groups), 2975, 2865, 1455, 1380 (methyl group), 3095, 1305, 950 (vinyl hydrogens), 2890 (methine hydrogen), and 1650 cm^{-1} (double bond).

The nmr spectrum gave peaks at δ^{CDCl_3} 6.0 (2 H) complex (vinyl protons), 4.4–3.9 (19 H) complex (ferrocenyl protons and methine proton), and 1.88 (3 H) doublet, J = 7.0 cps (methyl protons).

The electronic spectrum gave $\lambda_{max}^{95\% ethanol}$ 207 mμ (log ϵ 5.02), 272 (4.20), 330 sh (2.59), and 450 (2.59).

The mass spectrum[2] calculated for $C_{24}H_{24}Fe_2$[7] had values of P = 424 (100), P − 2 (12.7), P + 1 (32.0), and P + 2 (0.72). Values found were P = 424 (100), P − 2 (8.3), P + 1 (27.1), and P + 2 (0.8).

The structure assignment of 1,3-diferrocenyl-1-butene was further corroborated by the results obtained from ozonolysis.[3] The ozonide produced from 1,3-diferrocenyl-1-butene (100 mg, 0.236 mmole) was directly treated with lithium aluminum hydride to give a yellow solid (36 mg, 32% yield) which was shown by means of thin layer chromatography to consist of two components, one of which had an R_f identical with authentic hydroxymethylferrocene (**5**), while the other presumably was the unknown 2-ferrocenyl-1-propanol (**6**). The infrared and nmr spectra determined from the mixture were both consistent with the presence of only these two components.

Treatment of 1-Ferrocenylethanol with Acid-Washed Alumina in Ether at Room Temperature.—1-Ferrocenylethanol (419 mg, 1.93 mmoles) was added to a separatory funnel containing 4 g of acid-washed alumina and 15 ml of anhydrous ether. The acid-washed alumina was prepared by shaking 16 g of Alcoa alumina with 20 ml of water containing 1 ml of concentrated sulfuric acid followed by three successive washes with water. Activation of the alumina was accomplished by 30 min of heating over a medium Bunsen burner flame. After the ethereal solution of the carbinol was shaken with the alumina during 10 min at room temperature, the alumina was collected in a filter and washed with several portions of ether. Evaporation of the total ethereal solution left a red oil which was taken up in a minimum volume of hexane and carefully washed onto the top of an alumina (Alcoa) column. Elution with hexane provided **vinylferrocene**, 94 mg (22% yield), identified through its infrared spectrum. Elution with 1:1 (v/v) ethanol:hexane gave two bands. The faster-moving band yielded 1,3-diferrocenyl-1-butene, 144 mg (35% yield), while recovered **1-ferrocenyl-carbinol**, 36 mg (8.8% recovery), was obtained from the slower-moving band.

Treatment of 1-Ferrocenylethanol with Neutral Alumina in Refluxing Benzene.—A solution of 1-ferrocenylethanol (0.85 g, 3.7 mmoles) in 50 ml of benzene was mixed with 10 g of previously activated (100° for several hours) neutral alumina (Baker) and heated under gentle reflux during 2 hr. The material obtained from evaporation of the benzene solution was chromatographed on neutral alumina to give **vinylferrocene**, 0.33 g (42% yield), mp 48–49° (lit.[1,8,9] mp 45–48°, 48–49°, 49–50°).

Registry No.—**1**, 12125-65-4; **4** (*cis*), 12125-67-6; **4** (*trans*), 12125-66-5.

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[7] Calculations were based upon relative natural isotope abundances: "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Co., Cleveland, Ohio, 1965, p B-4 ff.

[8] F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).

