[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

Strained Small Ring Compounds: Bridgehead Substituted Bicyclo[2.1.1]hexanes[1]

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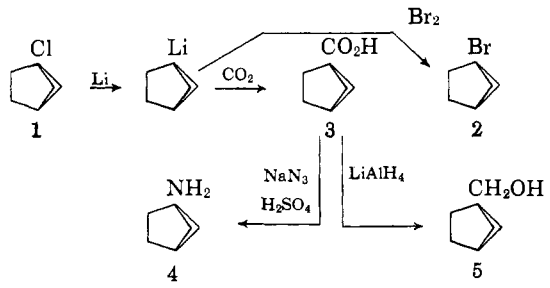
The preparation of a series of bridgehead substituted bicyclo[2.1.1]hexane derivatives is described. The basicity constant of the amine, the acid dissociation constant of the carboxylic acid, and the dipole moment of the chloride have been obtained and have been compared with compounds having less bond angle distortion. The data indicate an enhanced amount of s-character in the external orbital at the bridgehead. The solvolysis of the bridgehead bromide occurs at an unusually high rate and leads to an alkene. The solvolysis of bicyclo-[2.1.1]hexane-1-methyl tosylate occurs at an enhanced rate and gives about 90% internal return to bicyclo[2.2.1]-heptyl-1 tosylate. The reaction of the bridgehead substituted amine with nitrous acid has also been studied.

Bridgehead substituted bicyclic small ring compounds are of particular interest because the effects of bond angle deformation will be most noticeable at the bridgehead position. The availability of 1-chlorobicyclo[2.1.1]hexane (1)[3] has made it possible to prepare and study a series of bridgehead substituted bicyclo[2.1.1]hexanes.

The compounds of interest were prepared as follows: The chloride was converted to the lithium derivative and treated with either bromine or carbon dioxide giving 1-bromobicyclo[2.1.1]hexane (2) or bicyclo-[2.1.1]hexane-1-carboxylic acid (3). The acid (3) was converted to bicyclo[2.1.1]hexyl-1-amine (4) *via* the Schmidt reaction and to bicyclo[2.1.1]hexane-1-methanol (5) *via* lithium aluminum hydride reduction. In all cases, the retention of the bicyclo[2.1.1]hexane ring system could be shown by its characteristic n.m.r. spectrum.[3]



It will be convenient first to consider the physical properties of the compounds and then their chemical reactions. It is known[4] that bond angle deformation serves to decrease the basicity of amines, increase the acidity of carboxylic acids, and decrease the dipole moment of halides. For example, the basicities of cyclopropylamine, cyclobutylamine, and cyclopentylamine in 50% ethanol stand in the ratio 1:5:19[4]; the acidities of the corresponding acids stand in the ratio of 2:2:1[4,5]; and the dipole moments of cyclopropyl, cyclobutyl, and cyclopentyl bromides are 1.69, 2.09, and 2.20.[4] The change in properties can best be accounted for by assuming that bond angle deformation results in more s-character in the external bonds,[6] and that an sp^2 hybridized orbital is more electron withdrawing than an sp^3 hybridized orbital.[7] The same effect is also seen in the acidity of olefinic hydrogens in strained alkenes.[8]

The basicity of the amine 4, and of some related amines was determined in water and in 50% ethanol. The data are shown in Table I. It may be seen that

TABLE I

BASICITY CONSTANTS FOR SOME AMINES AT 25°

Amine	Solvent	$K_b \times 10^5$[a]	$K_b \times 10^5$ (lit.)	Ratio
Ammonia	Water	2.0	1.8[b,c]	1
Cyclohexylamine	Water	41	43.7[b,d]	20
Bicyclo[2.2.1]heptyl-1-amine	Water	16		8
Bicyclo[2.1.1]hexyl-1-amine	Water	2.0		1
Cyclohexylamine	50% ethanol	12	6.8[a,e]	20
Bicyclo[2.1.1]hexyl-1-amine	50% ethanol	0.57		1

[a] Based on observed pK_b value, not corrected for ionic strength. [b] Thermodynamic basicity constants. [c] Lange, "Handbook of Chemistry," Handbook Publishers, Sandusky, O., 7th Ed., 1949, p. 1408. [d] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932). [e] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951).

the ratio of basicities is independent of solvent, and that bicyclo[2.1.1]hexyl-1-amine is markedly less basic than the other amines. The bicyclohexylamine and cyclopropylamine appear to be the least basic of all simple saturated primary amines. The same trend is found in the acid dissociation constants of the bridgehead carboxylic acids (Table II). One might expect that

TABLE II

ACID DISSOCIATION CONSTANTS FOR SOME CARBOXYLIC ACIDS AT 25°[a]

Acid	Solvent	K_a	Ratio
Cyclohexanecarboxylic	50% ethanol	3.2×10^{-7}	1.00
Adamantane-1-carboxylic	50% ethanol	1.55×10^{-7}	0.48
Bicyclo[2.2.2]octane-1-carboxylic	50% ethanol	1.80×10^{-7}	0.56
Cyclohexanecarboxylic	Water	1.3×10^{-5}	1.0
Bicyclo[2.2.1]heptane-1-carboxylic	Water	1.3×10^{-5}	1.0
Bicyclo[2.1.1]hexane-1-carboxylic	Water	3.5×10^{-5}	2.6

[a] The data for 50% ethanol are taken from H. Stetter and J. Mayer, *Ber.*, **95**, 667 (1962), and J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953).

these acids should be less acidic than cyclohexanecarboxylic acid in view of the generally lower acidity of acids having the carboxyl group on a tertiary center.[9] It can be seen that if solvent effects are small, the bi-

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(2) (a) Department of Chemistry, Yale University. (b) Taken from part of the dissertation submitted by B. R. L. to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree.

(3) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961); K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

(4) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951).

(5) This situation with respect to the carboxylic acids is somewhat complex. In ethanol, the dissociation constants of the cyclo-C_3-, C_4-, and C_5-carboxylic acids are in the ratio of 2.0:1.4:1, whereas in water the ratio is 1.4:1.6:1.0. The changes arise from the fact that the constant for cyclopropanecarboxylic acid, like acrylic acid, changes more rapidly with a change in $1/\epsilon$ than do the other cycloalkanecarboxylic acids (M. Kilpatrick and J. G. Morse, *J. Am. Chem. Soc.*, **75**, 1854 (1953)).

(6) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(7) A. D. Walsh, *ibid.*, **43**, 60 (1947).

