above 300 mμ.[15] In those alcohols in which one asymmetric carbon carried a methyl and the other an ethyl (3-phenyl-2-pentanol and 2-phenyl-3-pentanol), the situation is reversed, and the *erythro* isomer possesses a maximum above 300 mμ and the *threo* none. For the alcohols in which a phenyl is attached to each asymmetric carbon (1,2-diphenyl-1-propanol and 1,2-diphenyl-2-methyl-1-butanol), neither diastereomer possesses a maximum, and for most of the region examined, the *threo* isomers have higher rotations than the *erythro*. Plots of the inverse of $[\alpha]$ against λ^2 for representative compounds gave lines which were not straight, but deviations from linearity were small.

Other Physical Properties.—The refractive indices of those diastereomers that are liquids at room temperature (compounds II–V and VIII) were taken, and are recorded in Table III. In all compounds measured the *erythro* isomers possess the higher refractive index.

Enough densities of these alcohols were determined to establish that no generalizations could be made correlating density and configuration. It is noted that in most cases the melting points of the *erythro*-alcohols[3] and their esters[3] tend to be higher than those of the *threo*-alcohols, but enough exceptions are known to prevent this generalization to be used for diagnostic purposes.

(15) Measurements could not be made lower than 300 mμ because of the considerable light absorption of the aromatic system. The shapes of the dispersion curves without maxima above 300 mμ suggest that maxima do appear at somewhat lower wave lengths.

TABLE III

INDICES OF REFRACTION OF DIASTEREOMERIC ALCOHOLS

Compound	Configuration	$n^{25}D$
3-Phenyl-2-butanol (II)	*erythro*	1.5167
3-Phenyl-2-butanol (II)	*threo*	1.5159
2-Phenyl-3-pentanol (III)	*erythro*	1.5121
2-Phenyl-3-pentanol (III)	*threo*	1.5113
3-Phenyl-2-pentanol (IV)	*erythro*	1.5106
3-Phenyl-2-pentanol (IV)	*threo*	1.5097
4-Phenyl-3-hexanol (V)	*erythro*	1.5088
4-Phenyl-3-hexanol (V)	*threo*	1.5072
1,2-Diphenyl-2-methyl-1-butanol (VIII)	*erythro*	1.5698
	threo	1.5694

Experimental

The footnotes of Tables I, II and III indicate the types of instruments, solvents and conditions of measurement for the infrared and n.m.r. studies. The data for the rotatory dispersion curves were taken in a Rudolph photoelectric spectropolarimeter model 200 S-80 equipped with a RCA IP 28 photomultiplier tube and a Xenon arc lamp. Readings were taken at 700, 650, 589 and 550 mμ, each 20 mμ's from 520 to 380, and each 10 or 5 mμ from 380 to 300 mμ. The polarimeter tube was 0.5 dm. with quartz windows. The slit width of the Beckman spectrometer was increased gradually to give approximately constant readings, which were taken by the symmetrical angles method.[16]

The 2-phenylbutane-3-*d* used in this investigation contained 91% deuterium, and its preparation and analysis will be reported in a future publication.

(16) W. Heller in A. Weissberger's "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, 2nd edition, Vol. 1, Chapter 23.

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE RESEARCH DIVISION OF ETHICON, INC.]

Stereochemistry of Diels–Alder Adducts. III. The Preparation and Rearrangement of Some Brominated Derivatives of Norbornanecarboxylic Acids

BY WERNER R. BOEHME

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2-*exo*-Bromonorbornane-2-*endo*-carboxylic acid and its derivatives were obtained *via* the Diels–Alder reaction of cyclopentadiene with α-bromoacrylic acid and subsequent reduction of the double bond or by bromination of norbornane-2-*endo*-carbonyl chloride. Bromination of norbornane-2-*endo*-carboxylic acid, however, gave the rearranged 2-*exo*-bromonorbornane-1-carboxylic acid as the sole product. 2-*exo*-Bromonorbornane-2-*endo*-carboxamide undergoes rearrangement upon heating above its melting point or upon treatment with dilute alcoholic alkali to form 2-*exo*-bromonorbornane-1-carboxamide. Catalytic or chemical hydrogenolysis of the isomeric bromoamides gives norbornane-2-*endo*-carboxamide and norbornane-1-carboxamide, respectively.

