Diels-Alder Reaction between Dimethylfulvene and Vinylene Carbonate. Configurational Assignments of and Magnetic Anisotropic Studies in Adducts and Related Compounds[1]

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Nine new 7-isopropylidenebicyclo[2.2.1]hept-5-ene 2,3-disubstituted derivatives were synthesized. Successful approaches include the reaction of dimethylfulvene with vinylene carbonate to afford exo and endo diastereo-isomers of 7-isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-diol carbonate, 1a and 1b, in the ratio of 3:2, respectively. Hydrolysis of 1a and 1b gave the corresponding diols, 2a and 2b. Treatment of the latter two with thiocarbonyldiimidazole resulted in the formation of the thionocarbonate, 3a and 3b. Catalytic hydrogenation of 1a, 2a, 2b, and 3a reduced the $\Delta^{5,6}$ double bond. As expected, the $\Delta^{5,6}$ double bond showed a shielding effect on the isopropylidene methyl protons, a deshielding on the H-2,3 exo pair, and a shielding influence on the corresponding endo pair. Desulfurization–decarboxylation of 3 with trimethyl phosphite or Raney nickel to produce 7-isopropylidenebicyclo[2.2.1]hepta-2,5-diene (4) was unsuccessful. Anisotropic effects of the double bonds on cyclopropyl protons in 7,7-dimethylenebicyclo[2.2.1]hept-5-ene and -hepta-2,5-diene are discussed.

Various aspects of the nuclear magnetic resonance spectra of bicyclo[2.2.1]heptane ring systems have been studied in recent years. Initial investigations[3] furnished relations between spin–spin coupling constants of ring protons and the stereochemistry. Fraser[4] established a method of configurational assignment in 5- and 6-substituted norbornenes.

Effects of magnetic anisotropy[5] of the double bond on the bridge methylene protons in norbornene and nonbornadiene, however, have been inconsistent and anomalous. Tori and coworkers[6] in 1964 incorrectly ascribed the multiplets centered at τ 8.92 and 8.67 to the H-7 syn and H-7 anti, respectively. This assignment was based on the anticipated larger diamagnetic shielding of the double bond for H-7 syn compared to H-7 anti. This assignment was later reversed,[7] since long-range coupling was observed between the multiplet at τ 8.67 and H-5,6 endo pair; stereospecific coupling between the latter and H-7 syn in accord with the "W-letter" rule[3e,8] was responsible for this reassignment. More recently, other workers[9] have clearly

demonstrated that H-7 syn in nonbornene absorbs[10] at lower field than H-7 anti, thus confirming Tori's later results.[7] Furthermore, in norbornadiene,[6] the bridge methylene protons experience an unusual deshielding and appear at τ 8.02, whereas in norbornane these protons absorb at τ 8.80. If the additivity principle of shielding effects could be applied, the signal of bridge methylene protons should appear at τ 8.80. This unexpected shielding and deshielding influence of the bridge protons prompted us to undertake the present study.

We originally wished to synthesize 7-isopropylidene derivatives of norbornane, norbornene, and norbornadiene to study the anisotropic effects of the double bonds on the isopropylidene methyl protons and see if unusual deshielding similar to that observed in norbornadiene is encountered. This aim, however, could not be accomplished, since we were not successful in synthesizing these compounds.

This paper reports (i) syntheses and configurational assignments of 7-isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-diol carbonates and their derivatives, and (ii) anisotropic effects of the $\Delta^{5,6}$ double bond on the isopropylidene methyl protons and H-2,3 exo–endo pairs. In addition, effects of the double bonds on the chemical shifts of the cyclopropyl protons in 7,7-dimethylenebicyclo[2.2.1]hept-5-ene[15] and -hepta-2,5-diene have been examined and the results compared with those of Tori[6,7] on norbornanes.

Results and Discussion

The reaction of dimethylfulvene with vinylene carbonate afforded a mixture of exo and endo isomers of

(1) (a) This work constituted, in part, the Ph.D. dissertation of M. Z. Haq, University of Ottawa, Ottawa, Canada, 1967, and was done under the supervision of Professor Robert R. Fraser. The author wishes to thank Professor Fraser for his stimulating guidance during the course of this work, for kindly suggesting that he submit the paper as sole author, and for providing invaluable comments and suggestions on the manuscript. Financial help of the National Research Council of Canada in support of this work is also gratefully acknowledged. (b) M. Z. Haq, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, ORGN-100.

(2) Meloy Laboratories, Inc., 6715 Electronic Drive, Springfield, Va. 22151.

(3) (a) W. D. Kumler, N. J. Schoolery, and F. B. Bruchter, Jr., *J. Amer. Chem. Soc.*, **80**, 2533 (1958); (b) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *ibid.*, **81**, 6305 (1959); (c) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (d) M. M. Anderson and P. M. Henry, *Chem. Ind. (London)* 2053 (1961); (e) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); (f) K. B. Wiberg, B. R. Lowny, and B. Nist, *ibid.*, **84**, 1954 (1962); (g) K. L. Williamson, *ibid.*, **85**, 516 (1963); (h) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963); (i) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Amer. Chem. Soc.*, **85**, 2513 (1963); (j) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965); (k) F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *ibid.*, **89**, 4431 (1967).

