results in decreased reactivity. Similar consideration of ground state interactions are used to explain the polar effects operative in the highly exothermic abstraction of a hydrogen atom by the chlorine atom,[17-23] and probably explain the positive Hammett ρ-value observed for the addition of the nucleophilic styryl radical to substituted styrenes.[4]

A slight reshuffling of the data in Table I brings to the fore another very well-behaved feature of the reaction under study. If the substituted propenes (I), butenes (II), and pentenes (III) are considered as separate reaction series, and a ρ^*-value is calculated for the addition of the trichloromethyl radical to the double bond in each series, by plotting log k_X/k_{OH} vs. σ^* for the group X, then it is possible to observe the effect on ρ^* of the interposition of a methylene group between the reaction site and the polar substituent. This treatment represents a slight modification of the original formulation of the Hammett–Taft relationship, but since the σ^*-value represents the inductive electron-withdrawing power of an atom or group of atoms, the treatment is perfectly valid. In Tables II, III, and IV the pertinent reactivity data are presented, and in Table V the ρ^*-values for the three reaction series are indicated. From the ρ^*-values in Table V it would appear that the interposition of a methylene group between the polar substituent and the double bond decreases the ρ^*-value by a factor of 2.5 ($\rho^*_{n=3} = {}^1/_{2.5}\rho^*_{n=2}$, $\rho^*_{n=2} = {}^1/_{2.5}\rho^*_{n=1}$). In the limited number of pertinent classical Hammett studies involving aromatic compounds, it has been found that the interposition of a methylene group decreases the ρ-value by a factor of about 2.3 (varying from 1.7 to 2.9 in four examples).[44] These results tend to confirm the contention expressed in an earlier paper[12] that the observed ρ-values for the addition of the trichloromethyl radical to substituted 3-phenyl-1-propenes and 4-phenyl-1-butenes of -0.29 and -0.20, respectively, are unexpectedly close together considering the presence of an additional insulating methylene group in the latter series. The two ρ-values differ by a factor of only 1.45.

Although the results discussed in this paper are in no way startling, it is nonetheless gratifying to see the regularity of the effects on reactivity of a vinyl group toward the trichloromethyl radical brought about by systematic structural changes in the rest of the molecule.

(44) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

TABLE II
RELATIVE RATES OF ADDITION OF $Cl_3C\cdot$ TO $XCH_2CH=CH_2$ AT 69.5°

X	σ^*	Rel. k
CN	$+3.64^a$	0.51 ± 0.04^c
Br	$+2.80^a$	0.64 ± 0.05
OH	$+1.55^a$	1.00
OCH_3	$+1.46^a$	0.99 ± 0.02
CH_2CN	$+1.30^b$	$1.03 \pm .03$
CH_2Br	$+1.00^b$	$1.15 \pm .10$
CH_2OH	$+0.555^b$	$1.51 \pm .05$

^{a} Ref. 32, p. 615. ^{b} Ref. 32, p. 619. ^{c} Average deviation.

TABLE III
RELATIVE RATES OF ADDITION OF $Cl_3C\cdot$ TO $XCH_2CH_2CH=CH_2$ AT 69.5°

X	σ^*	Rel. k
CN	$+3.64^a$	0.69 ± 0.02^c
Br	$+2.80^a$	0.76 ± 0.07
OH	$+1.55^a$	1.00
CH_2CN	$+1.30^a$	0.95 ± 0.10
CH_2Br	$+1.00^b$	$1.03 \pm .07$
CH_2OH	$+0.555^b$	$1.16 \pm .03$
n-C_4H_9	-0.130^b	$1.10 \pm .07$

^{a} Ref. 32, p. 615. ^{b} Ref. 32, p. 619. ^{c} Average deviation.

TABLE IV
RELATIVE RATES OF ADDITION OF $Cl_3C\cdot$ TO $XCH_2CH_2CH_2CH=CH_2$ AT 69.5°

X	σ^*	Rel. k
CN	$+1.30^a$	0.92 ± 0.01^c
Br	$+1.00^a$	0.87 ± 0.02
OH	$+1.55^a$	1.00
n-C_3H_7	-0.115^b	1.09 ± 0.04

^{a} Ref. 32, p. 615. ^{b} Ref. 32, p. 619. ^{c} Average deviation.

TABLE V
ρ^*-VALUES FOR THE REACTIONS
$X(CH_2)_nCH=CH_2 + Cl_3C\cdot \rightarrow X(CH_2)_n\dot{C}HCH_2CCl_3$ AT 69.5°

n	ρ^*	r^a
1	-0.15 ± 0.01	-0.99
2	$-.06 \pm .01$	$-.95$
3	$-.024 \pm .005$	$-.91$

^{a} Correlation coefficient.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, SAN DIEGO, LA JOLLA, CALIF.]