As part of a program designed to synthesize highly hindered trisubstituted acetic acids of bicyclic systems,[1] we have studied the stereochemistry of some halogenated norbornanecarboxylic acids and the rearrangement of 2-*exo*-bromonorbornane-2-*endo*-carboxamide.[2]

The rearrangement of 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid (I, R = OH) and its methyl ester (I, R = OCH_3) upon hydrogenolysis has been described by Kwart and Null.[3] These authors reported the formation of norbornane-1-carboxylic acid (IV, R = OH) upon catalytic hydrogenation of 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid in the presence of dilute methanolic potassium hydroxide and palladium–charcoal catalyst and the formation of 1-carbomethoxynorbornane (IV, R = OCH_3) upon chemical reduction of 2-*exo*-bromo-2-*endo*-carbomethoxynorbornane (I, R = OCH_3) with zinc and acetic acid. It has been shown[2] recently that no rearrangement takes place upon either catalytic or chemical hydrogenolysis and that the bromonorbornanecarboxylic acid and its ester reported by Kwart and Null were already rearranged prior to hydrogenolysis.

Bromination of norbornane-2-*endo*-carbonyl chloride (III, R = Cl)[4] in boiling thionyl chloride solu-

(1) W. R. Boehme, E. Schipper, W. G. Scharpf and J. Nichols, THIS JOURNAL, **80**, 5488 (1958).

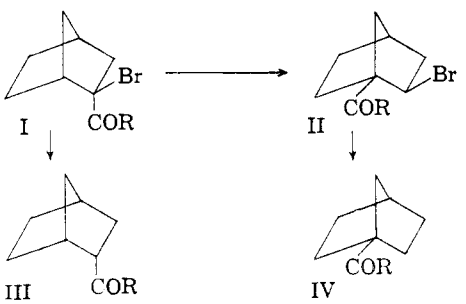
(2) For a preliminary communication describing this rearrangement see W. R. Boehme, *ibid.*, **80**, 4740 (1958).

(3) H. Kwart and G. Null, *ibid.*, **80**, 248 (1958).

(4) K. Alder, G. Stein, M. Liebmann and E. Rolland, *Ann.*, **514**, 197 (1934).

tion gave 2-*exo*-bromonorbornane-2-*endo*-carbonyl chloride (I, R = Cl). When the bromoacyl halide was treated with anhydrous ammonia in cold ether or toluene the corresponding amide, 2-*exo*-bromonorbornane-2-*endo*-carboxamide (I, R = NH_2), was obtained. The structure of the latter was established by hydrogenolysis to norbornane-2-*endo*-carboxamide (III, R = NH_2)[1,5] with either zinc and acetic acid[6,7] or catalytically in the presence of methanol and palladium–calcium carbonate catalyst. 2-*exo*-Bromonorbornane-2-*endo*-carboxamide was observed to resolidify when heated above its melting point (120–121°) and remelting occurred at about 160°. When it was heated at 150–160° for three minutes 76% of an isomeric bromocarboxamide (II, R = NH_2; m.p. 173–174°) was obtained from the melt. The rearrangement of I (R = NH_2) to II (R = NH_2) is also catalyzed by alkali. A solution of 5% potassium hydroxide in 95% methanol completely rearranged 2-*exo*-bromonorbornane-2-*endo*-carboxamide to its isomer (II, R = NH_2) in six hours at room temperature. Hydrogenolysis of the latter by either chemical or catalytic means gave norbornane-1-carboxamide (IV, R = NH_2). Compound IV (R = NH_2) was identified by elementary analysis, the mixed melting point behavior and a comparison of the infrared spectrum with that of an authentic sample prepared from norbornane-1-carboxylic acid (IV, R = OH)[8,9] *via* the acid chloride. Upon saponification IV (R = NH_2) gave norbornane-1-carboxylic acid.