(8) K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957); G. L. Closs and L. E. Closs, *ibid.*, **83**, 1003 (1961).

(9) J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938).

cyclo[2.1.1]hexane-1-carboxylic acid has a dissociation constant five times as large as the relatively strain-free bicyclo[2.2.2]octane-1-carboxylic acid. Solvent effects on the dissociation constants will be investigated when all of the compounds in the series (bicyclo[1.1.0]-butane-, bicyclo[1.1.1]pentane-, and bicyclo[3.1.1]-heptane-) are in hand. In the above case the effects are larger than those observed in comparing cyclopropane derivatives with other cycloalkyl compounds.

The dipole moments of the chloride 1 and of some related chlorides are given in Table III. Normally, the dipole moment of a tertiary chloride is 0.05–0.10 D. higher than that for a secondary chloride.[10] Thus, the value for 1-chlorobicyclo[2.2.1]heptane would be expected to be larger than that for cyclohexyl chloride, whereas it is essentially the same. A further small decrease in dipole moment is observed on going to the bicyclohexyl chloride. The change here is not as large as in going from cyclopropyl chloride to cyclopentyl chloride ($\Delta\mu = 0.3$[11]).

TABLE III

DIPOLE MOMENTS OF SOME CHLORIDES[b]

Compound	Dipole moment, D.
Chlorobenzene	1.60 ± 0.01[a]
Chlorocyclohexane	2.18 ± .01
1-Chlorobicyclo[2.2.1]heptane	2.17 ± .01
1-Chlorobicyclo[2.1.1]hexane	2.11 ± .01

[a] The value obtained previously (B. I. Spinrad, *J. Am. Chem. Soc.*, **68**, 617 (1946)) is 1.60 D. [b] These data were kindly determined by Dr. N. Lowry, to whom we express our appreciation.

Each of the above sets of measurements has indicated a change in the hybridization of the bridgehead orbital. The extent of the change is not clear, but it is hoped that further measurements on the full set of bicyclic compounds will allow an estimation of the change.

We may next consider the effect of bond angle deformation on the reactivity of the compounds. The solvolytic reactivity of bridgehead substituted bromides has received considerable attention. It is found that the relative reactivity of *t*-butyl bromide, 1-bromoadamantane, 1-bromobicyclo[2.2.2]octane, and 1-bromobicyclo[2.2.1]heptane are $1:10^{-3}:10^{-7}:10^{-14}$.[12] The large difference in rate was accounted for by assuming that the carbonium ion-like activated complex in an SN1 reaction preferred a planar conformation, and that it was destabilized when the ring system prevented the attainment of planarity. The difference between the compounds reflects the difference in rigidity of the ring systems, the most rigid being least able to approach coplanarity.

The rate of solvolysis of 1-bromobicyclo[2.1.1]-hexane was determined in 40% ethanol and was compared with that of 1-bromobicyclo[2.2.2]octane. The data are given in Table IV. It can be seen that both compounds react at the same rate and have the same activation parameters. Thus the bicyclohexyl bromide is 10^7 times more reactive than the 1-bromobicyclo[2.2.1]heptane, whereas the former is the more highly strained, and presumably the more rigid system.

TABLE IV

RATES OF SOLVOLYSIS OF BRIDGEHEAD BROMIDES IN 40% ETHANOL

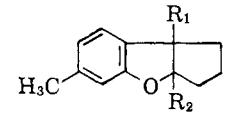
Compound	T, °C.	$k_1 \times 10^5$, sec.$^{-1}$	$\Delta H^{\pm}$	$\Delta S^{\pm}$
1-Bromobicyclo[2.2.2]-octane	96.8	5.99 ± 0.28	23.7[a]	−15[a]
1-Bromobicyclo[2.1.1]-hexane	96.7	6.03 ± .09	23.8	−14
	85.2	2.06 ± .03		

[a] M. Finkelstein, Ph.D. Thesis, Yale University, 1955.

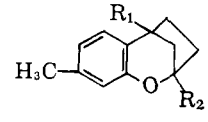
The product of the solvolysis of 1-bromoadamantane, and of the bicycloheptyl and octyl bridgehead bromides, is the corresponding alcohol, and no detectable amount of ring cleavage or other type of reaction has been observed. In the case of 1-bromobicyclo[2.1.1]hexane, no alcohol was found as the result of the solvolysis, and the product was unsaturated. The product formed in the reaction with silver ion at room temperature appeared to be methylcyclopentadiene.

The solvolysis of 1-chlorobicyclo[2.1.1]hexane and of 1-chlorobicyclo[2.2.1]heptane was studied in *m*-cresol. The rate constant for the former at 204° was 1.3×10^{-4} sec.$^{-1}$, and that for the latter at 322° was 5×10^{-7} sec.$^{-1}$. When the reaction of the former was carried out to 80% reaction, 81% of nonphenolic products was obtained. The main component (64%) had the empirical formula $C_{13}H_{16}O$, but the n.m.r. spectrum indicated that it was not a bridgehead substituted bicyclo[2.1.1]hexane.

The spectrum indicated no olefinic hydrogens. Integration of the spectrum indicated that there were only three aromatic protons rather than the four required for a *m*-cresyl ether. The remaining thirteen protons were found as: one at 6.74 τ, three at 7.75 τ, three at 8.55 τ, and six as a broad multiplet between 8–8.5 τ. The three protons at 7.75 τ must be attributed to the methyl group attached to the aromatic ring, and the group of three protons at 8.55 τ presumably also arises from a methyl group which is attached to a tertiary center since it is unsplit. The single proton at 6.74 τ is probably either attached to a benzylic carbon or to a carbon bearing an ether function. The aromatic protons appeared as an AB system plus one unsplit proton. The structures which are compatible with these data are 6 and 7.

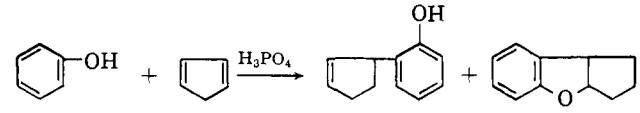


6a, $R_1 = CH_3$, $R_2 = H$
b, $R_1 = H$, $R_2 = CH_3$



7a, $R_1 = CH_3$, $R_2 = H$
b, $R_1 = H$, $R_2 = CH_3$

If methylcyclopentadiene were formed as a product of the solvolysis, products of the above type would be expected. For example, phenol and cyclopentadiene react in the presence of phosphoric acid to give the coumaran, 2,3-cyclopentano-2,3-dihydrobenzofuran.[13] In view of this conversion, which is a simple acid-catalyzed alkylation and ring closure, the more



probable structure for the cresolysis product is 6a or b.

