

and dried solution there was obtained 210 mg. (79%) of a solid, m.p. 154–155°, which had m.p. 155–156° when recrystallized from 95% ethanol. This product was identical with an authentic specimen of diphenylmaleic anhydride, prepared from phenylacetonitrile.³⁸ Identity was established by comparison of infrared spectra and by m.p. of the mixture of substances.

Dehydrochlorination of α,α' -Diphenylsuccinyl Chloride.—To a deoxygenated solution of 6 g. (1.76 mmoles) of diphenylsuccinyl chloride in 130 ml. of dry benzene, there was quickly added, under a nitrogen atmosphere, 7.91 g. (7.82 mmoles) of triethylamine. The mixture rapidly colored and was brilliant crimson in 1 hour. The infrared spectra of samples of the supernatant benzene solution taken after 3 and 20 hr. were identical and showed no band at 4.8 μ but maxima at 5.72, 5.85 and 6.18 μ . The reaction mixture was filtered and the benzene solution filtrate washed suc-

cessively with three 50-ml. portions of 1.2 *N* hydrochloric acid, three 100-ml. portions of water, 10% sodium carbonate solution, water and finally dried.

Evaporation of the benzene solution left a gummy oil residue from which, after extraction with 95% ethanol, 100 mg. of a bright yellow solid was obtained, m.p. >360°. After three recrystallizations from chloroform this solid had m.p. 394–396° and $\lambda_{\text{max}}^{\text{KBr}}$ 5.65 μ .

Anal. Found for solid of m.p. 394–396°: C, 80.79; H, 4.21; mol. wt., 531 (isothermal dist. from CHCl_3).

From the ethanol extract mentioned above several fractions, ca. 1.1 g. total weight, of m.p.'s less than 100° were obtained. None was examined further. Another yellow solid product, ca. 0.5 g. and of m.p. below 100°, was isolated by aqueous washing of the precipitated triethylamine hydrochloride and in part by gradual precipitation from the acid wash of the original benzene solution.

(38) C. L. Reimer, *Ber.*, **131**, 742 (1880).

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Ionic Reactions in Bicyclic Systems. I. The Preparation and Assignment of Configuration of the Isomeric Bicyclo[3.2.1]oct-3-en-2-ols and Bicyclo[3.2.1]octan-2-ols

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Deamination of *endo*-5-aminobicyclo[2.2.2]oct-2-ene (I) and acetolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (IV) give derivatives of *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa). *endo*-(*equatorial*)-Bicyclo[3.2.1]oct-3-en-2-ol (IIb) and the isomeric bicyclo[3.2.1]octan-2-ols (VI) have been prepared and their configurations established.

This paper describes the synthesis, properties and configurational assignments of the isomeric bicyclo[3.2.1]oct-3-en-2-ols (II) and the isomeric bicyclo[3.2.1]octan-2-ols (VI). These compounds were of interest in a study of carbonium ion (solvolytic) reactions in [2.2.2]- and [3.2.1]bicyclic systems.

Several years ago the conversion of *endo*-5-aminobicyclo[2.2.2]oct-2-ene (I) to bicyclo[3.2.1]oct-3-en-2-ol (II) by nitrous acid deamination was reported by Wildman and Saunders.² The structure of the deamination product was determined by oxidation to bicyclo[3.2.1]oct-3-en-2-one (III) and reduction to a bicyclo[3.2.1]octan-2-ol (VI).² However, the configuration of the product was not established. In the present work it was found that II produced by deamination of I has the *exo* or axial configuration (IIa). Solvolysis of the *endo*-*p*-toluenesulfonate (IV) also gives derivatives of *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa). Because of the availability of *endo*-bicyclo[2.2.2]oct-5-en-2-ol (V) and thus of the corresponding *p*-toluenesulfonate IV the latter transformation represents a convenient stereoselective synthesis of IIa. As indicated by the structural illustrations, IIa can be converted to its epimer IIb by oxidation to the ketone III and subsequent reduction of the carbonyl group. The unsaturated [3.2.1]bicyclic alcohols II can be converted to their saturated analogs VI by reduction of the double bond.

The Synthesis of the Isomeric Bicyclo[3.2.1]oct-3-en-2-ols (II).—*endo*-5-Aminobicyclo[2.2.2]oct-2-ene (I) was prepared from *endo*-5-carboxybi-

cyclo[2.2.2]oct-2-ene hydrazide by the Curtius reaction. The latter was prepared from ethyl *endo*-bicyclo[2.2.2]oct-2-en-5-carboxylate obtained from the reaction of cyclohexadiene with ethyl acrylate.³ A similar synthesis of I has been reported recently.⁴

The *endo*-amine I was converted to *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa) in two ways: aqueous nitrous acid deamination² and nitrous acid deamination in acetic acid followed by saponification of the resulting acetate. The products obtained by the two routes were indistinguishable. Physical properties of the deamination product IIa (including the infrared spectrum) were unchanged by chromatography (Florisil) or recrystallization of the *p*-nitrobenzoate derivative to a constant melting point. However, as will be shown later, there is evidence that this product is not completely homogeneous.

The axial [3.2.1]bicyclic alcohol IIa was also prepared from *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (IV) which in turn was prepared from the corresponding alcohol V. The latter was obtained from its acetate which was prepared from cyclohexadiene and vinyl acetate.⁵ The *endo*-*p*-toluenesulfonate IV derived from V was contaminated with about 10% of a more reactive isomer which was removed readily by recrystallization from ethanol. *endo*-Bicyclo[2.2.2]oct-5-en-2-ol (V) purified by recrystallization of its *p*-nitrobenzoate derivative apparently was homogeneous and gave pure *p*-toluenesulfonate IV (identical with material from which the reactive isomer had been removed).

The infrared spectrum of a 0.1 *M* solution of the

(1) (a) Socony-Mobil Co. Fellow, 1956–1957. (b) Wisconsin Alumni Research Foundation Fellow 1956–1958; National Science Foundation Fellow 1958–1960.

(2) W. C. Wildman and D. R. Saunders, *J. Am. Chem. Soc.*, **76**, 946 (1954).

(3) R. Seka and O. Trampusch, *Ber.*, **75**, 1379 (1942).

(4) C. A. Grob, K. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(5) K. Alder and H. Rickert, *Ann.*, **543**, 1 (1940).

pure *endo*-alcohol V in carbon disulfide contained three bands in the hydroxyl region: 3617 ± 2 (non-hydrogen bonded hydroxyl), 3593 ± 1 (intramolecular hydrogen bond with double bond)⁶ and 3490 ± 50 cm^{-1} (intermolecular hydrogen bond).⁷ Tenfold dilution of the solution did not affect the extinction coefficient of the 3593 cm^{-1} band but resulted in the disappearance of the 3490 ± 50 cm^{-1} band. The presence of an intramolecular hydrogen bond, which must involve the hydroxyl group and the double bond,⁶ establishes the configuration of the alcohol V and thus of the corresponding *p*-toluenesulfonate IV.

