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.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Dr. P. L. Fuchs for helpful suggestions and Dennis Wood for the synthesis of **1b**.

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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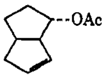
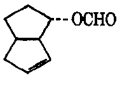
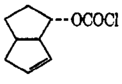
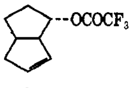
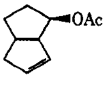
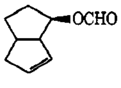
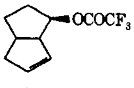
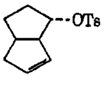
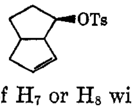
[1] I. Tabushi, K. Fujita, and R. Oda, *J. Org. Chem.*, **35**, 2383 (1970).

esters as well as the exo and endo alcohols were observed to be singlet-like). The downfield or upfield signal showed ABK_1 or ABK_2K_3 pattern, respectively, though the patterns were fairly complex by virtue of additional remote couplings. In order to gain further insights, the bridgehead allyl methine proton (H_1; see Figure 1), which appeared at τ 6.65 as a broad multiplet, was irradiated. The downfield signal (H_8) was simplified to the AB pattern with fine structure by the decoupling from H_1, while upfield signal (H_7) kept ABK_2K_3 pattern with fine structure although it was slightly simplified by the removal of the remote coupling with H_1. The result of the decoupling is shown in Figure 2. Thus the upfield or downfield signal was assigned to the proton at C_7 (H_7) or at C_8 (H_8), respectively. In order to investigate the substituent effect on the splitting, locations and coupling patterns of olefinic proton signals of the *endo-3.3.0*-7-en-2-yl esters were measured (Table I). Coupling constants, J_{AK_1}, J_{BK_2}, and J_{BK_3}, of the esters were observed to be practically equal (1.6 Hz). Coupling parameters of the AB pattern were obtained from the chemical shifts of band centers of the four peaks by the ordinary procedure.[2] Neither coupling constant nor chemical shift showed appreciable temperature dependency from 0 up to 100°. The temperature insensitivity seems to show that the carbonyl group actually rotates around the single bond under the condition of the nmr measurements (*i.e.*, even at 0°).[3] The chemical shift of H_8 in the *endo-3.3.0*-7-en-2-yl ester was most sensitive to the nature of acyl residue (Figure 3). This finding suggests not only that H_8 is in closer proximity to the substituent than H_7 in the endo ester consistently with the assignment made from the decoupling experiment, but also that the chemical shift difference ($\tau_7 - \tau_8$) results mainly from the deshielding of H_8, even though it is also probable that the shielding of H_7 contributes to the chemical shift difference to some extent. The chemical shift difference, $\Delta\tau$ 0.28 − 0.38, seems to indicate that the through-space magnetic anisotropic effect is the major factor of the observed chemical shift difference rather than the through-bond effect (the acyl residue is separated from H_7 or H_8 by five or six bonds, respectively), by considering that such a large chemical shift difference, $\Delta\tau$ 0.28 − 0.38, is neither seen in the open-chain analog, *trans*-hept-5-en-2-one, with the chemical shift difference of the olefinic protons to be far less than $\Delta\tau$ 0.1, nor in ω-substituted alkanes.

TABLE I
COUPLING PARAMETERS OF VINYL PROTONS OF *cis*-BICYCLO[3.3.0]OCTENE DERIVATIVES

Registry no.		τ_7[a]	τ_8[a]	$\Delta\tau$[b]	$J_{H_7H_8}$[c]	J_{AK_i}[d]
40132-71-6		4.63	4.34	0.293	6.0	~1.6
40132-72-7		4.59	4.28	0.307	6.0	~1.6
40132-73-8		4.62	4.30	0.318	5.9	~1.6
40132-74-9		4.61	4.23	0.377	~6.0	~1.6
40132-75-0		4.36	4.36	~0	~6.0[f]	2.0[f]
40132-76-1		4.36	4.36	~0	~6.0[f]	2.0[f]
40132-77-2		4.29	4.29	~0	~6.0[f]	2.0[f]
40132-78-3		4.64	4.36	0.283	~6.0	~1.6
40132-79-4		4.59	4.38	0.213[e]	~6.0	~1.6