(4) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(5) Magnetic anisotropic effects can be calculated employing Nakagawa and coworkers[5] equation provided that the molecular geometry is known.

(6) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(7) K. Tori, A. K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, **No. 1**, 9 (1966).

(8) For a review, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(9) (a) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Amer. Chem. Soc.*, **90**, 3721 (1968); (b) A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968).

(10) The reverse should be expected according to the suggestions of Jackman,[11] Pople,[12] and ApSimon and coworkers.[13] For a detailed account of magnetic anisotropy of the double bond and theoretical consideration, see ref 11–14.

(11) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, p 83.

(12) (a) J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962); (b) *ibid.*, **37**, 60 (1962).

(13) (a) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Chem. Commun.*, **No. 12**, 359 (1966); (b) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, and W. B. Whalley, *Tetrahedron*, **23**, 2375 (1967).

(14) H. Conroy in "Advances in Organic Chemistry: Methods and Results," R. A. Raphael, C. E. Taylor, and H. Wynberg, Ed., Interscience, New York, N. Y., 1960, p 265.

(15) Synthetic procedures known.[16]

(16) K. Alder, H. J. Ache, and F. H. Flock, *Chem. Ber.*, **93**, 1888 (1960).

TABLE I

NMR SPECTRAL DATA IN τ UNITS[a] OF 7-ISOPROPYLIDENEBICYCLO[2.2.1]HEPTANE DERIVATIVES

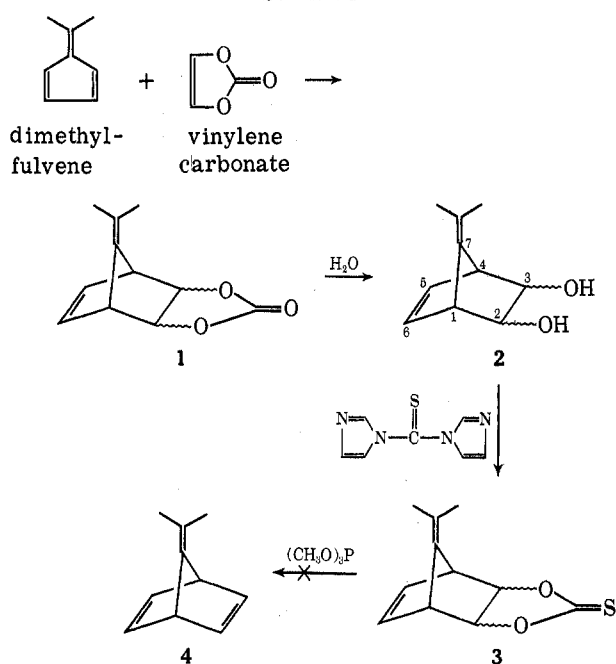| Compd	H-5, H-6	OH	H-2, H-3	H-1, H-4	H methyls
1a	3.81		5.60	6.50	8.33
	(t, sp 2 Hz)		(s)	(t, sp 2 Hz)	(s)
1b	3.70		5.22	6.32	8.42
	(t, sp 2 Hz)		(t, sp 2 Hz)	(qi, sp 2 Hz)	(s)
2a	3.82	7.12	6.34	6.84	8.34
	(t, sp 2 Hz)	(br s)	(s)	(t, sp 2 Hz)	(s)
2b	3.62	7.46	5.92	6.50	8.46
	(t, sp 2 Hz)	(br s)	(t, sp 2 Hz)	(qi, sp 2 Hz)	(s)
3a	3.78		5.18	6.37	8.35
	(t, sp 2 Hz)		(s)	(t, sp 2 Hz)	(s)
3b	3.64		4.82	6.21	8.41
	(t, sp 2 Hz)		(t, sp 2 Hz)	(qi, sp 2 Hz)	(s)

[a] Peak multiplets are represented by br, broad band; m, multiplet; qi, quintet; s, singlet; sp, spacing; t, triplet.

the adduct 1 in the ratio of 3:2, respectively (Scheme I). This conclusion was based on the nmr spectrum of the product, which showed two sets of bands (four peaks each) in the intensity ratio of 3:2. Fractional crystallization of the mixed adduct 1 gave pure carbonates 1a and 1b. Hydrolysis of 1a and 1b gave rise to 2a and 2b, which on treatment with thiocarbonyl-diimidazole resulted in the formation of 3a and 3b, respectively. Compounds 5a, 6a, 6b, and 7a (see Table II) were prepared by the catalytic reduction of 1a, 2a, 2b, and 3a, respectively.