The Wagner–Meerwein rearrangement is a rather common reaction in the bicyclic series.[10] A 2-substituted norbornane is rearranged to its mirror image[11] but rearrangement of a 2,2-disubstituted derivative results in a separation of the substituents. Thus, rearrangement of 2,2-dichloronorbornane[8,9] leads to 1,2-dichloronorbornane and, in the more complex camphane series, the transformation of 2,2-dichlorocamphane to 2,4-dichlorocamphane[12,13] can be attributed to a succession of Wagner–Meerwein rearrangements. On this basis the rearrangement product of 2-*exo*-bromonorbornane-2-*endo*-carboxamide (I, R = NH_2) is designated as 2-*exo*-bromonorbornane-1-carboxamide (II, R = NH_2).



When norbornane-2-*endo*-carboxylic acid (III, R = OH) was brominated by the Hell–Volhard–Zelinsky procedure[14] in the presence of a small amount of phosphorus trichloride, 2-*exo*-bromonorbornane-1-carboxylic acid (II, R = OH) was obtained as the sole product of the reaction. Catalytic hydrogenolysis of this acid in the presence of aqueous potassium hydroxide solution and palladium–charcoal gave norbornane-1-carboxylic acid (IV, R = OH) in high yield. Thus, bromination of norbornane-2-*endo*-carbonyl chloride proceeds normally whereas bromination of the corresponding acid is accompanied by rearrangement.

2-*exo*-Bromonorbornane-1-carbonyl chloride (II, R = Cl) was prepared from the acid II (R = OH) and thionyl chloride. This acid chloride, upon ammonolysis, gave the bromocarboxamide II (R = NH_2) and, upon treatment with methanol, 2-*exo*-bromo-1-carbomethoxynorbornane (II, R = OCH_3) was obtained. The ester II (R = OCH_3) was also obtained by esterification of 2-*exo*-bromonorbornane-1-carboxylic acid (II, R = OH) with diazomethane. When compound II (R = OCH_3) was reduced either chemically or catalytically there was obtained 1-carbomethoxynorbornane which was saponified to norbornane-1-carboxylic acid (IV, R = OH). 2-*exo*-Bromonorbornane-2-*endo*-carbonyl chloride (I, R = Cl) and methanol, on the other hand, gave 2-*exo*-bromo-2-*endo*-carbomethoxynorbornane (I, R = OCH_3) whose structure was established by hydrogenolysis to 2-*endo*-carbomethoxynorbornane (III, R = OCH_3)[15] and by saponification to norbornane-2-*endo*-carboxylic acid (III, R = OH).[4]

The Diels–Alder reaction of cyclopentadiene with α-bromoacrylic acid gave a mixture of stereoisomeric 5-bromo-2-norbornene-5-carboxylic acids from which one of the isomers was separated by fractional crystallization. While our investigation was under way Alder and his co-workers[16] showed this isomer to be 5-*exo*-bromo-2-norbornene-5-*endo*-carboxylic acid by means of the iodolactonization reaction[17] and selectively hydrogenated the double bond in the presence of ethyl acetate and platinum oxide to form 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid (I, R = OH). The condensation of cyclopentadiene with methyl α-bromoacrylate gave a mixture of stereoisomeric 5-bromo-5-carbomethoxy-2-norbornenes which, however, could not be saponified without extensive decomposition. Catalytic hydrogenolysis of 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid (I, R = OH) gave only norbornane-2-*endo*-carboxylic acid (III, R = OH). With diazomethane it gave the ester I (R = OCH_3) whose infrared spectrum was identical with that of the ester obtained from 2-*exo*-bromonorbornane-2-*endo*-carbonyl chloride (I, R = Cl) and methanol.

