give 48 mg. (27%) of IIIa, m.p. 198°. The analytical sample, m.p. 202° (sharp), was obtained by recrystallization from ethyl acetate. The infrared spectrum (KBr) had bands at 2750, 1712 (aldehyde), 2237 (nitrile), and 1728, 1236 cm.$^{-1}$ (acetate). The n.m.r. spectrum ($CDCl_3$) had doublets in the vinyl proton region at δ 5.97 (J = 6 c.p.s.) and 6.28 (J = 6 c.p.s.). The aldehyde proton appeared as a singlet at δ 9.70.

Anal. Calcd. for $C_{25}H_{31}NO_3$: C, 76.30; H, 7.94; N, 3.56. Found: C, 75.75; H, 7.98; N, 3.68.

A semicarbazone was prepared, m.p. 230–231°.

Anal. Calcd. for $C_{26}H_{34}N_4O_3$: C, 69.30; H, 7.61; N, 12.44. Found: C, 69.39; H, 7.80; N, 12.27.

Adduct IIIb of I with Methyl Acrylate.—A mixture of 200 mg. of I, 0.5 ml. of freshly distilled methyl acrylate, and a trace of hydroquinone was heated in a sealed evacuated tube to 115° for 7 days. The mixture was then transferred to a round-bottom flask and heated on a steam bath at 25 mm. for 1 hr. The residue, in benzene solution, was chromatographed over 30 g. of Merck alumina. Passage of 250 ml. of a 1:1 mixture of benzene–chloroform through the column eluted a fraction which crystallized from methanol to yield 174 mg. (69%) of IIIb, m.p. 160–163°. The analytical sample was prepared by repeated recrystallizations from methanol followed by two recrystallizations from 2-propanol: m.p. 169–170°; ν^{Nujol} 2250 (nitrile), 1735, 1740 cm.$^{-1}$ (ester C=O). The n.m.r. spectrum (CCl_4) had peaks in the vinyl proton region at δ 5.88 (J = 6 c.p.s.) and 6.20 (J = 6 c.p.s.).

Anal. Calcd. for $C_{26}H_{33}NO_4$: C, 73.73; H, 7.85; N, 3.31. Found: C, 73.69; H, 7.80; N, 3.05.

Attempted Diels–Alder Reaction of I with Vinyl Acetate.—A mixture of I, vinyl acetate, and a trace of hydroquinone was heated in a sealed evacuated tube at 110° for 95 hr. Work-up of the reaction mixture resulted only in recovery of I. In a second run conducted at 185° for 47 hr., the product appeared to be largely polymeric. No adduct could be isolated.

Attempted Diels–Alder Reaction of I with Methyl Vinyl Ether.—A mixture of I, methyl vinyl ether, and a trace of N-phenyl-2-naphthylamine were sealed under nitrogen in a stainless steel bomb fitted with a glass liner and heated to 200–208° for 24 hr. The product appeared to be polymeric. Similarly, heating I with methyl vinyl ether and a trace of hydroquinone at 185° for 48 hr. resulted, after work-up, in the recovery of a large amount of polymer and a trace amount of I.

Attempted Diels–Alder Reaction of I with *cis*-Dichloroethylene.—A mixture of I, *cis*-dichloroethylene, and a trace of hydroquinone was heated in a sealed evacuated tube at 185° for 24 hr. The diene component I was recovered quantitatively. When the reaction was run at 195° for 80 hr., polymer and I were isolated from the reaction mixture.

Attempted Diels–Alder Reaction of I with α-Chloroacrylonitrile.—Mixtures of I, α-chloroacrylonitrile, and trace amounts of hydroquinone were heated under nitrogen in one case at 110° for 22 hr., in other cases under reflux for 4 or 6 hr. In all cases at least 80% of the I employed was recovered.

Attempted Diels–Alder Reaction of I with Ethyl Azodicarboxylate.—A mixture of I, ethyl azodicarboxylate, and a trace of hydroquinone was heated at 100° for 6 hr. Routine work-up led to the recovery of unchanged I.

Heating I, ethyl azodicarboxylate, and a trace of N-phenyl-2-naphthylamine, under nitrogen, at 148° for 21 hr. led to the formation of a complex mixture (demonstrated by thin layer chromatography), but none of the desired adduct could be isolated.

Adduct V of I with 4-Phenyl-1,2,4-triazoline-3,5-dione (IV). A.—Equivalent quantities of I and IV[11] were mixed in acetone at room temperature. The red color characteristic of IV was completely discharged within 5 min.

B.—To a solution of 120 mg. (calculated) of 4-phenyl-1,2,4-triazoline-3,5-dione (IV), prepared *in situ*[11] in 30 ml. of dioxane, was added 110 mg. of I. The red solution was left at room temperature overnight, the color fading to a pale yellow. The solution was then evaporated to dryness under reduced pressure at room temperature. The resulting foam on trituration with methanol, at room temperature, gave adduct V as an off-white powder, m.p. 162.5–163.5° dec., yield 113 mg. Recrystallization from aqueous acetone gave an analytical sample: m.p. 164–165° dec.; ν^{Nujol} 1789 and 1739 (carbonyl), 1600 and 1501 cm.$^{-1}$ (phenyl). The n.m.r. spectrum ($CDCl_3$) showed a singlet at δ 7.38 (phenyl) and doublets in the vinyl proton region at δ 6.37 (J = 6 c.p.s.) and 6.59 (J = 6 c.p.s.).

Anal. Calcd. for $C_{30}H_{32}N_4O_4$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.28; H, 6.10, N, 10.58.

Acknowledgment.—We wish to express our appreciation to Syntex, S. A., for a generous gift of starting material.

Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. I. The Acid-Catalyzed Addition of Methanol and Acetic Acid to Bicyclo[3.1.0]hexene-2[1]

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Thermodynamically controlled acid-catalyzed addition of acetic acid or methanol to bicyclo[3.1.0]hexene-2 results in 4-acetoxycyclohexene or 4-methoxycyclohexene, respectively. Kinetically controlled addition of methanol results in predominantly *cis*- and *trans*-2-methoxybicyclo[3.1.0]hexane, with formation of small amounts of 4-methoxycyclohexene. Acid-catalyzed addition of methanol-*d* to bicyclo[3.1.0]hexene-2 proceeds stereospecifically *cis* to yield *trans*-3-deuterio-*trans*-2-methoxybicyclo[3.1.0]hexane.

