Identification of Olefin from Rearrangement Studies.—The olefin (0.55 g.) obtained from the acetolysis of the *p*-toluenesulfonate of IA (see paper I of this series) was treated in the usual manner with 2,4-dinitrobenzenesulfenyl chloride, and 0.65 g. of recrystallized product obtained, m. p. 81–82°, not depressed by admixture with the same derivative of an authentic sample of *cis*-2-phenyl-2-butene.

In the same way the olefin (0.12 g.) obtained from the acetolysis of the *p*-toluenesulfonate of IIA (see paper I of this series) was converted to the 2,4-dinitrobenzenesulfenyl chloride addition compound, wt. 90 mg. (recrystallized material), m. p. 81–82°, not depressed by admixture with an authentic sample of the same derivative of *cis*-2-phenyl-2-butene.

Acknowledgments.—The author wishes to thank Welton Burney for the analyses reported in this paper. The use of the reagent, 2,4-dinitrobenzenesulfenyl chloride was made possible through the kindness of N. Kharasch, who provided a sample of the substance and directions for its use, and who also made information available as to the direction of addition of the reagent to the carbon–carbon double bond.

Summary

1. The geometric isomers of 2-phenyl-2-butene have been prepared, configurational assignments have been made on the basis of physical properties, and solid derivatives have been prepared.

2. Evidence has been adduced for the stereospecific addition of 2,4-dinitrobenzenesulfenyl chloride to the carbon–carbon double bond.

3. The Chugaev reaction has been shown to be predominantly a *cis* elimination reaction in an acyclic system.

4. Evidence has been obtained for the relative configurations of all the stereoisomers of 3-phenyl-2-butanol, 2-phenyl-3-pentanol and 3-phenyl-2-pentanol.

5. The formation of olefin during the acetolysis of the *p*-toluenesulfonates of IA and IIA has been shown to be a non-stereospecific reaction.

LOS ANGELES, CALIFORNIA RECEIVED MARCH 14, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of Phellandral[1,2]

BY ROBERT L. FRANK, ROBERT E. BERRY AND ODETTE L. SHOTWELL

Most of the evidence concerning the structure of the terpene phellandral has indicated that this naturally occurring aldehyde is best represented by Structure X.[3,4,5] Cooke, Macbeth and Swanson[5b] have established the structure of the carbon skeleton by hydrogenation of phellandric acid to the known *cis*- and *trans*-hexahydrocuminic acids, and ultraviolet absorption spectra have located the double bond in the position α,β to the carbonyl group.[5a,6] This structure has now been confirmed by the synthesis of *dl*-phellandral through *dl*-phellandric acid, and the resolution of the racemic acid to the *d*-form corresponding to the acid obtained by oxidation of *d*-phellandral. The steps to the aldehyde are represented by Structures I–X.

The starting material, *p*-isopropylphenol (I), was best prepared by sulfonation of cumene, followed by alkali fusion. Methods involving nitration, reduction and diazotization or the alkylation of phenol resulted in mixtures of *o*- and *p*-isopropylphenols.

The hydrogenation and oxidation steps (I–II–III) were straightforward and gave yields of 96 and 82%, respectively.

In the preparation of the cyanohydrin acetate of 4-isopropylcyclohexanone (V) it was expected that treatment of the ketone with acetic anhydride and aqueous potassium cyanide[7] would lead directly to the cyanohydrin acetate. The reaction was tried on cyclohexanone as a model compound, and it was found to yield not the acetate but the cyanohydrin itself. The latter is resistant to acetylation by acetic anhydride, giving only 19% acetylation even in an excess of the reagent. Subsequent experiments showed that if one adds a trace of acetyl chloride to the acetic anhydride, the acetylation proceeds smoothly in good yields (64% with cyclohexanone). The conversion of 4-isopropylcyclohexanone (III) to the cyanohydrin acetate (V) was then carried out in two stages, but without purification of the intermediate cyanohydrin (IV), in a yield of 70%.

The method of Burns, Jones and Ritchie[8] and others[9] for the pyrolysis of esters gave excellent results with 4-isopropylcyclohexanone cyanohydrin acetate (V). The optimum temperature for our ester was 575–600°, which resulted in a small amount of charring in the pyrolysis tube, but nevertheless gave the highest yields (74%) of 4-isopropyl-1-cyano-1-cyclo-

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[1] Presented in part at the St. Louis meeting of the American Chemical Society, 1948, before the Division of Organic Chemistry.