Oxymercuration of Olefins. II. cis- and trans-Oxymercuration of Bicyclo[2.2.2]oct-2-ene

By T. G. Traylor

The oxymercuration of bicyclo[2.2.2]octene produces both cis- and trans-3-chloromercuribicyclo[2.2.2]octan-2-ol and no rearranged product, whereas under similar oxymercuration conditions norbornene gives only cis and cyclohexene only trans product. Hydroxymercuration of bicyclooctene in aqueous acetone is accompanied by cis-acetoxymercuration when mercuric acetate is used in high concentration or when sodium acetate is present. In glacial acetic acid oxymercuration of this olefin affords exclusively cis product. These and other data are presented as evidence that cis-oxymercuration of strained olefins occurs through an intermediate mercurinium ion. The results are consistent with a single intermediate leading to both cis and trans addition to bicyclooctene. This reaction also presents a simple synthesis of diastereomeric mercurials which are usually obtained with great difficulty.

Introduction

The oxymercuration of olefins, shown in eq. 1, displays kinetic and stereochemical behavior, solvent and

$$>C=C< + HgX_2 \xrightarrow{ROH} RO\overset{|}{C}-\overset{|}{C}HgX + HX \quad (1)$$

salt effects on rate and products, and structural effects which are typical of general electrophilic additions to double bonds.[1]
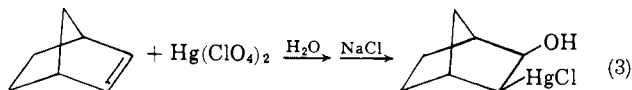
However, some notable differences between this and other electrophilic additions are apparent. For exam-

(1) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

ple, only 1,2-addition to butadiene occurs,[2] and addition

$$CH_2=CHCH=CH_2 + Hg(OAc)_2 \longrightarrow$$

$$\overset{\displaystyle OCH_3}{\underset{\displaystyle |}{AcOHgCH_2CHCH=CH_2}} \quad (2)$$
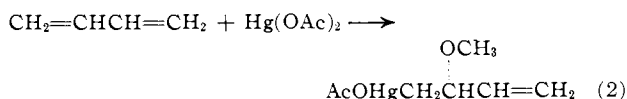
to bicycloheptenes (eq. 3)[3–5] does not lead to the usual rearrangement.

$$(3)$$

Both observations indicate that little carbonium ion character is developed on the olefinic carbon during oxymercuration. The difference between oxymercuration and other electrophilic additions is striking in another respect. Although mercuric salts are added to unstrained olefins to give exclusively *trans* addition products[3,4,6] (eq. 4), similar additions to a number of bicycloheptenes[3,4] produce exclusively *cis* products (eq. 3).

$$(4)$$

Thus, both *cis* and *trans* additions are quite general within specific structural limitations and two mechanisms of oxymercuration must be proposed, one leading to *cis* and the other to *trans* product. The present work was therefore undertaken to determine what structural features in the olefin lead to *cis*- or to *trans*-oxymercuration. One possibility is that strain in the olefin, rather than steric interaction of reagents with the bicyclic system, is responsible for *cis*-oxymercuration through the occurrence of a strained and thus very rigid and reactive mercurinium ion such as
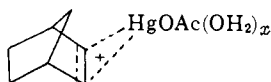
This argument predicts that unstrained bicyclic olefins should undergo *trans*-oxymercuration and very strained cyclic olefins should undergo *cis* addition of mercuric salts. Using the heats of hydrogenation[7] of norbornene (−33.1 kcal./mole), bicyclo[2.2.2]octene (−28.3 kcal./mole), and cyclohexene (−27.1 kcal./mole) as measures of olefin strain leads to the prediction that bicyclo[2.2.2]octene would be much less prone to *cis* addition than is norbornene and, in fact, bicyclo[2.2.2]octene was found to undergo both *cis*- and *trans*-oxymercuration. As a consequence of this result we were able to study the effects of solvent nucleophilicity and other variables on the stereochemistry of oxymercuration.

Results

The mercurials I–IV were prepared in this work, I–III by direct oxymercuration and IV by acetylation of III.

Preparation of *cis* (II) and *trans* (III) Oxymercuration Products.—The oxymercuration of bicyclo[2.2.2]-oct-2-ene can be carried out so as to isolate either pure

(2) K. H. McNeely and G. F Wright, J. Am. Chem. Soc., **77**, 2553 (1955).