The recent work of Winstein and Sonnenberg[3] on the trishomocyclopropenyl carbonium ion and the research of Roberts and co-workers[4] on bicyclobutonium ion intermediates stimulated our interest in electrophilic additions to bicyclo[3.1.0]hexene-2 (**1**). Two main alternative reaction pathways for electrophilic addition of HY to **1** appear to be available. For example, addition of HY to **1** might be expected to proceed through a trishomocyclopropenyl intermediate **2**, while addition in the reverse manner could conceivably produce intermediates analogous to bicyclobutonium ion intermediates such as **3** and **4**. Generation of **3** and **4** could result in the formation of five different structures (not including *cis–trans* isomers).[5] Thus it seemed to us that electrophilic additions to **1** would provide an opportu-

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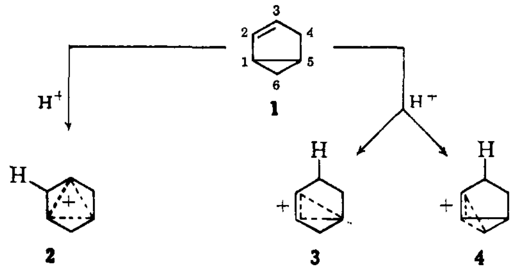
(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1964; Abstracts, p. 59S.

(2) National Defense Education Act Fellow, 1961–1964.

(3) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961); **83**, 3244 (1961).

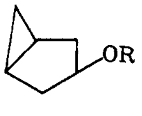
(4) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961).

(5) Formal analogy to the carbon scrambling found by R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts [*ibid.*, **81**, 4390 (1959)] would suggest that four bicyclobutonium ion intermediates in addition to **3** and **4** are possible, although they could not be formed directly from **1**.



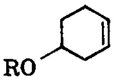
nity to make an interesting comparison between two reaction pathways each possibly involving a different nonclassical carbonium ion.

After abandoning the synthesis of the required starting olefin through use of the Simmons–Smith addition of methylene to cyclopentadiene due to low yields,[6] bicyclo[3.1.0]hexene-2 was synthesized by dehydration of either *cis*-3- or *cis*-2-bicyclo[3.1.0]hexanol (**5a** or **6a**) *via* the methyl xanthates (**5b** or **6b**) in 32 or 40% yield, respectively. Electrophilic addition of acetic acid to **1**, catalyzed by 1% sulfuric acid and carried out at either 25° or 118°, produces 4-acetoxycyclohexene (**7a**) as the only product. However, since *cis*-2-acetoxybicyclo[3.1.0]hexane (**6d**) is completely converted to **7a** in glacial acetic acid and 1% sulfuric acid at 25°, the structure of the addition product is probably dictated by thermodynamic control. Electrophilic addition of methanol, catalyzed by 20% sulfuric acid and carried out at reflux, results in 4-methoxycyclohexene (**7b**) as the sole product. The reaction conditions used for this addition were sufficient to cause complete isomerization of *cis*-2-methoxybicyclo[3.1.0]hexane (**6c**) to **7b**.

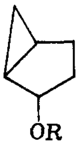


5a, R = H
b, R = CS_2CH_3
c, R = CH_3

6a, R = H
b, R = CS_2CH_3
c, R = CH_3
d, R = $COCH_3$

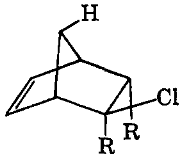


7a, R = $COCH_3$
b, R = CH_3



8a, R = H
b, R = CH_3

The use of milder reaction conditions resulted in less thermodynamic control. The addition of methanol to **1**, catalyzed by 20% sulfuric acid and carried out at 25° for 5 days, resulted in two components in a 30:70 ratio in the C_7-ether region as analyzed by vapor phase chromatography (v.p.c.). The infrared spectrum of the 30% component provided evidence that the bicyclo[3.1.0]hexyl ring system was present (ν_{max} 3070, 3040, 3000, and 1022 cm.$^{-1}$, no C═C absorption in the 1600–1650-cm.$^{-1}$ region, Table IV, Experimental). The n.m.r. spectrum showed a doublet at τ 6.27 due to the hydrogen α to the methoxyl group and a complex absorption region for the two methylene hydrogens of the cyclopropane ring at τ 9.40 to 10.15, which extends even further upfield than the absorption area for the corresponding hydrogens of bicyclo[3.1.0]hexane (τ 9.60–10.00). One might expect deshielding field effects for *cis*-2 and *cis*-3 substituents on the bicyclohexane ring upon the *syn*-C-6 hydrogen which are similar to the effect of the 5-*exo* chlorine on the C-7-*syn* hydrogen in *exo*-5-chloronorbornene derivatives[7] (**9**) and the effect of the *cis*-C-3-chlorine substituent of the dichlorocarbene–norbornene adduct (**10**) upon the *syn*-C-8 hydrogen.[8] This situation was found to prevail for a series of 2- and 3-bicyclo[3.1.0]hexyl epimers (Table IV), and, thus, it is not surprising that the infrared spectra of the 30% component and that of *trans*-2-methoxybicyclo[3.1.0]hexane, synthesized from the *trans*-2 alcohol (**8a**) using sodium and methyl iodide, proved to be identical and provided final confirmation of structure.



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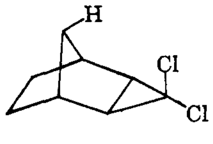

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The 70% component had the same retention time as 4-methoxycyclohexene (**7b**), but infrared analysis indicated that it was a mixture with 4-methoxycyclohexene as the major component. The additional absorption at 3070 and 3000 cm.$^{-1}$ suggested that the additional components(s) possessed the bicyclo[3.1.0]hexyl ring system. *cis*-2-Methoxybicyclo[3.1.0]hexane (**6c**) was prepared from *cis*-2 alcohol **6a** using sodium and methyl iodide. Infrared comparison of **6c** with the 70% component proved that this component was a binary mixture of 31% **6c** and 69% **7b**.

The results of the addition of methanol to bicyclo[3.1.0]hexene-2 carried out under various reaction conditions are summarized in Table I. The data obtained through study of some acid-catalyzed rearrangement reactions of *cis*-2-methoxybicyclo[3.1.0]hexane (**6c**) are listed in Table II and suggest that an important fraction of the 4-methoxycyclohexene, produced in the addition reaction, is formed by acid-catalyzed rear-

TABLE I

ADDITION OF METHANOL TO BICYCLO[3.1.0]HEXENE-2[a]

Run	Catalyst	Temp., °C.	Time	% yield 8b	6c	7b
1	20% H_2SO_4	67	7 hr.	0	0	100
2	20% H_2SO_4	25	5 days	30	22	48
3	0.4% *p*-TSA[b]	65	8 hr.	53	32	15

[a] All reactions were run in absolute methanol. [b] *p*-TSA = *p*-toluenesulfonic acid.