[2] This is the second communication on the chemistry of terpenes. For the first, see THIS JOURNAL, **71**, 1387 (1949).

[3] Schimmel's Report, 1904, Oct., p. 88; Simonsen, "The Terpenes," Cambridge University Press, 2nd edition, 1947, Vol. I, p. 308.

[4] Wallach, *Ann.*, **340**, 13 (1905); **343**, 33 (1905).

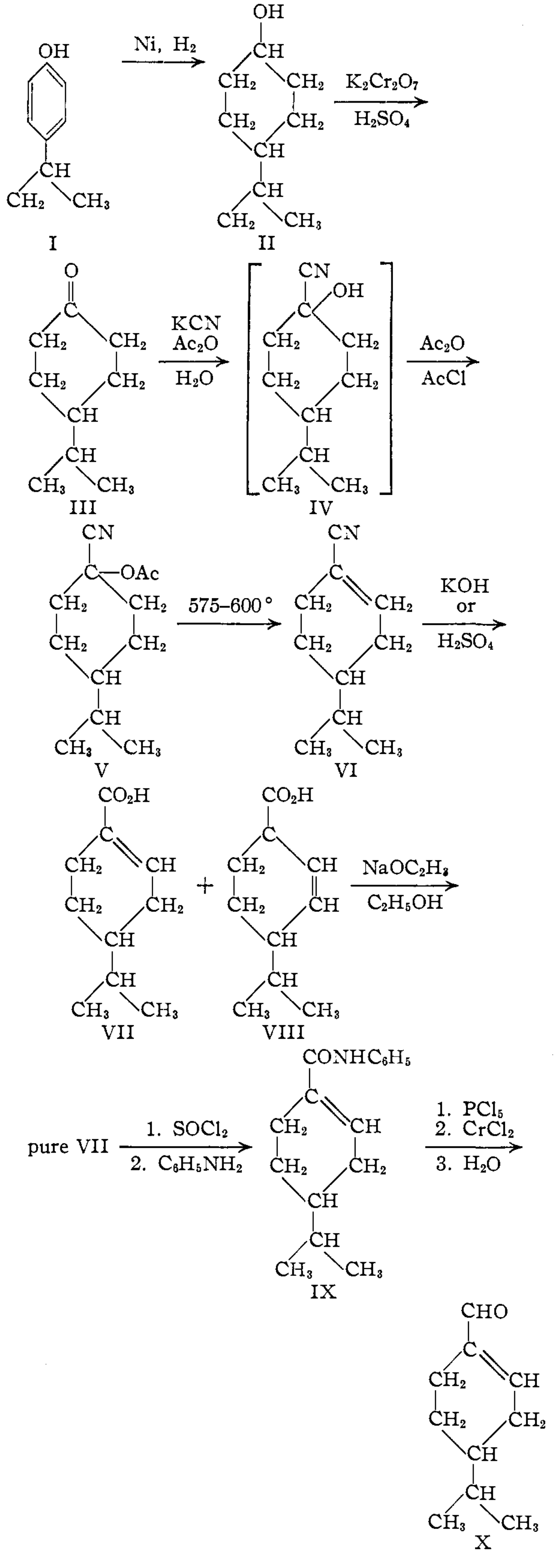
[5] (a) Cooke and Macbeth, *J. Chem. Soc.*, 1408 (1938); (b) Cooke, Macbeth and Swanson, *ibid.*, 808 (1940); (c) Burger and Macbeth, *ibid.*, 145 (1946).

[6] Evans and Gillam, *ibid.*, 565 (1943).

[7] Snyder, Stewart and Myers, THIS JOURNAL, **71**, 1055 (1949).

[8] Burns, Jones and Ritchie, *J. Chem. Soc.*, 400 (1935).