[a] τ value of H_7 or H_8 with TMS–$CHCl_3$ standard. [b] Chemical shift difference between two olefinic protons ($\tau_7 - \tau_8$) in ppm unit. [c] Observed coupling constant of two olefinic protons in cps units. [d] Observed coupling constants between an allylic proton and an olefinic one in cps units; these are observed to be almost equal. [e] The splitting seems to be attributable to the magnetic anisotropic effect of the tosyl residue. [f] From the comparison of the observed spectrum of the olefinic protons with the theoretical one calculated for the 5 spin system (H_1, H_{6x}, H_{6N}, H_7, and H_8) with the computer program, these couplings constants were obtained on the assumption that $\Delta\tau \approx 0$ cps, $J_{6x6N} = -13.50$ cps, and that all J_{Ak_i} were equal to each other.

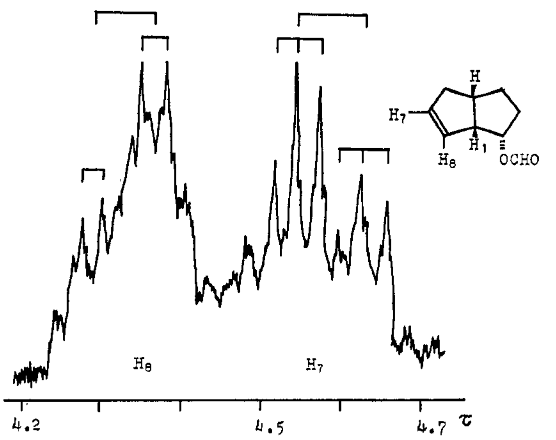


Figure 1.—Nmr spectrum of H_7 and H_8 of *endo-cis*-bicyclo[3.3.0]oct-7-en-2-yl formate measured at 60 MHz, with TMS–$CHCl_3$ internal standard.

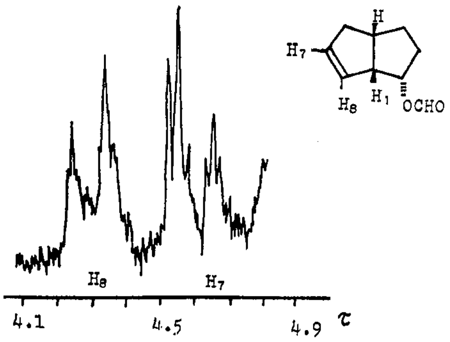


Figure 2.—Decoupled spectrum of H_7 and H_8 of *endo-cis*-bicyclo[3.3.0]oct-7-en-2-yl formate, from H_1 at τ 6.65.

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(2) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, p 310.

(3) Two other rationalizations are possible: (1) rotation is highly restricted even at room temperature and (2) the chemical shifts are insensitive to various rotomer species.

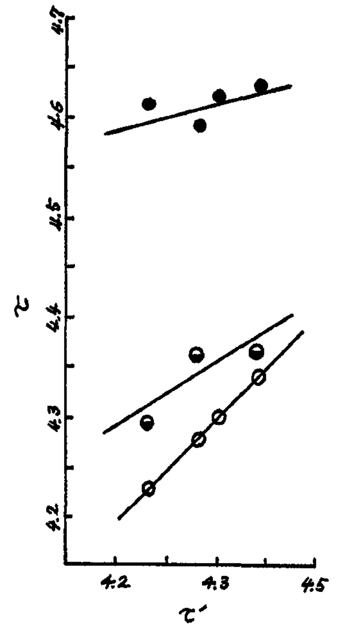

Figure 3.—Chemical shift of the olefinic proton of *endo*- or *exo*-*cis*-bicyclo[3.3.0]oct-7-en-2-yl ester (τ) *vs.* that of H_8 of *endo*-*cis*-bicyclo[3.3.0]oct-7-en-2-yl ester as a standard (τ); H_7 and H_8 of *exo*-*cis*-bicyclo[3.3.0]oct-7-en-2-yl ester (●), H_7 of *endo*-*cis*-bicyclo[3.3.0]oct-7-en-2-yl ester (◒), and H_8 of *endo*-*cis*-bicyclo[3.3.0]oct-7-en-2-yl ester (○).