Acetolysis of pure *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (IV) for ten half-lives (the kinetic results will be presented in another paper⁸) followed by saponification of the resulting acetate gave IIa in good yield. The product obtained in this way was slightly different from that obtained by deamination of I. For example, IIa derived from the tosylate melted 10 degrees lower than the deamination product. Moreover the *p*-nitrobenzoate melted about 7 degrees higher than that of the deamination product. The infrared spectra of the two *p*-nitrobenzoates were indistinguishable. However, the spectra of the alcohols were slightly different. That of the deamination product had several very weak bands which were absent in the spectrum of the alcohol derived from the pure *p*-toluenesulfonate.

It appears that the *exo*-(*axial*)-alcohol IIa prepared from pure *p*-toluenesulfonate IV is homogeneous. Gas chromatography gave a single sharp peak and the physical properties (including the infrared spectrum) were not changed by conversion to the *p*-nitrobenzoate derivative followed by saponification after several recrystallizations. The spectrum showed that this product was not contaminated with its epimer IIb. Hydrogenation of IIa prepared in this way gave pure *exo*-(*axial*)-bicyclo[3.2.1]octan-2-ol (VIa).

The nature of the impurity in IIa prepared by deamination of I remains obscure. The complete absence in the infrared spectrum of bands characteristic of *endo*-bicyclo[2.2.2]oct-5-en-2-ol (V) or *endo*-(*equatorial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIb) indicated these compounds were not present. It is perhaps significant in this connection that IIa prepared by solvolysis of *p*-toluenesulfonate IV from which the reactive contaminant had not been removed was essentially the same as that prepared by deamination. This suggests that the impurity in IIa, derived from impure *p*-toluenesulfonate IV and *endo*-amine I, results from the presence of *exo* isomer in the reactant. In other words, according to this idea, the two Diels-Alder reactions (preparation of I and V) give adducts containing the *exo* isomer which is not removed by the usual purification procedures. Presumably *endo*-amine I and *endo*-*p*-toluenesulfonate IV give pure IIa, and *exo*-amine and *exo*-*p*-toluenesulfonate give products isomeric with IIa which are extremely difficult to separate.

(6) P. v. R. Schleyer, D. S. Trifan and R. Baeska, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

(7) We are indebted to Professor R. West for the high resolution spectra and discussions concerning them.

(8) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961).

from IIa by conventional purification methods. In support of this view it is noteworthy that the Diels-Alder reaction of cyclohexadiene and acrylonitrile is not stereospecific (some of the *exo* adduct is formed)⁹ and that *exo*-bicyclo[2.2.2]oct-5-en-2-yl-amine and *p*-toluenesulfonate (by analogy with the *exo*-dehydronorbornyl analogs)¹⁰ would not be expected to give IIa.¹¹

Oxidation of pure *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa) with manganese dioxide¹² at room temperature gave bicyclo[3.2.1]oct-3-en-2-one (III).² The ultraviolet spectrum of the unsaturated ketone III was normal, *i.e.*, $\lambda_{\text{max}}^{\text{EtOH}}$ 227 (log ϵ 3.98). However the infrared spectrum (liquid film and solution) had a split carbonyl peak with strong absorption at 6.00μ and a medium intensity shoulder at 5.90μ . It appears that this doublet is not caused by contamination, since gas chromatography with several packings gave only one peak.

The infrared spectrum of the unsaturated ketone III, prepared from pure IIa, was slightly different from that of ketone derived from IIa prepared by deamination. The latter spectrum had several weak bands not present in that of pure ketone. This is additional evidence that IIa prepared by deamination was contaminated with structural isomers.

Reduction of the unsaturated ketone III with lithium aluminum hydride gave a mixture of the isomeric bicyclo[3.2.1]oct-3-en-2-ols (II) which consisted mostly of the equatorial isomer IIb. Contamination by the axial isomer IIa was indicated by the infrared spectrum and gas chromatography. Quantitative determination of the composition of the product was precluded because of broad overlapping peaks; however, it appeared that the product contained 10–15% of the axial isomer IIa. Reoxidation of this product (IIb) gave pure III which demonstrates that it is epimeric with IIa. Attempts to prepare a completely homogeneous sample of IIb were unsuccessful.

Reduction of III with sodium borohydride resulted in considerable (perhaps complete) reduction of the carbon-carbon double bond as well as the carbonyl group; *i.e.*, a mixture of the isomeric saturated [3.2.1]bicyclic alcohols (VI) was obtained. This result, although unusual, is not without precedent.¹⁴

The Synthesis of the Isomeric Bicyclo[3.2.1]octan-2-ols (VI).—Hydrogenation of the bicyclo[3.2.1]oct-3-en-2-ols (IIa and IIb) over 30% palladium-on-charcoal at atmospheric pressure (the procedure used earlier for hydrogenation of the deamination product)² resulted in absorption of only 50–60% of an equivalent amount of hydrogen. Each isomer (IIa and IIb) was converted in part to the corresponding saturated alcohol (VIa and VIb) and in part to bicyclo[3.2.1]octan-2-one (VII).

(9) K. Alder, K. Heimbach and R. Reubke, *Ber.*, **91**, 1516 (1958).

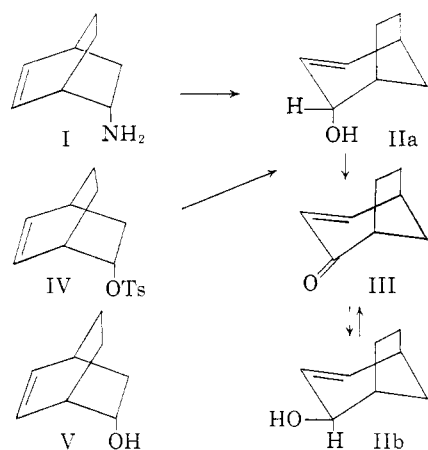
(10) J. D. Roberts, C. C. Lee and W. H. Sanders, Jr., *J. Am. Chem. Soc.*, **77**, 3034 (1955).

(11) There is evidence that participation by a double bond to form tricyclic compounds can occur in homoallylic [2.2.2]bicyclic systems¹² as well as in [2.2.1]bicyclic systems.¹⁰

(12) K. Alder, P. Brockhagen, C. Kaiser and W. Roth, *Ann.*, **593**, 1 (1955).

(13) R. M. Evans, *Quart. Revs.*, **13**, 61 (1959).