[9] (a) Schniepp and Geller, THIS JOURNAL, **67**, 54 (1945); (b) Ratchford and Fisher, *ibid.*, **69**, 1911 (1947).



hexene (*dl*-phellandronitrile, VI). The nitrile (VI) was assumed to have its unsaturation in the position α,β to the cyano group on the basis of its ultraviolet absorption spectrum (maxima at 212 mμ, log ϵ 3.95, and 271 mμ, log ϵ 2.01)[10,11] and on the basis of previous reports that rearrangement of the double bond seldom occurs in this type of pyrolysis.[12]

Hydrolysis of *dl*-phellandronitrile (VI) was accomplished under both alkaline and acidic conditions. In either case, however, mixtures resulted due to α,β–β,γ shifting of the double bond.[13] Saponification with 10% aqueous potassium hydroxide gave a mixture of solid acids, presumably VII and VIII, of m. p. 119–142°. Recrystallization from numerous solvents failed to effect separation. Hydrolysis with 75% sulfuric acid gave a similar mixture from which phellandric acid (VII) could not be isolated but which did give a 44% yield of an isomer we believe on the basis of infrared data to be the Δ^2 acid (VIII).

Various means, described in the Experimental Part, were used to obtain pure *dl*-phellandric acid (VII) from the mixture. Best results were obtained by refluxing the mixture in ethanolic sodium ethoxide to give an 80% yield of the pure Δ^1 acid (VII).

Reduction of *dl*-phellandric acid to *dl*-phellandral was accomplished readily, although in low yield (16% from the anilide), by the von Braun and Rudolph modification of the Sonn–Müller reduction.[14] The *dl*-phellandral was characterized by means of its physical properties and formation of its oxime, semicarbazone and 2,4-dinitrophenylhydrazone. Ultraviolet absorption spectra of the synthetic aldehyde and its semicarbazone corresponded with those reported for natural phellandral by Cooke and Macbeth[5a] and Evans and Gillam[6] (Fig. 1).

We were particularly interested in the properties of the oxime because of the structural similarity between phellandral and perilla-aldehyde. The *anti*-oxime of the latter has been reported to be 2000 times as sweet as sucrose.[15] We obtained only one oxime of *dl*-phellandral; it was not sweet.

Resolution of *dl*-phellandric acid (VII) was partially accomplished through its quinine salt. This salt reached constant rotation when the acid was about 56% resolved, and the resolution was completed by means of *l*-α-phenylethylamine.

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(10) Braude, *Ann. Repts. Chem. Soc.*, **42**, 122 (1945).

(11) Ultraviolet absorption spectra were kindly carried out by Mrs. Calvin Brantley using a Model D Beckmann spectrophotometer. The nitrile was dissolved in 95% ethanol, concentration 0.0192 g. per liter of solution.

(12) For example, the pyrolysis at 575° of the diacetate of pentamethylene glycol yields only 1,4-pentadiene, with apparently no shifting of the unsaturation into conjugation to form piperylene (see reference 9a).

(13) Boorman and Linstead, *J. Chem. Soc.*, 261 (1935).

(14) v. Braun and Rudolph, *Ber.*, **67**, 269 (1934).

(15) Kurukawa and Tomizawa, *J. Chem. Ind. Japan*, **23**, 342 (1920); (*C. A.*, **14**, 2839 (1920)).

The *d*-acid thus obtained was essentially identical in m. p. (143–144°) and rotation ($[\alpha]_D^{26}$ + 112.2°) with that obtained by oxidation of *d*-phellandral.[5b]

Experimental

All melting points are corrected.

p-Isopropylphenol (I).—Ninety grams (104 ml., 0.75 mole) of cumene and 83 g. (0.85 mole) of 95% sulfuric acid were heated with stirring for three hours on a steam-cone. The warm mixture was poured into 250 ml. of water, and 40 g. of sodium bicarbonate was added in small portions, followed by 105 g. of sodium chloride. Crude sodium p-cumenesulfonate, which precipitated on cooling, was collected on a suction filter, washed with 40 ml. of saturated aqueous sodium chloride, and dried for two days at 80°. It weighed 109 g.

A mixture of 960 g. (17.1 moles) of potassium hydroxide and 40 ml. of water was heated to 250° in a 3-l. iron pot fitted with a stirrer. To this was added with constant stirring over a period of one-half hour 360 g. (1.62 moles) of the impure sodium p-cumenesulfonate. The temperature was raised to 325° for ten minutes, then the contents immediately poured onto 3 l. of cracked ice. The resulting water solution was neutralized with concentrated sulfuric acid and steam distilled. Colorless crystals of p-isopropylphenol formed in the distillate. After drying in a vacuum desiccator for two days these weighed 118 g. (35% based on cumene), m. p. 58–59° (lit.,[16] 61°).