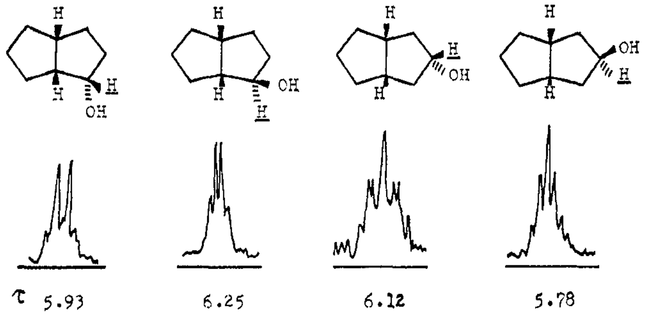

Figure 4.—Coupling patterns and chemical shifts of α protons of *cis*-bicyclo[3.3.0]octanols.

The enhanced through-space magnetic effect in the present system is largely attributable to its rigid structure. By assuming that the conformation of the *endo*-*3.3.0*-7-en-2-yl derivative is constructed with an envelope cyclopentane and a near-planar cyclopentene and has the substituent at C_2 quasiequatorial position, one may notice that the carbonyl group of the acyl residue can move to the position in close proximity to H_8 during the rotation and that the average effect of the magnetic anisotropy of the rotating carbonyl group causes a considerable deshielding of H_8 on the basis of a molecular model. While, for the conformation of C_2 quasiaxial substituent on the envelope cyclopentane ring or that of a half-chair cyclopentane ring, the anisotropic effect is expected to be small. For the esters of the *exo*-*3.3.0*-7-en-2-ol, the carbonyl group is expected to locate far from the two olefinic protons from the investigation of the molecular model. Therefore, no appreciable anisotropic effect is expected in these systems.

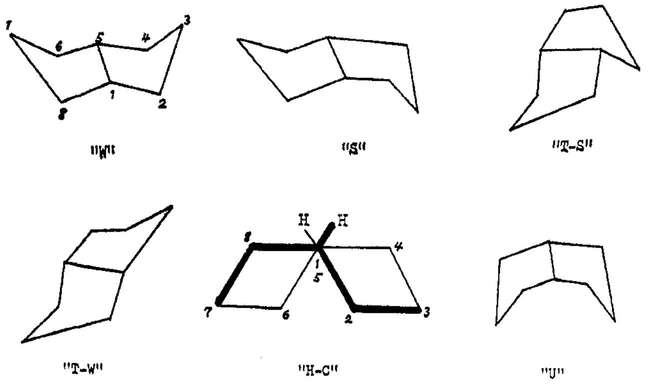

Figure 5.—Typical conformations of *cis*-bicyclo[3.3.0]octane framework.

Conformations of *cis*-Bicyclo[3.3.0]oct-2-ols and *cis*-Bicyclo[3.3.0]oct-7-en-2-ols.—Karplus predicted that the coupling of vicinal protons ($J_{HH'}{}^{vic}$) should vary with dihedral angle (ψ) according to the following equation.[4]

$$J_{HH'}{}^{vic} = 8.5\cos^2\psi - 0.28 \qquad 0° \leqq \psi \leqq 90°$$
$$= 9.5\cos^2\psi - 0.28 \qquad 90° \leqq \psi \leqq 180°$$

This equation was verified in many cases and used to identify configurational and conformational isomers.[5] Especially, the equation was shown to be successfully applied to six-membered ring;[6] but the factors other than the dihedral angle such as substituent effects were often shown to affect coupling constants.[7] Although the Karplus equation may not be strictly (numerically) applied to a five-membered ring, it seems to be allowed qualitatively to investigate the conformation or the configuration of the five-membered ring by means of the Karplus equation. We wish to discuss the conformations of the *cis*-bicyclo[3.3.0]-octane and the *cis*-bicyclo[3.3.0]oct-2-ene frameworks on the grounds of coupling constants of the α proton to hydroxyl group of the *3.3.0*-2- or -3-ols and the *3.3.0*-7-en-2-ols analyzed according to the equation. The observed nmr spectra of the α proton to hydroxyl group of the alcohols are shown in Figure 4. In order to analyze the coupling patterns in Figure 4, a reasonable assumption was made that each five-membered ring has envelope or half-chair conformation.[8] Five typical conformational models names as "*S*," "*W*," "*T-S*," "*T-W*," and "*H-C*" in Figure 5[1] were selected because of their expected stabilities. Other unstable conformers such as "*U*" were omitted, where C_3 and C_7 locate so close to suffer an unfavorable repulsive interaction between two nonbonded hydrogens (*endo*-

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[4] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); H. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).