When 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid was subjected to the conditions which brought about thermal isomerization of the bromocarboxamide I (R = NH_2), the infrared absorption spec-

(5) G. Komppa and S. Beckmann, *Ann. Acad. Sci. Fennicae*, **A39**, No. 7 (1934).
(6) E. Ott and K. Krämer, *Ber.*, **68**, 1655 (1935).
(7) K. Alder and F. Brochhagen, *Chem. Ber.*, **87**, 167 (1954).
(8) W. P. Whelan, Jr., Dissertation, Columbia University, 1952.
(9) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).
(10) A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956).
(11) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 254.
(12) J. Houben and E. Pfankuch, *Ann.*, **501**, 219 (1934).
(13) W. von E. Doering and E. F. Schoenewaldt, THIS JOURNAL, **73**, 2333 (1951).
(14) C. S. Marvel in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 523.
(15) H. Bode, *Ber.*, **70**, 1167 (1937).
(16) K. Alder, R. Hartmann and W. Roth, *Ann.*, **613**, 6 (1958).
(17) C. D. Ver Nooy and C. S. Rondestvedt, Jr., THIS JOURNAL, **77** 3583 (1955).

trum suggested that a partial rearrangement to 2-*exo*-bromonorbornane-1-carboxylic acid had taken place. 2-*exo*-Bromo-2-*endo*-carbomethoxynorbornane (I, R = OCH_3), however, appears to be quite stable under these conditions.

Experimental[18]

2-*exo*-Bromonorbornane-2-*endo*-carbonyl Chloride (I, R = Cl).—A solution of 46.2 g. (0.33 mole) of norbornane-2-*endo*-carboxylic acid[4] in 75 ml. of thionyl chloride was refluxed for 2 hours. Bromine (64.0 g., 0.4 mole) was added dropwise in 4 hours at the boiling point and refluxing was continued for one hour longer. Distillation through a short Vigreux column gave 67.8 g. (87%) of faintly yellow liquid, b.p. 103–109° (9 mm.); infrared absorption maxima[19]: 10.38(m), 10.53(s), 10.67(m), 10.96(w), 11.13(m), 11.31(s), 11.45(m), 11.74(s), 11.95(s), 12.33(m), 12.47(m), 12.97(s), 13.08(s), 13.23(m) and 13.98(s) μ.

Anal. Calcd. for $C_8H_{10}BrClO$: C, 40.45; H, 4.24. Found: C, 40.81; H, 4.63.

2-*exo*-Bromonorbornane-2-*endo*-carboxamide (I, R = NH_2).—A solution of 23.7 g. of 2-*exo*-bromonorbornane-2-*endo*-carbonyl chloride in 200 ml. of ice-cold toluene was saturated with gaseous ammonia. The suspension was allowed to stand overnight, heated on the steam-bath and filtered while hot. Upon cooling the filtrates deposited 7.9–9.8 g. (61–75%) of colorless crystals, m.p. 110–114°. Several recrystallizations from toluene raised the melting point to 120–121°; infrared absorption maxima: 9.83(s), 10.11(w), 10.40(w), 10.53(m), 10.72(m), 10.78(m), 11.31(w), 11.74(w), 12.22(w), 12.50(w), 12.79(w), 13.07(w), 13.59(m), 14.20(m) and 14.98(w) μ.

Anal. Calcd. for $C_8H_{12}BrNO$: C, 44.05; H, 5.55; N, 6.43; Br, 36.64. Found: C, 44.34; H, 5.62; N, 6.26; Br, 36.30.

