clusive evidence that the principal chlorine-binding reaction is not a free radical reaction associated with the peroxide-catalyzed polymerization of styrene, but is competing with it. Finally the α-phenethyl chloride formed in the presence of peroxide contains no more β-phenethyl chloride than that made in the absence of peroxide (see Table II, note *f*), a proportion too low to have been detected.[18]

The two polymer fractions from the peroxide run average 1.8% chlorine as compared with 4.75% reported by Ford, *et al.*, on their whole product (after assumed removal of phenethyl chloride, b.p. about 195°, by steam distillation). They gave no data on yields.

The low reactivity of styrene in chain transfer with hydrogen chloride is to be expected. The substituted benzyl radical involved should be less reactive than any saturated aliphatic radical in the crucial reaction 2.

Conclusions.—Table III permits comparison of factors which limit free radical additions of hydrogen chloride to unsaturated compounds. The reaction with ethylene is limited mostly by the endothermic nature of reaction (2). The result with styrene shows how the reactivity of the radical in reaction (2) further restricts reaction. Comparison of propylene and *t*-butylethylene shows that chain termination by transfer with allylic hydrogen atoms may be an equally critical factor when radicals sufficiently reactive to undergo reaction (2) are involved. The results with allyl chloride support the same conclusion and suggest that the ability of an unsaturated compound to polymerize with peroxides is a measure of the importance of the allyl termination mechanism in hydrogen chloride additions.

TABLE III

ABNORMAL ADDITION OF HYDROGEN CHLORIDE TO DOUBLE BONDS

Unsaturated compound	Chain length[a]	Reference
Ethylene	$\geq$30 at 26°	3a
Propylene	2 at 70°	
t-Butylethylene	>7 at 25°	4
Allyl chloride	22 at 80°	
Styrene	0 at 100°	

[a] Quantum yield of ethyl chloride from ethylene in vapor phase, moles of hydrogen chloride reacting by a free radical mechanism per mole of peroxide initially present in other instances. The decomposition of benzoyl peroxide was probably complete except with *t*-butylethylene.

Acknowledgment.—Mrs. D. K. Ladd, Miss Bess Rickman, and several members of the Analytical Chemistry Unit have contributed much of the experimental work.

SCHENECTADY, N. Y.

[18] J. Schramm, *Ber.*, **26**, 1709 (1893).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Oxidation of Bicyclo[2.2.2]octene-2 and Bicyclo[2.2.1]heptene-2[1]

BY H. M. WALBORSKY AND D. F. LONCRINI

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Bicyclo[2.2.2]octene-2 has been synthesized by a Diels–Alder condensation between ethylene and 1,3-cyclohexadiene. The olefin was oxidized to the epoxide and the *cis* and *trans* vicinal glycols. The anomalous behavior of bicyclo[2.2.1]-heptene-2 toward oxidation is discussed.

Introduction

Birch and Oldham[2] reported that the oxidation of bicyclo[2.2.1]heptene-2 by potassium permanganate gave the normal product, *cis*-cyclopentanedicarboxylic acid. However, when the olefin was oxidized by peracetic acid and the resulting glycol oxidized by chromic acid, 1,2,4-butanetricarboxylic acid and succinic acid were obtained. To account for the unpredicted result obtained by the chromic acid oxidation, the authors postulated a mechanism which involved the use of an intermediate with a double bond at the bridge-head.

The use of such an intermediate is questionable since this would represent a molecule of high energy as a result of the violation of Bredt's rule.[3] It was therefore of interest to repeat Birch's oxidation and to investigate the oxidation of bicyclo[2.2.2]octene-2 to determine whether or not this olefin would behave in an analogous anomalous manner.

Results and Discussion

Bicyclo[2.2.2]octene-2 was prepared in *ca.* 50% yield by the condensation of ethylene and 1,3-cyclohexadiene[4] in a high pressure vessel at 250°.[5] This method is a distinct improvement over the previously reported methods[6,7] which entailed seven to ten step procedures. The olefin was reduced catalytically to yield the saturated hydrocarbon, bicyclo[2.2.2]octane.

