** with $LiAlD_4$) and homonuclear decoupling experiments on **1a** confirm the above assignments and following couplings: $J_{5,6} = J_{4,5} = J_{1,6} = 7$ Hz, $J_{1,5} = J_{4,6} = 1$ Hz, $J_{3s,3a} = 7.5$ Hz, $J_{3s,4} = J_{3s,8} = 2$ Hz); mass spectrum m/e (rel intensity) 126 (55), 98 (35), 97 (30), 80 (85), 79 (100), 78 (30), 77 (35); ir (CCl_4) 3020, 2920, 2860, 1680 (w), 850 cm^{-1}.

Anal. Calcd for $C_7H_{10}S$: C, 66.61; H, 7.99. Found: C, 66.50; H, 7.81.

2-Thiabicyclo[2.2.2]octane (3).—To 1.0 g (7.8 mmol) of **1a** in 10 ml of absolute ethanol was added 4 g (80 mmol) of 100% hydrazine hydrate and a small amount of $CuSO_4$.[15] Oxygen was bubbled through the solution for 3 hr. The solution was filtered, diluted with 10 ml of water, and extracted with 2 × 10 ml of pentane. The pentane solution was washed twice with 10 ml of water and dried ($MgSO_4$). Evaporation gave 0.50 g (49%) of waxy solid: mp 200–205° (208–209° after sublimation; lit.[1a] 210–212°); nmr δ (CCl_4) 1.77 (m, 4 H), 1.92 (m, 3 H), 2.01 (m, 2 H), 2.45 (m, 1 H), 2.70 (d, J = 3 Hz, 2 H).

3-Oxo-2-thiabicyclo[2.2.2]oct-5-ene (4a).—A CCl_4 solution of **2a** prepared by refluxing 160 mg (2 mmol) of 1,3-cyclohexadiene with 0.15 ml (2 mmol) of thiophosgene for 1 hr and reducing the resulting mixture to one-half its volume in a stream of N_2 was hydrolyzed by preparative thin-layer silica gel chromatography. Sublimation gave 101 mg (36%) of colorless crystals: mp 65–67°; nmr δ (CCl_4) 1.5–2.4 (m, 4 H), 3.58 (m, 1 H), 4.15 (m, 1 H), 6.30 (td, J = 7.5, 2 Hz, 1 H), 6.67 (td, J = 7, 1.5 Hz, 1 H); ir (CCl_4) 3050 (w) 2960, 2940, 2870, 1680, 1615 (w) cm^{-1}.

Anal. Calcd for C_7H_8OS: m/e 140.02954. Found: m/e 140.02980.

7,7-Dimethyl-2-thiabicyclo[2.2.2]oct-5-ene (1b).—Using the method for preparing **1a**, 2.7 g (25 mmol) of 5,5-dimethyl-1,3-cyclohexadiene[9] and 1.9 ml (25 mmol) of thiophosgene on reduction with 1.9 g (50 mmol) of $LiAlH_4$ and purification by sublimation gave 1.2 g (31%) of solid **4a**: mp 60–63° (mp 67–68° after gc purification); nmr δ (CCl_4) 0.89 (s, 3 H), 1.25 (s, 3 H), 0.8–1.5 (m, 2 H), 2.34 (td, J = 9, 3 Hz, H-3-syn), 2.81 (dd, J = 9, 3 Hz, H-3-anti), 2.88 (d, J = 7 Hz, 1 H), 2.95 (m, 1 H), 6.07 (td, J = 7, 1 Hz, 1 H), 6.55 (br t, J = 7 Hz, 1 H).

Anal. Calcd for $C_9H_{14}S$: m/e 154.08162. Found: m/e 154.08168.

3-Oxo-7,7-dimethyl-2-thiabicyclo[2.2.2]oct-5-ene (4b).—The cycloadduct of 5,5-dimethyl-1,3-cyclohexadiene[9] (216 mg, 2 mmol) and thiophosgene (0.15 ml, 2 mmol) on hydrolysis by silica gel chromatography and purification by sublimation gave 112 mg (33%) **4b**: mp 106–109°; nmr δ (CCl_4) 1.11 (s, 3 H), 1.35 (s, 3 H), 1.49 (dd, J = 13.5, 4 Hz, 1 H), 1.87 (dd, J = 13.5, 2 Hz, 1 H), 3.44 (br t, J = 6 Hz, 1 H), 3.59 (br d, J = 6 Hz, 1 H), 6.26 (td, J = 7, 2 Hz, 1 H), 6.75 (td, J = 7, 1.5 Hz, 1 H); ir (CCl_4) 3070 (w), 2960, 2880, 1680, 1610 (w), 1380, 1360 cm^{-1}. Homonuclear decoupling experiments established the following couplings: $J_{1,6} = J_{4,5} = 6$ Hz, $J_{4,8} = 4$ Hz, $J_{1,5} = J_{4,8'} = 2$ Hz, $J_{4,6} = 1.5$ Hz, $J_{5,6} = 8$ Hz, $J_{8,8'} = 13.5$ Hz.