TABLE II

REARRANGEMENT OF *cis*-2-METHOXYBICYCLO[3.1.0]HEXANE, 6c[a]

Run	Catalyst	Time	Temp., °C.	% yield 8b	6c	7b
1	20% H_2SO_4	5 days	25	29	24	47
2	20% H_2SO_4	20 days	25	0	0	100
3	0.4% *p*-TSA	10 days	25	9	91	0
4	0.4% *p*-TSA	8 hr.	65	22	73	5
5	None	48 hr.	65	0	100	0

[a] All studies were run in absolute methanol.

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[6] This approach has been used successfully since by E. J. Corey and R. L. Dawson [*J. Am. Chem. Soc.*, **85**, 1782 (1963)] to prepare **1** in 5% yield.

[7] P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

[8] W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

TABLE III

ADDITION OF METHANOL TO BICYCLO[3.1.0]HEXENE-2[a]

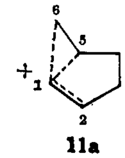
Run	Time, hr.	% yield 8b	% yield 6c	% yield 7b
1	0.5	55	45[b]	
2	2.0	54	39	7
3	4.0	52	35	13
4	4.0	52	34	13
5	6.0	51	34	15
6	8.0	49	31	20

[a] Catalyst, 0.1 *M* *p*-toluenesulfonic acid; 65°. [b] Combined value of **6c** and **7b**.

rangement of the 2-ethers **6c** and **8b**. Further evidence that this is true was obtained by studying the *p*-toluenesulfonic acid catalyzed addition of methanol to **1** at 65° using various reaction times. The results, listed in Table III, show that only about 7% of 4-methoxycyclohexene is formed in the 2-hr. run, while increasing percentages result with longer reaction times. Thus the maximum amount of **7b** which can be formed directly is 7%, but in fact the actual amount is probably less. If it is assumed that the acid-catalyzed rearrangement of **6c** is an SN1 process,[9] then the isomerization of **6c** to **8b** in which no detectable cyclohexenyl ether **7b** is formed (run 3, Table II) is a further illustration of the fact that very little **7b** is formed directly.[10]

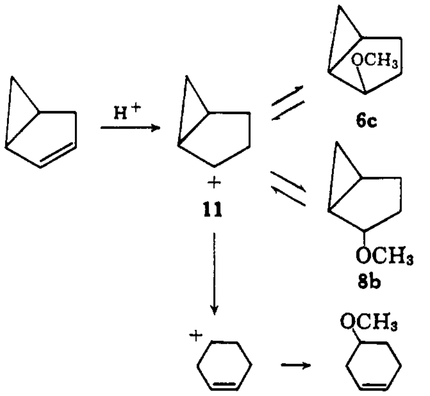
Particularly significant was the absence in the addition of methanol to **1** of the 3-ethers which could be detected easily if present in the C_7-ether fraction to an extent of 1%. The question arose as to whether they were formed and then rearranged, or whether they were not formed at all. To test this, *cis*-3-methoxybicyclo[3.1.0]hexane (**5c**) was subjected to the reaction conditions (20% sulfuric acid in methanol, 5 days, 25°) and found to be completely stable. Since the conjugate acid of the *cis*-3 ether might be expected to solvolyze more rapidly than the conjugate acid of the *trans*-3 ether,[3] the conclusion was drawn that none of the 3-ethers were formed in the addition reaction. Thus one can rule out a trishomocyclopropenyl carbonium ion (**2**), or a classical relative, as a product-determining intermediate.

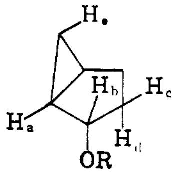
The acid-catalyzed addition of methanol to **1** might be represented most simply in terms of ion **11** which generates 2-ethers **6c** and **8b** reversibly and **7b**, *via* ion **12**, irreversibly. That **7b** is formed irreversibly was checked by subjecting it to the reaction conditions (20% sulfuric acid in methanol, 5 days, 25°) and finding, as expected,[11] that it is stable to rearrangement. However, it is clear that the 2-carbonium ion is more stable than the 3-carbonium ion in agreement with the results of Corey and Dawson[6] and of Winstein,[12] and therefore representation **11** is not completely adequate. The greater stability of the 2-carbonium ion may be rationalized as the result of electron donation by the cyclopropane ring to the electron deficient C-2 as in **11a**. Ion **11a** may, in fact, be the sole precursor of **6c**, **8b**, and **7b**. The positive charge must, however, be considerably localized at C-2 since attack at C-2 is favored over attack at C-5 by a factor of at least 12 to 1 and no products were observed resulting from attack at C-1 or C-6. Thus the product composition provides no evidence which requires bicyclobutonium ion intermediates **3** or **4** or other bicyclobutonium intermediates formed by rearrangement of **3** or **4**. One can not, however, rule out small cyclobutyl (bicyclo[2.2.0]hexyl) and bicyclo[2.1.1]hexyl contributions to the correct resonance picture for the 2-carbonium ion on the basis of the present evidence. It appears, then, that the 2-bicyclo[3.1.0]hexyl carbonium ion is similar to other substituted cyclopropylcarbinyl carbonium ions which do not rearrange under conditions of kinetic control.[4,9,13]



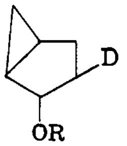
11a

The unique doublet at τ 6.27 (*J* = 5.1 c.p.s.) in the n.m.r. spectrum of *trans*-2-methoxybicyclo[3.1.0]hexane offered an opportunity to test the stereochemistry of the addition of methanol leading to this isomer. The splitting of the absorption of the *cis*-C-2 hydrogen (H_b in **13**) seemed to be most reasonably due to coupling with the *cis* hydrogen H_c.[14] This was verified by

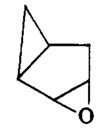




13a, R = CH_3
b, R = H



14a, R = CH_3
b, R = H



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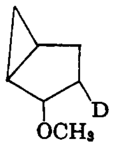

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[9] R. G. Pearson and S. H. Langer, *J. Am. Chem. Soc.*, **75**, 1065 (1953).