4-Isopropylcyclohexanol (II).—A solution of 187 g. (1.37 moles) of p-isopropylphenol in 250 ml. of ethanol (purified by stirring for three hours with 2 g. of Raney nickel) was hydrogenated over 6.0 g. of Raney nickel at 190° and 125-atm. pressure. Fractional distillation gave 189 g. (96%) of 4-isopropylcyclohexanol, b. p. 123–124° (40 mm.), n^{20}_D 1.4660 (lit.,[17] 1.4661).

4-Isopropylcyclohexanone (III).—To a solution of 59 g. (0.20 mole) of potassium dichromate in 455 ml. of water in a 1-l., three-necked flask fitted with a dropping funnel, a reflux condenser, a thermometer and a stirrer was added 80 g. (0.56 mole) of 4-isopropylcyclohexanol. Concentrated sulfuric acid (52 ml.) was added dropwise with stirring at such a rate that the temperature was kept between 55° and 60° (about 10 ml. of acid was added before the temperature began to rise). The reaction mixture was cooled to room temperature, the oily layer separated, and the aqueous layer extracted with ether. The oily layer and the extracts were combined, washed with 5% aqueous sodium hydroxide, then water, and dried over anhydrous magnesium sulfate. Fractional distillation in a 12-in. Fenske-type column gave 64.6 g. (82%) of 4-isopropylcyclohexanone, b. p. 90–91° (13 mm.), n^{20}_D 1.4560 (lit.,[17] 1.4552^{25}°). The semicarbazone, prepared according to the method of Shriner and Fuson,[18a] melted at 187–188° (lit.,[19] 187–188°).

Cyclohexanone Cyanohydrin.—A solution of 65 g. (1.00 mole) of potassium cyanide in 125 ml. of water was added dropwise with stirring to a mixture of 94 ml. (102 g., 1.00 mole) of acetic anhydride and 52 ml. (49 g., 0.50 mole) of cyclohexanone in a 1-l. flask fitted with a mechanical stirrer, a dropping funnel and a reflux condenser. During the addition the mixture was cooled in an ice-bath. Stirring was continued for fourteen hours at room temperature, after which the reaction mixture was homogeneous. Saturated aqueous sodium carbonate was added until the mixture was alkaline to litmus. A red oil separated during this time; it was removed, and the water layer extracted with three 50-ml. portions of benzene. The extracts and oil were combined, washed with three 50-ml. portions of 30% aqueous sodium bisulfite, dried over magnesium sulfate, and the benzene distilled at 15-mm. pressure. The residual oil crystallized when a spot on the flask was cooled with Dry Ice. It was purified by rapid distillation at 91–95° (2 mm.) from a Claisen flask to yield 47.7 g. (76%) of colorless liquid, n^{20}_D 1.4643, which crystallized on chilling. An analytical sample was prepared by washing these crystals with chloroform, ether and acetone; m. p. 35°.

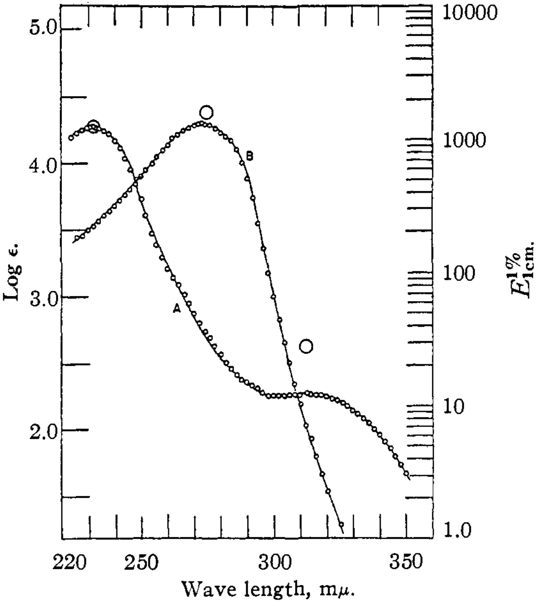

Fig. 1.—Ultraviolet absorption of *dl*-phellandral (A) (0.00418 g. per liter of ethanol solution) and its semicarbazone (B) (0.600 g. per liter of ethanol solution). The large circles represent the literature values (references 5a and 6).