[5] (a) For carbohydrate of six-membered ring: R. V. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **79**, 1005 (1957); *ibid.*, **80**, 6098 (1958). (b) For steroids: J. N. Shooley and M. T. Rogers, *ibid.*, **80**, 5121 (1958). (c) For halocyclohexanes: R. U. Lemieux and J. W. Lown, *Can. J. Chem.*, **42**, 893 (1964), and many other references.

[6] A. A. Bothner-By, "Advances in Magnetic Resonance," Vol. 1, Academic Press, New York, N. Y., 1965, p 195.

[7] (a) K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963); (b) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963); (c) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964); (d) P. Laszol and P. v. R. Schleyer, *ibid.*, **86**, 1964 (1964).

[8] Pitzer suggested that the envelope conformer was the most stable; later, Brutcher and Hoffmann claimed that the half-chair conformer was more stable than the envelope. See K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959); E. V. Brutcher, Jr., and W. Bauer, Jr., *ibid.*, **84**, 2232 (1962); R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

H_8 and *endo*-H_7).[9] In the conformational models, dihedral angles between the α proton and the adjacent protons were varied, the corresponding $J_{HH'}{}^{vic}$'s were estimated by the Karplus equation, and then coupling patterns were reconstructed. By this "trial and error" procedure, conformations with the best agreement with the observed patterns were found out as shown in Table II. The best agreement was obtained by assuming "*W*" conformations for the *exo*-*3.3.0*-2-ol, the *endo*-*3.3.0*-3-ol and the *endo*-*3.3.0*-3-ol and "*S*" conformation for the *endo*-*3.3.0*-2-ol. The result is the same as that obtained from our previous investigation of the nmr shielding effect, where the other five-membered ring ($C_1C_5C_6C_7C_8$) was assumed to have an envelope conformation as shown in Figure 5. The change of the favorable conformation from "*W*" to "*S*" is explicable by steric repulsion between 2-*endo*-hydroxyl group and *endo*-H_8 proton in the *endo*-*3.3.0*-2-ol. This repulsion is minimized by the conformational change of the 2-*endo*-hydroxyl group from the quasiaxial position to the quasiequatorial one. This result is consistent with the investigation for the conformation of 2-*endo*-ethyl-*cis*-bicyclo[3.3.0]octane-2,3-diol reported by E. Ghera,[10] where the bicyclooctane framework has "*S*" conformation due to the repulsion between bulky 2-*endo*-ethyl group. Chemical shifts and coupling patterns of the α proton (H_2) observed in the spectra of the *3.3.0*-7-en-2-ols are listed in Figure 6, respectively. The results of the conformational investigation of the *3.3.0*-7-en-2-ols by the similar procedure as that of the *3.3.0*-2- and -3-ols are shown in Table III, where the unsaturated ring ($C_1C_5C_6C_7C_8$) was assumed to have nearly planar conformation. "*S*" conformation was again concluded to be favored for the *endo*-*3.3.0*-7-en-2-ol, while the best agreement with the observation was obtained for "*H-C*" conformation in the case of the *exo*-*3.3.0*-7-en-2-ol (Figure 5).

TABLE II

OBSERVED COUPLING CONSTANTS AND ROUGHLY ESTIMATED DIHEDRAL ANGLES OF *cis*-BICYCLO[3.3.0]OCT-2- AND -3-OLS

endo- *3.3.0*-2-Ol[a] (24454-38-4)	*exo*- *3.3.0*-2-Ol[a] (23359-88-8)	*endo*- *3.3.0*-3-Ol[a] (24454-40-8)	*exo*- *3.3.0*-3-Ol[a] (24454-39-5)
$H_{2x}H_1$ ~20°	$H_{2N}H_1$ ~130°	$H_{3x}H_{2x(4x)}$ ~35°	$H_{3N}H_{2x(4x)}$ ~110°
(J ~ 7.0 cps)	(J ~ 4.4 cps)	(J ~ 5.4 cps)	(J ~ 3.5 cps)
$H_{2x}H_{3x}$ ~30°	$H_{2N}H_{3N}$ ~25°	$H_{3x}H_{2N(4N)}$ ~155°	$H_{3N}H_{2N(4N)}$ ~10°
(J ~ 5.6 cps)	(J ~ 6.5 cps)	(J ~ 7.5 cps)	(J ~ 8.0 cps)
$H_{2x}H_{3N}$ ~150°	$H_{2N}H_{3x}$ ~145°		
(J ~ 7.4 cps)	(J ~ 6.0 cps)		
"*S*"[a]	"*W*"[a]	"*W*"[a]	"*W*"[a]