Attempts to produce 4 through the reaction of 3 with trimethyl phosphite[17] or Raney nickel were unsuccessful. Attempted oxidative decarboxylation[18] of 7-isopropylidenebicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic acid[19] using lead tetraacetate also failed.

Configurational Assignments of 7-Isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-diol Carbonate (1) and Its Derivatives.—Elemental analysis and mass, infrared, and nmr spectral data confirmed the gross structure of 1 (see Experimental Section for details). In 1a a singlet at τ 5.60 (2 protons) was ascribed to the H-2,3 endo pair, since no coupling with the bridgehead protons is observed.[4] In 1b,[20] there appeared a triplet at τ 5.22 (2 protons) reasonably ascribed[3a-e,4,6,9] to the H-2,3 exo pair now spin coupled to the bridgehead protons; the latter now appeared as a quintet. The configurations of 2a, 2b, 3a, and 3b follow from their precursors and were confirmed by the multiplicities of the H-2,3 pair (see Experimental Section and Table I).

Reduction Products of 7-Isopropylidenebicyclo[2.2.1]-hept-5-ene-2,3-diol Carbonate (1) and Its Derivatives.—The structures of the hydrogenation products 5a, 6a, 6b, and 7a follow from their respective unsaturated counterparts and were confirmed by their elemental analyses and infrared and nmr spectral data (see Ex-

(17) Olefinic bonds can be obtained smoothly from 1,2-diols. See E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, **85**, 2677 (1963).

(18) Numerous examples of oxidative decarboxylation of dicarboxylic acids to produce double bonds including examples in bicyclic systems are known, *e.g.*, (a) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **43**, 1390 (1960); (b) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963); (c) E. J. Corey and J. Casanova, Jr., *Ibid.*, **85**, 165 (1963); (d) R. Criegee, C. O. Edens, Jr., and B. Graham in "Newer Methods of Preparative Organic Chemistry," Interscience, New York, N. Y., 1948, p 1.

(19) (a) D. Craig, J. J. Shipman, J. Kiehl, F. Widmer, R. Fowler, and A. Hawthorne, *J. Amer. Chem. Soc.*, **76**, 4573 (1954); (b) K. Alder and R. Ruhrmann, *Justus Liebigs Ann. Chem.*, **566**, 1 (1950).

(20) An elemental analysis of 1b itself was not obtained since it was available in very small quantity, but the diol 2b, which was derived from 1b on hydrolysis, analyzed correctly. This, therefore, established the structure of 1b as well.

SCHEME I[a]

[a] 1a = exo carbonate; 1b = endo carbonate; 2a = exo hydroxyls; 2b = endo hydroxyls; 3a = exo thionocarbonate; 3b = endo thionocarbonate; 5a = 1a, 6a = 2a, 6b = 2b, and 7a = 3a, respectively, with double bond at C-5 reduced in each case.

perimental Section). In a representative example of the nmr spectrum of 5a, a singlet at τ 5.57 was assigned to the H-2,3 endo pair. The bridgehead protons appeared as a triplet at τ 7.20 due to the coupling with the H-5,6 exo pair. The multiplets centered at τ 8.57 and 8.79 were ascribed to the H-5,6 exo and H-5,6 endo pairs, respectively, in accordance with the known chemical shifts of these protons in similar systems.[7]

Magnetic Anisotropic Effects of the Double Bond in Derivatives of 1.—Anisotropic effects of the $\Delta^{5,6}$ double bond on the isopropylidene methyl protons and on the H-2,3 exo–endo pairs in the reduction products of 1 and its derivatives merit discussion. Changes in the chemical shifts of various protons upon hydrogenation are obtained from Tables I and II and are summarized in Table III. It can be seen that isopropylidene methyls which lie above the plane of the double bond absorb at lower field in all the dihydro compounds (5a, 6a, 6b, and 7a) than in their unsaturated counterparts. Thus the $\Delta^{5,6}$ double bond exerts a diamag-

TABLE II

Nmr Spectral Data in τ Units[a] of Reduction Products of 7-Isopropylidenebicyclo[2.2.1]heptane Derivatives

Compd	OH	H-2, H-3	H-1, H-4	H-5, H-6 (exo)	H-5, H-6 (endo)	H methyls
5a[b]		5.57	7.20	8.57	8.79	8.27
		(s)	(t, sp 2 Hz)	(m)	(m)	(s)
6a	7.47	6.31	7.43	8.63	8.82	8.29
	(br)	(s)	(distorted t)	(m)	(m)	(m)
6b	7.28	6.15	7.14	8.68	9.12	8.36
	(br)	(t, sp 2 Hz)	(br)	(m)	(m)	(s)
7a		5.22	7.05	8.51	8.77	8.29
		(s)	(t, sp 2 Hz)	(m)	(m)	(s)

[a] Peak multiplets are represented by br, broad band; m, multiplet; qi, quintet; s, singlet; sp, spacing; t, triplet. [b] In CCl$_4$.