(3) (a) T. G. Traylor and A. W. Baker, Tetrahedron Letters, **No. 19**, 15 (1959); (b) J. Am. Chem. Soc., **85**, 2746 (1963).

(4) M. M. Anderson and P. M. Henry, Chem. Ind. (London), 2053 (1961).

(5) H. Kwart and L. Kaplan, J. Am. Chem. Soc., **76**, 4072 (1954).

(6) T. G. Traylor and S. Winstein, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 81-O.

(7) R. B. Turner, "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths, London, 19 9, pp. 76–77.
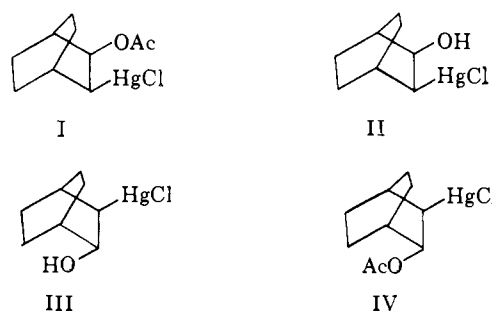
cis-2-chloromercuribicyclo[2.2.2]octan-3-ol (II) or the corresponding pure *trans* isomer III.

The *cis* isomer II (m.p. 155–156°) is best prepared by treating the olefin with an equimolar amount of mercuric acetate in acetic acid for a few minutes to produce I′, then pouring the resulting solution into excess aqueous sodium hydroxide to hydrolyze the acetate, and finally precipitating II by acidifying the solution with hydrochloric acid.


$$(5)$$
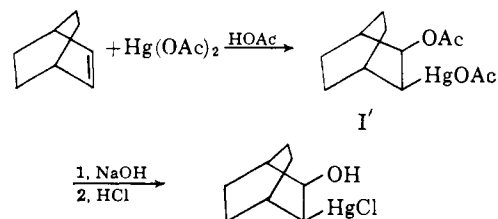
The acetate I was isolated as an oil which solidified at about 10° and is differentiated from the acetate IV (see below) in having a doublet carbonyl peak in the infrared. The *trans*-hydroxymercurial III (m.p. 172–172.5°), which is much less soluble in most solvents than the *cis* isomer, is quite easily isolated from mixtures of the two, obtained as described below, by recrystallization from chloroform, carbon tetrachloride, or heptane–ethyl acetate.

$$(6)$$
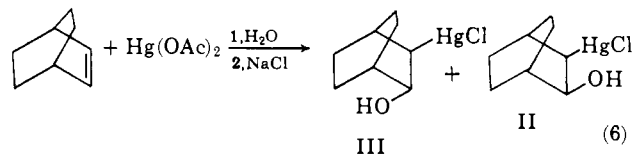
Structure Proof.—The infrared spectra of II and III indicate much greater intermolecular hydrogen bonding in III than in II as shown in the hydroxyl peaks at 2.9 μ. This suggests that II has the *cis* and III the *trans* configuration.

In some cases the stereochemistry of oxymercuration can be established by observing the size of the coupling constants between the hydrogens on the carbons containing the hydroxyl and chloromercuri groups.[4] Although a coupling constant, $J = 10$ c.p.s., was observed for the hydrogen α to the hydroxyl group ($\tau = 6.73$) in II, this doublet was poorly resolved and the corresponding hydrogen could not be resolved in III, presumably due to resplitting.

The structures of II and III were conclusively demonstrated by reducing both II and III to pure bicyclo[2.2.2]octan-2-ol, identified by comparison with an authentic sample, and by comparing the hydroxyl

$$(7)$$
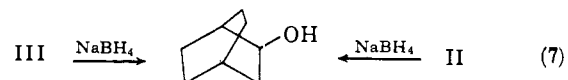
stretching frequencies of II and III with that of bicyclooctanol. The previous paper[3b] of this series established that *cis*-hydroxymercurials have hydroxyl stretching frequencies about 20 cm.$^{-1}$ lower and the

trans isomers only 6–10 cm.$^{-1}$ lower than the parent alcohol. The data in Table I, therefore, demonstrate that II has the *cis* and III the *trans* configuration of the two groups. Thus, the acetate I has the *cis* and IV the *trans* configuration as indicated.