[a] With respect to the abbreviation, see text. Registry numbers are in parentheses.

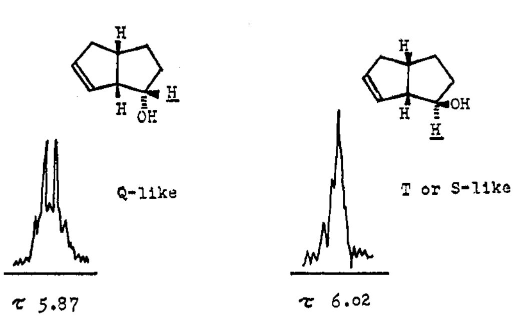


Figure 6.—Coupling patterns and chemical shifts of *cis*-bicyclo-[3.3.0]oct-7-en-2-ols.

TABLE III

OBSERVED COUPLING CONSTANTS AND ROUGHLY ESTIMATED DIHEDRAL ANGLES OF *cis*-BICYCLO[3.3.0]OCT-7-EN-2-OLS

endo-*3.3.0*-7-En-2-ol[a]	*exo*-*3.3.0*-7-En-2-ol[a]
$H_{2x}H_1$ ~20°	$H_{2N}H_1$ ~45°
(J ~ 7.2 cps)	(J ~ 4.3 cps)
$H_{2x}H_{3x}$ ~25°	$H_{2N}H_{3x}$ ~95°
(J ~ 6.3 cps)	(J ~ 0.2 cps)
$H_{2x}H_{3N}$ ~145°	$H_{2N}H_{3N}$ ~25°
(J ~ 6.3 cps)	(J ~ 6.8 cps)
"*S*"[a]	"*H-C*"[a]

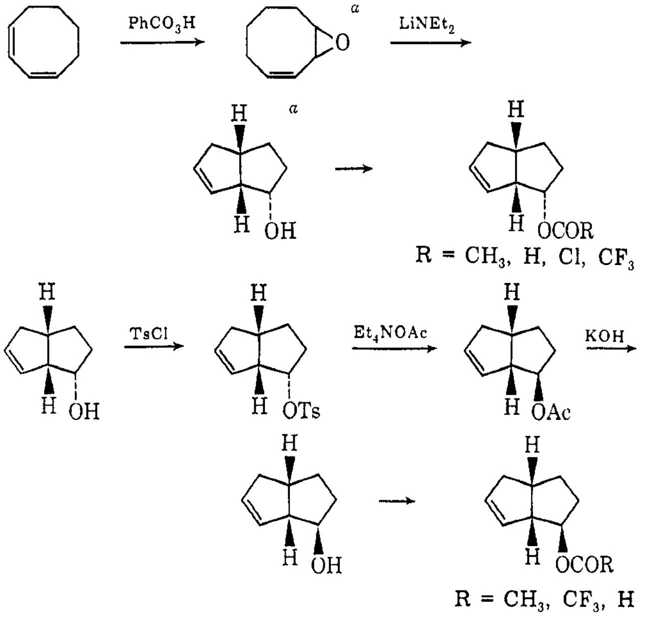
[a] With respect to the abbreviation, see text.

Experimental Section

Preparation of the Compounds for Nmr Measurements *exo*- and *endo*-*cis*-Bicyclo[3.3.0]octan-2- and -3-ols and Their Acetates.—The preparation of the alcohols and their acetates were described elsewhere.[1] A general scheme of the preparation of the *3.3.0*-7-en-2-yl derivatives is described in Scheme I.

SCHEME I

PREPARATION OF DERIVATIVES OF *cis*-BICYCLO[3.3.0]OCT-2-ENE



[a] See ref 10.