TABLE III

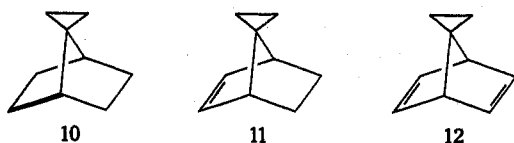Changes in Chemical Shift $(\Delta\tau)$[a] on Hydrogenation

Compd	H-2, H-3 (exo)	H-2, H-3 (endo)	H methyls
1a → 5a		−0.03	−0.06
2a → 6a		−0.03	−0.05
3a → 7a		+0.04	−0.06
2b → 6b	+0.23		−0.10

[a] $\Delta\tau = \tau_2 - \tau_1$, where τ_1 = the chemical shift in the unsaturated compound, and τ_2 = the chemical shift in the dihydro compound.

netic (shielding) effect on the isopropylidene protons. This result is in accord with the familiar shielding phenomenon[11] of the double bond above its plane.

The H-2,3 exo pair lies near the plane of the double bond and should, therefore, be expected to be shifted downfield, whereas the corresponding endo pair lying below the plane of the double bond should be expected[21] to be shifted upfield by the double bond. Inspection of Table III reveals that the $\Delta^{5,6}$ double bond exerts a paramagnetic (deshielding) effect on the H-2,3 exo pair and in two cases out of three a diamagnetic effect on the H-2,3 endo pair. These results serve to substantiate Fraser's earlier findings.[4] The fact that **3a** on hydrogenation shows a positive rather than negative $\Delta\tau$ may be a result of the anisotropic effect of the thionocarbonate group. A previous exception had also been noted by Wong and Lee.[23]

Anisotropic Effects of Double Bonds on Cyclopropyl Protons in 11 and 12.—Anisotropic effects of the double bonds on the chemical shifts of cyclopropyl protons in 7,7-dimethylenebicyclo[2.2.1]hept-5-ene[15] (**11**) and -hepta-2,5-diene (**12**) have been examined. Singlets for these protons in **10** and **12** appeared at τ 9.58 and

9.57, respectively (see Experimental Section). Multiplets centered at τ 9.62 and 9.71 in **11** are assigned to

the two anti and syn cyclopropyl protons, respectively; this assignment is suggested by the geometry of **11**, in which the syn cyclopropyl protons lie above the plane of the double bond and thus experience an appreciable diamagnetic shift. The anti cyclopropyl protons are almost insensitive[24a] to the anisotropy of the double bond. This observation is contrary to the reported paramagnetic shift for the H-7 syn and diamagnetic shift for the H-7 anti in norbornene.[7] Furthermore, the present study reveals no anomalous deshielding of the cyclopropyl protons in going from **10** to **12**, whereas an unusual deshielding of the bridge methylene protons was reported in proceeding from norbornane (τ 8.80) to norbornadiene (τ 8.02). Our results are consistent with the shielding phenomenon of the double bond, but differ from those of Tori because of the difference in orientation of the respective protons in the two systems. This study, qualitatively, demonstrates that geometric factors in norbornanes are important in affecting the chemical shifts of protons at the 7 position and is consistent with previous work.[9a,24b]

In summary, we have (i) synthesized and established configurations of several 7-isopropylidenebicyclo[2.2.1]-hept-5-ene 2,3-disubstituted derivatives, (ii) observed a diamagnetic effect of the $\Delta^{5,6}$ double bond on the seven isopropylidene methyls, and on the H-2,3 endo and a paramagnetic effect on the H-2,3 exo, and (iii) found a diamagnetic effect of the $\Delta^{5,6}$ double bond on the seven cyclopropyl syn protons in 7,7-dimethylenebicyclo[2.2.1]hept-5-ene. The results are consistent with the predicted anisotropic effects of the double bond.

Experimental Section[25]

7-Isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-diol Carbonate (Exo and Endo Isomers 1a and 1b).—Dimethylfulvene[26] (10.6 g,

(21) ApSimon and coworkers[22] find no significant influence of C–H anisotropy on shielding effects of the carbonyl group on substituting the latter for CH$_2$ group in a series of steroids [see also J. Homer and D. Callaghan, *J. Chem. Soc. A*, 439 (1968)]. Thus in our [2.2.1] system where the geometry is similar in olefinic and dihydro derivative, the C–H bond effect should not be an influence.

(22) J. W. ApSimon and H. Beierbeck, *Can. J. Chem.*, **49**, 1328 (1971).

(23) E. W. Wong and C. C. Lee, *ibid.*, **42**, 1245 (1964).

(24) (a) The magnitude of shielding on the anti cyclopropyls is small (0.04 ppm) and could fall within the error (±0.02 ppm) involved in the determination of peak positions in this case. (b) N. Inamoto, S. Masuda, K. Tori, K. Aono, and H. Tanida, *Can. J. Chem.*, **45**, 1185 (1967).