Hydrogenolysis of 2-*exo*-Bromonorbornane-2-*endo*-carboxamide (I, R = NH_2). **Procedure A.**—One-half gram of 2-*exo*-bromonorbornane-2-*endo*-carboxamide was dissolved in 5 ml. of acetic acid. One gram of zinc dust was added in portions during 10 minutes with stirring. Stirring was continued for one hour longer, 25 ml. of water was added and the mixture was allowed to stand overnight. The suspension was extracted with ether and the extracts were evaporated. Several crystallizations of the residue from water gave glistening plates of norbornane-2-*endo*-carboxamide (III, R = NH_2), m.p. 210–211° (reported[1] m.p. 210.5–211.5°).

Procedure B.—A solution of 2.5 g. of 2-*exo*-bromonorbornane-2-*endo*-carboxamide in 150 ml. of methanol containing 4 ml. of 5% palladium chloride solution and 2.0 g. of precipitated calcium carbonate was hydrogenated at 3 atm. pressure. The suspension was filtered and the solvent was removed by distillation. Several crystallizations of the residue from water gave norbornane-2-*endo*-carboxamide (III, R = NH_2), m.p. 210–211°.

Rearrangement of 2-*exo*-Bromonorbornane-2-*endo*-carboxamide (I, R = NH_2).—(a) Ten and one-half grams of 2-*exo*-bromonorbornane-2-*endo*-carboxamide was heated rapidly with stirring to 150–160° in a preheated oil-bath and held at this temperature for three minutes. The cooled melt, upon crystallization from toluene, gave 8.0 g. (76%), m.p. 172–173.5°. For analysis a sample was recrystallized from toluene, m.p. 173–174°; infrared absorption maxima: 10.15(w), 10.45(m), 10.63(m), 10.80(w), 11.74(w), 12.14(w), 12.68(w), 13.10(w), 13.30(w) and 14.49(m) μ.

Anal. Calcd. for $C_8H_{12}BrNO$: C, 44.05; H, 5.55; N, 6.43; Br, 36.64. Found: C, 44.28; H, 5.62; N, 6.34; Br, 36.76.

(b) One-fourth gram of 2-*exo*-bromonorbornane-2-*endo*-carboxamide was dissolved in 20 ml. of methanol containing 2.0 ml. of 50% aqueous potassium hydroxide. The solution was allowed to stand at room temperature for 6 hours and evaporated on a watch glass in an air-stream. The residue then was extracted with hot toluene. Upon cooling, the extract deposited a crystalline product (m.p. 169–171°) which was recrystallized from toluene, m.p. 173–174°.

2-*exo*-Bromonorbornane-1-carboxylic Acid (II, R = OH).—A mixture of 60.0 g. (0.43 mole) of norbornane-2-*endo*-carboxylic acid (prepared by hydrogenation of 2-norbornene-5-*endo*-carboxylic acid[15] in the presence of acetic acid and palladium oxide at 3 atm. pressure), 1 ml. of phosphorus trichloride and 73.6 g. (0.46 mole) of bromine was heated in an oil-bath at 75–80° for 8 hours. An additional 36.8 g. (0.23 mole) of bromine then was added and heating was continued for 4 hours longer at 75–80°. The reaction mixture, which solidified on cooling, was crystallized from isoöctane or from toluene. The colorless product (43.0 g., m.p. 141–143° from toluene) was recrystallized twice (31.0 g., m.p. 150–151° from toluene); infrared absorption maxima: 10.19(m), 10.50(s), 10.62(s), 10.78(s), 11.00(m), 11.83(m), 12.16(w), 13.05(w) and 13.50(s) μ.

Anal. Calcd. for $C_8H_{11}BrO_2$: C, 43.85; H, 5.06. Found: C, 43.58; H, 5.31.

An additional 28.5 g. (m.p. 147–149°) was obtained by working up the filtrates. 2-*exo*-Bromonorbornane-1-carboxylic acid boils with decomposition at approximately 100–118° (0.1 mm.).

2-*exo*-Bromonorbornane-1-carbonyl Chloride (II, R = Cl).—2-*exo*-Bromonorbornane-1-carboxylic acid (10.0 g.) and 10 ml. of thionyl chloride were refluxed for two hours and distilled through a short Vigreux column. The colorless distillate (7.8 g., 72%, b.p. 122–126° (9 mm.)) solidified to a granular cake (m.p. 50–52°) on cooling. A sample recrystallized from pentane melted at 51.5–52.5°; infrared absorption maxima: 10.20(m), 10.46(m), 10.63(m), 10.79(m), 10.93(w), 11.30(w), 11.72(s), 12.16(s), 12.36(s), 13.07(m), 13.49(s), 14.00(m) and 14.93(w) μ.

Anal. Calcd. for $C_8H_{10}BrClO$: C, 40.45; H, 4.24. Found: C, 40.36; H, 4.14.

2-*exo*-Bromonorbornane-1-carboxamide (II, R = NH_2).—A solution of 2.5 g. of 2-*exo*-bromonorbornane-1-carbonyl chloride in 50 ml. of anhydrous ether was saturated with gaseous ammonia. The solvent was allowed to evaporate and the residue was extracted with hot toluene. Upon cooling, the toluene solution deposited 2-*exo*-bromonorbornane-1-carboxamide (m.p. 168–169°) which was recrystallized from toluene, m.p. 173–174°.

Hydrogenolysis of 2-*exo*-Bromonorbornane-1-carboxamide (II, R = NH_2).—Reduction of 2-*exo*-bromonorbornane-1-carboxamide by either procedure a or b above gave norbornane-1-carboxamide (IV, R = NH_2), m.p. 234–236° from water.

Saponification of the hydrogenolysis product by refluxing with 20% potassium hydroxide solution and subsequent acidification with hydrochloric acid precipitated norbornane-1-carboxylic acid, m.p. 108–110°. When crystallized from pentane it melted at 111–112° (reported m.p. 112–113°,[8] 113.8–115.5°[9]).

Norbornane-1-carboxamide (IV, R = NH_2).—A solution of 5.0 g. of norbornane-1-carboxylic acid[8,9] in 50 ml. of chloroform and 10 ml. of thionyl chloride was refluxed for 2 hours. The chloroform and excess thionyl chloride were removed by distillation under reduced pressure. The residue of norbornane-1-carbonyl chloride (4.7 g.) was dissolved in 100 ml. of anhydrous ether and saturated with gaseous ammonia. The suspension was allowed to evaporate and the residue was crystallized from water, m.p. 235–236°.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.75; H, 9.25; N, 9.92.

5-Bromo-5-carbomethoxy-2-norbornene.—A solution of 138 g. (0.835 mole) of methyl α-bromoacrylate,[20] 82.5 g. (1.25 moles) of freshly distilled cyclopentadiene and 0.5 g. of hydroquinone in 100 ml. of toluene was heated at 125° for 10 hours in sealed glass tubes. Fractionation of the light brown liquid gave 171.7 g. (89%), b.p. 94–95° (4.5 mm.), $n^{25}D$ 1.5123.

Anal. Calcd. for $C_9H_{11}BrO_2$: C, 46.77; H, 4.80. Found: C, 47.04; H, 4.86.

2-*exo*-Bromonorbornane-2-*endo*-carboxylic Acid (I, R = OH).—5-*exo*-Bromo-2-norbornene-5-*endo*-carboxylic acid (m.p. 157–158°) was prepared by a method similar to that

(18) Melting points are uncorrected. Analyses and infrared spectra by Mr. E. R. Hoffmann and Miss Mary Grace Comfort of these laboratories.

(19) Infra-red spectra were determined with a model 21 Perkin-Elmer spectrophotometer. Solids were measured as potassium bromide pellets and liquids as capillary films between potassium bromide plates.

