Registry No.—Disiamylborane, 1069-54-1; D-galactono-γ-lactone, 2782-07-2; D-glucono-δ-lactone, 90-80-2; D-erythronolactone, 13016-40-5.

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A Three-Step Synthesis of Fichtelite from Abietic Acid

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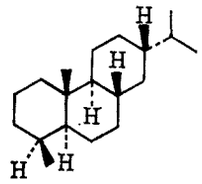
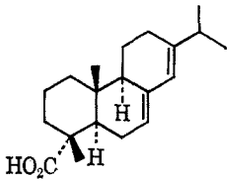
In connection with the proof of the course of a polyolefinic cyclization,[1] we had occasion to develop a convenient synthetic source of authentic fichtelite (I).[2] The following scheme is a somewhat condensed version of one of the approaches described by Burgstahler and Marx.[3]

For the first step of our synthesis we employed the known conversion of abietic acid (II), by reduction of the diamylamine salt with lithium in ammonia, into



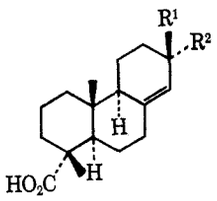
I



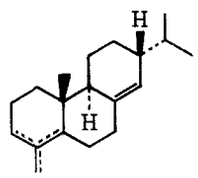
II

$\Delta^{8(14)}$-dihydroabietic acid [III, R^1 = H; R^2 = $CH(CH_3)_2$].[3,4] Four recrystallizations of the crude product afforded, in 24% yield, material, mp 197–198°, $[\alpha]^{26}D$ −24°, which is of only moderate purity.[3]

The second step involved decarboxylation of the dihydro acid by the pyridine–copper salt catalyzed[5] reaction with lead tetraacetate to give, in 76% yield, the diene mixture IV. This type of decarboxylative elimination reaction has been used before in the resin acid series and has been shown to give mainly the isomer with an exocyclic bond.[3,6] It is noteworthy that in our hands the Kochi decarboxylation procedure,[5] when applied to the known[3,7a] tetrahydroabietic acid, mp 182°, that is obtained on hydrogenation of III [R^1 = H, R^2 = $CH(CH_3)_2$], afforded the monoolefinic mixture (8,14-dihydro IV) in 76% yield.



III



IV

The third step amounted simply to catalytic hydrogenation of the diene mixture over platinum oxide in acetic acid. It seemed probable that the stereochemical course of this reaction would be predictable on the basis of the known propensity of such systems with an 8,14-olefinic bond to undergo β hydrogenation[3,7] and of such systems containing an olefinic bond involving C-4 to undergo α hydrogenation.[3] This expectation was realized in that the vapor phase chromatogram of the hydrogenation product showed only two peaks, in the ratio 3:7. The substance corresponding to the latter (major) peak, on separation by preparative vapor phase chromatography, crystallized in the collection tube. This material on a single recrystallization from methanol, melted at 45.8–46.1°, $[\alpha]^{26}D$ +19°. A mixture of this product with a sample of natural fichtelite[8] (I), mp 45.8–46.1°, $[\alpha]^{26}D$ +19°, melted at 45.8–46.1°. The infrared spectrum, as well as the nmr spectrum and gas chromatographic behavior of the synthetic material, was identical with that of the natural product.

For a somewhat simplified preparation of fichtelite in higher over-all yields, it was found that the total crude dihydroabietic acid of the first step could be employed. The hydrogenation product of the third step was shown by gas chromatographic analysis to contain 50% fichtelite. From this mixture it was possible to isolate fichtelite either by preparative gas chromatography or simply by repeated recrystallization from ether–methanol.

Experimental Section[9]

$\Delta^{8(14)}$-Dihydroabietic Acid [III, R^1 = H; R^2 = $CH(CH_3)_2$].—The following is essentially the procedure described by Kennedy.[4b] To a mixture of 400 ml of anhydrous ether and 400 ml of liquid ammonia (distilled from sodium) was added 40.0 g of the diamylamine salt of abietic acid ($[\alpha]^{25}D$ −60°).[10] The resulting light

(1) W. S. Johnson, N. P. Jensen, and J. Hooz, *J. Am. Chem. Soc.*, **88**, 3859 (1966).

(2) J. Simenson and D. H. R. Barton, "The Terpenes," Vol. III, University Press, Cambridge, England, 1952, p 337.

