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Hydrogenation of Acetophenone to Cyclohexylmethylcarbinol in the Presence of Solvent

BY V. N. IPATIEFF AND B. B. CORSON

Acetophenone can be selectively hydrogenated in isopentane solution to a 70% yield of cyclohexylmethylcarbinol[1] but the conditions must be controlled carefully.

Experimental

A 3350 cc. bomb was charged with 200 cc. of acetophenone, 400 cc. of isopentane, 40 g. of nickel catalyst,[2] and 100 kg./sq. cm. of hydrogen. The bomb was rotated for six hours at 100°. The product was distilled through a Podbielniak column with a reflux ratio of 10/1. The isopentane was first evaporated. The residue consisted of 20% (by vol.) of ethylbenzene (b. p. 135–137°; $n^{20}D$ 1.4925), 7% of intermediate fraction (b. p. 137–189°; $n^{20}D$ 1.4874), 70% of cyclohexylmethylcarbinol (b. p. 189–190°; $n^{20}D$ 1.4688), and 3% of bottoms ($n^{20}D$ 1.4940).

The ethylbenzene fraction contained about 1% of ethylcyclohexane on the basis of its refractive index and solubility in cold 15% fuming sulfuric acid.

(1) Cyclohexylmethylcarbinol has previously been made through the Grignard reaction (Bouveault, *Bull. soc. chim.*, [3] **29**, 1049 (1903); Sabatier and Mailhe, *Compt. rend.*, **139**, 343 (1904).

(2) The catalyst was a kieselguhr supported nickel (about 70% of nickel) which had been reduced at 430°.

The redistilled cyclohexylmethylcarbinol showed the following constants: b. p. 189.4–189.8° at 761 mm.; $n^{20}D$ 1.4677; d^{20}_4 0.925. *Anal.* Calcd. for $C_8H_{16}O$: C, 74.9; H, 12.6; mol. wt., 128. Found: C, 74.8; H, 12.5; mol. wt., 126.

When an isopentane solution of acetophenone was heated for six hours at 75°, the product was a mixture of 8% of ethylbenzene and 92% of an approximately 50/50 mixture of phenylmethylcarbinol and cyclohexylmethylcarbinol, and when the hydrogenation temperature was 50° the product was mainly unchanged acetophenone.

In the absence of solvent, and using reduced copper as catalyst[3] at 225°, 95% of the product was ethylbenzene. Using cyclohexane as solvent at 100°, the product was a mixture of ethylbenzene, the two alcohols, and acetophenone.

Summary

Acetophenone has been selectively hydrogenated in isopentane solution to cyclohexylmethylcarbinol.

(3) Prepared by reduction in hydrogen at 225° and ordinary pressure of Kahlbaum–Schering granular copper oxide (nickel content, 0.1%).

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 1, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF BOTANY, UNIVERSITY OF MINNESOTA]

Pseudo-eleostearic Acid[1]

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Moore[2] has shown that prolonged saponification of linseed oil induces a partial isomerization of its spectroscopically inactive liquid linolenic acid to an absorptive crystalline substance, m. p. 77°, bearing a striking resemblance to the eleostearic acids in the position and intensity of its absorption band and in its failure to form an ether-insoluble hexabromide.

In the course of a spectroscopic study of isomerism in the fatty acids[3] we found it expedient to determine the constitution of this compound, the oxidation products of which, consisting of sebacic, oxalic and butyric acids, establish its structure as 10,12,14-octadecatrienoic acid-1. The shift to a conjugated configuration induced by alcoholic alkalies is thus analogous to the rearrangement of linoleic acid under similar treatment.[4] Like the eleostearic acids (9,11,13-octadecatrienoic acids),[5] the new isomer adds only two molecules of bromine easily, the introduction of the third requiring considerable time or exposure to ultraviolet light. However, its maleic anhydride addition product is not homogeneous and could not be separated into its clearly defined individual components. This points to the geometric configuration of the parent substance as the *trans-trans-trans* or *trans-cis-trans* isomer, either of which may form more than one condensation product.[6]

Since the completion of this investigation, we

(1) This work was supported by grants from the Hormel Foundation, the National Live Stock and Meat Board, and the Graduate School of the University of Minnesota.