The oxidation of bicyclo[2.2.2]octene-2 (I) was carried out in the manner

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[1] This was presented in part before the 5th Southeast Regional Meeting of the American Chemical Society in New Orleans, La., December 10, 1953.

[2] S. Birch, W. Oldham and E. Johnson, *J. Chem. Soc.*, 818 (1947).

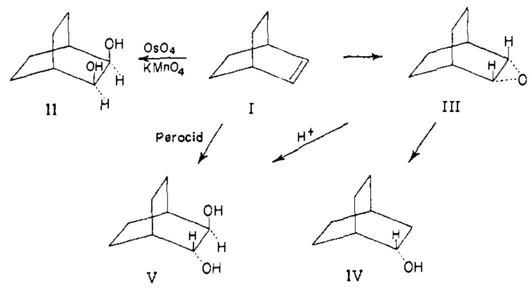
[3] J. Bredt, *Ann.*, **437**, 1 (1924).

[4] This procedure is a modification of the method of Tom (T. B. Tom with C. Boord and K. Greenlee, The Ohio State University Ph.D. Thesis, 1948). P. Wilder, Ph.D. Thesis (January, 1950) at Harvard with R. Woodward, report a similar preparation.

[5] The procedure described in this paper was developed in the laboratories of Dr. M. S. Newman at The Ohio State University.

[6] R. Seka and O. Tramposch, *Ber.*, **75B**, 1379 (1942).

[7] G. Komppa, *ibid.*, **68B**, 1267 (1935).



When I was oxidized by osmium tetroxide or potassium permanganate, *cis*-2,3-dihydroxybicyclo[2.2.2]octane was obtained. The glycol II gave a positive periodate test and yielded *cis*-1,4-cyclohexanedicarboxylic acid upon oxidation by nitric acid. The infrared spectrum shows the expected intramolecular hydrogen bonding, due to the *cis* OH, as shown by the fact that the ratio of the intensities of the two bands, due to the free and bonded OH, is independent of concentration (Fig. 1.)[8]

The oxidation of I by performic acid produced *trans*-2,3-dihydroxy-bicyclo[2.2.2]octane (V). The glycol V, upon oxidation, yielded the same dicarboxylic acid as that obtained from II. This glycol also gave a positive periodate test and its infrared spectrum revealed strong absorption due to the hydroxyl groups, but an absence of intramolecular hydrogen bonding, as exemplified by the fact that the ratio of the intensities of the two bands is dependent on the concentration (Fig. 1).

Epoxidation of I by perphthalic acid gave a quantitative yield of 2,3-epoxybicyclo[2.2.2]octane (III). Hydrolysis of III with formic acid, followed by saponification, produced the *trans*-glycol V. Reduction of III by lithium aluminum hydride yielded bicyclo[2.2.2]octanol-2 (IV).

The oxidation of I indicated a normal behavior of this olefin to peracid oxidation. This is in direct contrast to the behavior of bicyclo[2.2.1]heptene-2, whose glycol, produced by peracid oxidation, did not yield the expected *cis*-1,3-cyclopentanedicarboxylic acid.

Oxidation of bicyclo[2.2.1]heptene-2 (VI) by peracetic acid produced a glycol which did not give a periodic acid test, thus demonstrating that we were not dealing with a vicinal glycol.[9]

In light of recent work on the bicyclo[2.2.1]heptyl system,[10] the fact that bicyclo[2.2.1]heptene-2 does not yield a vicinal glycol becomes understandable.

The initial step in the peracid oxidation is undoubtedly the formation of an epoxide[11] which, under the acidic conditions of the reaction, is opened to give a non-classical ion (A $\rightleftarrows$ B $\rightleftarrows$ C). Reaction of the non-classical ion with solvent will yield VIII or IX (if there is a hydride shift) or a mixture of both. Both VIII and IX would give a negative periodate test.

