chromatographed over 200 g of Woelm (neutral, grade I) aluminum oxide. Elution with ether–ethanol (20:1) gave a crude solid which was purified by recrystallization from cyclohexane to give 2 g (17%) of Ic, mp 120–125°.

Acknowledgment.—The authors are indebted to the National Cancer Institute for U. S. Public Health Service Grant CA-07806, which supported this investigation. We also are grateful to Dr. Bernard Friedman, Sinclair Oil Co., for a generous supply of several olefins and to the Stauffer Chemical Co. for the phenylphosphonous dichloride.

Alumina-Catalyzed Dehydration of 1-Ferrocenylethanol. Formation of 1,3-Diferrocenyl-1-butene

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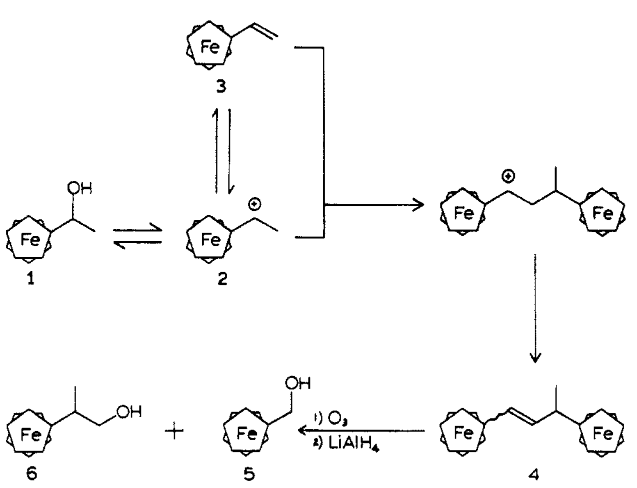
In 1961, Schlögl and Mohar[1] reported that a brief, room-temperature treatment of 1-ferrocenylethanol (**1**) with acidic Woelm alumina (Brockmann activity I) provided a mild means of effecting dehydration of the carbinol to vinylferrocene (**3**) in about 50% yield. We have found that relatively slight variations in the procedure leads to the formation of 1,3-diferrocenyl-1-butene (**4**).

Thus treatment of 1-ferrocenylethanol with acidic alumina (Merck) in refluxing benzene during 2 hr gave the olefin (**4**) in 77% yield. The structure of the product, possibly a mixture of the *cis* and *trans* forms, was established by the spectrometric data determined from the red, viscous liquid. Its mass spectrum[2] displayed the parent ion peak at 424, and the relative intensities of the P − 2, P + 1, and P + 2 peaks were found to be consistent with the molecular formula, $C_{24}H_{24}Fe_2$. The nmr spectrum showed the presence of the two vinyl protons, the methyl group attached to methine carbon, and the 19 other protons as a broad array of complex signals. The disubstituted, conjugated, olefinic linkage was also clearly indicated in the electronic and infrared spectra obtained from the purified reaction product. The structural assignment was also strengthened by the results obtained from ozonolysis.[3] Lithium aluminum hydride reduction of the ozonide produced from a portion of the purified reaction product gave rise to a two-component mixture; one of which was shown to be hydroxymethylferrocene (**5**), while the other component presumably was the unknown alcohol (**6**).

The formation of 1,3-diferrocenyl-1-butene may be rationalized in terms of the 1-ferrocenylethyl cation (**2**) as illustrated in Scheme I. This rationalization is supported by the fact that both **3** and **4** were obtained when the reaction was carried out for only 30 min at room temperature. A more complete description of the mechanism is not possible, however, principally because of the difficulty in assigning the detailed role which the alumina must play. In this regard it is interesting to note that the use of alkaline alumina, even in refluxing benzene for 2 hr, produces only vinylferrocene and not 1,3-diferrocenyl-1-butene.