[10] M. Hanack and H. J. Schneider [*Tetrahedron*, **20**, 1863 (1964)], in a complementary study published simultaneously with the presentation of our results (ref. 1), have demonstrated that the methanolysis of Δ^2-cyclopentenylcarbinyl *p*-toluenesulfonate produces *cis*- and *trans*-2-methoxybicyclo[3.1.0]hexane, Δ^2-cyclopentenylcarbinyl methyl ether, and no 4-methoxycyclohexene.

[11] M. Hanack and W. Keberle, *Ber.*, **96**, 2937 (1963).

[12] Footnote 13 in ref. 6.

[13] H. Hart and P. A. Law, *J. Am. Chem. Soc.*, **86**, 1957 (1964); **84**, 2462 (1962); H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959); H. Hart and R. A. Martin, *ibid.*, **82**, 6362 (1960); R. A. Sneen and A. L. Baron, *ibid.*, **83**, 614 (1961).

[14] (a) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963); (b) K. L. Williamson, *ibid.*, **85**, 516 (1963); (c) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, **No. 4**, 185 (1963).

synthesis of **14a**, adapting a synthetic route reported by Corey.[6]

trans-2,3-Epoxybicyclo[3.1.0]hexane (**15**) was reduced with lithium aluminum deuteride in 90% yield to give a mixture of the deuterated *trans*-2 (**14b**) and *trans*-3 alcohols. The *trans*-2 alcohol was separated by v.p.c. and the methyl ether **14a** was prepared from it, using sodium and methyl iodide, in 80% yield. The n.m.r. spectrum of **14a** showed one tertiary proton as a singlet at τ 6.28, three protons of the methoxy group at 6.72, two tertiary protons and three methylene protons (7.89 to 8.76), and two methylene protons on a cyclopropane ring (9.42 to 10.17). The integration corresponding to five protons in the τ 7.89 to 8.76 region indicated 95–100% deuteration since this region shows an integration corresponding to six protons in the undeuterated analog **8b**. A similar picture was obtained by comparison of the n.m.r. spectra of the *trans*-2 alcohols **14b** and **8a**. The spectrum of **8a** exhibited a doublet at τ 5.78 (J = 4.5 c.p.s.) while deuterated **14b** showed only a singlet at 5.88. Thus it is clear that the splitting of H_b is due to H_c as anticipated.

Since derivatives of norbornene containing a variety of electronegative substituents in the *endo*-5 position exhibit coupling constants for the *exo*-5 and *exo*-6 protons of 7.4–9.3 c.p.s.,[14a,b] and derivatives of *exo*-2-norbornanol show a range of 6.6–7.0 c.p.s. for the coupling constants of the *endo*-2 and *endo*-3 protons,[14c] it appears that the lower coupling constant for J_{bc} in **13** must be due to a difference in geometry. If the cyclopentane ring in **13** is puckered so that C-2 is displaced downward and C-3 upward from the average plane of the cyclopentane ring, then the dihedral angle for H_a–C–C–H_b approaches 80°, the angle for H_b–C–C–H_c approaches 20° and that for H_b–C–C–H_d approaches 100° as determined using a Dreiding model. This conformation of the bicyclo[3.1.0]hexane ring would explain the reduced coupling constant J_{bc} and the lack of coupling of H_b to either H_a or H_d.[15] The puckering of **13** into somewhat of a dish form is not unreasonable since it would decrease the more serious nonbonded interactions (H_a–O, H_e–H_b, and the two symmetrically situated interactions on the opposite side of the ring) while puckering in the opposite direction would increase them.

The n.m.r. spectrum of the *trans*-2 ether resulting from the *p*-toluenesulfonic acid-*d* catalyzed addition of methanol-*d* to bicyclo[3.1.0]hexene-2 (95–100% deuterated as evidenced by an integration corresponding to five protons in the τ 7.89 to 8.76 region) still showed the characteristic doublet at 6.27 (J = 5 c.p.s.). Thus the structure of the product must be **16**, which is the result of *cis* addition of CH_3OD. No *trans* addition product **14a** could be detected, although as much as 10% could have gone undetected. This *cis* addition of methanol to bicyclo[3.1.0]hexene-2 represents another example for the growing list of stereospecific *cis* polar additions to olefins.[14c,16] The mechanistic implications of this *cis* addition are presumably similar to those discussed for the systems studied by Dewar, Cristol, and Kwart.

Experimental[17]

Bicyclo[3.1.0]hexene-2.—Δ^2-Cyclopentenol was prepared by the method of Alder and Flock.[18] *cis*-2-Bicyclo[3.1.0]hexanol was prepared according to the directions given by Dauben and Berezin.[19] Methyl 2-bicyclo[3.1.0]hexyl xanthate was prepared by the procedure of Alexander and Mudrak.[20]

A 63.5-g. (0.338 mole) sample of xanthate was placed in a 100-ml., one-necked flask equipped with a distillation head and a receiver immersed in a Dry Ice trap. The flask was heated by means of a heating mantle and decomposition was first observed at a dry flask temperature of 150°. The reaction flask was held at this temperature for 1 hr. and then the temperature was gradually increased until a few drops of yellow oil were collected in the receiver. The receiver was allowed to warm slowly to room temperature. Distillation of the material which had collected in the receiver on an 18-in. semimicro spinning-band column gave 10.6 g. (0.133 mole, 39.2% of product, b.p. 70–71° at atmospheric pressure). The infrared spectrum of this material showed typical absorption for cyclopropane (C–H frequency at 3055 and ring absorption at 1020 cm.$^{-1}$) and double bond (C=C at 1595 and *cis*-hydrogens on a double bond at 715 cm.$^{-1}$) moieties.[21] The n.m.r. spectrum contained two olefinic protons (τ 4.03 and 4.58), two methylene protons α to a double bond (τ 7.60), two tertiary protons (τ 8.33), and two methylene protons on a cyclopropane ring (τ 9.17 and 10.17). An analytical sample was isolated by v.p.c. using a 27-ft. Dow–Corning QF-1 column.

Anal. Calcd. for C_6H_8: C, 89.94; H, 10.06. Found: C, 89.93; H, 10.25.

An alternate synthetic route to bicyclo[3.1.0]hexene-2 was realized through the pyrolysis of the methyl xanthate of *cis*-3-bicyclo[3.1.0]hexanol. Δ^3-Cyclopentenol was prepared by the method of Brown and Zweifel.[22] *cis*-3-Bicyclo[3.1.0]hexanol was prepared by the procedure of Winstein and Sonnenberg.[3] The methyl xanthate preparation and pyrolysis were carried out in the same manner as described for *cis*-2-bicyclo[3.1.0]hexanol, resulting in a 32% yield of bicyclo[3.1.0]hexene-2 (based upon xanthate). The over-all yield of desired olefin was not so good by this alternate route owing to the lower yield obtained in the first step. A 70–80% yield of Δ^2-cyclopentenol was realized using the Alder and Flock method,[18] while the yield of Δ^3-cyclopentenol by the Brown and Zweifel method[22] was only 15–20%.