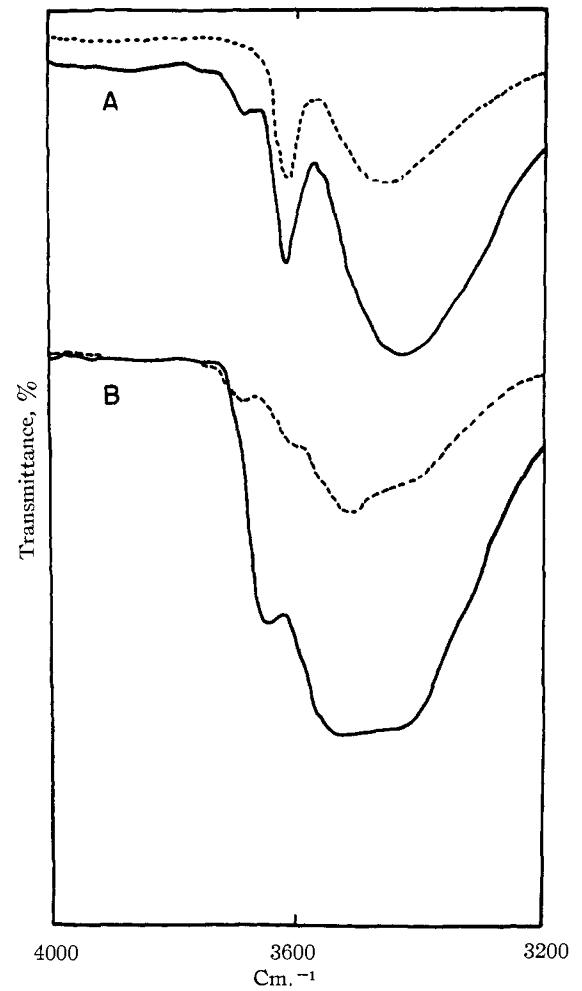
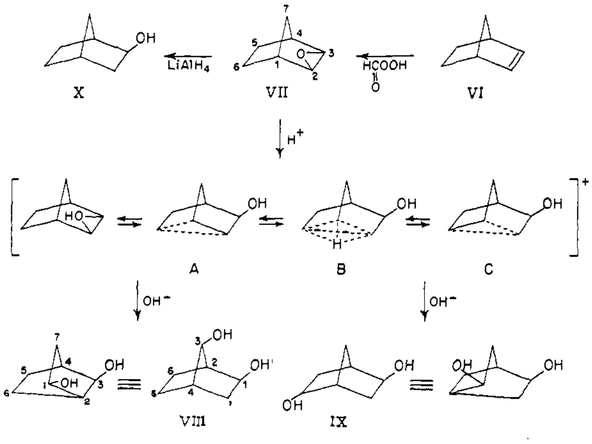


Fig. 1.—Infrared absorption spectra (Perkin-Elmer infrared spectrometer: 0.1 mm. cell length): A, *trans*-2,3-dihydroxybicyclo[2.2.2]octane; ——, saturated solution in chloroform (% transmission: free OH, 59.6; bonded OH, 45.7); ------, fivefold dilution (% transmission: free OH, 73.4; bonded OH, 72.4). B, *cis*-2,3-dihydroxybicyclo[2.2.2]-octane; ——, saturation solution in chloroform (% transmission: free OH, 49.0; bonded OH, 31.6); ------, fivefold dilution (% transmission: free OH, 84.5; bonded OH, 67.2).

We have tentatively assigned structure VIII to the glycol obtained by peracid oxidation of VI.



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[8] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

[9] A similar observation has recently been made on the per acid oxidation of dicyclopentadiene; M. Gates and S. P. Malchick, *ibid.*, **76**, 1378 (1954).