(20) C. S. Marvel and J. C. Cowan, THIS JOURNAL, **61**, 3156 (1939).

of Alder and co-workers[16] and hydrogenated to 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid (m.p. 131–132°, reported[16] m.p. 134°) in the presence of acetic acid and platinum oxide catalyst; infrared absorption maxima: 10.45(m), 10.60(s), 10.70(s), 11.08(s), 11.32(s), 11.79(m), 12.38(m), 12.87(m), 13.08(m), 13.72(s) and 15.32(m) μ.

Hydrogenolysis of 2-*exo*-Bromonorbornane-2-*endo*-carboxylic Acid (I, R = OH).—One-fourth gram of 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid was dissolved in an ice-cold solution of 0.5 g. of potassium hydroxide in 25 ml. of methanol and hydrogenated[21] in the presence of palladium–charcoal catalyst at 3 atm. pressure. The catalyst was removed by filtration and the solvent was distilled under reduced pressure. The residue was taken up in 10 ml. of water and acidified with concentrated hydrochloric acid. The precipitated norbornane-2-*endo*-carboxylic acid (m.p. 58–60°) was recrystallized from pentane, m.p. 65–66° (reported[4] m.p. 65–66°).

2-*exo*-Bromo-2-*endo*-carbomethoxynorbornane (I, R = OCH_3). (a) **From I (R = Cl).**—A solution of 25 g. of 2-*exo*-bromonorbornane-2-*endo*-carbonyl chloride in 100 ml. of cold methanol was allowed to stand for one hour at room temperature and the solvent was removed by distillation under reduced pressure on the steam-bath. The residue was taken up in ether, washed with saturated sodium bicarbonate solution and dried superficially by shaking for several minutes with anhydrous magnesium sulfate. Distillation of the ether solution gave 22.0–23.2 g. (90–95%), b.p. 97–99° (5 mm.), $n^{24.5}$D 1.5043; infrared absorption maxima: 10.33(w), 10.54(w), 10.63(m), 10.87(m), 11.33(w), 11.58(w), 11.77(w), 12.12(w), 12.35(w), 12.80(w), 13.08(w), 13.30(w), 14.45(m) and 14.55(m) μ.

Anal. Calcd. for $C_9H_{13}BrO_2$: C, 46.37; H, 5.62. Found: C, 46.42; H, 5.36.

(b) **From I (R = OH).**—One gram of 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid was dissolved in ether and esterified with an excess of diazomethane in ether. When the evolution of nitrogen had subsided the solution was distilled under reduced pressure. The distillate (1.0 g.) boiled at 120–121° (28 mm.), n^{25}D 1.5041.

Hydrogenolysis of 2-*exo*-Bromo-2-*endo*-carbomethoxynorbornane (I, R = OCH_3).—Reduction of 2-*exo*-bromo-2-*endo*-carbomethoxynorbornane with hydrogen in the presence of methanol, palladium chloride and calcium carbonate or with zinc and acetic acid by the procedures employed for the reduction of compound I (R = NH_2) gave 2-*endo*-carbomethoxynorbornane (III, R = OCH_3), b.p. 70–71° (5 mm.), $n^{24.5}$D 1.4630 (reported[15] b.p. 82° (15 mm.)).

Saponification of the debrominated ester by refluxing for one hour with 20% aqueous potassium hydroxide solution and subsequent acidification with concentrated hydrochloric acid gave norbornane-2-*endo*-carboxylic acid (m.p. 65–66° from pentane).

2-*exo*-Bromo-1-carbomethoxynorbornane (II, R = OCH_3).—An excess of ethereal diazomethane (from 21.5 g. of N-methyl-N-nitroso-*p*-toluenesulfonamide) was added dropwise to a solution of 10.5 g. of 2-*exo*-bromonorbornane-1-carboxylic acid in 250 ml. of ether. Distillation of the solution after the reaction had subsided gave 10.9 g. (98%), b.p. 117–118° (5 mm.), $n^{24.5}$D 1.5055; infrared absorption maxima: 10.18(m), 10.25(m), 10.32(s), 10.59(s), 10.71(m), 11.01(m), 11.79(m), 12.18(w), 12.45(m), 13.05(m) and 13.39(m) μ.