Addition of Acetic Acid to Bicyclo[3.1.0]hexene-2.—The method of Cristol and co-workers[23] was adapted for this system. In a 100-ml. flask equipped with a magnetic stirrer was weighed 2.00 g. (0.025 mole) of bicyclo[3.1.0]hexene-2. To this reaction flask was added 15.3 g. of glacial acetic acid and 0.1 ml. of 96% sulfuric acid. A reflux condenser was attached to the flask and the reaction mixture was heated at reflux and stirred for 2 hr.

The mixture was then cooled to room temperature and twice the volume of cold water was added. The solution was extracted several times with ethyl ether and the combined ether extracts were washed with water, 5% sodium carbonate solution, water, and saturated sodium chloride solution. After drying over magnesium sulfate, the ether was removed by distillation, and a total of 1.0 g. (29%) of product was obtained by vacuum distillation. The infrared spectrum of this product showed typical absorption for an acetate group (C=O at 1745 and C–O at 1240 and 1040 cm.$^{-1}$) and a double bond (C=C at 1650 and *cis* hydrogens on a double bond at 748 cm.$^{-1}$). This spectrum was similar but not identical with that of a known sample of 3-acetoxycyclohexene. The n.m.r. spectrum contained two olefinic protons (τ 4.40), four methylene protons α to a double bond (τ 7.80), two methylene protons β to a double bond (τ 8.17), one tertiary proton (τ

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5.00), and three protons of the acetate methyl group (τ 7.98). This product was greater than 99% pure by v.p.c. as analyzed on a 20-ft. Dow-Corning 200 column.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.71; H, 8.50.

The addition of acetic acid to bicyclo[3.1.0]hexene-2 was also done at room temperature in a similar manner. The reaction mixture was stirred at room temperature for 30 hr. The only product isolated (0.8 g., 23%) from this reaction was 4-acetoxycyclohexene.

***cis*-2-Acetoxybicyclo[3.1.0]hexane.**—The procedure described by Fieser was followed for the preparation of this compound.[24] Acetic anhydride (10 g., 0.1 mole) and *cis*-2-bicyclo[3.1.0]-hexanol (5.0 g., 0.05 mole) were heated at reflux with a small amount of sodium acetate (0.2 g.) for 4 hr. Water was added and the reaction solution was extracted with several portions of ether. The combined ether extracts were washed with water, 5% sodium carbonate solution, and water, and then dried over magnesium sulfate.

After the removal of the ether using a rotary evaporator, distillation of the remaining material on an 18-in. semimicro spinning-band column gave 3.5 g. (0.025 mole, 50%) of product, b.p. 65–68° (15 mm.). The infrared spectrum of this material showed typical absorption for the bicyclic C–H (3075, 3040, and 3005 cm.$^{-1}$) (see Table IV) and the acetoxy group (1725, C=O, and 1250 cm.$^{-1}$, C–O). An analytical sample was separated and collected using a 10-ft. Carbowax 1500 column.

TABLE IV

CHARACTERISTIC INFRARED AND N.M.R. ABSORPTION BANDS OF 2- AND 3-BICYCLO[3.1.0]HEXYL EPIMERS

Compd.	C-H stretching frequencies, cm.$^{-1}$	Cyclopropane frequency, cm.$^{-1}$	N.m.r. cyclopropane methylene, τ
Bicyclo[3.1.0]hexane	3055, 3025, 2995	1022	9.60–10.00
cis-2-Bicyclo[3.1.0]hexanol	3070, 3030,[a] 3000	1020	9.32–9.89
trans-2-Bicyclo[3.1.0]hexanol	3070, 3030, 2995	1020	9.39–10.10
cis-3-Bicyclo[3.1.0]hexanol	3078, 3030,[a] 3003	1022	9.30–9.84
trans-3-Bicyclo[3.1.0]hexanol	3060, 3030, 2997	1026	9.50–10.14
cis-2-Methoxybicyclo[3.1.0]-hexane	3070, 3030,[a] 3000	1020	9.36–9.83
trans-2-Methoxybicyclo[3.1.0]-hexane	3070, 3040, 3000	1022	9.40–10.15
cis-3-Methoxybicyclo[3.1.0]-hexane	3075, 3030,[a] 3000	1020	9.48–9.73
trans-3-Methoxybicyclo[3.1.0]-hexane	3071, 3037, 2995	1029	9.50–10.20
cis-2-Chlorobicyclo[3.1.0]hexane	3070, 3040,[a] 3000	1025	9.35–9.67
trans-2-Chlorobicyclo[3.1.0]-hexane	3060, 3035, 3000	1025	9.34–10.00
cis-3-Chlorobicyclo[3.1.0]hexane	3070, 3035,[a] 3000	1015	9.07–9.64
trans-3-Chlorobicyclo[3.1.0]-hexane	3060, 3040, 3000	1025	9.44–10.00

[a] Absorption band enhanced relative to epimer.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.56; H, 8.79.

Rearrangement Study. *cis*-2-Acetoxybicyclo[3.1.0]hexane.—A sample of *cis*-2-acetoxybicyclo[3.1.0]hexane was subjected to the conditions of the acetic acid additions to bicyclo[3.1.0]-hexene-2. In both cases (reflux and at room temperature) the only product isolated was 4-acetoxycyclohexene in 33% yield.

Addition of Methanol to Bicyclo[3.1.0]hexene-2.—The procedure of Cristol and co-workers[23] was adapted for this system.