(14) F. Sondheimer and Y. Klubansky, *Tetrahedron*, **5**, 15 (1959).

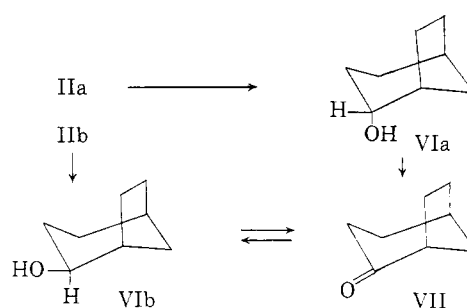


Evidently the conversion of the unsaturated alcohols II to the saturated ketone VII involves an intramolecular transfer of hydrogen on the catalyst surface. This rather unusual transformation is similar to that reported by Cope and co-workers¹⁵ who observed that hydrogenation of 5-cyclodecenol over palladium-on-charcoal gives cyclodecanone.

In contrast to the results with palladium-on-carbon, hydrogenation of IIa over palladium-on-barium sulfate resulted in the uptake of an equivalent amount of hydrogen. The reduction product contained only a trace of ketone and was purified by conversion to the *p*-nitrobenzoate which was recrystallized to constant melting point (only one recrystallization required) and saponified. From all indications the axial saturated alcohol VIa prepared in this way is homogeneous. Both the infrared spectrum and gas chromatography showed that it did not contain any of the epimer VIB. The physical properties are in excellent agreement with those recently reported for this compound.¹⁶

Under these conditions the equatorial unsaturated alcohol IIb absorbed only 50% of the hydrogen required for conversion to the saturated alcohol VI and gave a mixture of VI and ketone VII. The alcohol was separated from the ketone by conversion to the *p*-nitrobenzoate which was recrystallized only once (to avoid fractionation of the isomeric alcohols) and saponified. Gas chromatography showed that the resulting product was a pure binary mixture consisting of 70% of the equatorial alcohol VIB and 30% of the axial alcohol VIa. This product would be expected to contain much more of the axial isomer than the sample of IIb from which it was prepared because the unsaturated axial alcohol IIa is reduced quantitatively to VIa whereas the unsaturated equatorial alcohol gives at most a 50% yield of VIB (the rest is converted to ketone). Oxidation of the pure axial alcohol VIa and of the mixture of equatorial VIB and axial alcohol (derived from IIb) gave the same ketone, bicyclo[3.2.1]octan-2-one (VII).

Failure to obtain homogeneous *endo*-(equatorial)-bicyclo[3.2.1]octan-2-ol (VIB) by the above route led to investigation of its preparation from the bicyclic ketone VII by the method recently reported



by Walborsky and co-workers,¹⁶ *i.e.*, reduction of the ketone VII with lithium in ammonia. In the present work the ketone VII was prepared by chromic acid oxidation of pure axial alcohol VIa which was prepared by reduction of pure IIa. From all indications (infrared spectra and properties of derivatives) the ketone VII was homogeneous. The reduction product was purified by conversion to the *p*-nitrobenzoate derivative¹⁶ which was recrystallized to constant melting point and saponified. That the alcohol obtained in this way was homogeneous was shown by (a) gas chromatography, (b) the infrared spectrum and (c) the clean first-order solvolytic behavior of the *p*-toluenesulfonate derivative.⁸

Configurational Assignments to the Isomeric Unsaturated (II) and Saturated (VI) [3.2.1]Bicyclic Alcohols.—The structure of bicyclo[3.2.1]octan-2-one (VII) has been established unequivocally.¹⁷ Thus, conversion of the unsaturated (II) and saturated (VI) pairs of alcohols to this ketone shows they are 2-substituted [3.2.1]bicyclic alcohols. The position of the double bond in II is established by oxidation (without rearrangement) to an α,β -unsaturated ketone ([3.2.1]bicyclic α,β -unsaturated ketones other than III are not possible).

The configurational assignments for the unsaturated [3.2.1]alcohols (II) are based on several observations. It is significant in this connection that solvolysis of *endo*-bicyclo[2.2.2]oct-2-en-5-yl *p*-toluenesulfonate (IV) and deamination of the corresponding amine I are stereospecific (*i.e.*, only one isomer of the bicyclo[3.2.1]oct-3-en-2-yl derivative is formed). This product would be expected to have the axial configuration IIa because stereospecific solvolytic reactions involving Wagner-Meerwein rearrangements usually result in inversion of the carbon atoms from which and to which migration occurs¹⁸ (*cf.* the stereospecific conversions of bicyclo[2.2.1]hept-7-yl *p*-bromobenzenesulfonate to *exo*-bicyclo[3.2.0]hept-2-yl acetate¹⁹ and *exo-cis*-bicyclo[3.3.0]oct-2-yl *p*-bromobenzenesulfonate to *exo*-bicyclo[3.2.1]octan-8-ol²⁰).

(17) K. Alder and E. Windemuth, *Ber.*, **71**, 2404 (1938).

(18) P. D. Bartlett, Chapt. I in H. Gilman's "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953.

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

(20) A. C. Cope, J. M. Grisar and P. E. Peterson, *ibid.*, **82**, 4299 (1960).

(21) The configurations assigned on this basis alone are not unequivocal. Exceptions to the rule of inversion at the migration origin have been observed, *e.g.*, see S. Weinstein and N. J. Holness, *ibid.*, **77**, 3054 (1955). Moreover, in the present system stereospecific conversion of IV to the equatorial [3.2.1]bicyclic product would result if solvent attacked C₅ instead of C₁. In this case substitution (of solvent for the migrating ethylene bridge) would resemble an S_N2' process

(15) A. C. Cope, R. J. Cotter and G. G. Roller, *J. Am. Chem. Soc.*, **77**, 3598 (1955).

(16) A. A. Youssef, M. E. Baum and H. M. Walborsky, *ibid.*, **81**, 4709 (1959).