[10] J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); S. Winstein and D. Trifan, *ibid.*, **74**, 1147 (1952).

[11] D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 386.

This is based on the following evidence: When VI is carefully oxidized by peracetic acid, the epoxide VII which is formed was shown to be of the *exo*-configuration, since lithium aluminum hydride reduction yielded the *exo* alcohol.[12] Hydrolysis of the oxide produced the same glycol as did the peracid oxidation. This therefore establishes the configuration of the hydroxyl group at carbon atom 3 as shown in VIII. Thus, if the next hydroxyl group enters at position 1, the configuration[10,13] of the glycol would be as shown in VIII. If, on the other hand, there is a hydride shift, then the glycol produced would have the configuration IX. The fact that the glycol gives a cyclic acetal with *p*-nitrobenzaldehyde would favor structure VIII for the glycol produced. The acetal was produced in 84% yield and repeated attempts to find IX which would be produced by a hydride shift were unsuccessful. To assure that no rearrangement occurred during the formation of the acetal, which was formed under acidic conditions, the acetal was hydrolyzed and the original glycol was recovered unchanged.

The failure to obtain abnormal products from the oxidation of I can be explained on a similar basis. It has previously been demonstrated that the bicyclo[2.2.2]octyl system does not readily form a non-classical ion.[14] The reason suggested for this observation was that the bicyclo[2.2.1]heptyl system is strained, whereas the bicyclo[2.2.2]octyl is not,[15] and that the driving force for the formation of the non-classical ion may be mainly due to the relief of strain in going to the ion. If, indeed, the bicyclo[2.2.2]octyl system does not form a non-classical ion, then one would expect the formation of normal products in the peracid oxidation of I and in the hydrolysis of III, which has been found to be the case.

Experimental[16]

Bicyclo[2.2.2]octene-2 (I).—Cyclohexadiene-1,3[17] (100 g., 2 moles) and a few crystals of hydroquinone were placed in a glass-lined high pressure bomb (one-liter capacity) and ethylene introduced under 1200 lb. of pressure. The bomb was shaken and heated to 250° for 24 hours. Upon completion of reaction 750 lb. of ethylene had been absorbed and the bomb contents were extracted with pentane. The solvent was removed by distillation through a 12″ column and the residue distilled to yield 120 g. (1.1 moles, 56%) of product, b.p. 128–134°, m.p. 111–112°; literature[6] reports m.p. 113–114°. Yields in several runs ranged from 34–56%.

Bicyclo[2.2.2]octane.—To a solution of 1 g. of bicyclo-[2.2.2]octene-2 dissolved in 20 cc. of methanol was added 100 mg. of 10% palladium-on-charcoal. The mixture was shaken for two hours under 40 lb. of hydrogen pressure in a Parr apparatus. After removal of the catalyst, 100 cc. of water was added to the alcoholic solution and extracted once with 50 cc. of pentane. The pentane was dried over anhydrous magnesium sulfate and distilled through an efficient column. The residue was sublimed to yield 0.9 g. (0.008 mole, 87%) of product, m.p. 168–171°.

***trans*-Bicyclo[2.2.2]octane-2,3-diol (V).**—To a solution of 5 g. (0.04 mole) of bicyclo[2.2.2]octene-2 dissolved in 20 cc. of formic acid and 30 cc. of ether was added, with stirring, 7.5 g. of 30% hydrogen peroxide. After the initial exothermic reaction subsided, the reaction mixture was refluxed for four hours. The solution was evaporated to dryness *in vacuo* and the residue saponified with alcoholic potassium hydroxide. The alcoholic solution was diluted with water and extracted with ether. The ether extract was dried, the solvent stripped and the residue sublimed to yield 4.5 g. (0.032 mole, 80%) of diol. After one recrystallization from acetonitrile it gave m.p. 261–262°. The product gave a positive periodic acid test.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 66.97; H, 9.63.