SCHEME I



An important aspect of this work, in addition to providing a convenient means for the preparation of 1,3-diferrocenyl-1-butene, lies in the fact that all previously reported dimerizations arising from ferrocenylcarbinyl cations are believed to occur *via* radical coupling processes.[4] The present work represents the first-recognized case of a dimerization to which the radical coupling mechanism does not apply, but one which appears to be best-explained in terms of the ionic addition mechanism.

Experimental Section

General.—Temperature measurements were not corrected. Infrared, electronic, and nmr spectra were determined, respectively, on a Perkin-Elmer Model 337 spectrometer, a Perkin-Elmer Model 202 spectrometer, and a Varian A-60 spectrometer. Standard references[5] were used in guiding the interpretation of the spectrometric data.

Treatment of 1-Ferrocenylethanol with Acid-Washed Alumina in Refluxing Benzene.—1-Ferrocenylethanol (0.85 g, 3.7 mmoles), dissolved in 50 ml of benzene, was mixed with 10 g of acid-washed alumina (Merck), which was previously activated (100° for several hours). The mixture was heated under reflux during 2 hr and then allowed to cool to room temperature. After the blue-green alumina was collected in a filter, it was washed with several small portions of benzene. The original benzene filtrate was combined with the washings, and the whole evaporated to **1,3-diferrocenyl-1-butene** (**4**), 0.60 g (77% yield). A portion of the deep red liquid was molecularly distilled [55° (air-bath, 0.25 mm)] to obtain a sample from which the following data were obtained.[6]

The infrared spectrum gave ν^{CCl_4} 3095, 1105, 1000 (ferrocenyl

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[1] K. Schlögl and A. Mohar, *Naturwiss.*, **48**, 376 (1961).

[2] Obtained through the courtesy of Dr. H. M. Fales, National Heart Institute, to whom we acknowledge our sincere thanks.

[3] A general procedure for the ozonolysis of olefinic systems containing a ferrocenyl group, which avoids destruction of the latter, has been recently developed in this laboratory, the details of which will be published elsewhere.

[4] For examples and discussion see, M. Rosenblum, "Chemistry of the Iron Group Metallocenes," John Wiley and Sons, New York, N. Y., 1965, p 121 ff.

[5] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958; K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962; R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966; L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959; J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall Co., Inc., Englewood Cliffs, N. J., 1965; R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

[6] The infrared spectrum of the initially obtained reaction product did not differ significantly from that determined with the distilled material, indicating a relatively high purity of the former.

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 $\delta^{\mathrm{CDCl_3}}$ 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 $\lambda_{\max}^{95\%\,\mathrm{ethanol}}$ 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).

[9] G. R. Buell, W. E. McEwen, and J. Kleinberg, *ibid*, **84**, 40 (1962).

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

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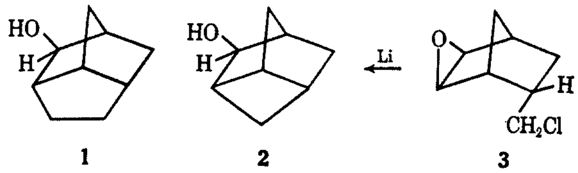
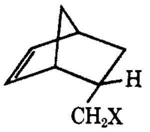
We would like to report a new synthesis of the interesting tricyclic alcohol 2-*exo*-brendanol (**1**). At the inception of this project, this ring system was unreported and represented a challenging synthetic problem. In addition, it was desired to explore the scope of the ring-closure reaction (**3**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

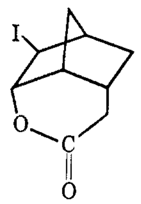


1 **2** **3**

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

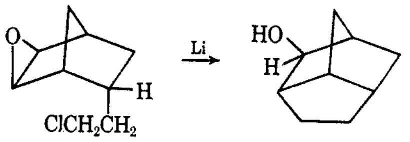


4a, X = CO_2H
b, X = CH_2OH
c, X = CH_2Cl



5

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



6 **1** (1)

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.

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.