Among other things the (a) composition of the hydride reduction product of the unsaturated ketone III, (b) relationship with the saturated analogs, and (c) relative gas chromatography retention times are consistent with the present assignments. In a system of this type, reduction of the ketone III with lithium aluminum hydride would be expected to result in preponderant formation of the *endo* or equatorial isomer IIb^{22a}; cf. conversion of norcamphor to *endo*-norborneol.^{22b}

Because the unsaturated [3.2.1]alcohols IIa and IIb can be converted to the corresponding saturated isomers VIa and VIb, structural assignments in one series will apply to the other. The present assignments are consistent with those recently proposed¹⁶ for the saturated bicyclic alcohols VI on the basis of (a) rates of saponification of the isomeric acetates and (b) equilibration studies. As has been pointed out,¹⁶ it is significant that the infrared spectra of the saturated alcohols are consistent with this assignment. The relative retention times in gas chromatography are also in agreement with this assignment. The equatorial isomers IIb and VIb have greater retention times on a polar column than do the corresponding axial isomers.²³

endo-(equatorial)-Bicyclo[3.2.1]oct-3-en-2-ol (IIb) is oxidized with chromic acid about six times faster than its epimer IIa in 90% aqueous acetic acid at 20.^{24a} It is interesting to note that this sequence is consistent with the idea^{24b,25} that equatorial allylic secondary alcohols, in contrast to their saturated analogs, may generally be oxidized more rapidly than their epimers. These relative reactivities would also be predicted by analogy with the relative rates of oxidation of the isomeric norborneols. In the latter system the *endo* isomer (which has the most hindered hydroxyl group) is oxidized about three times faster than the *exo* isomer at 30°.²⁶

Acknowledgment.—We are indebted to Professors J. Berson and A. Eschenmoser for helpful discussions.

Experimental²⁷

endo-5-Aminobicyclo[2.2.2]oct-2-ene (I).—Ethyl bicyclo[2.2.2]oct-2-en-5-carboxylate⁸ was converted to the hydrazide as follows. A solution of 180 g. of the ester and 200 g. of 99–100% hydrazine hydrate in 250 ml. of absolute ethanol was refluxed for 48 hr. The solution was concentrated to near dryness by distillation under reduced pressure. The yield of solid residue, after drying to constant weight under vacuum, was 168 g. (100%), m.p. 97–103°. This material was sufficiently pure to be used in subsequent steps. An analytical sample melted at 111.0–111.5° (aqueous ethanol).

and solvent would be expected to attack from the *exo* side (*cis* to the migrating group at C₁).

(22) (a) W. Klyne, "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1954, p. 54; (b) S. Beckman and R. Mezger, *Ber.*, **89**, 2738 (1959).

(23) For additional evidence bearing on these structural assignments see ref. 8 and H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961).

(24) (a) We are indebted to Professor Albert Eschenmoser for obtaining these rates. For a description of the method see J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **38**, 1529 (1955); (b) private communication from Professor Eschenmoser, 1958.

(25) G. Stork, in R. H. F. Manske's "The Alkaloids," Vol. VI, Academic Press, Inc., New York, N. Y., 1960, p. 223.

(26) H. Kwart and F. S. Francis, *J. Am. Chem. Soc.*, **81**, 2116 (1959).

(27) All melting points are corrected; sealed capillaries were used for the bicyclic alcohols.

Anal. Calcd. for C₈H₁₄N₂O: C, 65.03; H, 8.49. Found: C, 65.06; H, 8.44.

The amine I was prepared from the acid hydrazide: A solution of 75 g. (0.45 mole) of the hydrazide, m.p. 97–103°, in 680 ml. of water and 42 ml. of concentrated hydrochloric acid was covered with 500 ml. of ether and cooled to 0° in an ice-salt-bath. A solution of 34.5 g. (0.50 mole) of sodium nitrite in 75 ml. of water was added during a period of 7 min. to the stirred, cooled (0–9°) reaction mixture. The yellow ether layer, which contained the acid azide, was separated and the aqueous layer was extracted three times with 100-ml. portions of ether. The ether extract was washed with cold saturated aqueous sodium carbonate, dried (calcium chloride) and diluted with 200 ml. of absolute ethanol. The ether was removed by distillation from Drierite through a short Vigreux column, and the remaining solution (protected from moisture) was refluxed for 2.5 hr. After removal of the ethanol by distillation, the crude, oily urethan (88 g.) was converted to I by hydrolysis with methanolic potassium hydroxide.²⁸ The yield of I in the form of its hydrochloride after recrystallization from aqueous methanol was 31.8 g. (44%), m.p. 306–307° dec. (lit. m.p. 305–306° dec.,² 303–305°⁴).

The phenylthiourea derivative²⁹ of the amine melted at 171.5–172.0° (lit.² m.p. 168.5°).

When the reaction was carried out on a 1-mole scale, the yield dropped to 25% (presumably because the temperature could not be controlled well enough during the addition of sodium nitrite).

endo-Bicyclo[2.2.2]oct-5-en-2-ol (V).—The *endo*-alcohol V was prepared by the following modification of the method of Alder and Rickert.⁵ A mixture of 80 g. (1 mole) of 1,3-cyclohexadiene and 172 g. (2 moles) of freshly distilled vinyl acetate together with a few crystals of hydroquinone was sealed in a glass tube and heated in a metal bomb for 4 days at 180–190°. The unreacted low boiling material was removed under vacuum after which the main fraction (72 g.), b.p. 85–87° (8 mm.), was collected. This mixture of acetate and dicyclohexadiene was reduced with 10 g. of lithium aluminum hydride.³⁰ The product was purified by recrystallization from the minimum amount of 60–68° petroleum ether. The yield of alcohol, m.p. 157.5–163.5°, was 14.9 g. (23% based on cyclohexadiene). Sublimation (90°, aspirator vacuum) raised the melting point to 167.5–169.0° (lit.³¹ m.p. 166–167°).

The *p*-nitrobenzoate of V, prepared by a previously described procedure,³² melted at 109.8–110.8° after three recrystallizations from methanol followed by three from ethanol (69% yield) (lit.³¹ m.p. 108.5–109.5°). This material apparently is the pure *endo* isomer.

Anal. Calcd. for C₁₅H₁₈NO₄: C, 65.92; H, 5.53. Found: C, 66.20; H, 5.66.

The *p*-nitrobenzoate was saponified by refluxing 6.00 g. (0.022 mole) with 5.3 g. (0.095 mole) of potassium hydroxide in 110 ml. of methanol for 3 hr. After about half of the solvent was removed by distillation, the resulting mixture was diluted with 170 ml. of water and continuously extracted with pentane for 20 hr. Removal of the pentane left 2.26 g. (82%) of V, m.p. 167.0–168.8° (after two sublimations, 90°, aspirator vacuum). The infrared spectrum of this material was indistinguishable from that of material before conversion to the *p*-nitrobenzoate; infrared bands: 9.10, 9.40, 9.70, 9.90, 10.25, 10.75, 11.70, 12.20, 12.80, 14.10 and 14.40 μ (carbon disulfide). The high resolution infrared spectrum (see text) of V was obtained with a Perkin-Elmer model 112 single beam infrared spectrophotometer equipped with a lithium fluoride prism.⁷

Anal. Calcd. for C₈H₁₂O: C, 77.37; H, 9.74. Found: C, 77.23; H, 9.71.