The formation of methylcyclopentadiene as the product[14] results from a simple type of bond migration which may be symbolized as[15]

(10) A. Parts, *Z. physik. Chem.*, **B7**, 327 (1930); **B12**, 312 (1931).

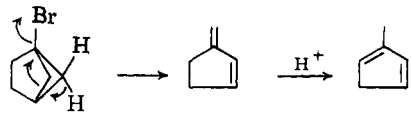
(11) M. T. Rogers and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 843 (1946).

(12) W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, Jr., *ibid.*, **75**, 1008 (1953); M. Finkelstein, Ph.D. Thesis, Yale Univ., 1955; P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

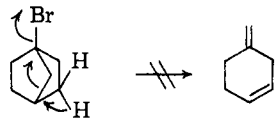
(13) A. R. Bader, *ibid.*, **75**, 5967 (1953).

(14) It still remains to demonstrate the formation of this compound as an intermediate by trapping it as the Diels–Alder adduct, or in some similar way. It was not possible to do this at the time the work was performed because of the small amount of material which was available. However, this point will receive consideration in our further study of this reaction which is under way.

(15) This is *not* to be interpreted as suggesting the mechanism of the reaction.



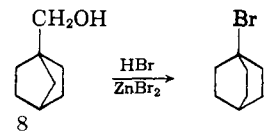
The bond angle deformation in this bromide is apparently high enough to favor this alternate mode of reaction. The same sort of process could be envisioned for 1-bromobicyclo[2.2.1]heptane, but here the product would be a nonconjugated diene, and the strain relief factor would not be as large as for the former bromide.



The contribution from the former factor may be assessed by examining the reaction of 1-bromobicyclo[3.1.1]heptane which would give a conjugated diene in this type of cleavage, and this study is in progress. Further discussion of the details of the reaction will be postponed until the work in progress has been completed.

A related reaction is that of the bridgehead substituted amine with nitrous acid. It has been found that apocamphylamine reacts smoothly with nitrous acid to give apocamphanol,[16] and that 1-norbornylamine also gives 1-norborneol (80%).[17] However, although the reaction of bicyclo[2.1.1]hexyl-1-amine with nitrous acid gave nitrogen evolution, bicyclo[2.1.1]hexan-1-ol was not obtained as a product. The major constituent of the product appeared to be derived from an alkene, and presumably the reaction led to the same kind of ring cleavage as in the solvolysis of the bridgehead bromide.

Another reaction involving the bridgehead position is the rearrangement of the bridgehead methanols. It has been observed that the reaction of bicyclo[2.2.1]heptane-1-methanol (8) with zinc bromide and hydrogen bromide leads to 1-bromobicyclo[2.2.2]octane,[17] and that the tosylate of 8 gives a somewhat enhanced rate of acetolysis.[18] However, the products



of this latter reaction were not determined.

The driving force in the rearrangement is relief of bond angle deformation, and the carbonium ion formed in the above case is the 1-bicyclo[2.2.2]octyl cation, which is one of the more favored of the bicyclic ions. With bicyclo[2.1.1]hexane-1-methanol, the driving force from strain relief would be greater than with the above compound, but the resultant carbonium ion, the 1-bicyclo[2.2.1]heptyl ion, is known to be very poor. One might then expect the rearrangement to proceed with difficulty. It was found that bicyclo[2.1.1]hexane-1-methyl bromide reacted with zinc bromide to give the rearranged bridgehead bromide under the conditions required for the reaction of bicyclo[2.2.1]heptane-1-methyl bromide.

In order to get a better idea of the relative reactivities of the two bridgehead methanols, both were converted to the tosylates, and the rates and products of acetolysis were studied. The results are summarized in Table V.

(16) P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939).
(17) W. P. Whelan, Jr., Ph.D. Thesis, Columbia University, 1952.
(18) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).

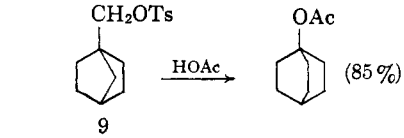
TABLE V

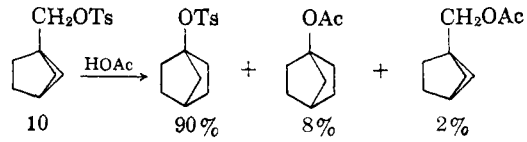
RATES OF ACETOLYSIS OF SOME NEOPENTYL TOSYLATES AT 80°

Tosylate	$k_1 \times 10^6$, sec.$^{-1}$	Rel. rate
Neopentyl[a]	0.17	1.00
Bicyclo[2.2.1]heptane-1-methyl	1.4 ± 0.1	8.0
Bicyclo[2.1.1]hexane-1-methyl	2.5 ± .1 (acetolysis)	
	30.5 ± .5 (tosylate rearrangement)	
	33 (total rate)	194

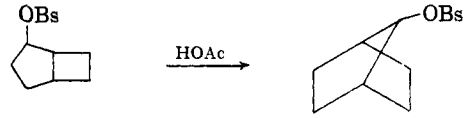
[a] Extrapolated from the data of S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

The reaction of 9 was normal and gave only acetate as





the product. The reaction of 10, on the other hand, gave essentially only bridgehead tosylate. The apparent total rate of reaction of 10 (ion-pair return plus acetate formation) was 24 times as great as that of 9. The reaction of 10 is similar to that of *exo*-bicyclo[3.2.0]heptyl-2-brosylate which gives predominantly internal return to 7-norbornyl brosylate.[19]



The marked difference between the two ring systems suggests that rearrangement occurs at an earlier stage of carbonium ion formation with 10 than with 9. This is reasonable in view of the destabilization of the 2-norbornyl cation, and further suggests that the reaction may possibly be best described as an internal rearrangement in which charge separation is minimized. This point will receive further study.

Finally, it should be noted that a displacement reaction by bromide ion in acetone on either tosylate is possible, leading to unrearranged bromide. The addition of bromide ion in the acetolysis of bicyclo[2.1.1]hexane-1-methyl tosylate leads to a reduction in the amount of bicyclo[2.2.1]heptyl-1-tosylate, and to the formation of some 1-bromobicyclo[2.2.1]heptane as well as unrearranged bromide.