TABLE I

HYDROXYL STRETCHING FREQUENCIES OF ALCOHOLS

| Instrument	Bicyclooctanol[b]	II	III	II	III
		Compound		Δν[a]	
Beckman IR-7	3621.6	3600.4	3615.3	21.2	6.3
Perkin–Elmer 421	....	3599.5	3614.5	22.1	7.1
Cary 90	....	3600.0	3615.0	21.6	6.6

[a] From bicyclooctanol. [b] Determined on both the sample supplied by Professor Walborsky and that prepared in this work.

Analysis of Mixtures of II and III.—The infrared spectra of these isomers are sufficiently different to permit approximate compositions of mixtures of the two to be determined. For this purpose the relative intensities (log (I_0/I) by the estimated base line technique[8]) of the 9.6-μ peak in II and the 9.8-μ peak in III were used.

Effect of Solvent and of Reagents on Stereochemistry of Addition.—The products of oxymercuration of bicyclooctene under a variety of reaction conditions are shown in Table II.

In order to show that the products listed in Table II are oxymercuration products and not the result of isomerizations or of destruction of one isomer, the product III was carried through the condition 3 and reisolated. The recovered product was not contaminated with II. Likewise the *trans*-acetate IV was treated with acetic acid and recovered unchanged by the same procedures which were used in the isolations of I and II.

The most striking result in Table II is the change from 50–50 *cis*- and *trans*-oxymercuration in water to exclusive *cis*-oxymercuration in acetic acid. The *cis*-acetate I was also produced by including acetate ion in the aqueous oxymercuration reaction mixture. However, the presence of acetate ion did not cause production of *trans*-acetate IV and reduced the amount of *trans*-hydroxymercurial III by only 10–15%.
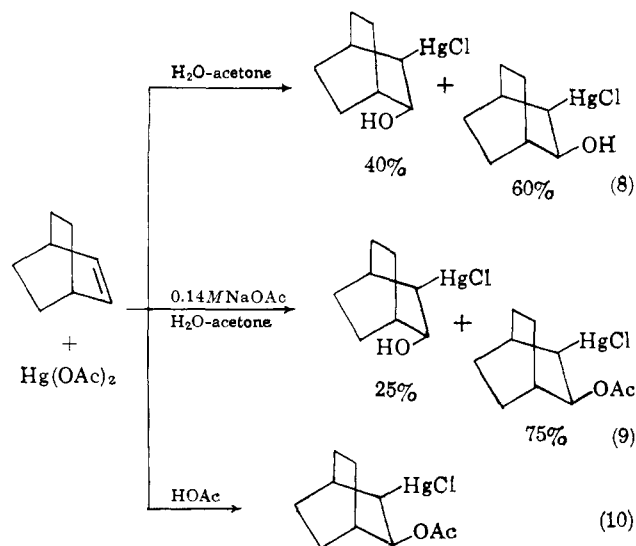
These results are consistent with the general observation that *cis*-oxymercurations with aqueous mercuric acetate produce some acetate product[3a] but that *trans*-oxymercurations do not.[1] However, if the solvent is a poor nucleophile, some *trans*-acetate is obtained. Thus,

(8) H. H. Nielsen and R. A. Oetjen, "Physical Methods in Chemical Analysis," Academic Press, Inc., New York, N. Y., 1950, p. 397.

TABLE II

EFFECT OF REACTION CONDITIONS ON PRODUCT COMPOSITION IN OXYMERCURATION OF BICYCLO[2.2.2]OCT-2-ENE

| Condition	Solvent	Concn. Hg(OAc)₂, mole/l.	Concn. NaOAc, mole/l.	Percentage composition of product			
				I	II	III	IV
1	H₂O	(0.1)[a]	...	0	50	50	0
2	H₂O–acetone[c]	.067	...	0	60	40	0
3	H₂O–acetone[c]	.09	...	Trace	60	40	0
4	H₂O–acetone[c]	.1	0.139	75[b]	0	25	0
5	HOAc	.37	...	(100)[b]	0	0	0

[a] Hg(OTos)(OH). [b] Identified by alkaline hydrolysis to II. [c] Fifty volume per cent each.

the addition of mercuric acetate to cyclohexene in water resulted in no acetate production but some acetate was obtained in *t*-butyl alcohol.
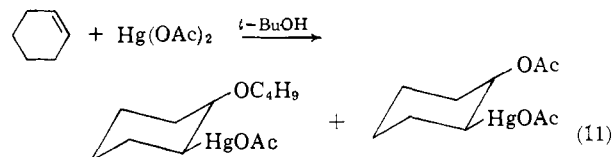
Discussion