***endo*-*cis*-Bicyclo[3.3.0]oct-7-en-2-ol.**—This alcohol was prepared from 3,4-epoxycyclooctene by isomerization with lithium diethylamide,[11] bp 90–95° (20 mm) [lit.[11] bp 93–96 (20 mm)].

***exo*- and *endo*-*cis*-Bicyclo[3.3.0]oct-7-en-2-yl Tosylates.**—A solution of 8 g (0.065 mol) of the *endo*-*3.3.0*-7-en-2-ol in 53.0 ml of pyridine was added to a solution of 22.9 g (0.120 mol) of *p*-toluenesulfonyl chloride with ice cooling and stirring. Then the mixture was stirred for 20 hr at room temperature. The reaction was quenched by the addition of 2 ml of cold water under ice cooling. The mixture was poured into 200 ml of cold water and extracted with seven portions of 200 ml of ether. The ether extracts were combined and washed with 1 N hydrochloric

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(9) For example, bicyclo[3.3.1]nonane framework was reported to have a serious repulsion between two endo protons attached to C_7 and C_3. See M. Dolber and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); W. A. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); W. D. K. Macrosson, J. D. Lark, C. A. Flegal, and L. M. Honing, *J. Org. Chem.*, **32**, 1372 (1967). Our calculation according to the extended Hückel method shows that "*U*" conformation is less stable than "*W*" one for *cis*-bicyclo[3.3.0]octane. Raman and ir spectra of the hydrocarbon suggested that "*S*" conformation was more stable than "*W*" and "*U*" ones: R. Granger, L. Bardet, C. Sablayrolles, and J.-P. Girard, *Bull. Soc. Chim. Fr.*, 4454 (1971).

(10) E. Ghera, *J. Org. Chem.*, **33**, 1042 (1948).

(11) J. K. Crandall and L.-H. Chang, *J. Org. Chem.*, **32**, 532 (1967).

acid and then saturated aqueous sodium bicarbonate solution. The ether layer was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was the practically pure tosylate (17.2 g). The ir spectrum (neat) did not show the absorption of OH stretching but the characteristic absorption of a tosylate: 1363 and 1177 cm^{-1}. The *exo-3.3.0*-7-en-2-yl tosylate was prepared by a similar procedure, ir 1360 and 1170 cm^{-1}.

***exo-cis*-Bicyclo[3.3.0]oct-7-en-2-yl Acetate.**—A mixture of 10.5 g of the *endo-3.3.0*-7-en-2-yl tosylate, 11.3 g of tetraethylammonium acetate, and 250 ml of acetone was refluxed for 22 hr. After evaporation of acetone, the residue was poured into 400 ml of water. Then the mixture was extracted five times with 200 ml portion of ether. The ether extracts were combined, washed with water, dried (Na_2SO_4), and concentrated. Distillation afforded 6.7 g of the *exo-3.3.0*-7-en-2-yl acetate: bp 69–73° (5 mm); ir, 1730, 1020, and 720 cm^{-1}, mass spectrum *m/e* 106 ($M^+ - CH_3CO_2H$) (the molecular peak, 166, was not observed).

***exo-cis*-Bicyclo[3.3.0]oct-7-en-2-ol.**—A mixture of 6.7 g of the *exo-3.3.0*-7-en-2-yl acetate, 2 g of sodium hydroxide, 2 drops of water, and 20 ml of methanol was refluxed for 10 hr. On cooling, the mixture was neutralized with concentrated hydrochloric acid. The precipitated sodium chloride was filtered off and the filtrate was concentrated. Distillation gave 3.8 g of the *exo-3.3.0*-7-en-2-ol: bp 79–83° (5 mm) [lit.[12] bp 71–72° (3 mm)]; ir (neat) 3360 cm^{-1}.

***endo-cis*-Bicyclo[3.3.0]oct-7-en-2-yl Acetate.**—A solution of 0.5 g of the *endo-3.3.0*-7-en-2-ol in 0.85 g of acetic anhydride was fluxed for 6 hr. The mixture was poured into 50 ml of saturated aqueous sodium bicarbonate solution and extracted with five 50-ml portions of ether. The ether extracts were combined, washed with water, dried (Na_2SO_4), and concentrated. Distillation afforded 0.6 g of the *endo-3.3.0*-7-en-2-yl acetate: bp 69–73° (6 mm); ir (neat) 1723, 790, and 765 cm^{-1}, mass spectrum *m/e* 106 ($M^+ - CH_3CO_2H$) (the molecular peak, 166, was not observed).