Experimental

Bicyclo[2.1.1]hexane-1-carboxylic Acid.—A suspension of 2 g. of lithium dispersion in mineral oil in 15 ml. of anhydrous cyclohexane, maintained under an oxygen-free nitrogen atmosphere, was heated to the reflux temperature, and a solution of 3.84 g. (33 mmoles) of 1-chlorobicyclo[2.1.1]hexane in 10 ml. of cyclohexane was added over a period of 30 min. with stirring. Stirring and heating was continued for 10 hr.

The solution was diluted with 30 ml. of cyclohexane and 40 ml. of purified anhydrous pentane and was cooled in an ice bath. The nitrogen stream was replaced by a stream of carbon dioxide which was dried with sulfuric acid and with Drierite. After carbonating for 2.5 hr., the mixture was treated with ethanol (2 ml.), water (10 ml.), and 6 *N* hydrochloric acid (35 ml.). The organic layer was separated and the aqueous layer was re-extracted with an additional 40 ml. of cyclohexane. The organic

(19) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **80**, 5895 (1958).

extract was washed with 6 *N* hydrochloric acid, and the acid was transferred to an aqueous phase with 5% sodium bicarbonate solution (two 25-ml. portions) and 5% sodium hydroxide solution (15 ml.). After the aqueous solution was washed with methylene chloride, it was acidified with hydrochloric acid and extracted with methylene chloride (four 50-ml. portions.) The solvent was removed by distillation through a glass helix packed column. Sublimation of the residue under reduced pressure gave 3.45 g. (83%) of bicyclo[2.1.1]hexane-1-carboxylic acid, m.p. 46.1–50.1°.

β-Phenylethylammonium bicyclo[2.1.1]hexane-1-carboxylate was prepared, and after two recrystallizations from ethyl acetate it had m.p. 151.0–154.4°. The acid regenerated from the amine salt melted at 50.7–52.4°.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.6; H, 8.0; neut. equiv., 126. Found: C, 66.4, 66.6; H, 7.8, 7.9; neut. equiv., 126.

The carboxamide was prepared and after two recrystallizations from ethanol–water had m.p. 236.6–238.4° (sealed tube).

Anal. Calcd. for $C_7H_{11}ON$: C, 67.2; H, 8.9; N, 11.2. Found: C, 66.9, 66.8; H, 9.1, 9.0; N, 11.5, 11.4.

1-Bromobicyclo[2.1.1]hexane.—Bicyclo[2.1.1]hexyl-1-lithium was prepared from 2.72 g. (23.3 mmoles) of 1-chlorobicyclo[2.1.1]-hexane as described above. After cooling, 40 ml. of pentane was added, followed by dropwise addition (over 15 min.) of 4.3 g. (27 mmoles) of bromine in 10 ml. of pentane with vigorous stirring. After an hour, 30 ml. of water was slowly added. The aqueous phase was extracted with 65 ml. of pentane, and the combined organic solutions were washed with 5% sodium thiosulfate solution, concentrated sulfuric acid, and with water. The dried solution was distilled through an 8-in. Vigreux column to remove the solvent, and the residue was distilled giving a forerun and 2.02 g. of bromide, b.p. 52–65° at 50 mm. Redistillation of both fractions gave 1.98 g. (53%) of crude 1-bromobicyclo-[2.1.1]hexane, b.p. 63.5–65° at 54 mm. The bromide was further purified by preparative vapor phase chromatography using a Silicone 710 column at 130°. The purified bromide was redistilled, b.p. 140–141°, $n^{24}D$ 1.4978.

Anal. Calcd. for C_6H_9Br: C, 44.7; H, 5.6; Br, 49.6. Found: C, 44.7, 44.8; H, 5.8, 5.6; Br, 49.7, 49.5.

1-Bromobicyclo[2.2.1]heptane.—The conversion of 4.50 g. (34.5 mmoles) of 1-chlorobicyclo[2.2.1]heptane to the lithium derivative and treatment with excess bromine gave 3.72 g. (57%) of 1-bromobicyclo[2.2.1]heptane, b.p. 76–78° at 31 mm., $n^{24}D$ 1.5079 (reported[17] b.p. 47.5–48° at 11 mm.).

Bicyclo[2.1.1]hexane-1-methanol.—With stirring, a solution of 1.00 g. (7.9 mmoles) of bicyclo[2.1.1]hexane-1-carboxylic acid in 25 ml. of anhydrous ether was added over 45 min. to a slurry of 1.68 g. (44 mmoles) of lithium aluminum hydride in 60 ml. of anhydrous ether. Stirring was continued for 1 hr. at room temperature, then the excess hydride was destroyed by the dropwise addition of 12 ml. of 40% Rochelle salt solution with ice cooling. The ether layer was decanted and the residual paste was washed with two 50-ml. portions of ether. The ether solution was dried and the solvent removed by distillation. Distillation of the residue gave 0.85 g. (96%) of the alcohol, b.p. 88–89° at 31 mm., $n^{26}D$ 1.4728.

Anal. Calcd. for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 74.7, 74.7; H, 10.7, 10.6.

Bicyclo[2.1.1]hexane-1-methyl Acetate.—A solution of 0.62 g. (5.5 mmoles) of bicyclo[2.1.1]hexane-1-methanol in 8 ml. of pyridine and 10 ml. of pentane was cooled in an ice bath, and 3 g. (40 mmoles) of acetyl chloride was added in small portions with stirring. After standing for 20 min., the mixture was diluted with 20 ml. of water. The mixture was extracted with four 20-ml. portions of pentane. The pentane solution was washed with ice–water, cold 3 *N* sulfuric acid (15 ml. in two portions), water, and 5% sodium bicarbonate solution. The dried pentane solution was distilled through a Vigreux column to remove solvent, and the residue was distilled giving 0.61 g. (73%) of the acetate, b.p. 79–80° at 18 mm. After redistillation, it had b.p. 77.5–78.5° at 18 mm., $n^{24}D$ 1.4487.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.1; H, 9.2. Found: C, 70.5, 70.3; H, 9.2, 9.2.

Bicyclo[2.2.1]heptane-1-methyl Acetate.—The treatment of 0.48 g. of bicyclo[2.2.1]heptane-1-methanol with acetyl chloride as described above gave 0.55 g. (87%) of the acetate, b.p. 82° at 10 mm. Redistillation gave material with b.p. 83° at 9 mm., $n^{24}D$ 1.4580.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.7, 71.5; H, 9.4, 9.5.