(25) Melting points were determined on a Leitz hot-stage apparatus and are uncorrected. Ir spectra were obtained on a Perkin-Elmer Infracord double beam instrument. Unless otherwise stated, nmr spectra were recorded in CDCl$_3$ on a Varian V4302 high-resolution spectrometer operating at 60 MHz. Tetramethylsilane was used as an internal standard and the spectra were calibrated by the side-band technique. Uv spectra were taken on a Perkin-Elmer ultraviolet–visible spectrophotometer. Vpc curves were obtained on a Perkin-Elmer gas chromatograph. Elementary analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

(26) (a) J. Thiele and H. Balhorn, *Justus Liebigs Ann. Chem.*, **348**, 5 (1906); (b) J. Thiele, *Chem. Ber.*, **33**, 666 (1900).

0.1 mol) was added dropwise[27] to a refluxing solution of vinylene carbonate[28] (8.6 g, 0.1 mol) in *p*-xylene (40 ml), under nitrogen, and the heating was continued for 18 hr. The solvent was then removed under vacuum; the residual syrup was distilled at 110–130° (0.05 mm) to give a pale yellow crystalline material (6.66 g, 35%). The nmr[29] spectrum of this material (CCl₄ + trace amount of CDCl₃) had two sets of absorptions in the intensity ratio of 2:3. The weaker set of bands appeared at 3.70 (t, H-5,6, sp 2 Hz), 5.22 (t, H-2,3, sp 2 Hz), 6.32 (qi, H-1,4, sp 2 Hz), and 8.42 (s, methyls). The more intense absorptions were at 3.81 (t, H-5,6, sp 2 Hz), 5.60 (s, H-2,3), 6.50 (t, H-1,4, sp 2 Hz), and 8.33 (s, methyls).

The mixture on recrystallization from carbon tetrachloride–petroleum ether (bp 30–60°) gave white crystals of pure **1a**: mp 108–109°; ir[30] (CHCl₃) 3050 (w), 1850, 1810 cm⁻¹ (vs); nmr, see Table I; uv (CH₃OH) λmax 207 nm (ε 2500); mol wt, 192 (mass spectrum). *Anal.* Calcd for C₁₁H₁₂O₃: C, 68.73; H, 6.29. Found: C, 68.99; H, 6.18. Compound **1b** was obtained by sublimation of the mixture at 35–40° (0.05 mm), followed by recrystallization from ether: mp 74–76°; ir[30] (CCl₄) 3050 (w) 1850, 1810 cm⁻¹ (vs); nmr, see Table I; uv (CH₃OH) λmax 207.5 nm (ε 3100); mol wt, 192 (mass spectrum).

exo-2,3-Dihydroxy-7-isopropylidenebicyclo[2.2.1]hept-5-ene (**2a**).—**1a** (358 mg, 1.865 mmol) was stirred with a solution of potassium hydroxide (10%) at room temperature for 2 hr. The solution was made acidic (HCl, 10%) and extracted with ether. The combined ether extracts were washed with water, dried (Na₂SO₄), and concentrated, giving a crystalline residue (300 mg, 84%) of **2a** which was recrystallized from CCl₄: mp 124–126°; ir[30] (CHCl₃) 3600–3300 (br), 3050 cm⁻¹ (w); nmr assignments in Table I; uv (CH₃OH) λmax 207 nm (ε 5000). *Anal.* Calcd for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.14; H, 8.32.

endo-2,3-Dihydroxy-7-isopropylidenebicyclo[2.2.1]hept-5-ene (**2b**).—The endo diol **2b** was obtained by the hydrolysis of the endo carbonate **1b** in exactly the same way as the exo diol **2a** from the exo carbonate, **1a**. **2b** after recrystallization from ethanol or sublimation [100–110° (0.05 mm)] afforded white crystals: mp 132–133°; ir[30] (CHCl₃) 3600–3300 (br), 3050 cm⁻¹ (w); nmr data in Table I; uv (CH₃OH) λmax 207 nm (ε 5400). *Anal.* Calcd for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.20; H, 8.46.

7-Isopropylidenebicyclo[2.2.1]hept-5-ene-*exo*-2,3-diol Thionocarbonate (3a).—A solution of **2a** (166 mg, 1.0 mmol) in *p*-xylene (5 ml) was heated under reflux with a solution of thiocarbonyldiimidazole[31] (178 mg, 1.0 mmol) in *p*-xylene (5 ml) for 0.5 hr. The reaction mixture was cooled and filtered and the solvent from the filtrate was evaporated to afford crystals of **3a** (200 mg, 96%). After sublimation [110–115° (0.05 mm)], needlelike crystals were obtained: mp 176–178°; ir[30] (CHCl₃), 3050 (w), 1330, 1300, 1275 cm⁻¹ (vs); see Table I for nmr data; uv (CH₃OH) λmax₁ 205 nm (ε 13,300), λmax₂ 241 nm (ε 19,900). *Anal.* Calcd for C₁₁H₁₂O₂S: C, 63.45; H, 5.81; S, 15.37. Found: C, 63.63; H, 5.73; S, 15.38.