Although nuclear magnetic resonance studies[9] have shown that the mercurinium ion (V) does not occur in
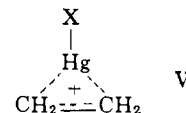
high concentration in aqueous solution, the kinetics and stereochemistry of addition to simple olefins indicate that this type of intermediate is involved in oxymercuration reactions.[1] Such an intermediate readily explains *trans* addition to simple olefins. However, a more detailed mechanism is necessary to accommodate the *cis*-oxymercuration of strained olefins.[3a,b,5]

In the previous paper[3b] of this series a general mechanism of electrophilic olefin addition was proposed in which a π-complex, in rapid equilibrium with olefin, undergoes *cis* or *trans* addition or rearrangement depending upon the electronegativity and complexing ability of the electrophile and on the rigidity of the olefin. Because mercury is not very electronegative and thus induces little carbonium ion character at the α-carbon, rearrangement does not occur during oxymercuration of the most strained olefins. It was suggested that *cis* addition to norbornenes was a result of resistance to twist about the carbon–carbon bond which is necessary for backside mercurinium ion opening as illustrated in Fig. 1 for norbornene.

A bicyclic olefin in which this C–C twist is easily accomplished would therefore be expected to undergo *trans* addition. With bicyclo[2.2.2]octene the strain is not completely removed (see heats of hydrogenation), but the twisted structure of the olefin lowers the energy of the transition state for backside attack on the ion relative to that for a similar attack on the bicycloheptene mercurinium ion. Therefore external attack on the bicyclooctene mercurinium ion by solvent may compete with frontside opening. On this basis the expected result was that the *trans* addition product should be favored in nucleophilic solvents and *cis* product should predominate in solvents of poor nucleophilicity. The observations of exclusive *cis* addition to this olefin in glacial acetic acid and *cis* + *trans* oxymercuration in aqueous acetone agree with this prediction.

Although a molecular four-center *cis* addition cannot be rigorously excluded at this time, a mechanism involv-

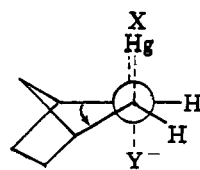(9) H. G. Tennent, private communication.

Figure 1.

ing a single intermediate leading to both *cis* and *trans* products is preferred. Furthermore, if the acetate I and hydroxymercurial II were formed by a molecular mechanism and the hydroxymercurial III by an ionic mechanism, it is difficult to explain the persistence of III in a sodium acetate solution where the equilibrium

$$Hg(OAc)_2 + H_2O \rightleftharpoons Hg^+(OH_2)(OAc) + OAc^- \quad (12)$$
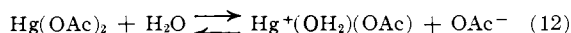
is shifted to the left.[10] Suppression of ionization or hydrolysis of mercuric acetate should favor molecular addition of mercuric acetate and at the same time suppress any ionic addition. Therefore the replacement of II by I upon sodium acetate addition should occur concomitant with a replacement of III by I. However, Table II shows that sodium acetate makes the change II to I essentially complete while repressing the formation of III only slightly and giving no detectable IV. These observations do not appear to support a molecular mechanism for *cis* oxymercuration. One of several possible ionic mechanisms[3b] which is consistent with the experimental findings is shown in Fig. 2.

Now that a delicate balance of *cis* and *trans* ionic addition to simple olefins is in hand, we plan a detailed study of solvent and salt effects on the rate and product composition in this reaction. In this way it may be possible to establish the nature of the mercurinium ion intermediate. The importance of olefin strain in determining stereochemistry of ionic addition will be further tested by observing the extent of *cis* addition to cyclobutene and cyclopropene.

It has recently been suggested that addition of hydrogen halides to double bonds, especially *cis* additions, proceeds through open carbonium ion–halide ion pairs.[11] That no open carbonium ion occurs in any of the *cis*-oxymercurations observed to date is shown by the absence of the very facile skeletal rearrangements usually observed in addition to bicycloheptenes or bicyclooctenes.[3b]

Experimental

Melting points were determined on a Thomas–Hoover melting point apparatus and are uncorrected.

Infrared spectra were taken on a Perkin–Elmer Infracord 137B except for the hydroxyl stretching frequencies which were determined on the instruments indicated in Table I. Nuclear magnetic resonance spectra were taken on a Varian A60 spectrometer.