(28) E. R. Buchman, A. O. Reims, T. Skei and M. J. Schlatter, *J. Am. Chem. Soc.*, **64**, 2696 (1942).

(29) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

(30) W. E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **72**, 147 (1950).

(31) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1953).

(32) H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, **76**, 5405 (1954).

The acid phthalate of V (purified *via* the *p*-nitrobenzoate) melted at 167.6–168.0° (ethyl acetate).

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.48; H, 6.07.

endo-Bicyclo[2.2.2]oct-5-en-2-yl *p*-Toluenesulfonate (IV).—To a stirred solution of 2.03 g. (0.016 mole) of crude *endo*-bicyclo[2.2.2]oct-5-en-2-ol (V), m.p. 157.5–163.5°, in 11 ml. of dry pyridine was added 3.42 g. (0.018 mole) of *p*-toluenesulfonyl chloride in one portion. The solution was chilled in an ice-bath prior to and during the addition of the acid chloride. When solution was complete, the reaction mixture was placed in a refrigerator for 48 hr. The excess acid chloride was decomposed by dropwise addition of 1 ml. of water and the resulting solution was poured into cold water. The crystalline product was collected by filtration, washed several times with cold water and dried under vacuum. After three recrystallizations from ether–pentane the yield was 3.87 g. (85%), m.p. 63.8–64.5°.

Anal. Calcd. for $C_{15}H_{16}O_3S$: C, 64.72; H, 6.52. Found: C, 65.01; H, 6.72.

Kinetic studies showed that this material was contaminated with a reactive isomer.⁸ Presumably this impurity was the *exo* isomer. Removal of the *exo* isomer from IV was effected in the following way. The crude solid was dissolved in the minimum amount of absolute ethanol at 50°. After heating the solution at 70° for 5 min. it was chilled in an ice-bath and seeded. The product was collected by filtration, washed several times with cold absolute ethanol and then with cold pentane. The ethanol recrystallization was repeated once and followed by recrystallization from ether–pentane. The yield of recovered pure product was 72%, m.p. 66.3–66.6°. The compound appeared to decompose after storage for several weeks in a refrigerator. Kinetic studies showed that this material was homogeneous.⁸

Anal. Calcd. for $C_{15}H_{16}O_3S$: C, 64.72; H, 6.52; solvolysis equiv., 278.4. Found: C, 65.01; H, 6.56; solvolysis equiv., 279.6 ± 1.6 (average of 9 determinations).⁸

The *p*-toluenesulfonate derived from pure V (purified *via* the *p*-nitrobenzoate) was prepared in the same way and purified by three recrystallizations from ether–pentane. The yield of pure product, m.p. 65.5–66.4°, was 85%. The solvolysis equivalent was 278.4.⁸

exo-(*axial*)-Bicyclo[3.2.1]oct-3-en-2-ol (IIa). A. By Aqueous Deamination of I.—The alcohol IIa was obtained as a yellow wax in 60–65% yield when an aqueous solution of the hydrochloride of *endo*-5-aminobicyclo[2.2.2]oct-2-ene (I) was treated with sodium nitrite according to the method of Wildman and Saunders.² After sublimation (50–55°, 0.5 mm.) the melting point was 102.0–108.0°.

B. By Deamination of I in Acetic Acid.—The method described by Roberts, *et al.*,³³ was used to deaminate I. By this method 22 g. of the hydrochloride of I was converted to 13.2 g. of a colorless liquid, b.p. 91–93° (18 mm.), n_D^{20} 1.4871. The infrared spectrum of this liquid had strong bands at 3.0 and 5.8 μ indicating that it was a mixture of alcohol IIa and the corresponding acetate.

The acetate was converted to *axial*-bicyclo[3.2.1]oct-3-en-2-ol (IIa) by reduction with lithium aluminum hydride.³⁰ Thirteen grams of the liquid mixture described above gave 9.4 g. (56% based on the amine hydrochloride) of IIa, which after sublimation (50–55°, 0.5 mm.) melted at 96–99°. The infrared spectrum of this material was the same as that of material prepared by method A.

The IIa described above (80 mg.) was chromatographed on Florisil. The eluent, 300 ml. of pentane–ether mixtures (0–3% ether), was collected in 25 fractions. The infrared spectra of fractions 3 and 24 were indistinguishable from that of the starting material below 12 μ and only slightly different at higher wave lengths.

The *p*-nitrobenzoate of IIa was prepared by a standard method³² and recrystallized to constant melting point from 90–100° petroleum ether. The melting point did not change after the first recrystallization. A 74% yield of the *p*-nitrobenzoate was obtained, m.p. 78–79° (lit.² m.p. 81–81.5°). The infrared spectra of samples from the first and fourth recrystallizations were identical.

The *p*-nitrobenzoate was saponified by a previously described procedure.³² After purification, 0.87 g. (78%) of IIa, m.p. 90–96° (with prior softening), was obtained from

2.5 g. of *p*-nitrobenzoate. The infrared spectrum of this material was identical with that of the alcohol isolated directly from the reaction mixture.

C. By Acetolysis of IV.—A solution of 25.05 g. (0.090 mole) of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (IV), m.p. 66.3–66.6°, and 4.061 g. (0.0495 mole) of sodium acetate in 450 ml. of anhydrous acetic acid was heated at 30.1°. After 2.5 hr. (25% reaction) 25 ml. of 1.0 *M* sodium acetate in acetic acid was added and the solution shaken several times. This was repeated after an additional 3 hr. and 40 min. (50% reaction). After a total of 72 hr. (*ca.* 11 half-lives for reaction) the reaction mixture was diluted with 1.5 l. of water and continuously extracted with pentane for 24 hr. The pentane extract was washed with dilute aqueous potassium carbonate and dried (magnesium sulfate). The pentane was removed by distillation and replaced with 500 ml. of 1.5 *M* methanolic potassium hydroxide. The resulting solution was refluxed for 1 hr., diluted with 500 ml. of water, and extracted with pentane for 24 hr. Removal of the pentane left 9.54 g. (85% based on starting tosylate) of IIa. The melting point after sublimation (90°, aspirator vacuum) was 85.5–87.0°. Gas chromatography of IIa (ethyl acetate solution) using a 30-inch Tide column (154°, helium flow rate 27 ml./min.) produced one peak (retention time 7 min.). However IIa and its epimer IIb were not resolved under these conditions.

The *p*-nitrobenzoate of IIa prepared by this route was obtained in 92% yield after recrystallization from methanol to a constant melting point (two recrystallizations were necessary) of 86.2–86.6° (lit.² m.p. 81–81.5°).

Anal. Calcd. for $C_{15}H_{16}NO_4$: C, 65.92; H, 5.53. Found: C, 66.14; H, 5.75.

