***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 prepared[32] 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 $C_{15}H_{17}NO_4$: 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 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 $C_8H_{14}O$: 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.

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

[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

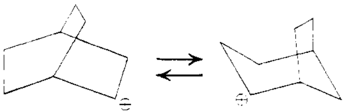
By Harlan L. Goering and Martin F. Sloan[1]

Received September 24, 1960

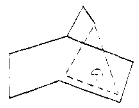
Deamination of 2-aminobicyclo[2.2.2]octane (III, X = NH_2) and hydrolysis of the corresponding [2.2.2]bicyclic *p*-toluenesulfonate (III, X = OTs) give mixtures of bicyclo[2.2.2]octan-2-ol (III, X = OH) and *exo*-(*axial*)-bicyclo[3.2.1]-octan-2-ol (IVa, X = OH). The isomeric *endo*-(*equatorial*)-bicyclo[3.2.1]octan-2-ol (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.

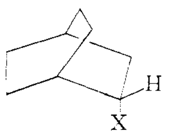


Ia Ib

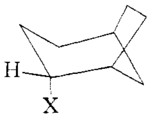


II

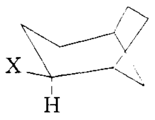
There are only a few reports in the literature concerning product studies of reactions involving this carbonium ion system. It has been observed[2] that 2-bromobicyclo[2.2.2]octane (III, X = Br) rearranges to 2-bromobicyclo[3.2.1]octane (IV, X = Br) when refluxed with silver bromide in carbon tetrachloride. This parallels the report[3] 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]



III



IVa



IVb

On the other hand, hydrolysis of bicyclo[2.2.2]-octan-2-yl *p*-bromobenzenesulfonate, bromide and chloride (III; = $O_2SC_6H_4Br$, Br and Cl) is reported to give the unrearranged product, [bicyclo2.2.2]octan-2-ol (III, X = OH).[4] Nitrous acid deamination of 2-aminobicyclo[2.2.2]octane (III, X = NH_2) 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 reversible[8] carbonium ion processes (*i.e.*, thermodynamic control) whereas the latter are irreversible[8] (*i.e.*, kinetic control). These results then suggest that the carbonium ion system gives

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[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).

[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.

bicyclo[2.2.2]octan-2-yl derivatives faster than the isomeric bicyclo[3.2.1]octan-2-yl derivatives but that the latter are more stable.

This analysis can also accommodate the reports that acid-catalyzed addition of acetic acid to bicyclo[2.2.2]octene (V)[4] and bicyclo[3.2.1]oct-2-ene (VI)[9] give bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc), if it is assumed that these are irreversible processes. However, it seems unlikely that these reactions (and the additions of hydrogen bromide and hydrogen chloride to V which also are claimed to give unrearranged adducts)[4] are irreversible carbonium ion processes.

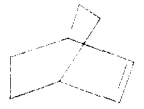
On the basis of the reports that irreversible carbonium ion reactions of bicyclo[2.2.2]octan-2-yl systems do not result in rearrangement, it has been concluded that the carbonium ion does not have a "non-classical" or bridged structure such as II.[4,5] This, of course, would not unequivocally rule out the bridged structure, but as has been pointed out,[5] a bridged ion would be expected to give rise to some of the more stable bicyclo[3.2.1] isomer.

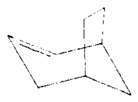
In other problems concerning the Wagner–Meerwein interconversion of bicyclo[2.2.2]- and [3.2.1]-octan-2-yl and octen-2-yl systems we investigated the rates and stereochemistry of solvolysis of the bicyclo[2.2.2]- and [3.2.1]-*p*-toluenesulfonates (III and IV, X = OTs)[10,11] and the stereochemistry of the deamination of 2-aminobicyclo[2.2.2]octane (III, X = NH_2).[12]

In the first of these studies it was discovered that under solvolyzing conditions the isomeric bicyclo-[2.2.2]octan-2-yl and *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonates (III and IVa, X = OTs) are interconverted by internal return.[11] Thus it is clear that the same products would have to result from the isomeric *p*-toluenesulfonates—the product compositions might differ for the two *p*-toluenesulfonates because some product is formed before equilibration of the unsolvolyzed *p*-toluenesulfonates is complete.

In the second study[12] it was found that deamination of optically active 2-aminobicyclo[2.2.2]octane gives an active product (alcohol). This, however, when oxidized gave an optically active ketone. Since active bicyclo[2.2.2]octan-2-ol cannot give an active ketone, it was obvious that this irreversible carbonium ion process (deamination) resulted in rearrangement.

Because of these findings we have reinvestigated the (a) deamination of the amine (III, X = NH_2), (b) acid-catalyzed addition of acetic acid to bicyclo[2.2.2]octene (V) and (c) hydrolysis of the *p*-toluenesulfonate (III, X = OTs). We have also investigated the acetolysis products of *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IVb, X = OTs). As mentioned above, the *axial-p*-toluenesulfonate (IVa, X = OTs) gives the same product as the [2.2.2]-*p*-toluenesulfonate (III, X = OTs) because of the rapid interconversion during solvolysis.


V


VI

Results

Deamination of 2-Aminobicyclo[2.2.2]octane (III, X = NH_2).—The bicyclic amine (III, X = NH_2) was prepared by hydrogenation of 5-aminobicyclo-[2.2.2]oct-2-ene.[10] Aqueous nitrous acid deamination of the amine gave bicyclooöctanol in 67% yield. Deamination of the amine (III, X = NH_2) in acetic acid followed by saponification of the resulting acetate gave bicyclooöctanol (65% yield) which had the same melting point and infrared spectrum as the product resulting from deamination with aqueous nitrous acid. Olefins were not detected; however, bicyclo[3.2.1]- and [2.2.2]octene are highly volatile[9,13] and may have been lost during isolation of the product.

The melting point of the deamination product was about ten degrees lower than that of pure bicyclo[2.2.2]octan-2-ol (III, X = OH). It was not depressed when mixed with pure III (X = OH) or changed by recrystallization or sublimation. The *p*-nitrobenzoate derivative, after recrystallization to constant melting point, melted about six degrees lower than pure bicyclo[2.2.2]octan-2-yl *p*-nitrobenzoate.

The infrared spectrum of the deamination product corresponded in detail to that of a binary mixture of bicyclo[2.2.2]octan-2-ol (III, X = OH) and *axial*-bicyclo[3.2.1]octan-2-ol (IVa, X = OH). The absence of bands characteristic of *equatorial*-bicyclo[3.2.1]octan-2-ol showed that this isomer was not present.

Gas chromatography also showed the deamination product to be a binary mixture of III and IVa (X = OH). However, the composition could not be determined by this method because the broad peaks were not completely resolved. The composition of the product was found to be 36% IVa (X = OH) and 64% III (X = OH) by infrared analysis. Control experiments showed that the deamination products (III and IVa, X = OAc and OH) are stable under the conditions of the deamination experiments.

Solvolysis of Bicyclo[2.2.2]octan-2-yl *p*-Toluenesulfonate (III, X = OTs) and *endo*-(*equatorial*)-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (IVb, X = OTs).—Bicyclo[2.2.2]octan-2-ol was prepared by saponification of the corresponding acetate which in turn was obtained by hydrogenation of the vinyl acetate–cyclohexadiene adduct.[10] The infrared spectrum of the alcohol and the *p*-toluenesulfonate derivative showed that they were not contaminated with isomeric bicyclo[3.2.1]octan-2-yl derivatives.

Pure bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (III, X = OTs) was allowed to solvolyze in 80% aqueous acetone at 50° for a period corresponding to at least 99% reaction (see reference 11 for rate data). A slight excess of pyridine was added at the outset to keep the solution from becoming acidic.

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[9] K. Alder, H. Krieger and H. Weiss, *Ber.*, **88**, 144 (1955).

[10] H. L. Goering, R. W. Greiner and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).

[11] H. L. Goering and M. F. Sloan, *ibid.*, **83**, in press (1961).

[12] M. F. Sloan, Ph.D. Thesis, University of Wisconsin, 1960.

[13] C. A. Grob, M. Ohta, E. Renk and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

The product, bicyclooöctanol (olefins were not detected), was isolated in 82% yield and purified by sublimation in such a way as to avoid fractionation. Gas chromatography and the infrared spectrum showed that the product was a pure binary mixture of bicyclo[2.2.2]octan-2-ol (III, X = OH) and *axial*-bicyclo[3.2.1]octan-2-ol (IVa, X = OH). This mixture contained 45% (infrared analysis) of the [3.2.1]isomer. The equatorial [3.2.1]isomer (IVb, X = OH) was not present. Because bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate and *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate are rapidly equilibrated (by internal return) during solvolysis it is apparent that both would give the same products.

endo-(*equatorial*)-Bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IVb, X = OTs)[10,11] was allowed to solvolyze for ten half-lives at 60° in acetic acid containing a slight excess of sodium acetate. Saponification of the resulting acetate gave pure *equatorial*-bicyclo[3.2.1]octan-2-ol (IVb, X = OH) in 96% yield. The melting point and infrared spectrum were the same as those of alcohol from which the equatorial *p*-toluenesulfonate was prepared.

Addition of Acetic Acid to Bicyclo[2.2.2]octene (V).—Bicyclo[2.2.2]octene (V) was prepared by Wolff–Kishner reduction of bicyclo[2.2.2]oct-5-en-2-one[13] which in turn was obtained by oxidation of *endo*-bicyclo[2.2.2]oct-5-en-2-ol.[10] The addition of acetic acid to V was catalyzed by 0.09 *M* *p*-toluenesulfonic acid. The crude product was saponified without purification and the unreacted olefin was removed by extraction with silver nitrate. The residual alcohol fraction, after purification by recrystallization, had an infrared spectrum that corresponded in complete detail to that of a ternary mixture of bicyclo[2.2.2]octan-2-ol (III, X = OH) and *axial*- and *equatorial*-bicyclo[3.2.1]octan-2-ol (IVa and IVb, X = OH). Gas chromatography (glycerol- and diglycerol-on-Celite) gave two peaks, IVa (X = OH) and a mixture of III and IVb (X = OH). From the relative intensities of the characteristic peaks in the infrared spectrum it appeared that there were about equal amounts of the three components.

When pure bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc) was submitted to the conditions of the addition experiment, rearrangement occurred. The product, after saponification and purification, had an infrared spectrum that was indistinguishable from that of the ternary mixture of III, IVa and IVb (X = OH) described in the preceding paragraph. This experiment shows that under the present conditions the addition is a reversible carbonium ion process.

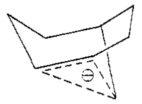
Discussion

The present work shows that both deamination of 2-aminobicyclo[2.2.2]octane (III, X = NH_2) and solvolysis of bicyclo[2.2.2]octan-2-yl *p*-toluene-sulfonate result in substantial rearrangement. These findings not only invalidate the earlier conclusions[4,5] concerning the nature of the cation but in fact indicate that a bridged ion (II), common to the bicyclo[2.2.2]octan-2-yl and *axial*-bicyclo[3.2.1]octan-2-yl systems, is involved.[14] In other words, the present results suggest that ionization involves participation by the bridging ethylene group.

Structure II for the ion nicely accounts for the stereochemical relationship between reactant and product. The usual relationship[15] is observed; *i.e.*, the atoms from which (C_1) and to which (C_2) migration occurs are inverted. It would indeed be difficult to explain the stereospecificity of the solvolysis in terms of the classical carbonium ion Ib. If this ion were the precursor for the bicyclo[3.2.1]-octyl product, formation of at least some of the more stable equatorial isomer would be expected. The bridged structure also accommodates the internal return phenomenon (interconversion of the isomeric *p*-toluenesulfonates III and IVa) associated with the solvolysis.[11] It should also be mentioned that the reactivities of the isomeric *p*-toluenesulfonates (III and IVb, X = OTs) are quite consistent with this picture.[11,16] That a bridged ion apparently is involved in this system is not surprising in view of the fact that analogous bridged ions are presumably involved in both the *exo*-2-norbornyl[14] and 7-norbornyl systems.[17]

A concerted process involving solvent attack at C_1 simultaneous with rearrangement and departure of the leaving group would also give the observed stereochemical result. In this connection it is significant that the kinetic experiments indicate nucleophilic participation by solvent is not involved.[11]

The completely stereospecific solvolysis of *endo*-(*equatorial*)-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IVb, X = OTs) is most interesting. This not only shows that different carbonium ions are involved in irreversible carbonium ion reactions of the epimeric bicyclo[3.2.1]octan-2-yl derivatives but suggests that in this case a bridged ion (VII) is also involved. According to this interpretation, with this isomer ionization involves participation by the bridging methylene group. It would be difficult to account for the stereospecificity (complete retention of configuration) on the basis of the classical carbonium ion Ib. On the other hand, attack by solvent at either of the two equivalent carbon atoms in VII would give the observed product, *i.e.*, the equatorial isomer. In another problem additional evidence that the symmetrical non-classical ion VII is involved in this system is being sought.



VII

Additional information concerning the nature of the intermediates in these systems results from the acid-catalyzed addition of acetic acid to bicyclo-

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(14) For leading references concerning bridged or "non-classical" carbonium ions see ref. 5 and 17.

(15) P. D. Bartlett, Chap. 1 in H. Gilman's "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953.

(16) Because the significance of internal return cannot be assessed quantitatively the true rates of ionization of the isomeric *p*-toluenesulfonates cannot be determined. However, the estimated rates are somewhat larger for each isomer than would be expected if the corresponding classical carbonium ion were the initially formed intermediate.

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

[2.2.2]octene, the only reversible carbonium ion process investigated. Under the conditions used in the present work (0.09 *M* HOTs, reflux six hours)[18] a ternary mixture of bicyclo[2.2.2]octan-2-yl (III, X = OAc) and *axial*-(IVa, X = OAc) and *equatorial*-bicyclo[3.2.1]octan-2-yl acetate (IV, X = OAc) is formed. The same ternary mixture is obtained when pure bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc) is submitted to the conditions of the addition reaction.[19]

The results presented in this paper indicate that a "non-classical" or bridged ion (II) results from the ionization of bicyclo[2.2.2]octan-2-yl and *exo*-(*axial*)-bicyclo[3.2.1]octan-2-yl derivatives. Apparently an isomeric bridged ion (VII) results from the ionization of *endo*-(*equatorial*)-bicyclo[3.2.1]octan-2-yl derivatives. If this interpretation is correct, the energy barrier between II and VII is sufficiently high so that in irreversible processes there is no interconversion (the products from III and IVa are different from those of IVb). However, under reversible conditions, *e.g.*, the acid-catalyzed addition of acetic acid and isomeric rearrangements (equilibration) of the acetates, the carbonium ions related to the isomeric bicyclo[3.2.1]octan-2-yl derivatives (II and VII) are interconverted.

Experimental

2-Aminobicyclo[2.2.2]octane (III, X = NH_2).—Hydrogenation[20] of 5-aminobicyclo[2.2.2]oct-5-ene[10] gave the hydrochloride of III (X = NH_2), m.p. > 320° (lit.[20] m.p. 345–350°), in 90% yield. The free amine (III, X = NH_2) melted at 143–144° (lit.[20] m.p. 140–141.5°).

Bicyclo[2.2.2]octan-2-ol (III, X = OH).—Hydrogenation of bicyclo[2.2.2]oct-5-en-2-yl acetate[10] over 10% palladium-on-carbon and then lithium aluminum hydride reduction[21] of the saturated acetate gave III (X = OH) in 25% yield (based on cyclohexadiene). After recrystallization from petroleum ether and sublimation (90°, aspirator vacuum) it melted at 220.9–222.2°(lit.[22,23] m.p. 216–217°); infrared bands: 9.15, 9.70, 10.20, 10.70, 11.00 and 11.80 μ (carbon disulfide). Bands characteristic of *equatorial*-bicyclo[3.2.1]-octan-2-ol (IVb, X = OH) (9.40, 9.60, 10.10 and 10.30 μ) and *axial*-bicyclo[3.2.1]octan-2-ol (IVa, X = OH) (10.40 μ) were absent.

The *p*-nitrobenzoate derivative, m.p. 107.6–108.0° (petroleum ether), was prepared by a previously described method.[24]

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.44; H, 6.22. Found: C, 65.58; H, 6.04.

Bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc) was prepared from the alcohol (anhydrous pyridine method)[25] in 81% yield, n^{25}_D 1.4725 (lit.[23] n^{20}_D 1.4712).

Bicyclo[2.2.2]octan-2-yl *p*-Toluenesulfonate (III, X = OTs).—The *p*-toluenesulfonate derivative was prepared from pure alcohol by a previously described method.[10] After recrystallization from 60–68° petroleum ether to a constant melting point, 54.2–55.0°, the yield was 2.80 g. (70%); infrared bands: 9.10, 10.10, 10.30, 10.85, 11.05, 11.50, 12.10, 12.30, 13.10, 14.20, 14.65 and 15.05 μ (carbon disulfide). Bands characteristic of *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IVb, X = OTs) (10.55, 11.30, 11.70 and 12.00 μ) and *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IVa, X = OTs) (10.65, 11.25, 11.75, 13.55 and 13.90 μ) were absent.

Anal. Calcd. for $C_{15}H_{20}O_3S$: C, 64.25; H, 7.19; solvolysis equiv., 280.4. Found: C, 64.41, H, 7.00; solvolysis equiv., 283.4 ± 1.3 (av. of 11 detn.[11]).

endo-(*equatorial*)-**Bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IVb, X = OTs)** was prepared from pure *equatorial*-bicyclo[3.2.1]octan-2-ol.[10] After two recrystallizations from an ether–pentane mixture the material melted at 80.1–80.8°, and the yield was 85%. Kinetic experiments[11] showed that this material was homogeneous; infrared bands: 10.55, 10.70, 10.95, 11.30, 11.40, 11.70, 12.00, 12.25, 13.55 and 15.05 μ (carbon disulfide).

Anal. Calcd. for $C_{15}H_{20}O_3S$: C, 64.25; H, 7.19; solvolysis equiv., 280.4. Found: C, 63.96; H, 7.21; solvolysis equiv., 281.2.

Bicyclo[2.2.2]octene (V).—Bicyclo[2.2.2]oct-5-en-2-one was prepared by oxidation of *endo*-bicyclo[2.2.2]oct-5-en-2-ol[10] with chromic acid.[26] After sublimation it melted at 75.0–83.5° (lit.[13] m.p. 79°). Bicyclo[2.2.2]octene, m.p. 116.4–117.5° (lit. m.p. 115–117°,[13] 111–112°[27]), was prepared by Wolff–Kishner reduction of the ketone.[13]

Deamination of 2-Aminobicyclo[2.2.2]octane (III, X = NH_2). A. In Water.—Deamination of the amine hydrochloride, m.p. > 320°, was carried out by the method described by Wildman and Saunders[20] for deamination of the hydrochloride of *endo*-5-aminobicyclo[2.2.2]oct-2-ene. After one recrystallization from petroleum ether the yield of bicyclooöctanol, m.p. 210.2–211.2° (*cf.* bicyclo[2.2.2]octan-2-ol, m.p. 220.9–222.2°), was 67%.

Pure bicyclo[2.2.2]octan-2-ol (III, X = OH), m.p. 220.9–222.2°, was submitted to the deamination conditions (methylamine hydrochloride, sodium nitrite and hydrochloric acid). After sublimation the recovered material (82% yield) melted at 221.1–222.1°. Its infrared spectrum was identical with that of the starting material.

B. In Acetic Acid.—To a stirred solution of 1.20 g. (0.00743 mole) of the amine hydrochloride in 8.5 ml. of dry acetic acid at room temperature was added 0.815 g. (0.0118 mole) of sodium nitrite over a period of 30 min. The two-phase (sodium chloride precipitates) mixture was allowed to stand at room temperature for 24 hr. Then an additional 0.200 g. of sodium nitrite was added, and the reaction was heated on a steam-bath for 1 hr. After cooling, it was poured into 30 ml. of cold 20% aqueous sodium hydroxide and extracted with pentane for 24 hours. The pentane solution of the acetate was washed with 5% hydrochloric acid and water. After drying, the pentane was removed by distillation and replaced with 40 ml. of 1 *M* methanolic potassium hydroxide. The resulting solution was refluxed for 1 hr., cooled and diluted with water, and then extracted with pentane for 24 hr. Removal of the pentane left 674 mg. of crude alcohol. After sublimation (90°, aspirator vacuum) the yield of product, m.p. 199.8–202.6°, was 66%. When mixed with bicyclo[2.2.2]octan-2-ol (m.p. 220.9–222.2°) the mixture melted at 206.7–212.2°. When mixed with *axial*-bicyclo[3.2.1]octan-2-ol[10] (m.p. 199.9–200.2°) the mixture melted at 197.8–202.0°. It was not changed by further recrystallization or repeated sublimations. The infrared spectrum was identical with that of the product from aqueous deamination (Part A).

Gas chromatography of the deamination product (ethyl acetate solution) using a 6-ft. column of 20% diglycerol-on-Celite (115°, helium flow rate 16 ml./min.) produced two broad, partially overlapping peaks with retention times of 19.5 and 21.5 min. The former was shown to be bicyclo[2.2.2]octan-2-ol (III, X = OH) and the latter *axial*-bicyclo[3.2.1] octan-2-ol(IVa, X = OH).

The infrared spectrum of the deamination product (alcohol) was an exact composite of those of bicyclo[2.2.2]octan-2-ol and *axial*-bicyclo[3.2.1]octan-2-ol. Bands characteristic of *equatorial*-bicyclo[3.2.1]octan-2-ol (9.40, 10.10 and

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(18) The conditions under which this reaction was claimed to give the unrearranged adduct were not described (ref. 4). These are essentially the conditions under which the addition of acetic acid to bicyclo[3.2.1]oct-2-ene is reported to give III (X = OAc) (ref. 9).

(19) Preliminary results (M. F. Sloan) indicate a similar mixture is obtained from bicyclo[3.2.1]oct-2-ene.

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10.30 μ[10]) were absent. Infrared analysis showed that the product consisted of 64 ± 2% bicyclo[2.2.2]octan-2-ol and 36 ± 2% *axial*-bicyclo[3.2.1]octan-2-ol.

The *p*-nitrobenzoate of the deamination product melted at 101.5–102.5° after single recrystallizations from aqueous ethanol and petroleum ether. When this derivative was mixed with bicyclo[2.2.2]octan-2-yl *p*-nitrobenzoate (m.p. 107.6–108.0°) the mixture melted at 104.0–106.5°.

Bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc) was submitted to the conditions of the deamination (methylamine hydrochloride, sodium nitrite, acetic acid). After saponification pure bicyclo[2.2.2]octan-2-ol, m.p. 220.6–221.8°, was isolated in 76% yield. The infrared spectrum was identical with that of an authentic sample.

Hydrolysis of Bicyclo[2.2.2]octan-2-yl *p*-Toluenesulfonate (III, X = OTs).—A solution of 3.00 g. (0.0107 mole) of III (X = OTs), m.p. 54.2–55.0°, in 55 ml. of 80% aqueous acetone containing 0.95 ml. (0.0117 mole) of pyridine was heated at 50° for 40 hr. This corresponds to over 99% reaction.[11] The solution was cooled and the acetone was allowed to evaporate under an air jet until crystallization of the product began. Water was added, and the mixture was extracted several times with ether. The ether extract was washed with 5% hydrochloric acid, then with water, and dried (magnesium sulfate). Removal of the ether left 1.113 g. (82%) of alcohol. After sublimation (90°, aspirator vacuum) the melting point was 204.4–205.6°.

Gas chromatography of the hydrolysis product (ethyl acetate solution) using a 6-ft. column of 20% diglycerol-on-Celite (115°, helium flow rate 16 ml./ min.) produced two broad, partially overlapping peaks. The retention times of these corresponded to bicyclo[2.2.2]octan-2-ol (III, X = OH) and *axial*-bicyclo[3.2.1]octan-2-ol (IVa, X = OH).

The infrared spectrum was similar to that of the product resulting from deamination of 2-aminobicyclo[2.2.2]octane, *i.e.*, a composite of the spectra of III and IVa (X = OH). Bands characteristic of *equatorial*-bicyclo[3.2.1]octan-2-ol (IVb, X = OH) were not present. Infrared analysis showed that the mixture consisted of 55 ± 2% III (X = OH) and 45 ± 2% IVa (X = OH).