All solvents and reagents were commercial reagent grade except for the bicyclo[2.2.2]oct-2-ene and the bicyclo[2.2.2]octan-2-ol which were kindly donated by Professor Harry Walborsky.

cis-2-Acetoxy-3-(chloromercuri)-bicyclo[2.2.2]octane (I).—A mixture of 0.220 g. (2.0 mmoles) of bicyclo[2.2.2]octene, 0.698 g. (2.2 mmoles) of mercuric acetate, and 6 ml. of glacial acetic acid was stirred 15 min. The mercuric acetate dissolved and the solution gave no mercuric oxide in aqueous alkali. This mixture was poured into a rapidly stirred solution of 0.2 g. of sodium chloride in 50 ml. of water at 0° to precipitate a colorless solid. This solid, which was filtered off and washed with ice water, melted at about 10° to a viscous oil. The oil, after drying under vacuum, weighed 0.683 g. (85%). The infrared spectrum in chloroform displayed carbonyl peaks at 5.74 and 5.80 μ whereas the corresponding *trans*-acetate had only one carbonyl peak. In addition, the *cis*-acetate I showed only traces of hydroxyl absorption.

(10) (a) P. Mahapatra, S. Aditya, and B. Prasad, *J. Indian Chem. Soc.,* **30**, 509 (1953); (b) E. G. Long and K. A. Kobe, *Ind. Eng. Chem.,* **43**, 2366 (1951).

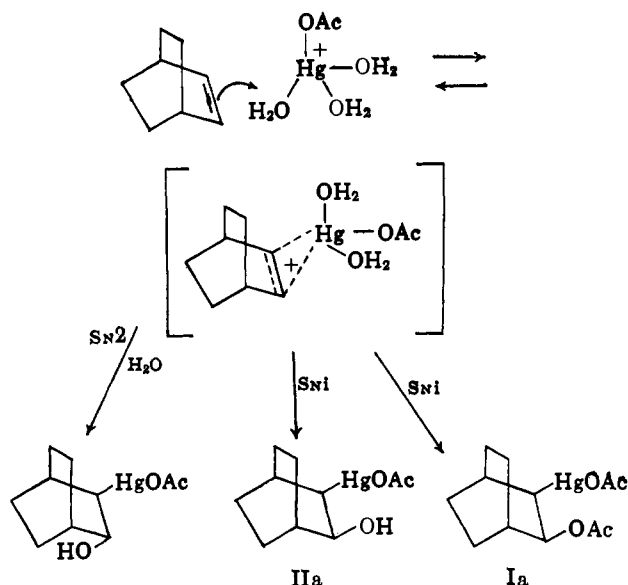(11) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.,* **84**, 2012 (1962).

Figure 2.

cis-2-(Chloromercuri)-bicyclo[2.2.2]octan-3-ol (II).—The acetoxymercuration above was repeated using twice the amounts of all reagents. The acetic acid solution was not poured directly into sodium chloride solution but was first poured into 50 ml. of 5.6 M sodium hydroxide solution. The resulting strongly alkaline solution was at 60–70° and was kept at this temperature for 15 min., then cooled and brought to pH 5 with concentrated hydrochloric acid. The resulting white precipitate was filtered off, washed with water, and dried over P_2O_5 *in vacuo*; yield 0.88 g. (60%). The infrared spectrum was identical with that of the purified product. The product was recrystallized from ethanol–water in two crops of 0.47 and 0.20 g., respectively, both melting at 155–156°. Analyses were obtained on another sample described below. The hydroxyl stretching frequency is shown in Table I.

trans-2-(Chloromercuri)-bicyclo[2.2.2]octan-3-ol (III).—A mixture of 0.55 g. (5 mmoles) of bicyclooctene, 1.08 g. (5 mmoles) of mercuric oxide, and 0.95 g. (5 mmoles) of *p*-toluenesulfonic acid monohydrate in 50 ml. of water was stirred 15 hr. with a magnetic stirrer. The olefin had disappeared and was replaced by a colorless crystalline solid. The mixture was made alkaline to dissolve the precipitate, reacidified with dilute hydrochloric acid, and about 1 g. of sodium chloride added. The resulting precipitate was dried and extracted with hot ethyl acetate. Heptane was added to the hot solution to cloud point and the solution cooled to give 0.18 g. of III, m.p. 172.0–172.5°. *Anal.* Calcd. for $C_8H_{13}OHgCl$: C, 26.6; H, 3.63. Found: C, 26.7; H, 3.85. Recrystallization from chloroform did not change the melting point or infrared spectrum. The spectrum in compound II has a large peak at 9.63 μ and a slight shoulder at 9.8 μ and III has a large peak at 9.8 μ with only a shoulder at 9.63 μ. These peaks could be used in either chloroform solution or in mineral oil mulls to estimate the compositions of mixtures of II and III which were obtained in most of the reported oxymercurations.