Anal. Calcd for $C_9H_{12}OS$: m/e 168.06082. Found: m/e 168.06095.

7,7-Dimethyl-2-thiabicyclo[2.2.2]oct-5-ene 2-Oxide.—By the method of Leonard and Johnson,[16] 154 mg (1 mmol) of **1b** gave on sublimation 141 mg (83%) of the sulfoxide: mp 125–127°; nmr δ (CCl_4) 0.98 (s, 3 H), 1.12 (s, 3 H), 0.8–1.6 (m, 2 H), 1.88 (br d, J = 13 Hz, 1 H), 3.1 (m, 1 H), 3.24 (dd, J = 13, 2.5 Hz, 1 H), 3.84 (br d, 6.5 Hz, 1 H), 6.18 (br t, 7 Hz, 1 H), 6.54 (br t, 7.5 Hz, 1 H).

Anal. Calcd for $C_9H_{14}OS$: m/e 170.07646. Found: m/e 170.07609.

4,6,7,7-Tetramethyl-2-thiabicyclo[2.2.2]oct-5-ene (8).—By the method used for the preparation of **1a**, 6.8 g (50 mmol) of 1,3,5,5-tetramethylcyclohexadiene[11] and 3.7 ml (48 mmol) of thiophosgene on reduction with 3.8 g (100 mmol) of $LiAlH_4$ gave after distillation [bp 68° (20 mm)] 3.0 g (33%) of **8**: nmr δ (CCl_4) 0.88 (s, 3 H), 1.18 (s, 3 H), 1.25 (s, 3 H), 0.8–1.3 (m, 4 H), 1.90 (d, J = 1.5 Hz, 3 H), 2.59 (m, 1 H), 5.42 (m, 1 H);

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mass spectrum *m/e* (rel intensity) 182 (55), 136 (25), 126 (93), 121 (100), 111 (85).

Anal. Calcd for $C_{11}H_8S$: C, 72.46; H, 9.95. Found: C, 72.44; H, 10.01.

4,6,7,7-Tetramethyl-2-thiabicyclo[2.2.2]oct-5-ene 2-Oxide (**9**).—By the method of Leonard and Johnson,[16] 100 mg (0.55 mmol) of **8** gave 98 mg (90%) of colorless crystals from pentane (at −78°): mp 70–73°; nmr δ (CCl_4) 0.93 (s, 3 H), 1.05 (s, 3 H), 1.25 (s, 3 H), 0.85–1.3 (m, 2 H), 1.90 (d, *J* = 1.5 Hz, 3 H), 1.69 (br d, *J* = 13 Hz, 1 H), 2.98 (d, *J* = 13 Hz, 1 H), 3.52 (m, 1 H), 5.85 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}OS$: *m/e* 198.10783. Found: *m/e* 198.10802.

A sample of **9** was reduced with $LiAlH_4$ in refluxing ether to give pure **8** by nmr comparison.

4,6,7,7-Tetramethyl-2-thiabicyclo[2.2.2]oct-5-ene 2,2-Dioxide (**10**).—Using the procedure of Johnson, Keiser, and Sharp,[3] 100 mg (0.55 mmol) of **8** gave 77 mg (65%) of colorless crystals from CCl_4: mp 116–118°; nmr δ (CCl_4) 0.98 (s, 3 H), 1.22 (s, 3 H), 1.43 (s, 3 H), 1.20 and 1.58 (ABq, *J* = 13.5 Hz, 2 H), 1.95 (d, *J* = 1.5 Hz, 3 H), 2.58 (br s, 2 H), 2.92 (br s, 1 H), 5.58 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O_2S$: *m/e* 214.10274. Found: *m/e* 214.10345.

3-Oxo-4,6,7,7-tetramethyl-2-thiabicyclo[2.2.2]oct-5-ene (**12**).—Compound **12** was prepared in 39% yield (155 mg) by the method used for **4a** and **4b** from the cycloadduct obtained from 272 mg (2 mmol) of 1,3,5,5-tetramethylcyclohexadiene[11] and 0.15 ml (2 mmol) of thiophosgene: mp 45–47° (48–49° after sublimation); nmr δ (CCl_4) 1.07 (s, 3 H), 1.21 (s, 3 H), 1.28 (d, *J* = 13 Hz, 1 H), 1.30 (s, 3 H), 1.68 (d, *J* = 13 Hz, 1 H), 1.95 (d, *J* = 1.5 Hz, 3 H), 3.12 (m, 1 H), 5.45 (m, 1 H); ir (CCl_4) 3030 (w), 2980, 2935, 2860, 1680, 1655 (sh), 1375, 1360 cm^{-1}.