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A New Synthesis of 2-*exo*-Brendanol[1]

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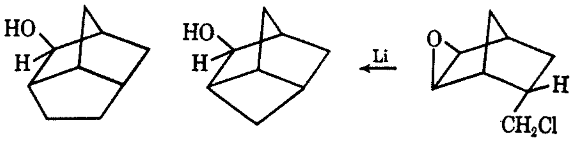
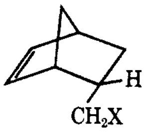
We would like to report a new synthesis of the interesting tricyclic alcohol 2-*exo*-brendanol (**1**). At the inception of this project, this ring system was unreported and represented a challenging synthetic problem. In addition, it was desired to explore the scope of the ring-closure reaction (**3** → **2**) developed for the synthesis of the tricyclo[3.2.1.0^{3,6}]octane system (**2**).[2]

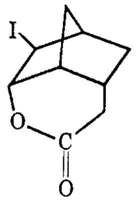


1 **2** **3**

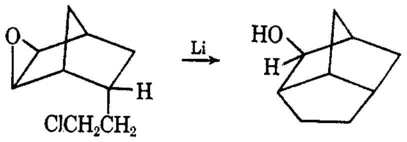
To this end, a synthesis of the homologous epoxide **6** was devised. Treatment of a mixture of *exo*- and *endo*-5-norbornene-2-acetic acids with iodine in basic solution yielded the iodo lactone **5** which on treatment with zinc and acetic acid generated the pure *endo* acid **4a**. Reduction of **4a** with lithium aluminum hydride yielded the carbinol **4b**,[3] which was converted to the corresponding chloride **4c** on treatment with thionyl chloride. The desired epoxide **6** was obtained on reaction of **4c** with buffered peracetic acid. Attempted cyclizations with magnesium and lithium ribbon were unfruitful.[4] The use of finely dispersed lithium[5] in tetrahydrofuran gave 50% yields of a volatile alcohol (eq 1). Gas chromatographic analysis revealed essentially one component. This material proved to be pure 2-*exo*-brendanol by comparison of its infrared and nmr spectra with those of an authentic sample.[6] Apparently, no substantial amounts of the isomeric ring system with a 2,5 bridge were formed.



4a, X = CO_2H
b, X = CH_2OH
c, X = CH_2Cl



5



(1)

6 **1**

Experimental Section

Microanalyses were performed by W. Manser, Herliberg, Switzerland, and by Micro-Tech Laboratories, Skokie, Ill. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Nuclear magnetic resonance data were obtained on a Varian Model A-60 spectrometer in carbon tetrachloride with tetramethylsilane as an internal standard. Infrared spectra were determined on either a Perkin-Elmer Model 137 spectrophotometer or a Beckman IR-5A spectrophotometer. Gas chromatograms were obtained on a Wilkens Aerograph Model A 90 P using a 15 ft by 0.25 in. (o.d.) aluminum column packed with 10% Carbowax 20M on Chromosorb G.

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[1] A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1615 (1965); A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Letters*, 2851 (1967); R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, **89**, 880 (1967).

[2] R. R. Sauers, R. A. Parent, and S. B. Damle, *ibid.*, **88**, 2257 (1966).

[3] E. Allred and Jr. Maicich, *Tetrahedron Letters*, **15**, 949 (1963).

[4] Cyclization attempts were carried out on an *exo*, *endo* mixture of the chloroethyl epoxide.

[5] Obtained from the Foote Chemical Co. as a 50% dispersion (<100 mesh) in hexane.

[6] We wish to acknowledge the invaluable assistance of Professor A. Nickon in providing unpublished data for this purpose.