Evaporation of the filtrate from III to dryness yielded 0.63 g. of mixed II and III containing 60–70% II. (Thus, the crude product contained about 50% of each isomer.) Recrystallization from ethyl acetate–heptane gave essentially unchanged mixture, m.p. 166–168°, and further recrystallization from isopropyl alcohol–water raised the m.p. to 168–169°. This product, which contained about 60% *cis* (II) mercurial was analyzed. *Anal.* Calcd. for $C_8H_{13}OHgCl$: C, 26.6; H, 3.63. Found: C, 26.8; H, 4.09.

Nuclear Magnetic Resonance Spectra.—In deuteriochloroform, compound III had a large peak around 8.33 τ and small peaks of about equal intensity at τ 5.64, 7.3, and 8.11. Compound II similarly had a large peak at 8.32 τ and small equal peaks at τ 5.65, 6.73, 7.28, and 8.03. The 6.73-τ peak appeared to be a doublet having a coupling constant of 10 c.p.s. This 6.73-τ doublet was also present in II and absent in III in hexadeuteriodimethyl sulfoxide.

Oxymercuration of Bicyclo[2.2.2]oct-2-ene in Aqueous Acetone.—A solution of 0.108 g. (1.0 mmole) of the olefin and 0.315 g. (0.99 mmole) of mercuric acetate in 15 ml. of 50 volume % aqueous acetone was stirred for 24 hr. The yellow precipitate which appeared initially slowly dissolved. The clear solution was evaporated to about 12 ml. and poured into a solution of 1 g. of sodium chloride and 1 g. of sodium bicarbonate in 25 ml. water to produce a colorless precipitate which, after washing and

drying, weighed 0.19 g. and melted at 171–172°. By comparing the infrared spectrum with those of I and II, it could be established that the mixture contained about 40% III and 60% II. This mixture had both 3615 and 3600 cm.$^{-1}$ peaks. A small amount was dissolved in warm chloroform, cooled in ice, and the precipitate filtered off and dried; m.p. 171–172°. The infrared spectrum of these crystals was identical with that of III.

Effect of Concentration of Mercuric Acetate.—When the preceding preparation was repeated at 50% higher concentration of reagents (0.091 M), a 75% yield (0.749 g.) of mixed mercurials was obtained which appeared to be 60–65% II and 35–40% III by infrared analysis. The product also had a small peak at 5.8 μ. This crude product was recrystallized from chloroform to yield 0.27 g. of a compound, m.p. 170–170.5° before and 172–172.5° after a second recrystallization from chloroform. The infrared spectrum in chloroform was identical with that of pure III.

The filtrate was evaporated to dryness to give a solid (IIa) whose infrared spectrum in chloroform was identical with that of pure II except that a carbonyl band having about the same intensity as the hydroxyl band appeared at 5.8 μ. Recrystallizing the product from 70% ethanol–30% water yielded a product of unchanged infrared spectrum, melting at 141–145°.

Effect of Added Acetate Ion on Oxymercuration Product Composition.—A 0.139 M solution of sodium acetate in fifty volume % aqueous acetone containing 0.192 g. (0.099 M) of bicyclooctene and 0.554 g. (0.097 M) of mercuric acetate was stirred for 30 hr. and evaporated to one-half its volume. After addition of 10 ml. of 6 N sodium hydroxide solution, the solution was heated to 50–60° for 10 min. to hydrolyze the acetate. About 1 g. of sodium chloride and enough concentrated hydrochloric acid to bring the solution to pH 5 were added. The precipitate which formed was filtered off and dried under vacuum; yield 2.13 g. (33%). The infrared spectrum indicated a mixture of 70% II and 30% III.

Identification of *cis*-**2-Acetoxy-3-(chloromercuri)-bicyclooctane (I) and** *trans*-**2-(Chloromercuri)-bicyclo[2.2.2]octan-3-ol (III) as the Products of Oxymercuration of Bicyclooctene in 0.14 M Sodium Acetate.**—The oxymercuration in 0.139 M sodium acetate above was repeated with 24-hr. reaction time. Evaporating the reaction mixture to half its volume in order to remove acetone produced a thick oil, which was separated by decanting the supernatant liquid and washed with water; 10 ml. of benzene was added to dissolve partially the oil and the mixture was evaporated, then dried over phosphorus pentoxide at 1 mm. pressure for 12 hr. to yield 0.55 g. of product (75% yield if the product were I). The infrared spectrum in a mineral oil mull indicated that this product contained about 25% of a hydroxy mercurial (II or III or a mixture). (The infrared spectra of the *cis*- and *trans*-acetoxymercurials were so similar that mixtures could not be analyzed by this method.) This product was dissolved in a minimum (5 ml.) of hot carbon tetrachloride and cooled to precipitate 74 mg. of pure *trans*-2-(chloromercuri)-bicyclo[2.2.2]-octan-3-ol (III) as indicated by its infrared spectrum. The infrared spectrum of the filtrate indicated that less than 25% of the hydroxymercurial remained as measured by the peak at 2.8 μ. This filtrate was evaporated to an oil, heated for 15 min. at 50° in 10 ml. of 2 N sodium hydroxide in 50% methanol, diluted with about 50 ml. of water, and acidified carefully with concentrated hydrochloric acid. The resulting precipitate was dried under vacuum over phosphorus pentoxide. An infrared spectrum in a mineral oil mull was identical with that of pure II. Therefore, the product of this reaction was about 75% I and 25% III with very little II or IV.