Mixture of 7-Isopropylidenebicyclo[2.2.1]hept-5-ene-*exo*-2,3- and -*endo*-2,3-diol Thionocarbonate (3a and 3b).—Starting from a mixture of **1a** and **1b**, a mixture of **2a** and **2b** was obtained. This mixture was then converted into the mixed thionocarbonates **3a** and **3b**. The crude crystalline material was sublimed at 120–130° (0.05 mm), giving a pure mixture of **3a** and **3b** in the ratio of 3:2 respectively, as shown by its nmr spectrum (Table I).

Attempted Desulfurization–Decarboxylation of 7-Isopropylidenebicyclo[2.2.1]hept-5-ene-*exo*- and -*endo*-2,3-diol Thionocarbonate Mixture, Using Trimethyl Phosphite.—The mixture of thionocarbonates **3a** and **3b** (1.04 g, 5.0 mmol) in trimethyl phosphite (10 ml, 85.0 mmol) in a two-neck flask equipped with a gas inlet tube and a condenser, was refluxed under nitrogen for 84 hr. The condenser, in turn, was connected to two traps containing carbon tetrachloride. A potassium hydroxide solution

(30 ml of 20%) was added to the reaction mixture and the contents were refluxed for 0.5 hr. The solution was extracted with ether several times and the ether extracts were washed with water and dried (Na₂SO₄). After evaporation of ether, a dark brown residue (50 mg) consisting of the starting material was obtained. The nmr spectra of materials in the two carbon tetrachloride traps did not show bands of the expected product, **4**.

Attempted Desulfurization–Decarboxylation of 7-Isopropylidenebicyclo[2.2.1]hept-5-ene-*exo*- and -*endo*-2,3-diol Thionocarbonate Mixture, Using Raney Nickel.—A solution of the exo and endo thionocarbonate mixture, **3a** and **3b** (95 mg), in ether (10 ml) was stirred with Raney nickel (60–90 mg) for 12 hr. The filtered ether solution, on evaporation, gave only the starting material as shown by its nmr spectrum. A complicated nmr spectrum of the reaction product was observed when the reaction was carried out for 2 hr in refluxing tetrahydrofuran or dioxane.

7-Isopropylidenebicyclo[2.2.1]heptane-*exo*-2,3-diol Carbonate (5a).—A solution of **1a** (50 mg) in ethanol (10 ml) was hydrogenated in the presence of Adams' catalyst (9 mg) at atmospheric pressure. One equivalent of hydrogen was taken up in 5 min. The solvent was removed under reduced pressure to obtain a white residue (48 mg, 95%). The product after sublimation at 90–100° (0.05 mm) melted at 113–114°: ir[30] (CCl₄) 1845, 1810 cm⁻¹ (s); nmr, see Table II; uv (CH₃OH) λmax 205 nm (ε 3100). *Anal.* Calcd for C₁₁H₁₄O₃: C, 68.02; H, 7.27. Found: C, 68.02; H, 7.12.

exo-2,3-Dihydroxy-7-isopropylidenebicyclo[2.2.1]heptane (**6a**). —Hydrogenation of **2a** (60 mg) in ethanol (10 ml) was carried out as described above. The solvent was removed, giving white amorphous material (56 mg, 92%); the product after sublimation at 80–90° (0.05 mm) afforded white crystals of **6a**: mp 96–97°; ir[30] (CCl₄) 3500 cm⁻¹ (br); nmr assignments in Table II; uv (CH₃OH) λmax 205 nm (ε 4300). *Anal.* Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.61; H, 9.47.

endo-2,3-Dihydroxy-7-isopropylidenebicyclo[2.2.1]heptane (**6b**). —A solution of **2b** (30 mg) in ethanol (10 ml) was hydrogenated. The product (28 mg, 92%) after sublimation at 90–100° (0.05 mm), had mp 129–130°; ir[30] (CCl₄) 3600–3300 cm⁻¹ (br); nmr, see Table II; uv (CH₃OH) λmax 205 nm (ε 3800). *Anal.* Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.21; H, 9.71.

7-Isopropylidenebicyclo[2.2.1]heptane-*exo*-2,3-diol Thionocarbonate (7a).—A solution of **3a** (66 mg) in ethyl acetate (15 ml) was hydrogenated as before; the uptake of hydrogen was extremely slow and was complete after 24 hr. The product (60 mg, 90%) was purified by sublimation at 100–110° (0.05 mm): mp 145–146°; ir[30] (CHCl₃) 1340, 1305, 1275 cm⁻¹ (vs); nmr, see Table II; uv (CH₃OH) λmax 205 nm (ε 8300) and 241 (14,300). *Anal.* Calcd for C₁₁H₁₄O₂S: C, 62.84; H, 6.71; S, 15.22. Found: C, 62.68; H, 6.57; S, 15.09.