(2) Moore, *Biochem. J.*, **31**, 142 (1937).

(3) Kass, Miller, and Burr *Proc. Am. Soc. Biol. Chem.*, **32**, 66 (1938).

(4) Kass, Miller and Burr, THIS JOURNAL, **61**, 482 (1939).

(5) Böeseken, *et al.*, *Rec. trav. chim.*, **46**, 619 (1927).

(6) Morrell and Davis, *Trans. Faraday Soc.*, **32**, 209 (1936).

have been informed[7] that in an independent preliminary study of the oxidation products of the new acid, designated by Moore[7] as "pseudo-eleostearic acid," Prof. T. P. Hilditch obtained sebacic acid and small amounts of monobasic acids having in impure condition an apparent equivalent of about 106. If the latter is assumed to be valeric acid (neutral equiv. 102), an allenic structure is suggested, which is contradicted by the pronounced absorption band at 270 mμ characteristic of the triply conjugated eleostearic acids.[8,9]

Moore[7] considers the spectroscopic activity and the production of sebacic acid indicative of the reorientation of the unsaturated linkages from the 9,12,15 positions of linolenic acid to the 10,12,14 configuration of pseudo-eleostearic acid.

Experimental

Formation of Pseudo-eleostearic Acid.—Moore's uncertain and prolonged saponification procedure, requiring the refluxing of the fatty acids with aqueous alcoholic potash for from seven to twenty-five days,[2] may be advantageously shortened to a matter of hours or minutes by the substitution of anhydrous butanol[4] or ethylene glycol, respectively, as the reaction medium, using approximately equal weights of the fatty acids and the alkali in four volumes of the solvent. The isomerization is completed in from six to twenty-four hours with the former and in from thirty to one hundred and twenty minutes with the latter, the reaction mixture then being acidified and the butanol removed by either steam or vacuum distillation and the glycol by simply washing the acids with water. The usual precautions against oxidation must be observed throughout, and the course of the reaction may be followed spectroscopically, dienometrically, or iodometrically, being considered complete when the absorption bands of the isolated aliquot samples of the mixed fatty acids reach a maximum at 230 and 270 mμ, their diene number exceeds 20, or their iodine number falls to about 150.

Six hundred and twenty-five grams of linseed oil fatty acids from which the solid acids were removed by two crystallizations from ligroin at −18° was refluxed under nitrogen for two hours with an equal weight of potassium hydroxide in 2.5 liters of anhydrous ethylene glycol. The mixture was then cooled, several hundred cc. of water added, and the refluxing resumed for a brief period to saponify the esters. (This step is essential when butanol is used as the solvent, since it shows a pronounced tendency toward esterification in the anhydrous state.) The soap solution was acidified, the fatty acids extracted with 1.5 liters of ligroin, and thoroughly washed with water. The dried ligroin solution was left overnight at −18°, when it deposited 25 g. of practically pure pseudo-eleostearic acid.

Pseudo-eleostearic Acid.—The acid precipitated easily from 85% alcohol as feathery crystals and from hexane as glistening scales. It was relatively insoluble in petroleum ether (30–35°), 1 g. requiring about 175 cc. for solution at 0°. Its m. p. was 77–79° (uncorr.), repeated crystallizations failing to narrow the melting point range, which was rapidly depressed and widened by exposure of the acid to air, so that three trials within two hours showed melting point ranges beginning successively at 75.5, 71.5, and 69° with a final maximum of 75°. The acid showed remarkable susceptibility to oxidation, quickly acquiring an acridly rancid odor and even its ligroin solutions becoming opalescent on boiling.

Anal.[10] Calcd. for $C_{18}H_{30}O_2$: C, 77.70; H, 10.79. Found: C, 77.78; H, 11.02.

The iodine number determinations by the Wijs or Hanus method gave values intermediate between two and three double bonds, rising with time and showing the recurring end-point and precipitation of iodine characteristic of the conjugated fatty acids.[11]

Hydrogenation of Pseudo-eleostearic Acid.—A mixture of the acid and platinum oxide catalyst in acetic acid was shaken for two hours in an atmosphere of hydrogen at room temperature and 40 lb. (3 atm.) pressure. The product was precipitated with water and after one recrystallization from 85% alcohol melted at 69.5–70°, showing no depression with a sample of authentic stearic acid.