A. Reflux Temperature, Sulfuric Acid Catalyst.—Bicyclo-[3.1.0]hexene-2 (2.0 g., 0.025 mole) was added to a mixture of 40.0 g. (1.25 moles) of absolute methanol and 10.0 g. (0.098 mole) of 96% sulfuric acid. The reaction mixture was refluxed (67° pot temperature) for 7 hr. and then cooled. The mixture was diluted with about 100 ml. of distilled water and extracted with three 50-ml. portions of ether. The combined ether extracts were washed with water, 5% sodium carbonate solution, water, and dried over magnesium sulfate. The ether was removed by distillation and a total of 0.8 g. (29%) of product was obtained by vacuum distillation. The vapor phase chromatograph of this product on a 25-ft. Carbowax 1500 column showed only one peak. The infrared spectrum of the product showed the typical ether absorption centered at 1100 and C=C absorption at 1645 cm.$^{-1}$ and was identical with that of an authentic sample of 4-methoxycyclohexene. The n.m.r. spectrum contained two olefinic protons (τ 4.43), one tertiary proton and three protons of the methoxy group (τ 6.72), four methylene protons α to a double bond (τ 7.95), and two methylene protons β to a double bond (τ 8.18). This spectrum was similar but not identical with that of 3-methoxycyclohexene.[25] An analytical sample was isolated by v.p.c. using the column listed above.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.86; H, 10.64.

B. Room Temperature, Sulfuric Acid Catalyst.—A 2.0-g. (0.025 mole) sample of bicyclo[3.1.0]hexene-2, 40.0 g. (1.25 moles) of absolute methanol, and 10.0 g. (0.098 mole) of 96% sulfuric acid were stirred at room temperature for 5 days. The reaction product (1.0 g., 37% yield) was isolated as previously described and showed two peaks on a 25-ft. Carbowax 1500 v.p.c. column in the ratio of 30 to 70. The infrared spectrum of the 30% peak had absorptions indicating that the bicyclic ring structure was present (C–H at 3070, 3040, and 3000 and cyclopropane at 1022 cm.$^{-1}$) (see Table IV) and showed ether absorption at about 1100 cm.$^{-1}$. This spectrum was identical with that of an authentic sample of *trans*-2-methoxybicyclo[3.1.0]hexane. The n.m.r. spectrum of the 30% component contained one tertiary proton as a doublet at τ 6.27 (J = 5.1 c.p.s.); three protons of the methoxy group, 6.70; two tertiary protons and four methylene protons, ranging from 7.93 to 8.90; and two methylene protons on a cyclopropane ring, 9.40 to 10.15. An analytical sample was isolated by v.p.c.

Anal. Calcd. for $C_7H_{12}O$: C, 74.97; H, 10.79. Found: C, 74.58; H, 10.83.

The infrared spectrum of the 70% peak showed that it was a mixture of 31% *cis*-2-methoxybicyclo[3.1.0]hexane (base line calculation at 830 cm.$^{-1}$) and 69% 4-methoxycyclohexene (by difference).

C. Reflux Temperature, *p*-Toluenesulfonic Acid Catalyst.—A mixture of 1.5 g. (0.019 mole) of bicyclo[3.1.0]hexene-2, 0.038 g. (0.0002 mole) of *p*-toluenesulfonic acid, and 10.0 g. (0.31 mole) of absolute methanol was heated at reflux for 8 hr. The mixture was cooled and the reaction products were isolated as previously described. The isolated products (0.11 g., 5%) showed two peaks by v.p.c. in the ratio of 53 to 47. The 53% peak was *trans*-2-methoxybicyclo[3.1.0]hexane; the 47% peak was a mixture of 69% *cis*-2-methoxybicyclo[3.1.0]hexane and 31% 4-methoxycyclohexene. The C_7-ether product analyzed by infrared as a mixture of 53% *trans*-2-methoxybicyclo[3.1.0]hexane (base line calculation at 710 cm.$^{-1}$), 32% *cis*-2-methoxybicyclo-[3.1.0]hexane (base line calculation at 760 cm.$^{-1}$), and 15% 4-methoxycyclohexene (base line calculation at 733 cm.$^{-1}$).

***cis*-2-Methoxybicyclo[3.1.0]hexane.**—Freshly cut pieces of metallic sodium (1.3 g., 0.05 g.-atom) were added to 300 ml. of anhydrous ethyl ether in a three-necked 500-ml. flask equipped with a stirrer and reflux condenser. A mixture of 4.9 g. (0.05 mole) of *cis*-2-bicyclo[3.1.0]hexanol in 50 ml. of anhydrous ether was added to the reaction flask. The reaction was stirred overnight at room temperature. After the pieces of unchanged sodium were removed physically, 14.2 g. (0.1 mole) of methyl iodide was added dropwise. The reaction mixture was stirred an additional 8 hr., filtered, and dried over magnesium sulfate. After the removal of the ether using a rotary evaporator, distillation of the remaining material on an 18-in. semimicro spinning-band column gave 1.3 g. (0.012 mole; 24%) of product, b.p. 54–56° (60 mm.). The retention time of the product was the same on a Carbowax 1500 v.p.c. column as that for 4-methoxycyclohexene. An analytical sample was isolated by v.p.c.

Anal. Calcd. for $C_7H_{12}O$: C, 74.97; H, 10.79. Found: C, 74.67; H, 10.78.

The infrared spectrum of this material showed typical absorption for the bicyclic C–H (3070, 3030, and 3000 cm.$^{-1}$), ether absorption at about 1100, and cyclopropane at 1020 cm.$^{-1}$. The n.m.r. spectrum of this material contained one tertiary proton α to the methoxy group with a complex splitting pattern centered at τ 5.9, three protons of the methoxy group, 6.70; two tertiary and four methylene protons, ranging from 8.00 to 9.00 τ; and two methylene protons on a cyclopropane ring,

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(24) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1957, p. 205.

(25) N.m.r. data and a standard sample of 3-methoxycyclohexene were kindly supplied by Richard E. McAtee.

9.36 to 9.83. In particular, the *cis*- and *trans*-2-methoxybicyclo[3.1.0]hexane isomers are distinguishable in the n.m.r. by the tertiary proton α to the methoxy group. This proton appears as a distinct doublet in the spectrum of the *trans* isomer (shifted somewhat upfield) and as a complex pattern in the spectrum of the *cis* isomer. This distinction characterizes the 2-epimers which are listed in Table IV. In addition, a deshielding effect of *cis* substituents upon the *syn*-C-6 hydrogen results in shifting the absorption band for the methylene hydrogens of the cyclopropane ring downfield, while the *trans* epimers exhibit an absorption area for the C-6 hydrogens similar to that of the parent bicyclo[3.1.0]hexane. A third distinguishing feature of the epimers considered in Table IV is that in each case the *cis* isomer exhibits an enhanced C–H stretching absorption at about 3035 cm.$^{-1}$ relative to the corresponding *trans* isomer.