(3) A. W. Burgstahler and J. N. Marx, *Tetrahedron Letters*, 3333 (1964); *J. Org. Chem.*, in press.

(4) (a) E. E. Royals, W. C. Bailey, and R. W. Kennedy, *ibid.*, **23**, 151 (1958); (b) R. W. Kennedy, Ph.D. Thesis, Emory University, 1956; University Microfilm 58-5153.

(5) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 1811 (1965).

(6) See *inter alia* W. A. Ayer, C. E. McDonald, and J. B. Stothers, *Can. J. Chem.*, **41**, 1113 (1963); J. W. Huffman and P. G. Arapakos, *J. Org. Chem.*, **30**, 1604 (1965).

(7) (a) W. Herz and R. N. Mirrington, *ibid.*, **30**, 3198 (1965); J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *ibid.*, **31**, 4128 (1966); (b) J. W. ApSimon, P. V. Demarco, and J. Lemke, *Can. J. Chem.*, **43**, 2793 (1965).

(8) We wish to thank Professor R. E. Ireland for providing us with a sample of natural fichtelite which originally came from Professor O. Jeger, whom we also thank.

(9) Melting points were taken on a Kofler hot-stage microscope unless otherwise indicated. Liquid film specimens were used for the infrared spectra which were determined on Perkin-Elmer 137 and 237B spectrophotometers. Nmr spectra were determined on a Varian A-60 spectrometer. Rotations were determined on 1% solutions in 95% ethanol with a Zeiss circle polarimeter 0.01. Analytical gas chromatographies were carried out on an Aerograph Hy-Fi (A-600) gas chromatograph equipped with a hydrogen flame detector; columns employed were 0.125 in. × 7.5 ft 5% SE-30 silicon rubber on 60–80 Chromosorb W, and 0.125 in. × 7.5 ft 15% Carbowax on 80–100 Chromosorb W. Preparative gas chromatographies were performed on an Aerograph Autoprep (A-700); columns employed were 0.375 in. × 20 ft 20% SE-30 silicon rubber on 60–80 Chromosorb W, and 0.375 in. × 20 ft 20% Carbowax on 45–60 Chromosorb W.

(10) This material was obtained by purification of technical abietic acid (Matheson Coleman and Bell) by the method of G. C. Harris and T. F. Sanderson, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 1.

yellow slurry was stirred while it was brought to reflux temperature; then 6.5 g of freshly scraped 2- to 4-cm pieces of lithium wire was added over a period of 20 min. The mixture was stirred under reflux for 1 hr, and 150 ml of absolute ethanol was then added slowly with stirring over a 1-hr period. The ammonia was removed by distillation through a water-cooled condenser. To the residue were added 150 ml of 95% ethanol, 600 ml of water, and 100 ml of concentrated hydrochloric acid. After standing for 14 hr at room temperature, the acidic mixture was cooled in an ice bath. The resultant precipitate, which was collected by filtration and washed well with water, amounted to 26.5 g (100% yield) of light tan crystals, mp 145–165°, $[\alpha]^{27}D$ +2°. Four recrystallizations of material of this quality from acetone gave a 24% recovery (lit.[4] 25–30%) of colorless, crystalline material, mp 197–198°,[11] $[\alpha]^{27}D$ −24° (lit. mp 195–197°, $[\alpha]D$ −26°;[3] mp 197–197.5°, $[\alpha]^{25}D$ −24.7° [4]).

Decarboxylation of $\Delta^{8(14)}$-Dihydroabietic Acid [III, R^1 = H; R^2 = $CH(CH_3)_2$] to Give the Diene Mixture IV.—In a dry, nitrogen-filled flask were placed 2.00 g of the aforementioned purified dihydroabietic acid (mp 197–198°), 4.0 g of lead tetraacetate, and 50 mg of cupric acetate. To this mixture were added 20 ml of anhydrous benzene (dried over molecular sieves) and 2.0 ml of dry pyridine (distilled from calcium hydride). The system was degassed, filled with nitrogen, and then stirred at reflux under nitrogen for 14 hr. The mixture was cooled and added to 150 ml of ether and 50 ml of water. Ferrous sulfate was added until the aqueous layer was saturated, and the mixture was then acidified with 10% hydrochloric acid. The ether layer was washed successively with three 100-ml portions of saturated brine, 50 ml of saturated sodium bicarbonate solution, and 100 ml of saturated brine, and was then dried over anhydrous magnesium sulfate. The residue, obtained on evaporation of the solvent, was chromatographed on 100 g of Woelm neutral alumina (activity II). Elution with 150 ml of pentane gave 1.30 g (76% yield) of the diene mixture IV. This mixture contained a significant proportion of terminal methylene isomer as evidenced by its infrared spectrum which exhibited strong bands at 6.10 and 11.2 μ. The column was further eluted with 300 ml of 4:1 pentane–methylene chloride containing 1% methanol to give 0.46 g (23% yield) of a material exhibiting strong bands at 5.78 and 8.05 μ (acetate) in the infrared spectrum.