***exo-* and *endo-cis*-Bicyclo[3.3.0]oct-7-en-2-yl Trifluoroacetates.**—Each trifluoroacetate was prepared from trifluoroacetic anhydride (1.5 ml) and the corresponding alcohol (0.2 g) by the similar procedure described above. The dried ether extract was concentrated under reduced pressure and used for nmr measurement without isolation. The ir spectrum of the nmr sample showed the absence of hydroxyl group and the presence of carbonyl group of trifluoroacetate: the exo isomer, 1775 cm^{-1}; the endo isomer, 1779 cm^{-1}.

***exo-* and *endo-cis*-Bicyclo[3.3.0]oct-7-en-2-yl Formates.**—A mixture of 0.2 g of the corresponding alcohol, 3 ml of formic acid, and 0.2 g of anhydrous sodium sulfate was heated at 80° for 4 hr. Then the mixture was poured into 150 ml of saturated aqueous sodium bicarbonate solution, extracted with four 50-ml portions of ether. The ether layer was washed with water, dried (Na_2SO_4), and concentrated. Distillation of the formate afforded the *exo-3.3.0*-7-en-2-yl formate, bp 84–86° (20 mm), ir (neat) 1718 cm^{-1}, mass spectrum *m/e* 106 ($M^+ - HCO_2H$) (the molecular peak, 152, was not observed), and the *endo-3.3.0*-7-en-2-yl formate, bp 73–74° (12 mm), $n^{22}D$ 1.4852, ir (neat) 1716 cm^{-1}, mass spectrum *m/e* (rel intensity) 152 (1.59, M^+), 106 (100, $M^+ - HCO_2H$).

***endo-cis*-Bicyclo[3.3.0]oct-7-en-2-yl Chloroformate.**—Dry phosgene gas was bubbled into a solution of 0.1 g of the *endo-3.3.0*-7-en-2-ol in 1 ml of carbon tetrachloride during 20 min at 15°. The solution was kept standing for 30 min at room temperature. Then dry nitrogen was bubbled for 15 min in order to purge excess phosgene and hydrogen chloride formed. The mixture was used for nmr measurement without isolation.

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Nuclear Magnetic Resonance Spectroscopy. The Carbon-13 Spectra of Some Cyclic Alkynes, Allenes, and Alkenes[1]

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The ^{13}C nuclear magnetic resonance (cmr) spectra of selected examples of cyclic alkynes, allenes, and alkenes are reported and discussed. The possible effects of diamagnetic anisotropy on the differences of carbon chemical shifts between cyclic and acyclic alkynes are considered. Other possible sources of carbon chemical-shift differences in these compounds are discussed.

The chemical shifts of sp-hybridized carbons have been of interest to nuclear magnetic resonance (nmr) spectroscopists for several years.[2–5] More recently, technological advances in the maintenance of stable magnetic fields and proton decoupling have made possible the resolution of the carbon resonances of the entire alkyne molecule, so that the substituent effects of the alkyne moiety on the chemical shift of neighboring carbons could be studied.[6,7] It was evident from these last studies that the triple bond appears to have a larger effect upon carbon than proton chemical shifts. The present study seeks to extend our knowledge of the effect of diamagnetic anisotropy in carbon chemical shifts, and to investigate the differences in the responses of protons and carbons to neighboring multiple bonds.

Experimental Section

The compounds used in this study were obtained from commercial sources or were prepared by known literature procedures. Data for the compounds are presented in Table I.

Carbon-13 chemical shifts were measured under conditions of full proton decoupling on a Varian digital frequency sweep spectrometer described previously.[8] Spectra were obtained in benzene solution. Chemical shifts were measured relative to internal cyclohexane (*ca.* 5%) and later referenced to external carbon disulfide by the relation $\delta_{CS_2} = \delta_{C_6H_{12}} + 166.2$ ppm.

Results

The carbon-13 chemical shifts are summarized in Table II. The assignments of resonances were based

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(1) Supported by the National Science Foundation, and by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences.

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