Bicyclo[2.1.1]hexane-1-methyl Tosylate.—To an ice–salt-cooled mixture of 1.68 g. (15 mmoles) of the alcohol in 17 ml. of dry pyridine was added 2.95 g. (15.5 mmoles) of reagent grade tosyl chloride. The mixture was swirled until solution was complete, and then placed in a refrigerator for 16 hr. The mixture was poured into 50 ml. of ice–water and extracted with a total of 125 ml. of ether in four portions. The combined ether extracts were washed with three portions of cold 6 *N* sulfuric acid, ice–water, and 2% sodium bicarbonate solution. The ether solution was dried, and the solvent was removed using a rotary evaporator. The tosylate slowly crystallized, giving 3.80 g. (95%) of the crude tosylate. The tosylate was recrystallized with 96% recovery from either ether–pentane or pentane and had m.p. 40.5–41.3°.

Anal. Calcd. for $C_{14}H_{18}O_3S$: C, 63.1; H, 6.8. Found: C, 62.9, 63.1; H, 6.5, 6.4.

Bicyclo[2.2.1]heptane-1-methyl Tosylate.—The treatment of 2.03 g. of bicyclo[2.2.1]heptane-1-methanol with tosyl chloride as described above gave 4.38 g. (96%) of the crude tosylate. After recrystallization from pentane–ether, and pentane, it had m.p. 76.5–77.1° (reported[18] 78.9–80°).

Bicyclo[2.1.1]hexane-1-methyl Bromide.—To a stirred refluxing solution of 2.40 g. (9.0 mmoles) of bicyclo[2.1.1]hexane-1-methyl tosylate in 10 ml. of reagent grade acetone was added 1.57 g. (18 mmoles) of anhydrous lithium bromide. Lithium tosylate precipitated about 4 min. after the addition of the bromide. After 13 hr., the acetone was removed by distillation through an 8-in. Vigreux column. The mixture was cooled, diluted with 30 ml. of water, and extracted with 150 ml. of ether and 100 ml. of pentane. The organic layer was washed with water, dried, and the solvent removed using the above column. Distillation of the residue gave 1.49 g. (94%) of the bromide, b.p. 78–79° at 35 mm., $n^{24}D$ 1.4946. Removal of the last trace of acetone was effected by vapor phase chromatography; redistillation gave the pure bicyclo[2.1.1]hexane-1-methyl bromide, b.p. 78–80° at 37 mm., $n^{25}D$ 1.4999.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.0; H, 6.3; Br, 45.7. Found: C, 48.2; H, 6.1; Br, 46.2, 46.1.

Bicyclo[2.2.1]heptane-1-methyl Bromide.—The reaction of 2.00 g. (7.1 mmoles) of bicyclo[2.1.1]heptane-1-methyl tosylate with 1.24 g. (14.3 mmoles) of lithium bromide under the conditions described above gave 1.23 g. (91%) of the corresponding bromide, b.p. 89° at 20 mm. Lithium tosylate precipitation occurred in about 1 hr. A redistilled sample had $n^{24}D$ 1.5041.

Anal. Calcd. for $C_8H_{13}Br$: C, 50.8; H, 6.9; Br, 42.3. Found: C, 50.7, 50.9; H, 6.9, 7.2; Br, 42.1, 42.0.

Bicyclo[2.1.1]hexyl-1-amine Hydrochloride.—Sodium azide (1.5 g., 23 mmoles) was added in portions over a period of 1 hr. to a stirred mixture of 1.91 g. (15.2 mmoles) of bicyclo[2.1.1]hexane-1-carboxylic acid, 46 ml. of C.P. chloroform, and 23 ml. of concentrated sulfuric acid at 45–50°. Stirring at 50–55° was continued for 2.5 hr. The mixture was cooled in ice, and 100 g. of ice was added with vigorous stirring. The chloroform layer was separated, and the aqueous layer was washed with two 50-ml. portions of chloroform. The acidic aqueous phase was thoroughly cooled and made alkaline by the addition of 50% sodium hydroxide. The amine was extracted with 100 ml. of 1:1 ether–pentane mixture and with two 50-ml. portions of pentane. The combined extracts were washed with water; then the amine was reextracted with 12% hydrochloric acid. Water and hydrochloric acid were removed using a rotary evaporator until the residue reached constant weight, giving 1.94 g. (96%) of crystalline bicyclo[2.1.1]hexyl-1-amine hydrochloride. Recrystallization from methanol–ethyl acetate gave 97% recovery of the hydrochloride; it did not melt below 250°.

Anal. Calcd. for $C_6H_{12}NCl$: C, 53.9; H, 9.1; N, 10.5. Found: C, 54.1, 54.2; H, 9.0, 8.9; N, 10.5, 10.4.

Deamination of Bicyclo[2.2.1]heptyl-1-amine.—A solution of 1.48 g. (10.0 mmoles) of bicyclo[2.2.1]heptyl-1-amine hydrochloride in 9 ml. of 10% acetic acid was cooled in an ice bath. A solution of 2.07 g. (30 mmoles) of sodium nitrite in 3.5 ml. of water was added in portions with swirling. Since gas evolution was relatively slow at 0°, cooling was discontinued at intervals, and used only for moderation of the reaction. A pale yellow oil formed. When gas evolution became sluggish, an additional 3 ml. of 10% acetic acid was added and the mixture was heated at 100° for 12 hr. After cooling, 5.0 g. of potassium hydroxide and 10 ml. of methanol were introduced; then heating was resumed for 4 hr. After cooling and dilution of the mixture with 40 ml. of water, the crude alcohol crystallized. It was extracted with ether (100 ml.) and pentane (200 ml.). The extracts were washed with water, 10% hydrochloric acid, 5% sodium bicarbonate, and water. After drying, the solvent was removed by distillation through a packed column. Sublimation of the residue gave 0.90 g. (80%) of 1-norborneol. The infrared spectrum was identical with that reported by Whelan.[17]

Deamination of Bicyclo[2.1.1]hexyl-1-amine.—The reaction of 1.34 g. (10.0 mmoles) of the amine hydrochloride with 2.07 g. (30 mmoles) of sodium nitrite was carried out as described above. Rapid gas evolution occurred at 0°; the mixture was kept at 0° for 0.75 hr. by which time a bright green oil had formed. An additional 3 ml. of 10% acetic acid was added and the mixture heated on a steam bath for 12 hr. Initially, the aqueous phase became yellow, then red, and finally black and tarry looking.