The *p*-nitrobenzoate was saponified by refluxing 7.00 g. (0.0256 mole) with 125 ml. of 1.0 *M* methanolic potassium hydroxide for 1 hr. The solution was diluted with 150 ml. of water and continuously extracted with pentane for 24 hr. Removal of the pentane left 3.09 g. (95% yield) of pure *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa), m.p. 87.2–88.2°. The infrared spectrum of this sample was the same as that of the alcohol obtained by saponification of the acetolysis product.

Anal. Calcd. for $C_{15}H_{16}O$: C, 77.37; H, 9.74. Found: C, 77.76; H, 9.95.

The infrared spectrum of IIa prepared by this method is only slightly different from that prepared by methods A or B. The spectra of the alcohol prepared by the latter two methods contained weak bands at 12.35, 12.60, 13.40, 13.60 and 14.45 μ . These bands were absent in the spectrum of IIa prepared by acetolysis of IV; infrared bands: 9.35, 9.55, 9.80, 10.00, 10.30, 10.60, 10.90, 11.25, 11.40, 11.80, 12.15, 13.10 and 14.25 μ (carbon disulfide).

Acetolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (Va) which had not been purified by ethanol recrystallization (*i.e.*, tosylate still contaminated with the reactive (*exo*) isomer), m.p. 63.6–64.4°, was carried out in the same way (saponification of the acetate was replaced by reduction with lithium aluminum hydride). The yield of IIa, m.p. 81.4–83.5°, after purification by sublimation (135°, aspirator vacuum) was 78%. The infrared spectrum contained weak bands at 12.60 and 13.40 μ which are not present in the spectrum of pure IIa.

The *p*-nitrobenzoate of this material melted at 81.5–82.5° (60–68° petroleum ether).

Bicyclo[3.2.1]oct-3-en-2-one (III).—Oxidation of *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIa), m.p. 85.5–87.0° (prepared by method C), with freshly prepared manganese dioxide³⁴ according to a previously described procedure³⁵ gave III in 60% yield, b.p. 76° (7 mm.), n_D^{20} 1.5123, λ_{max}^{EIOH} 227 μ ($\log \epsilon$ 3.98), lit.² λ_{max}^{EIOH} 227 μ ($\log \epsilon$ 3.9). The infrared spectrum contained a strong carbonyl peak at 6.00 μ with a medium intensity shoulder at 5.90 μ .

Gas chromatography under the following conditions resulted in only one peak: (a) 4-ft. column of 20% glycerol-on-Celite at 115°, (b) 8-ft. Tide column at 150°, and (c) 4-ft. column of 20% 1,2,3-tris-2-(cyanoethoxy)-propane-on-Celite at 155°; infrared bands: 7.20, 7.55, 7.70, 8.00, 8.20, 8.40,

(34) (a) O. Mancera, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.*, 2189 (1953); (b) F. Sondheimer, O. Mancera, M. Urguiza and G. Rosenkranz, *J. Am. Chem. Soc.*, 77, 4145 (1955).

(35) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, 77, 4042 (1955).

(33) J. D. Roberts, C. C. Lee and W. H. Saunders, *J. Am. Chem. Soc.*, 76, 4501 (1954).

8.60, 8.75, 9.05, 9.45, 9.60, 10.60, 10.90, 11.50, 11.90, 12.80, 13.80 and 14.50 μ (liquid film).

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.96; H, 8.15.

The 2,4-dinitrophenylhydrazine (dark orange-red needles) melted at 140.4–141.5° (ethyl acetate-ethanol).

Anal. Calcd. for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67. Found: C, 55.35; H, 4.84.

axial-Bicyclo[3.2.1]oct-3-en-2-ol (IIa) obtained by methods A or B above was oxidized by the same procedure. The infrared spectrum contained all of the bands present in the spectrum of pure III (see above). In addition there were weak bands at 8.95, 9.30, 11.65 and 13.50 μ . These are absent in the spectrum of the pure ketone.

endo-(*equatorial*)-Bicyclo[3.2.1]oct-3-en-2-ol (IIb).—Pure bicyclo[3.2.1]oct-3-en-2-one (III) was reduced with lithium aluminum hydride.³⁶ The yield of alcohol, m.p. 73.8–76.8°, after sublimation (90°, aspirator vacuum) was 92%.

The *p*-nitrobenzoate melted at 78.1–78.8° after four recrystallizations from methanol (67% yield). Further recrystallization did not change the melting point. When mixed with the *p*-nitrobenzoate (m.p. 86.2–86.6°) of the epimer IIa the resulting mixture melted at 78.0–85.0°.

Anal. Calcd. for $C_{18}H_{18}NO_4$: C, 65.92; H, 5.53. Found: C, 66.17; H, 5.70.

The *p*-nitrobenzoate was saponified by the method described above for the saponification of IIa *p*-nitrobenzoate. The yield of *endo*-(*equatorial*)-bicyclo[3.2.1]oct-3-en-2-ol (IIb), m.p. 77.5–80.5°, after two sublimations (90°, aspirator vacuum) was 98%.

Anal. Calcd. for $C_8H_{10}O$: C, 77.37; H, 9.74. Found: C, 77.19; H, 10.03.

The infrared spectrum of this alcohol was identical with that of the alcohol before conversion to the *p*-nitrobenzoate. This material contained about 15% of the *axial* isomer IIa; all of the peaks present in the spectrum of IIa were present although some were at greatly reduced intensity. Gas chromatography with a 4-ft. column of 20% glycerol-on-Celite (112°, helium flow rate 18 ml./min.) produced a broad peak (retention time, 24 min.). A shoulder on this peak at ca. 16 min. indicated the presence of the *axial* isomer IIa.

One-half gram of IIb (purified *via* the *p*-nitrobenzoate) was chromatographed with a column of 20 g. of alumina and eluted with ether in pentane (0–10% ether). The infrared spectra of the first and last fraction (92% of the alcohol was recovered) were identical with that of the alcohol before chromatography; infrared bands: 9.40, 9.50, 9.90, 10.10, 10.90, 11.90, 12.25, 12.60, 13.10, 13.60 and 14.55 μ (carbon disulfide).

endo-(*equatorial*)-Bicyclo[3.2.1]oct-3-en-2-ol (IIb) was oxidized with manganese dioxide by the method described above for the oxidation of IIa. The α,β -unsaturated ketone III was obtained in 50% yield, n_D^{25} 1.5122, $\lambda_{max}^{CHCl_3}$ 227 m μ ($\log \epsilon$ 3.95). The infrared spectra of III prepared from IIb was indistinguishable from that of III derived from IIa.