Methyl Pseudo-eleostearate.—Ten grams of the acid was dissolved in 100 cc. of 4% methyl alcoholic sulfuric acid and left overnight at room temperature. The solution was then refluxed briefly and finally extracted with ligroin from which 7 g. of the methyl ester, m. p. 41° after recrystallization from methanol or ligroin, precipitated on cooling. The residue was a yellow oil which partially solidified at 0° and yielded an additional 1.5 g. of impure ester. Saponification of the sharply melting ester produced the parent acid, the m. p. of which again was 77–79°. This spread evidently is due to the greater susceptibility of the acid to oxidation.

Disruptive Oxidation of Methyl Pseudo-eleostearate.—A modification of the procedures of Armstrong and Hilditch[12] and of Haworth[13] was used; 5 g. of the ester was dissolved in 130 cc. of purified acetone and 75 g. of powdered potassium permanganate added carefully. The mixture was boiled under reflux and an additional 10 g. of the oxidizing agent added to produce a permanent pink coloration. After three hours, the acetone was evaporated completely, the residue extracted four times with dilute potassium hydroxide solution and the alkaline extract concentrated somewhat. The green extract was decolorized with gaseous sulfur dioxide, acidified with a small quantity of dilute sulfuric acid and distilled to the incipient precipitation of the salts. The residue was thoroughly extracted with ether, which on evaporation left 1.5 g. of a practically white solid contaminated with a yellowish oil, the latter being removed by crystallization from water and charcoal to give an acid with a neutral equivalent of 101.5 and m. p. 131–133°. One recrystallization narrowed the melting

(7) Moore, private communication to G. O. Burr, March 24, 1939.

(8) Dingwall and Thompson, THIS JOURNAL, **56**, 899 (1934).

(9) Hulst, *Rec. trav. chim.*, **54**, 639, 644 (1935).

(10) All micro analyses herein reported were performed by Mr. J. W. Opie of the Department of Organic Chemistry.

(11) Böeseken and Gelber, *Rec. trav. chim.*, **46**, 158 (1927).

(12) Armstrong and Hilditch, *J. Soc. Chem. Ind.*, **44**, 43T (1924).

(13) Haworth, *J. Chem. Soc.*, 1456 (1929).

point to 132–133°, no depression with authentic sebacic acid, m. p. 133°, neut. equiv., 101.07.

The aqueous residue was extracted repeatedly with benzene, then treated with a few drops of bromine, cooled, and the precipitated salts filtered off and discarded. The sulfates were precipitated with barium chloride, the filtrate made alkaline, then acidified with acetic acid and treated with purified calcium nitrate. After several hours the fine precipitate was filtered off, dissolved in hydrochloric acid and reprecipitated with ammonium hydroxide. The white powder, 0.76 g., reduced acid permanganate instantly and left a residue of 36.67% after ignition (calcd. for $CaC_2O_4 \cdot H_2O$, 38.38%).

The distillate, which possessed a pronounced odor of butyric acid, was made alkaline and evaporated to a small volume. It was then acidified, thoroughly extracted with ether, the ether extract washed once with water, and dried overnight with Drierite after preliminary drying over sodium sulfate. Evaporation of the ether left 0.5 g. of a liquid, 0.4 g. of which distilled at 165°. This distillate was miscible with water in all proportions, had a neutral equivalent of 80 and formed a *p*-toluidide, m. p. 69–71° (butyric acid, neut. equiv. 88, *p*-toluidide m. p. 73°).

Bromination of Pseudo-eleostearic Acid.—A solution of 1.5 g. of the acid in 250 cc. of petroleum ether cooled to 0° was brought to a distinct orange color with bromine and left at 0° for three hours. About 0.1 g. of a white powder precipitated, melting at 90–95° from hexane solution. Recrystallization from 1–5 ether-ligroin solution raised the m. p. to 90–100° and further fractionation of the powder from hexane showed its major component to be a crystalline substance, m. p. 104–104.5°.