4-Methoxycyclohexene.—4-Chlorocyclohexanol was prepared from 1,4-cyclohexanediol by the method of Owen and Robins.[26] 4-Hydroxycyclohexene was prepared by the elimination of the elements of hydrogen chloride from 4-chlorocyclohexanol using alcoholic potassium hydroxide. 4-Methoxycyclohexene was prepared from the 4-hydroxycyclohexene, resulting from the elimination reaction, by the method described above for the synthesis of *cis*-2 ether **6c** in 44% yield. Analysis of this preparation by v.p.c. using a 25-ft. Carbowax 1500 column showed it to be a mixture of 63% 4- and 37% 3-methoxycyclohexene.[25] Since ether preparations from similar alcohols have been shown to be free of isomerization,[19,27] isomerization apparently occurred at some time during the first two steps of the preparation procedure. The 4-methoxycyclohexene peak was collected separately and its infrared spectrum was identical with that of the cyclohexenyl product obtained from the methanol addition reactions.

***cis*- and *trans*-2-Methoxybicyclo[3.1.0]hexane.**—A mixture of 89% *cis*-2-bicyclo[3.1.0]hexanol and 11% *trans*-2-bicyclo-[3.1.0]hexanol was prepared by lithium aluminum hydride reduction of 2-bicyclo[3.1.0]hexanone according to the procedure of Corey and Dawson.[6] This mixture was used to prepare *cis*- and *trans*-2-methoxybicyclo[3.1.0]hexane in 55% yield by the method described above for the *cis*-2-methyl ether. Analysis of the product mixture by v.p.c. on a 25-ft. Carbowax 1500 column showed it to be 14% *trans*-2-methoxybicyclo[3.1.0]-hexane and 86% *cis*-2-methoxybicyclo[3.1.0]hexane. The two peaks were collected separately from the chromatograph and their infrared spectra were identical with those of the *trans*-2 and *cis*-2 ethers obtained from the methanol addition reaction.

Rearrangement Study. *cis*-2-Methoxybicyclo[3.1.0]hexane.—Samples of *cis*-2-methoxybicyclo[3.1.0]hexane were subjected to the various conditions of the methanol addition to bicyclo-[3.1.0]hexene-2.

A. Room Temperature, Sulfuric Acid Catalyst.—A mixture of 2.0 g. (0.018 mole) of *cis*-2-methoxybicyclo[3.1.0]hexane, 40.0 g. (1.25 moles) of absolute methanol, and 10.0 g. (0.098 mole) of 96% sulfuric acid was stirred at room temperature for 5 days. The reaction products were isolated in 50% yield and analyzed by v.p.c. and infrared in the same manner as previously described. The ether mixture was 29% *trans*-2 ether, 24% *cis*-2 ether, and 47% 4-methoxycyclohexene.

In another experiment the same reaction mixture was allowed to stand at room temperature with frequent stirring for 20 days. Separation and analysis of the ether products showed only 4-methoxycyclohexene in 60% yield.

B. Room Temperature, *p*-Toluenesulfonic Acid Catalyst.—A mixture of 0.7 g. (0.0063 mole) of *cis*-2-methoxybicyclo[3.1.0]-hexane, 0.019 g. (0.0001 mole) of *p*-toluenesulfonic acid, and 5.0 g. (0.156 mole) of absolute methanol was stirred at room temperature for 10 days. Isolation of the reaction products gave a 50% yield and analysis showed 9% *trans*-2 ether, 91% *cis*-2 ether, and no evidence of 4-methoxycyclohexene.

C. Reflux Temperature, *p*-Toluenesulfonic Acid Catalyst.—A mixture of 0.7 g. (0.0063 mole) of *cis*-2-methoxybicyclo[3.1.0]-hexane, 0.016 g. (*ca.* 0.0001 mole) of *p*-toluenesulfonic acid, and 5.0 g. (0.156 mole) of absolute methanol was refluxed for 8 hr. Isolation of the ether reaction products gave a 55% yield and analysis showed 22% *trans*-2 ether, 73% *cis*-2 ether, and 5% 4-methoxycyclohexene.

D. Reflux Temperature, No Catalyst.—A 2.0-g. (0.018 mole) sample of *cis*-2-methoxybicyclo[3.1.0]hexane in 40.0 g. (1.25 moles) of absolute methanol was refluxed for 48 hr. Isolation (33% recovery) and analysis of the reaction product showed no change in the starting ether. Analytical procedures would have been able to detect a 1% change in the starting ether.

***cis*-3-Methoxybicyclo[3.1.0]hexane.**—*cis*-3-Methoxybicyclo[3.-1.0]hexane was prepared in 27% yield from *cis*-3-bicyclo[3.1.0]-hexanol using the method described for preparation of *cis*-2-methoxybicyclo[3.1.0]hexane. The infrared spectrum of this compound showed typical bicyclic C–H absorption (3075, 3030, and 3000 and cyclopropane at 1020 cm.$^{-1}$) and ether absorption centered at about 1100 cm.$^{-1}$. The n.m.r. spectrum of this ether contained one tertiary proton α to methoxy (complex multiplet centered at τ 6.20), three protons of the methoxy group (τ 6.84), four methylene protons (centered at τ 8.10), two tertiary protons (ranging from τ 8.68 to 9.00), and two methylene protons on a cyclopropane ring (τ 9.48 to 9.73). This material showed only one peak by v.p.c. on a 25-ft. Carbowax 1500 column.

Anal. Calcd. for $C_7H_{12}O$: C, 74.97; H, 10.79. Found: C, 74.70; H, 10.84.

Rearrangement Study. *cis*-3-Methoxybicyclo[3.1.0]hexane.—A mixture of 2.0 g. (0.018 mole) of *cis*-3-methoxybicyclo-[3.1.0]hexane, 40.0 g. (1.25 moles) of absolute methanol, and 10.0 g. (0.098 mole) of 96% sulfuric acid was stirred at room temperature for 5 days. The reaction product (45% recovery) was isolated and analyzed. The *cis*-3 ether was recovered unchanged as determined by v.p.c. and infrared analysis.