Sodium Borohydride Reduction of Bicyclo[3.2.1]oct-3-en-2-one (III).—To a stirred, ice-cooled solution of 5.00 g. (0.041 mole) of III in 90 ml. of methanol was added 1.71 g. (0.045 mole) of sodium borohydride during a 10-min. period. After the addition was complete, stirring was continued at room temperature for 2.5 hr. After addition of 20 ml. of water the resulting solution was heated on the steam-bath for 5 min. Further dilution with 140 ml. of water, extraction with pentane and then removal of the solvent, gave 5.062 g. of solid. A small portion was sublimed (90°, aspirator vacuum), m.p. 136.2–145.8°. The infrared spectrum contained only weak bands between 11.0 and 15.0 μ where *equatorial*-(IIb) and *axial*-bicyclo[3.2.1]oct-3-en-2-ol (IIa) absorb strongly. The spectrum and melting point did not correspond to either IIa or IIb or a mixture of them. The infrared spectrum indicated that the product was largely bicyclo[3.2.1]octan-2-ol (VI).

exo-(*axial*)-Bicyclo[3.2.1]octan-2-ol (VIa). **Method A.**—A solution of 2.90 g. (0.023 mole) of *axial*-bicyclo[3.2.1]oct-3-en-2-ol (IIa), m.p. 85.5–87.0°, in 25 ml. of methanol was hydrogenated at 25° and atmospheric pressure over 200 mg. of 30% palladium-on-carbon.³ After 2.5 hr., when about 50% of the calculated amount of hydrogen had been absorbed the reaction stopped. The catalyst was removed and the

methanolic solution was diluted with water and continuously extracted with pentane for 16 hr. The pentane solution was concentrated (distillation) until material began to crystallize. Cooling in Dry Ice yielded 1.49 g. of white solid, m.p. 177.8–181.0°. This material gave a positive (weak) 2,4-dinitrophenylhydrazine test, and its infrared spectrum contained a strong carbonyl peak at 5.85 μ .

The *p*-nitrobenzoate, m.p. 91.1–92.1° (methanol), was prepared from 1.40 g. of the alcohol-ketone mixture. Saponification by the method described for IIa *p*-nitrobenzoate followed by sublimation (90°, aspirator) gave 1.02 g. (73%) of *exo*-(*axial*)-bicyclo[3.2.1]octan-2-ol, m.p. 194.2–195.5°. The infrared spectrum of this material contained no carbonyl peak.

Evaporation of the pentane mother liquors from the hydrogenation experiment yielded 1.02 g. of an oily solid which gave a strong positive 2,4-dinitrophenylhydrazine test. This material was converted to the semicarbazone,²⁹ m.p. 171.2–171.4° (methanol-water). The melting point of this derivative was not depressed when mixed with an authentic sample of the semicarbazone of bicyclo[3.2.1]octan-2-one (VII), m.p. 171.4–171.9°. The infrared spectra of the two semicarbazones were identical.

Method B.—A solution of 3.018 g. (0.0235 mole) of *axial*-bicyclo[3.2.1]oct-3-en-2-ol (IIa), m.p. 85.5–87.0°, in 25 ml. of methanol was hydrogenated at 25° and atmospheric pressure over 200 mg. of 5% palladium-on-barium sulfate. After 2 hr., 98% of an equivalent amount of hydrogen had been absorbed, and the reaction stopped. The product was worked-up as described under method A. The yield of saturated alcohol VIa after sublimation (90°, aspirator) was 3.00 g. (98%), m.p. 190.0–192.0°. The infrared spectrum contained only a small carbonyl peak.

The *p*-nitrobenzoate (75% yield after two recrystallizations from pentane) melted at 94.0–94.6° (lit.¹⁶ m.p. 94–95°).

Saponification of the *p*-nitrobenzoate by the method described above for IIa-*p*-nitrobenzoate gave *axial*-bicyclo[3.2.1]octan-2-ol (VIa) in 99% yield, m.p. 199.9–200.2° (lit.¹⁶ m.p. 200–201°) after sublimation (90°, aspirator vacuum). The infrared spectrum contained no absorption at 9.40, 10.10, 10.30 and 11.00 μ where the *equatorial* isomer VIb absorbs strongly; infrared bands: 9.10, 9.20, 9.65, 9.85, 10.40, 10.75, 11.30 and 11.40 μ (carbon disulfide).

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.04; H, 10.77.

Gas chromatography of VIa (ethyl acetate solution) with a 4-ft. column of 20% glycerol-on-Celite (115°, helium flow rate 21 ml./min.) produced a single peak with a retention time of 16 min. Under these conditions, the epimer VIb had a retention time of 21 min.

Hydrogenation of *endo*-(*equatorial*)-Bicyclo[3.2.1]oct-3-en-2-ol (IIb).—*equatorial*-Bicyclo[3.2.1]oct-3-en-2-ol (IIb), m.p. 77.5–80.5°, was hydrogenated over 5% palladium-on-barium sulfate (see method B described above for the hydrogenation of the *axial* isomer, IIa). Hydrogen uptake stopped after about 50% of an equivalent amount of hydrogen had been absorbed. The solid isolated from the reaction mixture exhibited a strong carbonyl absorption in the infrared. After conversion to the *p*-nitrobenzoate followed by saponification there was obtained a 19% yield (based on IIb) of alcohol, m.p. 182.4–183.6°.

Gas chromatography of the alcohol (ethyl acetate solution) with a 4-ft. column of 20% glycerol-on-Celite (115°, helium flow rate 21 ml./min.) produced two peaks (retention times 16.5 and 20 min.). The first was *axial*-bicyclo[3.2.1]octan-2-ol (VIa) and the second *equatorial*-bicyclo[3.2.1]octan-2-ol (VIb). Relative peak areas indicated that the mixture contained 70% VIb and 30% VIa.

The results of hydrogenation over 30% palladium-on-carbon were similar. Hydrogen absorption ceased after about 50% of the calculated amount was consumed. After purification *via* the *p*-nitrobenzoate, the alcohol was isolated in 10% yield, m.p. 185.6–187.0°. This also was a mixture of the isomeric saturated alcohols VI consisting mostly of the *equatorial* isomer VIb.

Bicyclo[3.2.1]octan-2-one (VII).—*axial*-Bicyclo[3.2.1]octan-2-ol (VIa) m.p. 199.9–200.2°, was oxidized to VII in 89% yield using the procedure of Youssef, *et al.*¹⁶; m.p. 123.0–124.0° (lit.¹⁶ m.p. 127–129°). Purification *via* the semicarbazone¹⁶ was omitted.

The semicarbazone melted at 171.4–171.9° (methanol-water) (lit.¹⁶ m.p. 171–172°).