Spiro[2.4]hepta-1,3-diene.—Spiro[2.4]hepta-1,3-diene, bp 43–45° (70 mm) [lit.[16] bp 57° (100 mm)], was prepared according to the method of Alder and coworkers:[16] ir[30] (neat) 3120, 3050 cm⁻¹ (w); nmr[29] (CCl₄) 3.66 and 4.07 (two symmetrical multiplets for vinylics, 4 protons), 8.51 (cyclopropyl, s, 4 protons).

endo[32]-2,3-Dibromo 7,7-dimethylenebicyclo[2.2.1]hept-5-ene (**8**).—The reaction of spiro[2.4]hepta-1,3-diene with dibromoethylene was done in a Carius combustion tube, sealed under high vacuum. The adduct was purified by sublimation at 40–50° (0.05 mm): mp 73° (reported[16] mp 75°); ir[30] (CCl₄) 3110, 3050 cm⁻¹ (w); nmr[29] (CCl₄) 3.71 (t, H-5,6, sp 2 Hz), 5.48 (t, H-2,3 exo, sp 2 Hz), 7.43 (qi, H-1,4, sp 2 Hz), 9.46 (s, H cyclopropyls).

endo-2,3-Dibromo-7,7-dimethylenebicyclo[2.2.1]heptane (**9**).—Hydrogenation of **8** afforded white, crystalline material of **9** after sublimation at 80–90° (0.05 mm): mp 104° (reported[16] mp 76°); ir[30] (CCl₄) 3100 cm⁻¹ (w); nmr[29] (CCl₄) 5.33[33] (br, H-2,3 exo), 9.39 (s, H cyclopropyls).

7,7-Dimethylenebicyclo[2.2.1]heptane (10).—Debromination of **9** gave **10**: mp 40–42° (reported[16] mp 44°); ir[30] (CCl₄) 3100 cm⁻¹ (w); nmr[29] (CCl₄) 9.58 (s, H cyclopropyls), 8.5 (br m, 10 protons).

(27) Several preliminary experiments were carried out to establish optimum reaction conditions. Reactions in a Carius combustion tube or metallic bomb gave only black tarry material.

(28) M. S. Newman and R. W. Addor, *J. Amer. Chem. Soc.*, **75**, 1263 (1953).

(29) Signal positions in τ units; br, broad; m, multiplet; qi, quintet; s, singlet; t, triplet. Chemical shifts are accurate to ±0.02 ppm. All these assignments are confirmed by the integrated areas of various peaks.

(30) Abbreviations: br, broad; s, sharp; vs, very strong; w, weak.

(31) H. A. Staab and G. Walther, *Justus Liebigs Ann. Chem.*, **657**, 98 (1962).

(32) Alder, *et al.*, first reported **8** but did not comment on its configuration. On the basis of the triplet nature of the signal for H-2,3 due to coupling with the bridgehead protons, we have assigned the endo configuration to this compound.

(33) This unexpected downfield shift may result from the anisotropic effects of Br-2,3.

7,7-Dimethylenebicyclo[2.2.1]hept-5-ene (11).—Purification of 11, bp 57–60° (50 mm) [lit.[16] bp 63° (60 mm)], was accomplished by vpc (silicone oil column at 98°): ir[30] (CCl₄) 3100 (w), 3020 cm⁻¹ (w); nmr (CCl₄) 3.97 (t, H-5,6, sp 2 Hz), 7.92 (br, H-1,4), 8.22 (m, H-2,3 exo), 8.98 (m, H-2,3 endo), 9.62 (m, H cyclopropyls anti), 9.71 (m, H cyclopropyls syn).

7,7-Dimethylenebicyclo[2.2.1]hepta-2,5-diene (12).—Purification of 12, bp 30–31° (18 mm) [lit.[16] bp 37° (20 mm)], was achieved by vpc using a silicone oil column at 91°: ir[30] (CCl₄) 3100, 3010 cm⁻¹ (w); nmr[29] (CCl₄) 3.26 (t, H-2,3,5,6, sp 2 Hz), 7.08 (t, H-1,4, sp 2 Hz), 9.57 (s, H cyclopropyls).

Registry No.—**1a**, 35092-24-1; **1b**, 35129-58-9; **2a**, 35092-25-2; **2b**, 35092-26-3; **3a**, 35092-27-4; **3b**, 35092-28-5; **5a**, 35092-29-6; **6a**, 35092-30-9; **6b**, 35092-31-0; **7a**, 35092-32-1; dimethylfulvene, 2175-91-9; vinylene carbonate, 872-36-6.