Anal. Calcd. for $C_9H_{13}BrO_2$: C, 46.37; H, 5.62. Found: C, 46.25; H, 5.72.

Hydrogenolysis of 2-*exo*-Bromo-1-carbomethoxynorbornane (II, R = OCH_3).—Reduction of this ester by either of the procedures employed for compound I (R = NH_2) gave, after saponification with 20% aqueous potassium hydroxide solution and acidification with concentrated hydrochloric acid, norbornane-1-carboxylic acid (m.p. 111–112° from pentane).

Hydrogenolysis of 2-*exo*-Bromonorbornane-1-carboxylic Acid (II, R = OH).—An ice-cold solution of 21.9 g. of 2-*exo*-bromonorbornane-1-carboxylic acid and 16.8 g. of potassium hydroxide in 200 ml. of water was hydrogenated at 3–4 atm. pressure in the presence of palladium–charcoal catalyst. The absorption of hydrogen was complete in one hour and the catalyst was removed by filtration. The filtrate was acidified with concentrated hydrochloric acid, the precipitate was filtered off, washed with a little cold water and dried over calcium chloride *in vacuo*. The crude product (12.8 g., m.p. 109–111°) was purified by sublimation[8,9] *in vacuo* to give 12.2 g. (87%) of norbornane-1-carboxylic acid, m.p. 111–112°.

SOMERVILLE, N. J.

(21) L. F. Fieser and W. T. Huang, THIS JOURNAL, **75**, 4837 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Course of Bromination in Bicyclo[2.2.1]heptanecarboxylic Acids; the Observation of Rearrangement During a Reduction of β-Bromoacids

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The bromination of both *exo*- and *endo*-norbornane-2-carboxylic acids produced the identical bromoacid derivative using PCl_3 and Hell–Volhard–Zelinsky conditions. Bromination in thionyl chloride solution yielded an isomeric bromoacid derivative. The rearranged structure IIIc is assigned to the former and structure VI (R = H) to the latter on the basis of evidence of hydrogenolysis with palladium–charcoal–hydrogen, zinc–acetic acid, and lithium aluminum hydride and, finally, decisive evidence deduced from nuclear magnetic resonance measurements. Reversal of Wagner–Meerwein rearrangement is established for the course of $LiAlH_4$ hydrogenolysis of III. The higher rate of formation of the product on bromination of the *endo*-acid I is correlated with the greater ease of abstraction of an *exo* (equatorial) proton in the formation of the enolic intermediate in the bromination reaction. The hydrogenolysis reaction with zinc in acetic acid which involves the same intermediate apparently exhibits the same preference for equatorial attack. The formation of the rearranged bromoacid IIIc has also been noted to occur in good yield on direct bromination in the absence of PCl_3, $SOCl_2$ or any extraneous solvent. The ready solvolysis of the bromine in the bromoacid chloride of IIIa has been observed during attempts to prepare the pure bromoacid of IIIa. These and other results have been considered in a discussion of the factors that produce Wagner–Meerwein rearrangement of the IIIa bromoacid derivatives.

In the course of studies on the bromination of the *endo*- and *exo*-norbornane-2-carboxylic acids, hydrogenolysis of the common bromination product III under a variety of conditions was explored as a possible means of establishing the stereochemistry of the reaction. Treatment of the methyl ester of III with zinc and acetic acid furnished the norbornane-1-carboxylic ester (VIII) in good yield. Reduction of the ester III with lithium aluminum hydride, on the other hand, furnished the *endo*-2-methylolnorbornane (VII). These results permit two alternative interpretations: (a) either that hydrogenolysis with zinc–acetic acid had led to rearrangement, or (b) that carbon skeleton rearrangement had occurred in both the bromination and the lithium aluminum hydride