Anal.[20] Calcd. for $C_7H_{11}ON$: C, 67.17; H, 8.86. Found: C, 67.21; H, 8.88.

Cyclohexanone Cyanohydrin Acetate.—To 68 ml. (73 g., 0.75 mole) of acetic anhydride and 0.8 ml. of acetyl chloride heated to boiling was slowly added 85.0 g. (0.68 mole) of cyclohexanone cyanohydrin. The mixture was refluxed for one hour after the end of the addition; it turned dark red during this time. Direct fractional distillation gave 91.0 g. (80%) of product, b. p. 125° (13 mm.), which crystallized on cooling; m. p. 48° (lit.,[8] 48–49°).

The same experiment, carried out with acetic anhydride containing no acetyl chloride, yielded 19% of the cyanohydrin acetate.

4-Isopropylcyclohexanone Cyanohydrin Acetate (V).—Crude 4-isopropylcyclohexanone cyanohydrin was prepared by the method for cyclohexanone cyanohydrin, with the use of 90 ml. (98 g., 0.96 mole) of acetic anhydride, 60 g. (0.43 mole) of 4-isopropylcyclohexanone and 62 g. (0.96 mole) of potassium cyanide in 192 ml. of water. After removal of the benzene at 15 mm. from the extract of the product, the oil was refluxed for one hour with 41 ml. (44.0 g., 0.43 mole) of acetic anhydride and 0.5 g. of acetyl chloride. Fractional distillation then gave 65.5 g. (70%) of product, b. p. 145–147° (14 mm.). It crystallized on cooling; m. p. 43–44°. An analytical sample was prepared by four recrystallizations from methanol–water to yield colorless mica-like plates, m. p. 50.5–52.5°.

Anal. Calcd. for $C_{12}H_{19}O_2N$: C, 68.85; H, 9.15. Found: C, 68.86; H, 9.20.

4-Isopropyl-1-cyano-1-cyclohexene (*dl*-Phellandronitrile, VI).—Three hundred and fifty-seven grams (1.71

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[16] Paternò and Spica, *Gazz. chim. ital.*, **6**, 535 (1876).

[17] Cahn, Penfold and Simonsen, *J. Chem. Soc.*, 1366 (1931).

[18] (a) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd edition, 1948, p. 170; (b) p. 202; (c) p. 171.

[19] Vavon and Callier, *Bull. soc. chim.*, [4] **41**, 677 (1927).

[20] Microanalyses were carried out by Misses Emily Davis, Betty Alice Snyder and Theta Spoor, Mr. Maurice Dare and the Clark Microanalytical Laboratory.

moles) of the cyanohydrin acetate of 4-isopropylcyclohexanone was pyrolyzed by passing it through a vertical 18-mm. Pyrex tube filled with eight inches of glass beads. The temperature of the reaction was 575–600°; the ester was passed through the tube over a period of twelve hours at a rate of one drop every 3.5 seconds. There was some charring in the pyrolysis tube. Direct distillation of the product in a ten-inch Fenske-type column yielded 188 g. (74%) of colorless liquid, b. p. 118–120° (15 mm.); n^{20}D 1.4786; sp. gr. $^{20}_{20}$ 0.914; *MR* calcd. (using exaltation of 0.7): 46.2, found: 46.3.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.53; H, 10.14. Found: C, 80.37; H, 9.88.

Pyrolysis of a similar amount at 500° gave a 60% yield (based on unrecovered starting material) and a 31% recovery of starting material; at 565–575° the yield was 62% with no recovery of starting material.