Anal. Calcd. for $C_{18}H_{30}O_2Br_4$: C, 36.14; H, 5.02. Found: C, 35.73; H, 4.67.

The filtrate from the tetrabromides was treated with an additional portion of bromine and exposed to direct sunlight at room temperature. After twenty-four hours a partially crystalline precipitate appeared. Three successive extractions with boiling hexane yielded a total of 0.25 g. of white powders melting at (I) 125–135°, (II) 140–145°, and (III) 145–151°, respectively. The residue was taken up in ligroin (b. p. 90–95°) and finally recrystallized from ether, in which it is easily soluble, precipitating only in the ice–hydrochloric acid bath as scaly crystals, m. p. 152°. The ether mother liquor was evaporated and the residue combined with the hexane extract III, the mixture being recrystallized from ether to yield an additional crop of solid of m. p. 152°. Both portions were combined and recrystallized again from ether to yield 90 mg. of a crystalline material, m. p. 152–152.5°.

Anal. Calcd. for $C_{18}H_{30}O_2Br_6$: C, 28.50; H, 3.96. Found: C, 28.44; H, 4.17.

The hexane extracts I and II were combined and recrystallized from ligroin (b. p. 90–95°) without much improvement in melting point. However, 15 mg. of a crystalline substance of m. p. 148° was obtained from a 1 : 1 ether–petroleum ether solution. This was evidently the impure hexabromide, the mixed m. p. being 148–152°. Evaporation of the original ligroin mother liquor left only liquid bromides.

The hexabromide is apparently the only solid addition product obtained when pseudo-eleostearic acid is brominated in ultraviolet light; 0.4 g. of the acid in 15 cc. of purified carbon tetrachloride contained in a quartz test-tube was brominated at 0° to an orange color; an excess of one-third of the bromine consumed was added and the solution illuminated with a mercury arc at 50 cm. for one hour. The excess bromine was removed with amylene, the solvent evaporated at the vacuum pump, and the residual oil worked up with hexane. After twelve hours in the icebox, 50 mg. of a crystalline precipitate was obtained, melting at 145–148° after crystallization from ligroin (b. p. 90–95°). One recrystallization from ether raised the melting point to 152.5°. That ultraviolet light induces no isomerization of the parent acid was shown by the unaltered melting point and solubility behavior of a sample of pseudo-eleostearic acid similarly illuminated in a quartz container.

Addition of Maleic Anhydride.—An intimate mixture of equimolar quantities of pseudo-eleostearic acid and maleic anhydride was heated under nitrogen to 145°, when the yellow color of the melt was discharged. The reaction product set to a tacky, plastic mass on cooling. This was subdivided by repeated extraction with boiling hexane into a soluble granular solid and an insoluble sirup. The solid was redissolved several times in hexane, the less soluble sirup being removed each time. The final product was a white, poorly friable powder, sintering at 75° and melting at 77°, the melt becoming clear at 82°.

Anal. Calcd. for $C_{22}H_{32}O_5$: C, 70.21; H, 8.51. Found: C, 69.71; H, 8.21.

The residual sirup set to a brittle solid after complete evacuation of the solvent, and could then be ground to a coarse granular powder similar in melting point and appearance, except for a yellowish tinge, to the hexane extract. Both fractions were extremely soluble in alcohols, ether, acetic acid, and acetone, and were precipitated with ligroin as sirups that became solid on complete removal of the solvent. When the pseudo-eleostearic acid was heated with an excess of maleic anhydride either in the solid state or in a solvent, the reaction mixture remained liquid until the excess of reagent was removed either by distillation or with water, after which the characteristics of the product were those described.

Summary

Linolenic acid is partially converted by alcoholic alkalies into pseudo-eleostearic acid, 10,12,14-octadecatrienoic acid, m. p. 79°, methyl ester, m. p. 41°.

Pseudo-eleostearic acid forms mixed maleic anhydride addition products and mixed bromides, among them a tetrabromide, m. p. 104.5°, and a hexabromide, m. p. 152.5°.

MINNEAPOLIS, MINN. RECEIVED JULY 14, 1939