Preparation and Stereochemistry of 1-Methyl-2-methylenebenzonorbornene and 1,2-Dimethyl-2-benzonorbornenyl Derivatives

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Optically active 2-benzonorbornenone (1) has been converted to active 1-methyl-2-methylenebenzonorbornene (5) in five steps and the latter has been converted to active 1,2-dimethyl-*exo*-2-benzonorbornenol (4) and 1,2-dimethyl-*exo*-2-benzonorbornenyl methyl ether (6). Absolute configurations and rotations of 4, 5, and 6 are established by correlation with 1.

We have recently investigated the symmetry properties of ionic intermediates in the 1,2-dimethyl-2-benzonorbornenyl system[1] This paper reports our synthetic entry into this system and the correlation of optical configurations and rotations required for that investigation.

The 1,2-dimethyl-*exo*-2-benzonorbornenyl system was derived from 2-benzonorbornenone (1)[2] as outlined in Chart I. The key intermediate in this synthesis is 1-methyl-2-methylenebenzonorbornene (5), which was prepared from 1-methyl-2-benzonorbornenone (3) by

CHART I

1, −578°

2, −74°   3, +556°

4, +27°   5, +315°

6, +73°

the Wittig reaction. The latter was prepared from 1 by the series of reactions used earlier[3,4] to convert norcamphor to 1-methyl-2-norbornanone. This sequence involves conversion of 1 to 2-methyl-*endo*-2-benzonorbornenol (2) with methylmagnesium bromide followed by acid-catalyzed rearrangement of 2 in acetic acid to 1-methyl-*exo*-2-benzonorbornenyl acetate. This step results in configurational change of the bicyclic system, as illustrated in Chart I. Reductive cleavage of the acetate with lithium aluminum hydride followed by Oppenauer oxidation[5] of the resulting 1-methyl-*exo*-2-benzonorbornenol gave 3.

Absolute configurations and rotations[6] are shown in Chart I. These were determined directly starting with optically active 1. The absolute configuration and rotation of the latter had been established earlier.[2] Optically active 1 was prepared[2] by asymmetric hydroboration of benzonorbornadiene with tetraisopinocamphenyldiborane[7] followed by oxidation of the resulting active *exo*-2-benzonorbornenol. The most active samples were about 68% optically pure.

Optically active 5 was converted to active 1,2-dimethyl-*exo*-2-benzonorbornenol (4) by oxymercuration–demercuration[8] and to active 1,2-dimethyl-*exo*-2-benzonorbornenyl methyl ether (6) by methoxymercuration–demercuration.[9] There is evidence[3,7] that this type of addition does not result in rearrangement in a similar system, and from this and the reproducible changes in rotations, we conclude that these transformations do not result in loss of optical purity.

Experimental Section

Materials.—Racemic and optically active 2-benzonorbornenone (1) were prepared in about 80% yield from benzonorborna-

(1) H. L. Goering and J. V. Clevenger, to be submitted for publication.

(2) D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *J. Amer. Chem. Soc.*, **90**, 4877 (1968).

(3) H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and H. Humski, *J. Org. Chem.*, **34**, 624 (1969).

(4) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Amer. Chem. Soc.*, **83**, 3986 (1961).

(5) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).
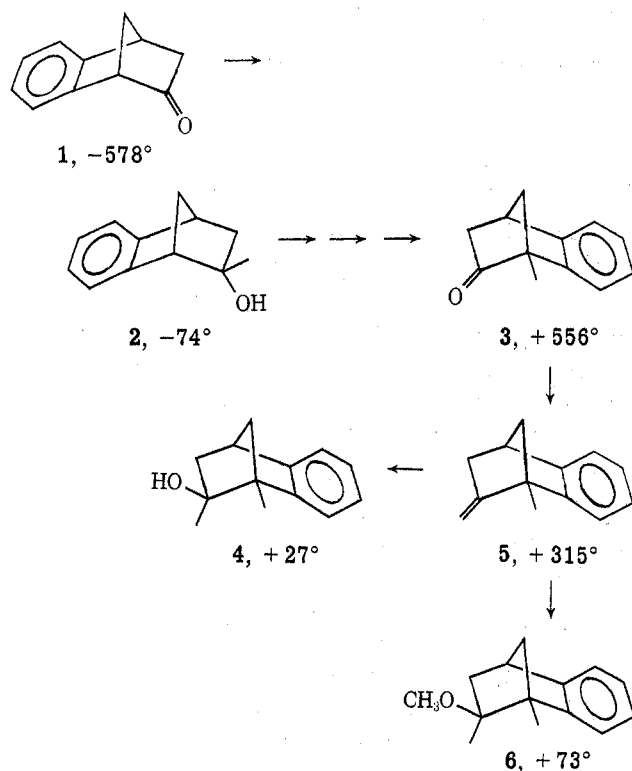
(6) Rotations are for chloroform solutions at 25°.

(7) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

(8) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967), and references cited therein.

(9) H. C. Brown and M.-H. Rei, *ibid.*, **91**, 5646 (1969).