Hydrolysis of 4-Isopropyl-1-cyano-1-cyclohexene. A. With Potassium Hydroxide.—A mixture of 188 g. (1.26 moles) of the nitrile, 141 g. (2.52 moles) of potassium hydroxide, and 3 ml. of 1-octanol (to prevent foaming) in 1271 ml. of water was refluxed for forty-eight hours. After forty hours most of the nitrile layer had disappeared. After cooling and filtration, the solution was acidified with concentrated hydrochloric acid. A light brown precipitate formed. This was dissolved in 1500 ml. of hot nitromethane. The mother liquor was extracted with 300 ml of nitromethane and the extract combined with the main hot solution. On cooling 136 g. of white platelets deposited; m. p. 119–142°. A second crop, 18.5 g., m. p. 83–118°, raised the total yield of mixed Δ^1- and Δ^2-4-isopropyltetrahydrobenzoic acids (VII and VIII) to 73%. Crystallizations from ethanol–water mixtures and from nitromethane did not raise nor narrow the m. p. range.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.57; H, 9.52.

B. With Sulfuric Acid.—To 25 g. of 75% sulfuric acid at 120° in a 200-ml. flask equipped with a stirrer, a dropping funnel and a reflux condenser was added dropwise 6.0 g. (0.04 mole) of 4-isopropyl-1-cyano-1-cyclohexene. The mixture was stirred at 110–120° for three hours, then poured into ice-water to give a brown precipitate. Two recrystallizations from ethanol–water, with the use of Darco, and one from dioxane–water (60:40) yielded 3.0 g. (44%) of colorless needles, m. p. 105°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.46; H, 9.73.

On the basis of its neutral equivalent, 172, and its infrared spectrum, kindly furnished by Mrs. J. L. Johnson, this acid is assumed to be Δ^2-4-isopropyltetrahydrobenzoic acid (VIII). The spectrum, obtained in Nujol suspension using a Perkin–Elmer Model 12B infrared spectrometer with rock salt optics, showed weak absorption bands at 702, 736, 1071, 1086, 1109, 1178, 1217, 1274, 1286, 1301, 1314 and 1371 cm.$^{-1}$ and strong bands at 1649 (unconjugated double bond) and 1680 cm.$^{-1}$ (carboxylic carbonyl group). No absorption was observed in the region of 1750–1800 cm.$^{-1}$, characteristic of γ-lactones.[21]

***dl*-Phellandric Acid** (VII).—Thirty-eight grams (1.6 gram-atoms) of sodium was dissolved in 1400 ml. of absolute ethanol in a 3-l. flask fitted with a reflux condenser. To this was added 136 g. (0.810 mole) of the mixture of acids, m. p. 119–142°, obtained by the alkaline hydrolysis above. A lumpy precipitate formed; the mixture was refluxed for three hours and allowed to stand overnight. About half the alcohol was removed by distillation, ice-water was added to the residue and the latter then carefully acidified with concentrated hydrochloric acid. Crystals formed in the mixture, which now had a total volume of 5 l. One recrystallization from 1400 ml. of nitromethane gave 109 g. (80% from the mixture, 58% from the nitrile) of colorless needles, m. p. 142–144° (lit.,[5b] 143–144°).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.03; H, 9.31.

Attempted lactonization of the Δ^2 acid[22] by heating a mixture of 10 ml. of 60% sulfuric acid with 0.5 g. of a sample of the mixed acids nearly to boiling for five minutes gave a recovery of the mixture, m. p. 104–135°.

In an experiment to esterify the Δ^2 acid[13] 3.0 g. (0.02 mole) of the same mixture was dissolved in 36 ml. of absolute ethanol, and 18 ml. of 1 *N* ethanolic hydrogen chloride was added. After five hours at room temperature and one-half hour of refluxing, the mixture was poured into ice-water, extracted with benzene, the benzene removed at 15 mm. pressure, and the residue recrystallized twice from nitromethane. The product, m. p. 142–143°, was the desired *dl*-phellandric acid, but weighed only 0.3 g. (10% from the mixture).

One milliliter (1.5 g.) of thionyl chloride was added to 0.57 g. of the mixture of Δ^1 and Δ^2 acids, and the resulting acid chloride mixture heated at 100–105° for two hours, then hydrolyzed by stirring in water at room temperature for three hours. The crystals, recrystallized from nitromethane, melted at 134–143°, indicating some concentration of the Δ^1 acid, but the recovery was less than 0.1 g.