The phenylurethan derivative gave m.p. 223–223.7° from acetonitrile. *Anal.* Calcd. for $C_{22}H_{24}N_2O_4$: C, 69.45; H, 6.36; N, 7.36. Found: C, 69.22; H, 6.45; N, 7.51.

The oxidation of the glycol with fuming nitric acid[18] yielded *cis*-1,4-cyclohexanedicarboxylic acid, m.p. and mixed m.p. 168–169°.

2,3-Epoxybicyclo[2.2.2]octane (III). With Monoperthalic Acid.—To a solution of 10.8 g. (0.1 mole) of bicyclo-[2.2.2]octene-2 in 100 cc. of dry ether, kept at −10°, was added 0.2 mole of monoperphthalic acid. The solution was kept at ice-box temperature for three weeks. The solution was washed successively with aqueous sodium bisulfite, sodium hydroxide and finally with water. After drying over anhydrous sodium sulfate, the solvent was removed *in vacuo*. The residue (12 g.) was recrystallized once from a water-methanol mixture and finally sublimed to yield 9 g. (75%) of product, m.p. 190–190.3°.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.46; H, 9.61.

With Peracetic Acid.—To a solution of 5 g. (0.045 mole) of bicyclo[2.2.2]octene-2 dissolved in 50 cc. of chloroform was added 17 cc. of 40% peracetic acid[19] to which 0.6 g. of anhydrous sodium acetate was added. The temperature was not allowed to rise above 20°. The chloroform layer was separated, washed with dilute potassium hydroxide, water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue sublimed to yield 2.5 g. (41%) of product, m.p. 189–190°.

Hydrolysis of 2,3-Epoxybicyclo[2.2.2]octane.—A solution of 1 g. (0.008 mole) of the oxide dissolved in 6 cc. of formic acid was refluxed for one hour. The formic acid was removed *in vacuo* and the residual oil was shaken overnight with 18 cc. of 10% sodium hydroxide. The solution was extracted with ether and the ether extract was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue sublimed to yield 0.95 g. (86%) of the *trans*-diol, m.p. 255–256°. Mixed m.p. with authentic sample gave no depression; the phenylurethan derivative, m.p. and mixed m.p. 223–224°.

***cis*-Bicyclo[2.2.2]octane-2,3-diol (II). Potassium Permanganate Method.**—To a solution of 10 g. (0.1 mole) of bicyclo[2.2.2]octene-2 dissolved in 100 cc. of acetone was added water until solution became turbid. Potassium permanganate (15 g.) was added slowly, with stirring, and the temperature was maintained between 0–10° by means of a salt-ice bath. The manganese dioxide was filtered and the filtrate treated with sodium bisulfite. The solution was then steam distilled to remove acetone and unreacted olefin. The residual aqueous solution was heavily salted and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and stripped *in vacuo*. The residue was recrystallized from acetonitrile to yield 2.8 g. (20%) of product, m.p. 254–255°.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.51; H, 10.01.

The phenylurethan derivative gave m.p. 247.8–248° from acetonitrile. *Anal.* Calcd. for $C_{22}H_{24}N_2O_4$: N, 7.4. Found: N, 7.8.

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[12] L. W. Trevoy and W. G. Brown, This Journal, **71**, 1675 (1949).

[13] In connection with this point, it is interesting to note that the *exo* alcohol which was obtained by Winstein and Trifan, ref. 10, by the solvolysis of bicyclo[2.2.1]heptyl-2-*p*-bromobenzenesulfonate can be obtained in 80% yield by hydrolysis of bicyclo[2.2.1]heptene-2 with 80% sulfuric acid. This indicates that both reactions go through a common intermediate.

[14] H. M. Walborsky, *Experientia*, **IX**, 209 (1953).

[15] K. Alder and G. Stein, *Ber.*, **67**, 613 (1934); G. Becker and W. H. Roth, *ibid.*, **67**, 627 (1934); K. Alder and H. F. Rickert, *Ann.*, **524**, 150 (1936); G. B. Kistiakowsky, *et al.*, This Journal, **57**, 65 (1935); **58**, 137, 146 (1936).