Stability of III to Oxymercuration Conditions. In Acetone–Water.—A mixture of 0.275 g. of mercuric acetate and 0.225 g. of the above mercurial III in 10 ml. of 50 volume % aqueous acetone was stirred 5 hr. and evaporated to half its volume. The solution was adjusted to pH 11 with sodium hydroxide, filtered, and acidified with HCl to precipitate a white solid. After filtration, washing, and drying under vacuum, this precipitate had an infrared spectrum identical with that of the starting *trans* compound. Recrystallization of this solid from chloroform did not change the infrared spectrum; the filtrate, after concentration and removal of two additional crops of III, showed no indication of the *cis*-mercurial II (at 9.6 μ). Because the *cis*-mercurial concentrates in the filtrate, this indicates no isomerization under oxymercuration conditions.

Recovery of III from Glacial Acetic Acid.—The *trans*-mercurial III used above (0.34 g.) was heated to 50° for 10 min. in 3 ml. of glacial acetic acid, cooled, and poured into 3 g. of sodium hydroxide in 10 ml. of water. The resulting solution was cooled, neutralized with concentrated hydrochloric acid, and the precipitate collected, washed with water, and dried. The 0.265 g. of recovered product displayed the same infrared spectrum as the starting *trans* compound.

Stability of *trans*-**2-Acetoxy-3-(chloromercuri)-bicyclooctane (IV) in Glacial Acetic Acid.**—About 20 mg. of sodium acetate and 0.218 g. of III were heated 30 min. at 90° in 6 ml. of acetic anhydride and the excess acetic anhydride and acetic acid removed under vacuum. The crystalline product was dried at 0.5 mm. pressure for 12 hr.; m.p. 120–127°. The infrared spectrum was exactly like that of I except that a single, sharp acetate peak occurred at 5.84 μ and there was a small hydroxyl peak at 2.8 μ.

This compound (90 mg.) was heated 10 min. at 40° in acetic acid and treated by the same procedure used in the hydrolysis and isolation of II. The 70 mg. of product had an infrared spectrum identical with that of pure III.

Mercuration of Cyclohexene in *t*-**Butyl Alcohol.**—This reaction was carried out by the method of Wright[12] with the exception that the mercuric acetate–cyclohexene–*t*-butyl alcohol mixture was stirred 4 hr. before the BF$_3$ etherate was added.

The crude product, *trans*-2-*t*-butoxycyclohexylmercuric chloride, had a carbonyl absorbance at 5.8 μ, about one-sixth as large as the absorbance at 3.4μ.

Reduction of the Bicyclooctene Oxymercuration Products.—The aqueous Hg(OTos)$_2$ oxymercuration procedure described above was repeated on a 10-mmole scale, and at the end of the reaction about 2 g. of sodium borohydride was added. The mixture was stirred for 14 hr. and the product extracted with 50 ml. of ether. Evaporation of the ether under vacuum produced 0.31 g. (25% yield) of pure bicyclo[2.2.2]octan-2-ol, m.p. 208–210°, having a hydroxyl stretching frequency of 3621.6 cm.$^{-1}$ and an over-all infrared spectrum identical with an authentic sample.[8]

When about 50 mg. of the product IIa was stirred with 1 g. of sodium borohydride in 8 ml. of 0.5 N sodium hydroxide for 4 hr. and the mixture extracted with carbon tetrachloride, the dried extract also had an infrared spectrum identical with that of authentic bicyclo[2.2.2]octan-2-ol except for a very small peak at 5.75 μ due to acetate from a trace of acetoxymercurial (I).

(12) G. F Wright, *Can. J. Chem.*, **28B**, 625 (1950).