***dl*-Phellandric Acid Anilide.**—One hundred grams (0.59 mole) of *dl*-phellandric acid, 500 ml. of dry benzene and 65 ml. (106 g., 1.50 moles) of thionyl chloride, connected to a suitable trap, were allowed to stand for forty-five hours. The benzene and excess thionyl chloride were removed *in vacuo*. The residual acid chloride was dissolved in 1800 ml. of dry benzene in a 3-l. flask and 163 ml. (166 g., 1.78 moles) of aniline was added directly. Some heat was evolved and a white precipitate of aniline hydrochloride formed. After four hours at room temperature, the mixture was filtered to remove the precipitate, and the filtrate evaporated in stages to yield successive crops of crystalline anilide. These were washed in turn with dilute hydrochloric acid, dilute aqueous sodium hydroxide and water. Recrystallization from 4.5 l. of high-boiling petroleum ether yielded 122 g. (84%) of product in the form of fine needles, m. p. 131–132°.

Anal. Calcd. for $C_{16}H_{21}NO$: C, 78.96; H, 8.70; N, 5.76. Found: C, 79.20; H, 8.48; N, 5.87.

***dl*-Phellandral.**—The method of von Braun and Rudolph[14] was followed closely. The imino chloride of *dl*-phellandric acid anilide was prepared from 50 g. (0.21 mole) of the anilide and 43 g. (0.21 mole) of phosphorus pentachloride. Chromous chloride solution was prepared in an atmosphere of carbon dioxide from 70 g. (0.41 mole) of red chromous acetate, kindly prepared by Messrs. Aaron Herrick and Marshall Hatfield,[23] and 275 ml. of 3 *N* hydrogen chloride in absolute ether. Addition of the imino chloride in 100 ml. of dry benzene to the chromous chloride solution gave a brown chromic chloride complex as described by von Braun and Rudolph. After hydrolysis of this and extraction of the aqueous layer with ether, the combined ether–benzene solutions were united with those of a second identical reduction. Evaporation at 15-mm. pressure yielded the Schiff base of *dl*-phellandral as a light brown residue. This was decomposed by means of 1 l. of 10% aqueous oxalic acid, and the *dl*-phellandral steam distilled in about 5 l. of water. The distillate, divided into convenient portions, was extracted four times with a total of 4 l. of ether. The extracts were dried over magnesium sulfate and fractionally distilled under nitrogen in a modified Claisen flask to give 10.4 g. (16%) of *dl*-phellandral, b. p. 103–105° (9 mm.); n^{20}D 1.4896 (lit. for *l*-isomer,[5a] 1.4897); sp. gr. $^{20}_{20}$ 0.944 (lit. for *d*-isomer,[3] 0.9412^{20}); *MR* calcd. (using exaltation of 0.77):[24] 46.5, found: 46.6.

Anal.[25] Calcd. for $C_{10}H_{16}O$: C, 78.88; H, 10.60. Found: C, 77.62, 77.64, 77.48; H, 9.79, 9.90, 10.28.

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[21] Thompson, *J. Chem. Soc.*, 328 (1948).

[22] Fittig, *Ann.*, **283**, 47 (1894).

[23] Hatfield, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., in press.

[24] v. Auwers and Eisenlohr, *J. prakt. Chem.*, **84**, 15 (1911).

[25] The analysis indicates the presence of phellandric acid, an expected result considering the ease of oxidation of phellandral (ref. 3).

The oxime, prepared according to the directions of Shriner and Fuson,[18b] melted at 76-77° when recrystallized as plates from ethanol-water.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.80; H, 10.25. Found: C, 72.03; H, 10.42.

Ultraviolet irradiation of the oxime in benzene solution for thirty-six hours resulted in complete recovery of the material melting at 76-77°.

The semicarbazone,[18a] shiny flakes when recrystallized from methanol, melted at 199.5-200.5°.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.16; H, 9.09. Found: C, 63.17; H, 9.12.

The 2,4-dinitrophenylhydrazone, prepared by the method of Shriner and Fuson,[18c] formed red microcrystals from absolute ethanol, m. p. 194.5-196°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: N, 16.87. Found: N, 16.80.

d-Phellandric Acid.—To a mixture of 2920 ml. of petroleum ether (80-110°) and 488 ml. of *n*-butyl alcohol were added 45 g. (0.27 mole) of *dl*-phellandric acid and 101 g. (0.27 mole) of quinine trihydrate. The solution was heated to 60°, filtered hot, allowed to cool slowly to room temperature and finally chilled overnight in an icebox. The precipitated salt was filtered and recrystallized from the same solvent mixture. A second 45-g. portion of acid was treated in the same manner, and the two batches of salt combined and recrystallized seven times. The rotation did not change during the last two crystallizations. There was obtained 24 g. of quinine salt, m. p. 141-143°, $[\alpha]^{25}_{D}$ −100° (0.0288 g./ml. of methanol).