[16] All melting points and boiling points are uncorrected. Analyses were performed by Elek Micro-analytical Laboratories, Los Angeles, Calif. All melting points were taken in sealed capillaries.

[17] K. Ziegler, *et al.*, *Ann.*, **551**, 110 (1942).

[18] O. Diels and K. Alder, *ibid.*, **475**, 137 (1929).

[19] A sample was kindly furnished by Becco Corp., Buffalo, N. Y.

With Osmium Tetroxide.—To a solution of 0.27 g. (0.0025 mole) of bicyclo[2.2.2]octene dissolved in 25 cc. of anhydrous ether and cooled to 0° was added a solution of 0.6 g. of osmium tetroxide and 1 cc. of pyridine dissolved in 25 cc. of anhydrous ether. The precipitated osmic ester was filtered, washed with dry ether and finally dissolved in 25 cc. of methylene chloride. The solution was stirred with 5 g. of mannitol, 0.6 g. of potassium hydroxide and 45 cc. of water for 14 hours. The aqueous layer was separated, saturated with sodium chloride and extracted with chloroform. The extract was washed with ammonium chloride, dried over anhydrous sodium sulfate and the chloroform removed *in vacuo*. The residue was crystallized from acetonitrile to yield 110 mg. (34%) of glycol, m.p. 254–255°.

The oxidation of the *cis*-glycol was performed in the same manner as described for the *trans*-glycol. *cis*-1,4-Cyclohexanedicarboxylic acid (0.6 g., 70%) was obtained, m.p. and mixed m.p. 168–169°.

Bicyclo[2.2.2]octanol-2 (IV).—To a solution of 1 g. of lithium aluminum hydride in 30 cc. of anhydrous ether was added with stirring 2.8 g. (0.022 mole) of 2,3-epoxybicyclo-[2.2.2]octane. The reaction mixture was stirred at room temperature for two days and then decomposed by pouring onto an ice–sulfuric acid mixture. The ether extract was washed with water, dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was sublimed to yield 2.8 g. (0.02 mole, quant.) of alcohol, m.p. 210–212° (S.T.).[6] The phenylurethan derivative gave m.p. 138–139°[6] and the *p*-bromobenzenesulfonate ester gave m.p. 79.6–80.4.[14]

Oxidation of the alcohol with chromic acid yielded the ketone, m.p. 172–173°.

The 2,4-dinitrophenylhydrazone derivative gave m.p. 166–167°.

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.31; H, 5.30; N, 18.52.

***exo*-2,3-Epoxybicyclo[2.2.1]heptane (VII).**—To a solution of 47 g. (0.5 mole) of VI[20] in 30 cc. of chloroform was added 125 cc. of 40% peracetic acid and 25 g. of sodium acetate. During the addition of the peracetic acid, the temperature was not allowed to rise above zero degrees, and this temperature was maintained for one hour after the addition had been completed. The reaction mixture was neutralized with 40% sodium hydroxide. The chloroform layer was separated, dried over anhydrous sodium sulfate and the solvent distilled. The residual oil was distilled to yield 38.6 g. (70%) of the epoxide, b.p. 155–158°, m.p. 125–127°.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.41; H, 9.26.

2,7-Dihydroxybicyclo[2.2.1]heptane (VIII). (A) By Hydrolysis of VII.—A solution of 2 g. (0.018 mole) of the oxide dissolved in 10 cc. of 88% formic acid was refluxed for one hour. The formic acid was removed *in vacuo* and the residual oil was shaken overnight with 25 cc. of 10% sodium hydroxide. The solution was extracted with ether and the ether extract was dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* yielded 1.6 g. (67%) of the diol, m.p. 179–181°. The diol gave a negative periodic acid test.