***endo*-2-Hydroxy-*exo*-3-iodo-*endo*-6-norbornaneacetic Acid Lactone (5).**—A mixture of 5-norbornene-2-acetic acids[7] was prepared from the Grignard reagent of 5-norbornene-2-methyl chloride.[3,7]

The crude acids (40 g, 0.26 mole) were dissolved in 300 ml of water which contained 18.4 g (0.278 mole) of potassium hydroxide and 15.4 g (0.183 mole) of sodium bicarbonate. A solution of 67.0 g (0.264 mole) of iodine and 82.0 g (0.493 mole) of potassium iodide in 300 ml of water was added with stirring over a period of 1 hr. The resulting mixture was stirred for an additional 0.5 hr at 25°. An additional 20 g of potassium hydroxide in 50 ml of water was added followed by solid sodium bisulfite until the iodine color was discharged. The mixture was cooled with ice and extracted with cold chloroform. The dried ($MgSO_4$) extracts were evaporated to give 55.7 g (76%) of the lactone **5**. Crystallization from absolute ethanol gave an analytical sample, mp 101.5–103°.

Anal. Calcd for $C_9H_{11}O_2I$: C, 38.87; H, 3.99; I, 45.64. Found: C, 39.09; H, 4.01; I, 45.93.

The infrared spectrum (mull) showed carbonyl absorption at 5.70 μ.

***endo*-5-Norbornene-2-acetic Acid (4a).**—The crude iodolactone **5** (55.0 g, 0.2 mole) was dissolved in 1.5 l. of glacial acetic acid and treated with three 10-g portions of zinc dust over a 1.5-hr period. The resulting mixture was stirred for 1 hr at 25°. The solids were removed by filtration and the filter cake was washed with additional acetic acid. The washings were combined with the filtrate and the acetic acid was evaporated *in vacuo*. The residue was dissolved in 250 ml of ether. After several washings with saturated ammonium chloride solution, the ether was dried ($MgSO_4$) and evaporated to give 29 g (96%) of crude **4a**. The infrared spectrum (film) of this material displayed carbonyl absorption at 5.80 and a *cis* double bond band at 13.80 μ.

A small sample was distilled for an analytical sample, bp 104–106° (2.05 mm) (lit.[7] *exo, endo* mixture: bp 143° (12–13 mm)); $n^{25}\text{D}$ 1.4890.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.97; H, 7.91.

Note: Great difficulty was encountered in repetition of this latter experiment without any obvious explanation. It was decided to work with the *exo, endo* mixture in the later stages for this reason. The procedure used is basically that of B. E. Tate and A. Bavely, *J. Am. Chem. Soc.*, 79, 6519 (1957).

***endo*-5-(β-Hydroxyethyl)norbornene (4b).**—The acid **4a** (27.5 g, 0.18 mole) in 200 ml of dry ether was added slowly with stirring to a slurry of 7.5 g (0.2 mole) of lithium aluminum hydride in 1.5 l. of dry ether. After addition was complete, stirring was continued for 1 hr at which time the excess reagent was destroyed by careful addition of water. The resulting slurry was filtered and the ether was removed by evaporation. Distillation of the residue gave 19.4 g (78%) of alcohol **4b**; bp 86.0–86.5° (1.7 mm), $n^{25}\text{D}$ 1.4919 (lit.[3] bp 93–94° (6 mm), $n^{25.3}\text{D}$ 1.4930).

The infrared spectrum showed *cis*-double bond absorption at 13.88 and a C–O stretching band at 9.47 μ.

Several attempts to obtain a carbon–hydrogen analysis gave results ~1.3% low in carbon perhaps due to moisture even after careful collection by gas chromatography.

***endo*-5-(β-Chloroethyl)norbornene (4c).**[8]—A solution of 4.0 g (0.029 mole) of alcohol **4b** in 15 ml of dry benzene and 2.0 ml of pyridine was cooled in an ice bath. A solution of 7.00 g (0.059 mole) of thionyl chloride in 10 ml of benzene was added with stirring over a period of 1 hr. Stirring at ~0° was continued for 0.5 hr. The excess thionyl chloride was destroyed by shaking the reaction mixture with ice. The aqueous phase was extracted with ether and the combined organic phases were evaporated to give 4.15 g (91%) of crude chloride **4c**. Distillation gave 2.53 g (53%) of pure product with bp 87–90° (14 mm); $n^{25}\text{D}$ 1.4984.