Anal. Calcd. for $C_{30}H_{40}N_2O_4$: C, 73.14; H, 8.18. Found: C, 73.34; H, 8.43.

The quinine salt was dissolved in chloroform and decomposed by shaking with 12 ml. of 5% aqueous potassium hydroxide. The chloroform layer was discarded. The aqueous layer was washed twice with chloroform and then acidified. The precipitated acid was collected on a filter, washed with water and air-dried. It weighed 6.4 g., $[\alpha]^{25}_{D}$ +63° (0.0223 g./ml. of methanol).

The partially resolved acid was dissolved in 300 ml. of a mixture of 1 volume of *n*-butyl alcohol to 20 volumes of petroleum ether (80-110°), and an excess of *l*-α-phenylethylamine was added. The mixture was heated on a steam-cone, then allowed to cool slowly as before. After eighteen recrystallizations from the same solvent mixture the rotation of the salt remained constant. There was obtained 1.27 g. of salt, m. p. 151-152°; $[\alpha]^{25}_{D}$ +70.0° (0.0266 g./ml. of methanol solution).

Anal. Calcd. for $C_{18}H_{27}NO_2 \cdot H_2O$: C, 70.32; H, 9.51. Found: C, 70.66; H, 9.58.

This salt was decomposed in the same manner as the quinine salt to yield optically pure *d*-phellandric acid, m. p. 143-144°, $[\alpha]^{26}_{D}$ +112.2° (0.02054 g./ml. of methanol solution) (lit.,[5b] m. p. 144-145°, $[\alpha]^{20}_{D}$ +112.8° (0.02083 g./ml. of methanol solution)).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.25; H, 9.62.

Summary

The structure of the terpene phellandral has been confirmed by the total synthesis of *dl*-phellandral and the resolution of *dl*-phellandric acid.

URBANA, ILLINOIS RECEIVED MAY 31, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Flavanones and Related Compounds. VI. The Polarographic Reduction of Some Substituted Chalcones, Flavones and Flavanones

BY T. A. GEISSMAN AND S. L. FRIESS[1]

The study of the behavior at the dropping-mercury electrode of substances belonging to the C_6–C_3–C_6 (flavonoid) group of naturally occurring plant substances[2] has been continued. A more detailed examination has been made of some of the questions raised in the earlier part of this work, and a study has now been made of a group of flavones having hydroxyl and acetoxyl groups in the 5-, 7- and 4′-positions.[3] In addition, fourteen flavanones and sixteen chalcones, containing hydroxyl, methoxyl and acetoxyl groups in various positions in both aromatic rings, were examined. In each group the parent compound was included.

The objectives of this study included (1) a correlation between the kind and degree of substitution and the resulting variation in the ease of reduction at the electrode; (2) an evaluation of the most probable electrode mechanism; and (3) an attempt to account for the observed $E_{1/2}$ values on the basis of the proposed electrode reaction and the relative degrees of resonance stabilization of the reactants and products of the electrode reaction.

Experimental

The polarographic runs were made in 50% buffer-50% isopropyl alcohol mixtures at a temperature of 25 ± 0.1°, the $E_{1/2}$ values being measured against the saturated calomel electrode (S.C.E.). The *p*H values recorded for the various buffer mixtures used in the polarographic runs are the nominal ones given by the Beckman *p*H meter. They are in general about 1 *p*H unit higher than those of the aqueous buffer solutions alone.

In the case of the chalcones, the polarograph, buffers and dropping-mercury electrode were those used in the earlier study. Later, a Fisher Electropode was used, the runs with the flavones and flavanones being made with this instrument.

The capillary used for the runs on the flavones

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[2] Engelkemeir, Geissman, Crowell and Friess, THIS JOURNAL, **69**, 155 (1947).

[3] Chalcones, flavones and flavanones are numbered as follows: