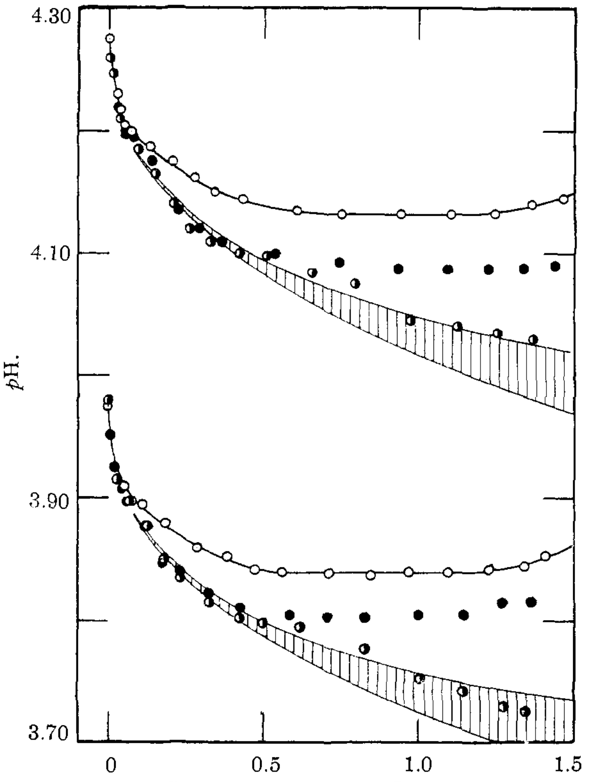

Fig. 1.—The effect of KCl, NH_4Cl and $C(NH_2)_3Cl$ on the pH of acetic acid–acetate mixtures. The upper curves represent the addition of KCl (○), NH_4Cl (◑), and $C(NH_2)_3Cl$ (●) to a solution initially containing 0.0561 *M* HOAc and 0.0208 *M* NaOAc. The lower curves represent the addition of the same salts to a solution of 0.0569 *M* HOAc and 0.0104 *M* NaOAc. The shaded areas show the possible location of these curves for an association constant of 0.5 between the cation and acetate ion. (Most of the experimental points for salt concentrations below 0.05 have been omitted in this figure.)

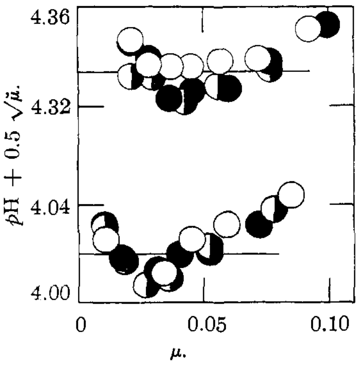

Fig. 2.—Extrapolation to zero ionic strength. The upper and lower curves have the same meaning as in Fig. 1. The experimental points are drawn with a radius of 0.005 pH unit, approximately one half the probable experimental error.

tassium and acetate ions, the pH at any concentration of KCl is given by equation 1

$$pH = pK - \log C^\circ_{OAc^-}/C^\circ_{HOAc} - \log y_{OAc^-}/y_{HOAc} + e \quad (1)$$

where *y* is used for activity coefficients (molarity scale) and *e* represents the sum of the errors due to changing liquid junction potentials and possible non-ideality of the glass electrode. The assumption of volume additivity does not introduce an error since only a ratio of concentrations is involved. In the experiments with ammonium and guanidinium ions the same equation applies, except that the concentration of acetate, C_{OAc^-}, is now lower than that calculated from the initial amount added, $C^\circ_{OAc^-}$, because of complex formation. If $\log y_{OAc^-}/y_{HOAc}$ and *e* are assumed at any given ionic strength to have the same value for each salt, then the pH difference between the curves for NH_4Cl and $C(NH_2)_3Cl$ and that for KCl is

$$\delta pH = -\log C^\circ_{OAc^-}/C_{OAc^-} \quad (2)$$

The concentration of undissociated cation acetate is $C^\circ_{OAc^-}\cdot((1 - C_{OAc^-})/C^\circ_{OAc^-})$. This quantity is much smaller than the concentration, C_s, of added salt, so that the association constant, in concentration units, becomes

$$K_C = \left(1 - \frac{C_{OAc^-}}{C^\circ_{OBc^-}}\right) \Big/ C_s \frac{C_{OAc^-}}{C^\circ_{OAc^-}} = (10^{-\delta pH} - 1)/C_s$$

The values of K_c calculated from the data vary from 0.2 to 0.4. Correction for activity coefficients leads to a value of K_a near 0.5. The shaded area of Fig. 1 encompasses theoretical curves of pH *versus* salt concentration based on this value of K_a, and making use of several possible assumptions regarding activity coefficients. Below concentrations of 0.5 *M* the theoretical curve is insensitive to these assumptions and the points for both ammonium and guanidinium ions fall along the curve within the experimental error. Above 0.5 *M* the pH difference due to guanidinium ion is less than predicted, suggesting that the value of the association constant between guanidinium and acetate ions may actually be less than 0.5.

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Rearrangement of 2-Aminobicyclo[2.2.2]octene-5 with Nitrous Acid

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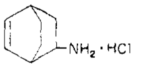
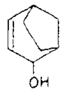
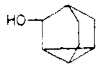
It is well known that the action of nitrous acid on aliphatic primary amines may give rise to a number of products, some possessing the original carbon skeleton and others with a rearranged structure. In view of the ease with which 2-aminobicyclo-[2.2.1]heptene-5 is converted to 3-hydroxynortricyclene[3] with nitrous acid, it seemed of interest to determine whether the homologous compound, 2-aminobicyclo[2.2.2]octene-5 (I) would form the unknown tricyclo[2.2.2.$0^{2,6}$]octan-3-ol (III) under similar conditions.



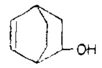
I



II



III



IV

Alcohols which might be anticipated as likely

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[2] Abstracted in part from a thesis submitted by D. R. Saunders in partial fulfillment of the requirements for the degree of Bachelor of Arts, Princeton University, May, 1953.

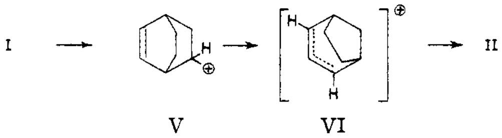
[3] W. Parham, W. T. Hunter and R. Hanson, THIS JOURNAL, **73**, 5068 (1951).

reaction products include the unrearranged bicyclo[2.2.2]-5-octen-2-ol (IV), tricyclo[2.2.2.$0^{2,6}$]octan-3-ol (III) and bicyclo[3.2.1]-3-octen-2-ol (II). A 61% yield of alcohol was obtained when I was treated with sodium nitrite and a trace of concentrated hydrochloric acid. The alcohol was converted to a phenylurethan, m.p. 126–126.5° and a *p*-nitrobenzoate, m.p. 81–81.5°. The melting point of the latter derivative eliminated IV as the correct structure for the product.[4]

When the alcohol was reduced at room temperature and atmospheric pressure with palladium-on-charcoal catalyst, one mole of hydrogen was absorbed to give a solid alcohol, m.p. 183–184°. The phenylurethan melted at 128–129°. These physical constants are in good agreement with the values reported for bicyclo[3.2.1]octan-2-ol by Doering and Farber[5] and Alder and Windemuth.[6]

Although it seemed extremely unlikely that rearrangement had occurred during the preparation of I, the structure of the amine was verified by reduction to 2-aminobicyclo[2.2.2]octane which had been prepared previously by Komppa[7] and Seka and Tramposch.[8]

Since IV is stable to hydrochloric acid under the conditions of the diazotization, it is established that the rearrangement occurs during the reaction with nitrous acid. The mechanism of the transformation can be explained in terms of the general carbonium ion theory. The allylic carbonium ion VI is formed by ethylene group migration to C_2. Addition of water to VI followed by loss of a proton would give II. Participation of an electron pair in the ethene group appears to be absent in the rearrangement since no tricyclic products could be isolated. Migration of the ethene group can be eliminated as a possibility for chromic acid oxidation of II gave an α,β-unsaturated ketone which showed a λ_{max} 227 mμ (log ϵ 3.9) and an infrared carbonyl band at 6.0 μ.



Experimental[9]

2-Aminobicyclo[2.2.2]octene-5 Hydrochloride (I).—By the procedure of Alder, Rickert and Windemuth,[10] 5.50 g. (0.036 mole) of 2-nitrobicyclo[2.2.2]octene-5 gave 4.51 g. (79%) of colorless plates, 302–306° dec. (sealed capillary). A small portion was sublimed and then recrystallized from aqueous acetone for analysis, m.p. 305–306° dec. (sealed capillary).

Anal. Calcd. for $C_8H_{14}NCl$: C, 60.17; H, 8.84; N, 8.77. Found: C, 60.16; H, 8.86; N, 8.58.

The **phenylthiourea** of I was prepared and recrystallized from aqueous ethanol, m.p. 168.5°.

Anal. Calcd. for $C_{15}H_{18}N_2S$: C, 69.72; H, 7.02; N, 10.84. Found: C, 69.58; H, 6.95; N, 10.66.

2-Aminobicyclo[2.2.2]octane.—A solution of 500 mg. (3.1 millimoles) of I in 10 ml. of ethanol was treated with 100 mg. of 30% palladium-on-charcoal catalyst and hydrogenated at atmospheric pressure and room temperature. The reduction stopped when 107% of the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration. The filtrate was concentrated in an air jet to a white solid that was triturated with ether and filtered to give 450 mg. (89%) of the hydrochloride which sublimed in a sealed capillary at 345–350° (reported[7] >300°). The free amine was precipitated as an oil from a solution of the hydrochloride by the addition of base. The product was extracted with ether and concentrated in an air jet to give a white solid, m.p. 139–141°, which was purified by sublimation, m.p. 140–141.5° (sealed capillary) (reported[7,8] 138–140°).

The **picrate** was prepared in ether and recrystallized from aqueous methanol as elongated, yellow prisms, m.p. 222–223° dec. (reported[7] 222–223° dec.).

Bicyclo[3.2.1]-3-octen-2-ol (II).—A solution of 1.60 g. (0.023 mole) of sodium nitrite in 5 ml. of water was added slowly to a cooled solution of 3.70 g. (0.023 mole) of I in 10 ml. of water. No test for nitrous acid was obtained with starch–iodide paper until two drops of concentrated hydrochloric acid had been added. The solution became cloudy and was allowed to stand in the refrigerator overnight. The solution was heated at 100° for four hours and the alcohol was removed by steam distillation. The distillate was extracted with ether. The ether layer was dried and concentrated to 1.77 g. (61%) of a pale yellow wax. This material was not characterized further but was converted to derivatives which could be handled more easily.

The ***p*-nitrobenzoate** was prepared and recrystallized from aqueous ethanol, m.p. 81–81.5°.

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.95; H, 5.53; N, 5.13. Found: C, 65.80; H, 5.68; N, 5.11.

The **phenylurethan** was prepared and recrystallized from petroleum ether, m.p. 126–126.5°.

Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.04; H, 7.05; N, 5.76. Found: C, 74.31; H, 7.26; N, 5.80.

Bicyclo[3.2.1]octan-2-ol.—A solution of 478 mg. (3.85 millimoles) of II in 10 ml. of ethanol was mixed with 100 mg. of 30% palladium-on-charcoal catalyst and hydrogenated at atmospheric pressure and room temperature. The catalyst was removed by filtration and the filtrate was concentrated to 430 mg. (89%) of white solid, m.p. 162–174°. Recrystallization from pentane gave white prisms, m.p. 183–184° (sealed capillary) (reported[5] 183–184°, 183°[6]).

The **phenylurethan** was prepared and recrystallized first from petroleum ether and then from aqueous ethanol, m.p. 128–129° (reported[6] 130°; 128–129.5°[5]).

Attempted Rearrangement of IV.—A suspension of 0.375 g. of IV,[4] m.p. 166–167°, in 5 ml. of water containing 5 drops of concentrated hydrochloric acid was allowed to stand 12 hours at 0° and then was heated on a steam-bath for 4 hours. The alcohol was steam distilled and extracted with ether. The ethereal solution was dried and concentrated to give a 68% yield of material that was identical with IV as proven by comparison of the infrared spectra.

Bicyclo[3.2.1]-3-octen-2-one.—Oxidation of 160 mg. of II with 100 mg. of chromic anhydride in aqueous acetic acid gave 81 mg. of colorless oil; λ_{max} 227 mμ (log ϵ 3.9). The infrared spectrum showed carbonyl absorption at 6.0 μ.

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[4] Two unequivocal syntheses of IV, m.p. 166–167°, have been achieved in this Laboratory. The *p*-nitrobenzoate of IV melted at 108.5–110°. W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, submitted for publication.

[5] W. von E. Doering and M. Farber, THIS JOURNAL, **71**, 1514 (1949).

[6] K. Alder and E. Windemuth, *Ber.*, **71**, 2404 (1938).

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

[8] R. Seka and O. Tramposch, *ibid.*, **75**, 1379 (1942).

[9] All melting points are corrected. Analyses by Clark Microanalytical Laboratories, Urbana, Illinois. We are indebted to Mrs. Iris Siewers of the National Heart Institute, Bethesda, Maryland, for infrared spectra of several of these compounds.

[10] K. Alder, H. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938).