After saponification and dilution as described above, the black mixture was steam distilled. The distillate was acidified with hydrochloric acid and extracted with 50 ml. of isopentane. The latter was washed with water, 5% sodium bicarbonate solution, and water. After drying, the isopentane was carefully removed by fractional distillation; essentially no residue remained. No amine hydrochloride was recovered upon evaporation of the hydrochloride acid solution indicating that complete deamination had occurred.

Solvolysis of 1-Bromobicyclo[2.1.1]hexane. A. Solvolysis in Aqueous Ethanol.—A solution of 0.22 g. of 1-bromobicyclo-[2.1.1]hexane in a mixture of 11 ml. of absolute ethanol and 7.5 ml. of 0.211 *N* sodium hydroxide was heated to reflux for 24 hr. Ethanol and other organic compounds were salted out with potassium carbonate and dried with anhydrous potassium carbonate. Separation of the mixture by vapor phase chromatography gave 0.09 g. of the starting bromide as the only isolable product.

B. Silver-Catalyzed Solvolysis in Aqueous Dioxane.—To a solution of 0.50 g. of silver nitrate in 2 ml. of water was added 0.24 g. of 1-bromobicyclo[2.1.1]hexane and 2 ml. of dioxane. Silver bromide formation began even before the dioxane was added. A copious precipitate was soon formed. The mixture was allowed to stand at room temperature for 1 hr. Attempts to isolate the organic products by extraction, fractionation of solvent, and vapor phase chromatographic separation failed; no component occurred in sufficient quantity for isolation. However, solvolysis was complete; 0.28 g. (100%) of silver bromide was collected.

C. Silver-Catalyzed Solvolysis in Aqueous Ethanol.—A mixture of 0.4 g. of 1-bromobicyclo[2.1.1]hexane, 0.5 g. of silver nitrate, 2 ml. of ethanol, and 1 ml. of water was allowed to stand at room temperature for 1 hr. with occasional swirling. Excess silver nitrate was precipitated by the addition of saturated sodium chloride. The silver halide was removed by filtration. The filtrate was extracted with about 1 ml. of carbon tetrachloride containing tetramethylsilane. The organic layer was washed twice with small portions of water, dried, and then the n.m.r. spectrum examined. Other than peaks corresponding to a small ethanol impurity, the major characteristic of the spectrum were bands in the vinyl region (mainly at 4.58–5.14 τ with a smaller amount of absorption at ~4.5 τ) and array of bands from 7.1–8.3 τ; especially intense at 7.62 τ. The infrared spectrum had strong bands at 3.29 and 6.13 μ. The solution was unsaturated to bromine.

Acetolysis of 1-Bromobicyclo[2.1.1]hexane.—A solution of 0.43 g. of the bromide and 0.50 g. of potassium acetate in 35 ml. of glacial acetic acid (1% acetic anhydride) was sealed in an ampoule and held at 160° for 81 hr. After cooling, the mixture was poured into 50 ml. of ice–water and extracted with a total of 250 ml. of pentane. The pentane solution was washed with water, and the latter was added to the original aqueous acetic acid phase. Gravimetric determination of the bromide in the aqueous solution gave 0.50 g. of silver bromide (100%). The pentane solution was washed with sodium bicarbonate and with water. After drying, the solvent was removed through a small column. The residue, which did not have a typical acetate odor, could only be evaporatively distilled at 140° and 0.5 mm. The sticky product discolored somewhat in air. It did not react with bromine, nor was there absorption in the vinyl region of the n.m.r. spectrum. Absorption at 5.70 and 8.05 μ in the infrared spectrum was weak, indicating only a small amount of acetate grouping in the product.

Solvolysis of 1-Chlorobicyclo[2.1.1]hexane in *m*-Cresol.—A solution of 0.50 g. (4.3 mmoles) of 1-chlorobicyclo[2.1.1]hexane in 7 ml. of *m*-cresol (distilled from zinc dust) was sealed in a tube and heated to 205° for 4.3 hr. This reaction time corresponded to about 83% reaction. On cooling, the mixture became bright vermilion. The tube was opened and poured into 5 ml. of water. The mixture was diluted with 100 ml. of pentane (three phases). The organic layers were treated with small portions of water until the extracts no longer gave a positive test for halide ion. Ether (20 ml.) was added to the two-phase organic system to effect miscibility; then the mixture was washed with 20 ml. of 50% sodium hydroxide to remove cresol and other phenolic products, and with water. After drying, the solvents were removed by distillation through an 8-in. Vigreux column. Distillation of the residue gave 0.53 g. (65% based on starting materials, 81% based on extent of reaction) of a colorless liquid, b.p. 74–76° at 0.5 mm. Vapor phase chromatography on a Silicone 710 column at 215° indicated at least seven components, but the major peak accounted for 64% of the mixture. This fraction was separated and redistilled. The n.m.r. spectrum of the product bore no resemblance to those of bicyclo[2.1.1]-hexane derivatives. By integration, the aromatic absorption corresponded to 2.98 protons, the methyl bands corresponded to 6.0 protons, and the 6.74 τ absorption to 1.00 protons. No bands appeared in the vinyl region.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.9; H, 8.6. Found: C, 82.8, 82.8; H, 8.4, 8.6.

1-Bromobicyclo[2.2.2]octane.—A solution of 1.30 g. of bicyclo[2.2.1]heptane-1-methanol, 6 ml. of 48% hydrobromic acid, and 8.3 g. of zinc bromide was heated at 100° for 5 hr. At intervals, sublimed materials were melted from the walls of the reaction vessel by immersion of the flask into the heating bath. The cooled mixture was diluted with 30 ml. of water and extracted with three 50-ml. portions of concentrated sulfuric acid, with 5% sodium bicarbonate solution, and with water. After drying and distillation of the solvent, sublimation of the residue gave 1.54 g. (79%) of the crude bromide, m.p. 60.6–63.0° (sealed tube) (reported[17] 59.5–62.0°). Examination by vapor phase chromatography with a silicone column indicated the presence of an impurity, presumably 1-bromobicyclo[3.2.1]-octane. A sample of 1-bromobicyclo[2.2.2]octane purified by gas chromatography followed by resublimation had m.p. 66.9–67.7° (sealed tube), and gave no evidence of inhomogeneity upon further chromatographic analysis. This material was used for the kinetic investigations.

Rearrangement of Bicyclo[2.1.1]hexane-1-methyl Bromide with Zinc Bromide.—The treatment of bicyclo[2.1.1]hexane-1-methyl bromide with zinc bromide at room temperature for 43 hr. gave only partial rearrangement. Therefore a mixture of 0.67 g. of the bromide and 0.38 g. of anhydrous zinc bromide was placed in a stoppered tube and heated at 60° for 18.5 hr. The mixture was diluted with 5 ml. of water and extracted with pentane (3 × 20 ml.) and a 1:1 pentane–ether mixture (10 ml.). The solution was dried and the solvent removed through a small column. Distillation of the residue gave 0.53 g. (79%) of a bromide, b.p. 72° at 26 mm., $n^{25}D$ 1.5071. The infrared and n.m.r. spectra were identical with those for 1-norbornyl bromide.

Rearrangement of Bicyclo[2.2.1]heptane-1-methyl Bromide with Zinc Bromide.—The reaction of 0.65 g. of the bromide with 0.26 g. of zinc bromide under the conditions given above gave 0.48 g. of a liquid bromide, b.p. 92–93° at 23 mm. The infrared and n.m.r. spectra indicated only partial rearrangement. Gas chromatographic analysis indicated 36% rearrangement.

Acetolysis of Bicyclo[2.2.1]heptane-1-methyl Tosylate.—A mixture of 1.80 g. (6.4 mmoles) of the tosylate and 0.75 g. (7.7 mmoles) of potassium acetate in 60 ml. of glacial acetic acid (1% acetic anhydride) was heated at reflux temperature for 60 hr. The cooled solution was diluted with 250 ml. of ice–water and extracted with four 100-ml. portions of pentane and 100 ml. of ether. The organic extracts were washed with water, sodium bicarbonate solution, and water. After drying, the solvent was distilled through a short column and the residue was distilled giving 0.92 g. (85%) of acetates, b.p. 83–85° at 10 mm. Saponification with methanolic potassium hydroxide gave a crystalline alcohol which was sublimed once and had m.p. 201–207° (sealed tube). The infrared spectrum of this material was identical with that reported[17] for bicyclo[2.2.2]octan-1-ol except for a small absorption of 9.75 μ which suggested bicyclo[3.2.1]octan-1-ol as a minor impurity. Vapor phase chromatographic examination of the alcohol also indicated only a trace of impurity.

Acetolysis of Bicyclo[2.1.1]hexane-1-methyl Tosylate.—A solution of 2.00 g. (7.5 mmoles) of the tosylate and 0.89 g. (9.1 mmoles) of potassium acetate in 70 ml. of glacial acetic acid (1% acetic anhydride) was heated at reflux temperature for 60 hr. The work-up was the same as given above, and gave only 0.09 g. (8%) of an acetate, b.p. ~65° at 11 mm., and a large residue which did not distill (or decompose) even up to 140°.

The residue was crystallized with some difficulty from pentane–ether giving 1.50 g. (75%) of a tosylate. The n.m.r. spectrum of this material was very similar to those of 1-chloro- and 1-bromonorbornane, and the infrared spectrum was identical with that previously reported for 1-norbornyl tosylate.[20] A sample recrystallized three times from ether–pentane had m.p. 29.2–29.8°.

Anal. Calcd. for $C_{14}H_{18}O_3S$: C, 63.1; H, 6.8. Found: C, 62.7, 62.8; H, 6.3, 6.5.

The acetate fraction was shown by vapor phase chromatography to have two components in the ratio 78:22. The retention time of the minor component and of bicyclo[2.1.1]hexane-1-methyl acetate were the same and the structure was confirmed by noting characteristic bands in the n.m.r. spectrum of the mixture. The infrared spectrum of the major product, separated by vapor phase chromatography, was identical with that of 1-norbornyl acetate.

Acetolysis of Bicyclo[2.1.1]hexane-1-methyl Tosylate with Added Lithium Bromide.—A mixture of 1.27 g. (4.8 mmoles) of the tosylate, 0.80 g. (8.2 mmoles) of potassium acetate, and 2.00 g. (23 mmoles) of anhydrous lithium bromide in 150 ml. of glacial acetic acid (1% acetic anhydride) was heated to reflux for 40 hr. The work-up was the same as given above. After the solvent had been removed, the volatile materials were collected in a Dry Ice–acetone cooled trap by evacuation to ~0.5 mm. for 2 hr. at 25–30°. The residue, 0.71 g., gave 0.60 g. (47%) of 1-norbornyl tosylate on crystallization from ether–pentane.

(20) C. J. Norton, Ph.D. Thesis, Harvard University, 1955.

The volatile products were examined by vapor phase chromatography using a silicone column at 120°. Separation of the major product gave 0.20 g. (24%) of bromides; at the same time, the ratio of 1-norbornyl acetate to bicyclo[2.1.1]hexane-methyl acetate was found to be 87:13 and the ratio of bromides to acetates was 91:9. Since 1-norbornyl bromide and bicyclo[2.1.1]hexane-1-methyl bromide could not be separated by vapor phase chromatography, the extent of rearrangement was determined by examining the n.m.r. spectrum of the mixture. There was about 25% of unrearranged bromide in the mixture.

Kinetic Experiments. Materials.—Practical grade *m*-cresol was distilled from zinc dust, collecting the portion having b.p. 88–89° at 9 mm. The 40% ethanol was prepared by mixing two volumes of C.P. absolute ethanol with three volumes of carbon dioxide-free distilled water and had n^{23}D 1.3543. The glacial acetic acid used contained 1% acetic anhydride in order to ensure the absence of water.

The chlorides and bromides were purified by vapor phase chromatography followed by redistillation or resublimation. The tosylates were purified by recrystallization.

Solvolysis of Bridgehead Chlorides in *m*-Cresol.—Approximately 0.03 *M* solutions of the chlorides in *m*-cresol were prepared and 5-ml. portions were sealed in ampoules. They were heated for appropriate times in a micro-Carius furnace and the temperature was determined using a thermocouple. After cooling, the contents of a tube was transferred to a beaker using 40 ml. of reagent grade acetone and the chloride was titrated potentiometrically at 0° with standard 80% ethanolic silver nitrate solution (0.01 *N*). At 322°, the rate constant for 1-chlorobicyclo[2.2.1]heptane was $4.9 \pm 1.3 \times 10^{-7}$ sec.$^{-1}$, whereas at 204°, the rate constant for 1-chlorobicyclo[2.1.1]-hexane was $1.25 \pm 0.08 \times 10^{-4}$ sec.$^{-1}$.