Lithium Aluminum Deuteride Reduction of *trans*-2,3-Epoxybicyclo[3.1.0]hexane.—To a solution of 1.05 g. (0.025 mole) of lithium aluminum deuteride in 30 ml. of dry ether was added dropwise a solution of 2.5 g. (0.025 mole) of *trans*-2,3-epoxy-bicyclo[3.1.0]hexane[6] in 10 ml. of dry ether. After the addition had been completed, the reaction was heated at reflux for 1 hr. The excess deuteride was decomposed by dropwise addition of water, and sufficient excess water was added to give a granular precipitate. The resulting suspension was filtered and the precipitate was washed thoroughly with ether. The ether was removed from the combined filtrate and washings using a rotary evaporator. Analysis of this product (2.3 g., 90% yield) using a 10-ft. Carbowax 1500 column showed 61% *cis*-3-deuterio-*trans*-2-bicyclo[3.1.0]hexanol and 39% *cis*-2-deuterio-*trans*-3-bicyclo[3.1.0]hexanol. The n.m.r. spectrum of *cis*-3-deuterio-*trans*-2-bicyclo[3.1.0]hexanol showed one tertiary proton α to hydroxyl as a singlet at τ 5.88, hydroxyl hydrogen at 6.18, a five-proton band 7.84–8.77 (indicating 95–100% deuteration), and two cyclopropane methylene hydrogens, 9.45–10.17.

***cis*-3-Deuterio-*trans*-2-methoxybicyclo[3.1.0]hexane.**—*cis*-3-Deuterio-*trans*-2-methoxybicyclo[3.1.0]hexane was prepared from the corresponding alcohol in 80% yield using the method described for the preparation of *cis*-2-methoxybicyclo[3.1.0]-hexane. The n.m.r. spectrum of this compound showed one tertiary proton (singlet) at τ 6.28, three protons of the methoxy group at 6.72, two tertiary protons and three methylene protons at 7.89 to 8.76, and two methylene protons on a cyclopropane ring at 9.42 to 10.17. The integration corresponding to five protons in the τ 7.89 to 8.76 region indicated 95–100% deuteration since this region shows an integration corresponding to six protons if no deuterium is present.

Methanol-*d* Addition to Bicyclo[3.1.0]hexene-2.—Methanol-*d* (99% deuterated by infrared analysis) was prepared by the method of Hobden, *et al.*[28] *p*-Toluenesulfonic acid-*d* was prepared by the hydrolysis of *p*-toluenesulfonyl chloride with D_2O. Bicyclo[3.1.0]hexene-2 (1.5 g.) was treated with 10 ml. of 0.4% *p*-toluenesulfonic acid-*d* in methanol-*d* at reflux for 20 hr. The isolated methyl ethers (30% yield) showed 40% *trans*-2 and 60% *cis*-2 ether and 4-methoxycyclohexene by v.p.c. The *trans*-2 ether was isolated by v.p.c. and analyzed by n.m.r. The n.m.r. spectrum showed one tertiary proton as a doublet at τ 6.27 (J = 5 c.p.s.) and five protons in the 7.89–8.76 region. An integration corresponding to five protons in this region demonstrated 95–100% deuteration of the sample as an integration corresponding to six protons in this region is found if no deuterium is present.

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Transmission of Substituent Effects in Bicyclo[2.2.2]octanes and Aromatic Analogs[1,2]

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A series of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the corresponding aromatic acids have been synthesized and their dissociation constants determined potentiometrically in 50 vol.% ethanol–water. From these data σ'-, σ_p-, σ_m-, σ_R-, and σ_I-constants are derived. The results for charged substituents supplement existing data. The derived constants are examined in terms of the Kirkwood–Westheimer cavity model and attention is focused on the role of external dielectric constant in determining the apparent σ-constants of charged substituents.

An important problem of physical organic chemistry is the correlation of the effect of substituents on free-energy changes involved in rate processes and equilibria. Although this is fundamentally a quantum mechanical problem, in practice it is usually reduced to finding that set of simplified concepts and associated parameters that most accurately mirror the experimental results. Thus, substituent effects have been decomposed into various combinations of inductive, field, polarizability, and resonance effects.[4-8]

One of the most fruitful approaches available for understanding substituent effects in saturated systems is the Kirkwood–Westheimer cavity model. Although it has severe theoretical and practical limitations,[9,10] it appears to be the most basic model available[11] and is the only one that considers the solvent explicitly.

This paper presents pK data on a series of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the corresponding *meta*- and *para*-substituted benzoic acids. These data, which supplement published data on the same system, are discussed in terms of inductive and resonance parameters and in terms of a simple Kirkwood–Westheimer model.

TABLE I

THERMODYNAMIC pK VALUES IN ETHANOL–WATER (50 VOL.%)

Benzoic acid substituent	Thermodynamic pK	Statistically corrected pK
H	5.80 ± 0.01	5.80
m-COOH	5.14 ± 0.02	5.44
m-COO$^-$	6.33 ± 0.01	6.03
p-COOH	4.90 ± 0.01	5.20
p-COO$^-$	6.27 ± 0.01	5.97
p-COOEt	5.20 ± 0.01	5.20
p-N(CH$_3$)$_3$I	4.46 ± 0.02	4.46
4-Substituted bicyclo[2.2.2]octane		
H	6.79[a]	6.79
COOH	6.07 ± 0.02	6.37
COO$^-$	7.27 ± 0.02	6.97
COOEt	6.38 ± 0.00	6.38
N(CH$_3$)$_3$$^+$	5.43 ± 0.02	5.43
NH$_3$$^+$	5.64 ± 0.03	5.64

[a] Calculated from Roberts[12] apparent pK of 6.74.

Results and Discussion

σ-Constants.—The thermodynamic dissociation constants of the substituted bicyclic and aromatic acids measured in this work (see Experimental for details) are recorded in Table I along with the statistically corrected constants. All of the constants were determined in 50 vol. % ethanol–water. It should be noted that the value reported for the parent bicyclic monoacid is based on the apparent pK of Roberts[12] with an added activity coefficient correction of +0.05, which is the estimated difference in pK between the apparent and thermodynamic pK values of benzoic acid. The internal consistency of the data validates this assumption. The deviations recorded in Table I represent the reproducibility of several determinations. While the absolute pK's recorded may be in error by as much as 0.1 pK unit, the ΔpK's of any two acids are presumably reliable to about the sum of their deviations, *i.e.*, to about ±0.04 pK units.

Where comparisons are possible the present results agree reasonably well with those of Holtz and Stock[13] and with those of Roberts.[12] The agreement of the data with those of Lewis and Ritchie[14] is unsatisfactory in the present solvent 50 vol.% ethanol–water but these authors have remarked that their indicator method is insensitive in this media. Their extensive data in less aqueous solvents can be correlated satisfactorily with our results.

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(11) A hierarchy of models can be envisioned in which the substituent and functional group are first embedded in an unvarying continuum, next in an environment divided into separately continuous solvent and substrate parts, and on to environments of increasingly higher degree of structure.

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