(36) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

endo-(*equatorial*)-Bicyclo[3.2.1]octan-2-ol (VIb).—The lithium in ammonia reduction of bicyclo[3.2.1]octan-2-one (VII), m.p. 123.0–124.0°, was carried out by the method described earlier.¹⁶ The crude alcohol was isolated in 97% yield.

The *p*-nitrobenzoate of the crude alcohol was prepared³² in 96% yield. The melting point after two recrystallizations from pentane was 80.0–80.4° (lit.¹⁶ m.p. 83–84°). Further recrystallization from pentane or methanol did not change the melting point.

Anal. Calcd. for C₁₅H₁₇NO₄: C, 65.44; H, 6.23. Found: C, 65.35; H, 6.14.

Saponification of the *p*-nitrobenzoate followed by two sublimations (90°, aspirator vacuum) gave pure *endo*-(*equatorial*)-bicyclo[3.2.1]octan-2-ol (VIb) in 97% yield, m.p. 175.7–176.7° (lit.³⁷ m.p. 174–175°). The infrared spectrum

(37) The melting point of this compound was incorrectly reported as 194–195° in ref. 16; private communication from H. M. Walborsky.

contained no peaks at 9.65 and 10.75 μ where the epimer VIa absorbs strongly; infrared bands: 9.10, 9.40, 9.60, 9.85, 10.05, 10.10, 10.30, 10.40, 10.70, and 11.00 μ (carbon disulfide).

Anal. Calcd. for C₈H₁₄O: C, 76.14; H, 11.18. Found: C, 75.86; H, 11.08.

Chromatography of 512 mg. of VIb with a column of 20 g. of Alcoa alumina using increasing amounts of ether in pentane (0–30% ether) as eluent resulted in 88% recovery of material. All of the material was eluted with 30% ether–pentane. The infrared spectra of the first and last fractions were the same as that of the alcohol before chromatography.

Gas chromatography of VIb (ethyl acetate solution) with a 4-ft. column of 20% glycerol-on-Celite (115°, helium flow rate 21 ml./min.) gave one peak (retention time 21 min.). Under these conditions the axial isomer VIa had a retention time of 16 min.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Ionic Reactions in Bicyclic Systems. II. Carbonium Ion Reactions in Bicyclo[2.2.2]-octane and Bicyclo[3.2.1]octane Derivatives

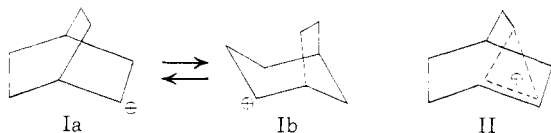
BY HARLAN L. GOERING AND MARTIN F. SLOAN¹

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Deamination of 2-aminobicyclo[2.2.2]octane (III, X = NH₂) and hydrolysis of the corresponding [2.2.2]bicyclic *p*-toluenesulfonate (III, X = OTs) give mixtures of bicyclo[2.2.2]octan-2-ol (III, X = OH) and *exo*-(*axial*)-bicyclo[3.2.1]octan-2-ol (IVa, X = OH). The isomeric *endo*-(*equatorial*)-bicyclo[3.2.1]octan-2-ol (IVb, X = OH) is not formed in these reactions. Acetolysis of *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IVb, X = OTs) proceeds with complete retention of configuration (*equatorial* acetate is the only substitution product). Acid-catalyzed addition of acetic acid to bicyclo[2.2.2]octene gives a ternary mixture of bicyclo[2.2.2]octan-2-yl, and *axial*- and *equatorial*-bicyclo[3.2.1]octan-2-yl acetates (III, IVa and IVb; X = OAc).

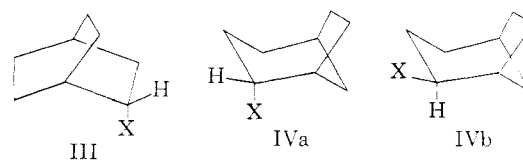
Introduction

Bicyclo[2.2.2]octan-2-yl (III) and *exo*-(*axial*)-bicyclo[3.2.1]octan-2-yl (IVa) systems are related to the same carbonium ion system. The latter can be represented as (a) an equilibrium between the two classical structures I or (b) a bridged "non-classical" cation II. In addition to ionization reactions of 2-substituted bicyclo[2.2.2]- and [3.2.1]-octanes, this carbonium ion system can be produced by protonation of bicyclo[2.2.2]- and [3.2.1]octenes.



There are only a few reports in the literature concerning product studies of reactions involving this carbonium ion system. It has been observed² that 2-bromobicyclo[2.2.2]octane (III, X = Br) rearranges to 2-bromobicyclo[3.2.1]octane (IV, X = Br) when refluxed with silver bromide in carbon tetrachloride. This parallels the report³ that hydration of bicyclo[2.2.2]octene (V) with aqueous sulfuric acid also results in rearrangement and gives bicyclo[3.2.1]octan-2-ol (IV, X = OH). The configurations of these products were not determined. These results have been quoted as evidence that

bicyclo[3.2.1]octane systems are more stable than the isomeric [2.2.2]bicyclic systems.^{4–6}



On the other hand, hydrolysis of bicyclo[2.2.2]octan-2-yl *p*-bromobenzenesulfonate, bromide and chloride (III; = O₂SC₆H₄Br, Br and Cl) is reported to give the unrearranged product, [bicyclo[2.2.2]octan-2-ol (III, X = OH).⁴ Nitrous acid deamination of 2-aminobicyclo[2.2.2]octane (III, X = NH₂) also is reported to give the unrearranged alcohol III (X = OH) as the major product.⁷ However, in this case it was recognized that the product is not homogeneous.⁷ As has been pointed out,^{4,5} these results are not necessarily inconsistent with those mentioned in the preceding paragraph. The first two reactions are reversible⁸ carbonium ion processes (*i.e.*, thermodynamic control) whereas the latter are irreversible⁸ (*i.e.*, kinetic control). These results then suggest that the carbonium ion system gives

(4) H. M. Walborsky, *Experientia*, **9**, 209 (1953).

(5) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(6) W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **80**, 1956 (1958).

(7) M. Farber, Ph.D. Thesis, Columbia University, 1949.

(8) Reversible carbonium ion processes are those in which the products are formed reversibly from the intermediates, *i.e.*, the intermediates are formed repeatedly. In irreversible processes the intermediates are converted to products irreversibly.

(1) Wisconsin Alumni Research Foundation Fellow 1956–1958; National Science Foundation Fellow 1958–1960.

(2) W. E. Doering and M. Farber, *J. Am. Chem. Soc.*, **71**, 1514 (1949).

(3) M. S. Newman and Y. T. Yu, *ibid.*, **74**, 507 (1952).