Solvolysis of Bridgehead Bromides in 40% Ethanol.—Approximately 0.01 *M* solutions of the bromides in 40% ethanol were prepared and 5-ml. portions were sealed in ampoules. Tubes for a single run were immersed in a bath simultaneously and withdrawn at regular intervals. The samples were titrated with 0.0116 *N* sodium hydroxide solution to a phenolphthalein end point. The rate constants are given in Table IV.

Acetolysis of Bridgehead Carbinyl Tosylates.—Approximately 0.03 *M* solutions of the tosylates in glacial acetic acid were heated at 80.1°, and at regular intervals, 25-ml. aliquots were removed and cooled. Titration with standard sodium acetate in glacial acetic acid (0.05 *N*) was performed to the bromphenol blue end point. The rate constants were given in the Discussion section.

In order to determine the rate of internal return to the 1-norbornyl tosylate, the tosylates were recovered from the aliquots titrated above in the following fashion. The sample was diluted with 75 ml. of ice–water and then extracted with two 50-ml. portions of ether and 25 ml. of pentane. The combined organic extract was washed with cold sodium bicarbonate solution and with ice–water. The organic solution was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator at room temperature. The acetate was removed by evacuation at 0.1 mm. for 1 hr. The remaining tosylate mixture was dissolved in reagent grade carbon tetrachloride and the composition was determined from the integrated n.m.r. spectrum. There are sufficient differences in spectra between the two compounds to permit an accurate determination of the rate constant.

Ionization Constants of Carboxylic Acids and Amines.—Water was redistilled from alkaline potassium permanganate and protected from atmospheric carbon dioxide by Ascarite tubes. The 50% ethanol was prepared by mixing equal volumes of U.S.I. absolute ethanol and water.

Four buffers were used for standardization of the Beckman model G pH meter: Beckman pH 7.00 and 10.00 prepared buffer solutions; 0.05 *M* potassium acid phthalate (pH 4.01); and 0.01 *M* borax (pH 9.18), all at 25°.

Cyclohexanecarboxylic acid and cyclopropanecarboxylic acid were redistilled before use. Bicyclo[2.1.1]hexane-1-carboxylic acid and bicyclo[2.2.1]heptane-1-carboxylic acid were purified as the β-phenethylamine salt and resublimed.

Reagent grade ammonium chloride was used. The stable amine hydrochlorides (recrystallized from methanol and ethyl acetate) were used in order to avoid the problem of weighing the free amines which are rather susceptible to carbonate formation.

The equivalence points of approximately 0.01 *N* stock solutions of the acid were accurately determined by potentiometric titration. The concentration of amine hydrochloride was determined from the weight of material used. A number of samples of each solution were exactly half neutralized with 0.2114 *N* sodium hydroxide under nitrogen. After reaching equilibrium at 25°, the pH of the solutions was determined. The pH meter was standardized with appropriate buffers before and after each series of measurements. In aqueous solution the pK_a's of acetic, cyclohexanecarboxylic, and cyclopropanecarboxylic acids were found to be 4.72, 4.88, and 4.80, respectively: the reported values are 4.75, 4.90 and 4.83.[5,9] The data are summarized in Tables I and II.

Dipole Moment Measurements.—Analytical reagent grade benzene was shaken with several portions of concentrated sulfuric acid, water, dilute sodium hydroxide solution, and water. After being dried over calcium chloride, it was distilled and a center fraction, b.p. 80–81°, n^{25}D 1.4980, was collected. Chlorobenzene was distilled once before use and had n^{27}D 1.4583. 1-Chlorobicyclo[2.1.1]hexane was distilled immediately before use and had b.p. 121°, n^{27}D 1.4612.

A Dipolemeter DMO1 (Wissenshaftlich Technische Werkstatten), kindly made available by Dr. A. Huitric of the Pharmacy Department, University of Washington, was employed for the measurements. Calibration was carried out in the manner suggested by the manufacturer using cyclohexane, benzene, and di-*n*-butyl ether. The data were treated using the method of Halverstadt and Kumler.[21] The data are summarized in Table III.

(21) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

The Tricyclo[2.2.2.0^{2,6}]octan-3-ols and Derivatives. Preparation, Structure, and Reactivity Studies[1]

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Acetolysis of arenesulfonates of *exo*-bicyclo[2.2.2]oct-5-en-2-ol (**2a**) proceeds with a substantial amount of anchimeric assistance by the double bond. The major product in buffered medium was determined to be *endo*-tricyclo[2.2.2.0^{2,6}]octan-3-yl acetate (**5c**), whereas the minor products were retained acetate **2d** and *axial*-bicyclo[3.2.1]oct-6-en-2-yl acetate (**10**). The results indicate that **2a** and **5a** represent a unique pair of homoallylic isomers, in which the carbonium ion intermediate(s) for their interconversion is attacked from the *exo* direction (retention) at C-5 and from the *opposite side* (steric approach control) at C-2. The epimeric tricyclic alcohol **7a** has been prepared by sodium borohydride reduction of tricyclo[2.2.2.0^{2,6}]octan-3-one (**6**). The stereochemistry of the tricyclanols **5a** and **7a** was determined by equilibration studies, n.m.r. spectral data, and hydrogenolysis. Both tricyclic acetates **5c** and **7c** undergo rapid, quantitative, acid-catalyzed isomerization to bicyclic isomers. Products of the acetolysis of the *p*-nitrobenzoates of **5a** and **7a** have been determined. A convenient preparative route to **5c** is available *via* the lead tetraacetate decarboxylation of *exo*- and *endo*-5-carboxybicyclo[2.2.2]oct-2-ene. The homoallylic isomers in this system are compared to the related cholesteryl and dehydronorbornyl analogs.

In a recent manuscript,[2] we noted that hydrolysis of the monobromide fraction isolated from the reaction of N-bromosuccinimide with bicyclo[2.2.2]oct-2-ene afforded substantial amounts of a tricyclo[2.2.2.0^{2,6}]-octan-3-ol (**1**). This product was postulated as having resulted from solvolysis of *exo*-5-bromobicyclo[2.2.2]-

(1) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1–5, 1963, p. 52M.

(2) N. A. LeBel, J. E. Huber, and L. Zalkow, *J. Am. Chem. Soc.*, **84**, 2226 (1962).