Anal. Calcd for $C_9H_{13}Cl$: C, 69.00; H, 8.36; Cl, 22.64. Found: C, 68.60; H, 8.18; Cl, 23.58.

6-(β-Chloroethyl)-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (6).—A solution of 4.0 g (0.0256 mole) of chloride **4c**[9] in 70 ml of chloroform was cooled in an ice–salt bath. A solution of 3.0 g of sodium acetate in 16.0 ml of 40% peracetic acid was added over 15 min.[10] After stirring for an additional 2.5 hr at 15°, the mixture was neutralized with 20% sodium hydroxide solution. The layers were separated and the aqueous phase was extracted three times with chloroform. The combined extracts were dried ($MgSO_4$) and distilled. A residue was obtained which was purified by evaporative distillation at 0.4 mm. There was obtained 3.42 g (79%) of **6**.[9]

Anal. Calcd for $C_9H_{13}OCl$: C, 62.61; H, 7.59; Cl, 20.53. Found: C, 62.38; H, 7.46; Cl, 20.54.

The infrared spectrum (film) showed strong absorption at 11.75 μ, characteristic of epoxides.[11]

***exo*-2-Hydroxytricyclo[4.2.1.$0^{3,7}$]nonane (1).**—A three-necked flask was fitted with a gas inlet tube, a condenser, and a pressure-equalized dropping funnel. The entire apparatus was flame dried under a nitrogen stream. The nitrogen was flushed by a helium stream. A slurry of 4.0 g (~0.36 g-atom) of lithium dispersion[5] in 50 ml of dry tetrahydrofuran was added to the flask. A solution of 2.8 g (0.0162 mole) of **6** in 30 ml of tetrahydrofuran was added over 10 min with continuous agitation by a magnetic stirrer. The resulting mixture was heated at reflux for 42 hr after which it was poured onto crushed Dry Ice. Dilute hydrochloric acid was added until the resulting solution was acidic to litmus. The water layer was extracted with ether and the combined extracts were washed with sodium bicarbonate solution. The dried extracts were evaporated carefully to yield a light yellow residue. Sublimation of this material at 100° using an oil pump gave 1.0 g (53%, based on 85% epimeric purity) of a semisolid. Purification by gas chromatography (>90% homogeneity) gave a white solid, mp 129–130° (lit.[6] 133.5–134.5°). The infrared and nmr spectra of this material were identical with those of authentic samples.[6]

Registry No.—1, 14805-44-8; **4a**, 14734-13-5; **4b**, 14734-14-6; **4c**, 14734-15-7; **5**, 14734-16-8; **6** (*exo*), 14754-85-9; **6** (*endo*), 14754-86-0.

Acknowledgments.—Financial support from the Colgate-Palmolive Co. and the National Institutes of Health (RG-08701) is gratefully acknowledged.

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[7] K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

[8] C. R. Noller and R. A. Bannerot, *J. Am. Chem. Soc.*, **56**, 1563 (1934).

[9] An *exo*, *endo* mixture (15:85) was used in this experiment and the product was carried through the cyclization steps without separation into the pure *endo* isomer.

[10] H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

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L-Proline-N-oxalic Anhydride[1]

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As part of an investigation of oxalyl derivatives of α-amino acids,[2] we have prepared the cyclic N-oxalic anhydride (I) of L-proline by treatment of the amino acid in an inert solvent with excess oxalyl chloride. To our knowledge, the only N-oxalic anhydride of an α-amino acid previously reported is that of 4-carbomethoxy-5,5-dimethylthiazolidine-2-carboxylic acid, obtained in the same manner.[3]

In both of these cases the N atom acylated was in the form of a secondary amine in a five-membered ring.

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[1] Journal Paper No. J-5677 of the Iowa Agricultural and Home Economics Experiment Station, Ames, Iowa, Project No. 1384. Abstracted from the Ph.D. Thesis of R. E. Worthington, Iowa State University, Ames, Iowa, 1961.

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