Acetolysis of *equatorial*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (IVb, X = OTs).—A solution of 500 mg. (0.00178 mole) of IVb (X = OTs), m.p. 80.1–80.8°, and 155 mg. (0.00189 mole) of sodium acetate in 9 ml. of anhydrous acetic acid was heated at 60° for 9 days (over 99% reaction).[11] After cooling, the solution was poured into water and the resulting mixture was extracted with pentane for 24 hr. The pentane was removed by slow distillation and replaced with 25 ml. of 1 *M* methanolic potassium hydroxide. After the resulting solution had refluxed for 1 hr., it was diluted with water and extracted with pentane for 24 hr. Removal of the pentane followed by sublimation (90°, aspirator vacuum) gave 217 mg. (96%) of *equatorial*-bicyclo[3.2.1]octan-2-ol (IVb, X = OH), m.p. 176.0–178.7°. The infrared spectrum was identical with that of authentic IVb (X = OH).[10]

Addition of Acetic Acid to Bicyclo[2.2.2]octene (V).—A solution of 512 mg. (0.00473 mole) of V in 10 ml. of 0.092 *M* *p*-toluenesulfonic acid in acetic acid was refluxed for 6 hr. Then solid sodium acetate was added to the cooled solution and the resulting solution was diluted with water and extracted with pentane for 14 hr. The pentane was removed by slow distillation and replaced with 25 ml. of 1*M* methanolic potassium hydroxide. After the resulting solution had refluxed for 1 hr., it was diluted with water and extracted with pentane for 24 hr. The pentane extract was washed with two 5-ml. portions of 20% aqueous silver nitrate, then with water, and dried (magnesium sulfate). Removal of the solvent followed by sublimation (90°, aspirator vacuum) of the residual solid gave 360 mg. (59%) of alcoholic material, m.p. 191.5–193.8°. After one recrystallization from petroleum ether the melting point was 199.4–201.5°.

The infrared spectrum of the product was a composite of those of bicyclo[2.2.2]octan-2-ol (III, X = OH) and *axial*- and *equatorial*-bicyclo[3.2.1]octan-2-ol (IVa and IVb, X = OH). The relative intensities of the bands at 11.80 μ (III), 10.10 μ (IVb) and 10.40 μ (IVa) indicated that approximately equal amounts of the three components were present.

Bicyclo[2.2.2]octan-2-yl acetate (III, X = OAc) was submitted to the conditions of the addition reaction. The yield of product, after one sublimation, was 68%, m. p. 194.5–196.8°. The infrared spectrum was indistinguishable from that of the alcohol resulting from saponification of the adduct obtained from the addition of acetic acid to V.

Infrared Analysis.—The compositions of the binary mixtures of III and IVa (X = OH) were determined by a previously described method.[28] The transmittance of samples was arbitrarily set at 100% at 2.4 μ for the calculations. The spectra of 10% carbon disulfide solutions of the samples were determined with a Baird model B double beam infrared spectrophotometer equipped with a sodium chloride prism. The same set of cells was used for all of the determinations. The method was checked with three synthetic mixtures of III and IVa (X = OH). The average difference between the experimental and actual values of the compositions of these three samples was 1.7%.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

Organic Ions in the Gas Phase. VIII. Bicycloheptadiene

BY SEYMOUR MEYERSON, JOHN D. MCCOLLUM AND PAUL N. RYLANDER

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Evidence has been reported that the three C_7H_8 isomers, toluene, cycloheptatriene-1,3,5 and spiro[2.4]heptadiene-1,3, dissociate under electron impact to a common $C_7H_7^+$ species, the tropylium ion. Furthermore, energetics data on toluene and cycloheptatriene have been interpreted as reflecting decomposition to this common product from a common excited state, $C_7H_8^{+*}$, of the molecular ion. Both suggestions have now been extended, on the basis of mass-spectral and energetics evidence, to include a fourth isomer, bicyclo[2.2.1]heptadiene-2,5. This compound exhibits also a major competing dissociation path, which resembles a reverse Diels–Alder reaction and leads to $C_5H_6^+$ and C_2H_2.

Evidence has been reported that the $C_7H_7^+$ ion formed from toluene under electron impact is the completely symmetrical tropylium ion, and that it results from dissociation of an excited ionized molecule, $C_7H_8^{+*}$, in which the eight hydrogen atoms have almost completely lost identity.[1,2] Pronounced similarity of the mass spectra of two isomeric compounds cycloheptatriene-1,3,5 and spiro[2.4]heptadiene-1,3 to that of toluene has suggested[2,3] that all three compounds dissociate to give a common $C_7H_7^+$ species—the tropylium ion. For toluene and cycloheptatriene, the energies of the $C_7H_8^{+*}$ intermediates were found equal within experimental error; a single intermediate thus seems common to the two systems.[2]

If the similar behavior of these isomers arises from identical reaction intermediates, the same behavior might be expected from other C_7H_8 iso-

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