Anal. Calcd for $C_{11}H_6OS$: C, 67.30; H, 8.22. Found: C, 67.46; H, 8.18.

Compound **12** was also obtained by basic hydrolysis (addition of pyridine followed by H_2O) of the diene–thiophosgene cycloadduct.

Registry No.—**1a**, 40168-94-3; **1b**, 40168-95-4; **1b** 2-oxide, 40317-79-1; **2a**, 40168-96-5; **3**, 280-41-1; **4a**, 40168-97-6; **4b**, 40168-98-7; **8**, 40168-99-8; **9**, 40169-00-4; **10**, 40169-01-5; **12**, 40169-02-6; 1,3-cyclohexadiene, 592-57-4; thiophosgene, 463-71-8; 5,5-dimethyl-1,3-cyclohexadiene, 33482-80-3; 1,3,5,5-tetramethylcyclohexadiene, 4724-89-4.

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Nuclear Magnetic Resonance Studies on *cis*-Bicyclo[3.3.0]oct-7-en-2-yl Derivatives. A Long-Range Magnetic Anisotropic Effect on Olefinic Protons by Endo Carbonyl Group

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Considerable chemical shift differences ($\Delta\tau$ 0.29–0.37) of olefinic protons were observed in the nmr of some esters of *endo-cis*-bicyclo[3.3.0]oct-7-en-2-ols, while the olefinic protons of the corresponding exo esters did not show such chemical shift differences. This difference was considered to result from a remote through-space magnetic anisotropic effect of the endo acyl residue; *i.e.*, the remote effect in the present system was attributable to the rigid structure of the bicyclo[3.3.0]octene skeleton which allowed the endo carbonyl group to move to the position in close proximity to H_8 and to cause the considerable deshielding effect on H_8 (and also the shielding effect on H_7 to some extent), but did not allow the exo carbonyl group to do so. The conformations of *exo-* and *endo-cis*-bicyclo[3.3.0]octan-2-ols, *exo-* and *endo*-bicyclo[3.3.0]octan-3-ols, and *exo-* and *endo-cis*-bicyclo[3.3.0]oct-7-en-2-ols were assigned as *W* and *S*, *W* and *W*, and *H-C* and *S* type, respectively, on the ground of the coupling constants of α proton to hydroxy group according to the Karplus equation.

In the previous report, we have discussed the conformations of *exo-* and *endo-cis*-bicyclo[3.3.0]oct-2- and -3-yl derivatives (hereafter abbreviated as the *exo-* and *endo-3.3.0*-2 and -3 derivatives, respectively) on the basis of the calculations of the shielding effects in nmr spectroscopy by means of McConnell's equation.[1] In the present manuscript, we wish to report the investigation of the nmr coupling pattern of the α proton to the hydroxyl group in the *3.3.0*-2-ols which is in accord with our previous conclusion.[1] We also wish to describe an interesting observation of chemical shift difference of olefinic protons of some esters of *endo-cis*-bicyclo[3.3.0]oct-7-en-2-ol (hereafter abbreviated as the *endo-3.3.0*-7-en-2-ol, and so on). Such a difference was not observed in nmr of the *exo-3.3.0*-7-ene-2 derivatives. These observations seem to be useful to determine the stereochemistry at C_2 position in the *cis*-bicyclo[3.3.0]oct-7-en-2-yl derivatives and related compounds. The coupling patterns of the olefinic protons were investigated by the decoupling technique, and the substituent effect on the difference was also evaluated. This difference was considered to result from a remote through-space magnetic anisotropic effect of the carbonyl group of the acyl residue on the olefinic protons.

Results and Discussion

Chemical Shift Difference of Olefinic Protons of *endo-cis*-Bicyclo[3.3.0]oct-7-en-2-ol Derivatives.—Nmr measurements were carried out in carbon tetrachloride where τ values were determined on the basis of a TMS–chloroform internal double standard, using 60-MHz and 100-MHz nmr spectrometers. A spectrum of olefinic protons of the *endo-3.3.0*-7-en-2 formate is shown in Figure 1 as a typical example. As is shown in the figure, a remarkable chemical shift difference was observed for the esters of the *endo-3.3.0*-7-en-2-ol, while it was not observed for the exo esters (the signals of olefinic protons of the exo

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