Fichtelite. A. From the Diene Mixture IV.—A 1.30-g portion of the aforementioned diene mixture IV was hydrogenated for 35 min at atmospheric pressure in 70 ml of glacial acetic acid in the presence of 325 mg of platinum oxide. Hydrogen uptake had ceased after 20 min. The mixture was filtered, and the combined filtrate and washings were concentrated, ether was added, and the solution was washed with saturated sodium bicarbonate solution, followed by saturated brine, and then dried over magnesium sulfate. Evaporation of the solvent gave 1.22 g (92% yield) of colorless oil. The gas chromatogram (SE-30, 165°) of this product exhibited two peaks in the ratio 3:7 at retention times of 19 and 22 min. The major fraction, which was separated by preparative gas chromatography over SE-30 at 210°, crystallized in the collection tube and melted at 42.5–45.0°. One recrystallization from methanol gave an 85% recovery of long, colorless blades, mp 45.8–46.1°, $[\alpha]^{26}D$ +19°. A mixture of this product with a sample of natural fichtelite,[8] mp 45.8–46.1°, $[\alpha]^{26}D$ +19°, also melted at 45.8–46.1°. The infrared spectrum, as well as the nmr spectrum and the gas chromatographic behavior of the synthetic product, was also identical with that of the natural material.

As an alternative to preparative gas chromatography for the separation of fichtelite from the 3:7 mixture, recrystallization from ether–methanol at −20° could be employed. No seed crystals were necessary. Two such recrystallizations of the crude mixture gave a 56% recovery of material melting at 40.5–42.5°, which was shown by gas chromatographic analysis to be 90% pure. Seven more recrystallizations gave a 19% recovery of fichtelite (mp 45.8–46.1°), which was more than 99% pure.

B. From Crude Dihydroabietic Acid.—A 2.00-g portion of the aforementioned total crude acid (mp 145–165°) was decarboxylated with 4.0 g of lead tetraacetate in 40 ml of benzene in the presence of 2 ml of pyridine and 50 mg of cupric acetate according to the procedure described above. The crude product was heated in a nitrogen atmosphere at a temperature that was gradually increased from 100 to 175° over a period of 45 min. The temperature was then maintained at 175° for 1 hr in order to decompose the acetate contaminant (see above). The residue was chromatographed on 60 g of Woelm neutral alumina (activity III). Elution with 100 ml of pentane gave 1.53 g (90% yield) of diene mixture, which was hydrogenated for 1 hr at atmospheric pressure in acetic acid in the presence of 400 mg of platinum oxide. Hydrogen uptake had ceased after about 30 min. The product amounted to 1.54 g of almost colorless oil. The gas chromatogram (Carbowax, 190°) exhibited three peaks in the ratio of 1:2:1 with retention times of 24.0, 28.0, and 30.5 min. The major fraction was shown to correspond to fichtelite by the identity of its gas chromatographic retention time with that of authentic material and by separation by preparative gas chromatography. Four recrystallizations of the crude mixture from ether–methanol at −20° gave a 22% recovery of material melting at 42–44.0°, which was shown to be 90% pure by gas chromatography. Five additional recrystallizations gave a 7% recovery (6% over-all yield from abietic acid) of fichtelite (mp 45.8–46.1°), which was shown to be at least 99% pure. A recrystallization scheme, which employed no seed crystals, also gave an over-all yield from abietic acid of approximately 6%. Fichtelite of 98.5% purity (by gas chromatography) melts at the same place as samples of higher purity obtained by further recrystallization.

Registry No.—I, 2221-95-6; II, 514-10-3; III [R^1 = H; R^2 = $CH(CH_3)_2$], 2221-96-7.

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(11) This melting point was taken in a sealed evacuated capillary tube under nitrogen on a Hershberg melting point apparatus.