Hydrolysis of the epoxide with dilute sulfuric acid gave a 40% yield of the same diol.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.62; H, 9.52.

The phenylurethan derivative gave a melting point 222–222.5° from acetonitrile. *Anal.* Calcd. for $C_{21}H_{22}N_2O_4$: C, 68.83; H, 6.05. Found: C, 69.26; H, 6.33.

(B) **Performic Acid Oxidation of VI.**—To a solution of 10 g. (0.1 mole) of VI dissolved in 100 cc. of ether and 33 cc. of formic acid was added, with stirring, 20 cc. of 30% hydrogen peroxide. After the initial exothermic reaction subsided, the reaction mixture was stirred overnight. The solution was concentrated *in vacuo* and the residue saponified with alcoholic sodium hydroxide. The solution was diluted with water and extracted with ether. The ether extract was dried, solvent stripped, and the residue recrystallized from ether–petroleum ether to yield 10 g. (77%) of diol, m.p. 179–181°.

Peracetic acid oxidation of VI gave a 20% yield of the diol.

Bicyclo[2.2.1]heptyl-2,7-*p*-nitrobenzylidine Acetal.—To a solution of 7.8 g. (0.051 mole) of *p*-nitrobenzaldehyde dissolved in 80 cc. of dry benzene was added 7 g. (0.055 mole) of crude VIII and a catalytic amount of *p*-toluenesulfonic acid. The solution was distilled until the volume was reduced to 30 cc. and the remaining solvent was stripped *in vacuo*. The solid residue was crystallized from petroleum ether (30–60°) to yield 11.2 g. (84.5%) of the acetal, m.p. 96.8–97.4°.

Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.79; N, 5.36. Found: C, 64.30; H, 5.84; N, 5.40.

The acetal was hydrolyzed by adding 4 g. of the acetal to a solution of 4 g. of 2,4-dinitrophenylhydrazine in 15 cc. of concd. sulfuric acid, 30 cc. of water and 30 cc. of ethanol. The mixture was warmed on the steam-bath for five minutes. The solid 2,4-dinitrophenylhydrazone was filtered and the filtrate was neutralized with solid potassium carbonate. The solution was extracted with ether. The ether extract was dried and evaporated to yield 1.2 g. (63%) of VIII, m.p. and mixed m.p. of the phenylurethan derivative 221–222°.

***exo*-Bicyclo[2.2.1]-heptanol-2 (X).**—To a solution of 2.3 g. of lithium aluminum hydride in 100 cc. of N-ethylmorpholine was added, with stirring, 5.5 g. (0.05 mole) of VII dissolved in 25 cc. of N-ethylmorpholine. The reaction mixture was stirred and heated (95°) for 15 hours. The excess lithium aluminum hydride was decomposed with water and the mixture was steam distilled. The distillate was extracted with ether. The ether extract was washed with dilute hydrochloric acid, water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was sublimed to yield 4.3 g. (77%) of X, m.p. 126–127°.[10] The *p*-bromobenzenesulfonate ester derivative gave m.p. 54.5–57°.[10] The phenylurethan derivative gave a m.p. 146–146.8°.[21]

With Sulfuric Acid on VI.—To a solution of 12 cc. of concentrated sulfuric acid and 6 cc. of water was added 6 g. (0.06 mole) of VI. The mixture was shaken, with periodical cooling, until homogeneous. The solution was diluted with water and extracted with ether. The ether extract was dried and evaporated *in vacuo*. The solid residue was crystallized from petroleum ether (30–60°) to yield 5.6 g. (80%) of *exo*-alcohol, m.p. 125–126°; the phenylurethan derivative m.p. and mixed m.p. 145–146°.

Tallahassee, Florida

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(20) L. M. Joshel and L. W. Butz, This Journal, **63**, 3350 (1941).

(21) K. Alder, *Ber.*, **71**, 2451, 2458 (1938); lit. m.p. 145–146°.