

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA, IOWA CITY]

Synthesis of *cis*-9-Octadecene, 9-Octadecyne and 9,10-Octadecane-diolBY F. E. DEATHERAGE¹ AND H. S. OLCOTT²

For several years, this Laboratory has been interested in the autoxidation of fats and its retardation by antioxidants. Hamilton and Olcott³ described the autoxidation of purified oleic acid and related compounds. In continuation of this work, it was considered advisable to study the autoxidation of *cis*-9-octadecene, the hydrocarbon corresponding to oleic acid.

Except for a brief reference by Böeseken and Belifante⁴ to an impure product, this compound has not been described. It has now been synthesized in relatively pure form from oleyl alcohol. The alcohol was converted to oleyl bromide by means of phosphorus tribromide. The Grignard reagent was then prepared and decomposed with dilute hydrochloric acid to give the desired hydrocarbon. This was further purified by brominating, distilling off the saturated hydrocarbons and regenerating the octadecene by treating the dibromo-octadecane with zinc.

The work of Dupont⁵ suggested that 9-octadecyne could be hydrogenated quantitatively to *cis*-9-octadecene. 9,10-Dibromooctadecane was heated with potassium hydroxide in *n*-amyl alcohol and the 9-octadecyne was obtained from the resulting products by fractional distillation. The reduction to the octadecene was unsatisfactory.

A third possible method of synthesis was based upon obtaining the two isomeric 9,10-octadecane-diols by the reduction of nonyloloin,⁶ which in turn was obtained by the condensation of *n*-butyl pelargonate, according to the method of Hansley.⁷ However, of the two possible diols (α = low melting, β = high melting), only the β -form (m. p. 127°) was obtained pure. Conversion to the dibromide and treatment of this with zinc did not give the desired hydrocarbon in suitable yield and purity.

(1) From a portion of a thesis presented by F. E. Deatherage to the Faculty of the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) Hamilton and Olcott, *Ind. Eng. Chem.*, **29**, 217 (1937).

(4) Böeseken and Belifante, *Rec. trav. chim.*, **45**, 914 (1926).

(5) Dupont, *Bull. soc. chim.*, [5] **3**, 1030 (1936).

(6) Another product, probably 9-octadecanone, was also formed in this reduction.

(7) Hansley, *This Journal*, **57**, 2303 (1935).

Experimental

Oleyl Alcohol.—This was prepared according to the method given in "Organic Syntheses."⁸

Oleyl Bromide.—(One mole) 268 g. of oleyl alcohol was dissolved in 750 cc. of carbon tetrachloride in a 2-liter Erlenmeyer flask; 270 g. (1 mole) of phosphorus tribromide mixed with 75 cc. of carbon tetrachloride was added over a period of forty-five minutes. The mixture became warm and much hydrogen bromide was evolved. The mixture was refluxed overnight on a hot-plate, during which time an orange, semi-solid gum precipitated. One hundred grams of charcoal was then added, the mixture was shaken, filtered, and the carbon tetrachloride removed by distillation under reduced pressure (water pump). The residual oleyl bromide was dissolved in 1200 cc. of light petroleum ether and washed several times with dilute sodium bicarbonate and then with 30% methanol until neutral.

After removal of the petroleum ether, the crude bromide was distilled at a pressure of 0.2 mm. The yield of oleyl bromide, boiling at 160–175° and 0.2 mm., varied from 65 to 90% of the theoretical. The same procedure could be followed with larger and proportionate amounts.

Oleylmagnesium Bromide and Crude *cis*-9-Octadecene.—12.3 g. (0.5 mole) of clean magnesium shavings and 1 liter of anhydrous ether were placed in a 2-liter, three-necked, round-bottomed flask equipped with an efficient condenser and stirrer; 166 g. (0.5 mole) of oleyl bromide was added to the reaction mixture by means of a dropping funnel and at such a rate as to maintain a vigorous reaction. The mixture was refluxed for two hours after all of the bromide had been added. The ether was then removed by distillation, and the Grignard was hydrolyzed by the cautious addition of 5% hydrochloric acid containing ammonium chloride. The hydrocarbon was taken up in light petroleum ether and washed free of acid with water. The petroleum ether was then distilled off to give a practically quantitative yield of *cis*-9-octadecene contaminated with saturated hydrocarbons.

9,10-Dibromo-octadecane.—To the crude octadecene, in twice its volume of chloroform and at a temperature below 10°, bromine was slowly added to excess; the excess was removed by a few drops of crude octadecene. The residue, after distilling off the chloroform, was dibromo-octadecane and saturated hydrocarbons. The latter were removed by distillation at 0.2 mm. from a flask surrounded by an oil-bath maintained at 165°. This temperature permitted the distillation of the saturated hydrocarbons and yet was low enough to prevent decomposition of the dibromide. The residual liquid dibromide, obtained in almost quantitative yield, was used without further purification.

***cis*-9-Octadecene.**—Four times its weight of anhydrous *n*-amyl alcohol and an excess of zinc dust were added to the

(8) *Org. Syntheses*, **15**, 51 (1935).

9,10-dibromo-octadecane and the mixture was refluxed overnight. The excess zinc was removed from the hot solution by filtration. The clear solution was washed twice with dilute hydrochloric acid, then with water until neutral. After removing the amyl alcohol by distillation, the resulting octadecene was fractionated. The fraction boiling at 125–140° and 0.1–0.2 mm. accounted for 80–90% of the crude octadecene. Bromine addition by the method of Yasuda⁹ indicated 3.89 mmol. of double bond per g. (theoretical, 3.97 mmol. per g.). Hence, the preparation was about 97.5% *cis*-9-octadecene: d_{41} 0.782, m. p. –2–0°.

Anal. Calcd. for $C_{18}H_{36}$: C, 85.62; H, 14.38. Found: C, 85.43; H, 14.41.

That the method employed to remove the saturated hydrocarbons from octadecene caused little, if any, inversion from the *cis* to the *trans* compound may be inferred from the work of Lucas and his co-workers¹⁰ on the 2-butenes. More direct evidence that the double bond has the same configuration as that in oleic acid is furnished by comparative autoxidation studies of the hydrocarbon, oleic acid, its esters, and oleyl alcohol which will be reported elsewhere.

9-Octadecyne.—Twenty-nine grams of 9,10-dibromo-octadecane was dissolved in 100 cc. of anhydrous amyl alcohol and heated with 16 g. of potassium hydroxide at 120° for two hours. After washing the solution to the neutral point, the amyl alcohol was removed by steam distillation and the residue was fractionated at 0.45 mm.; 3.5 g. of 9-octadecyne distilled at 142 ± 2°. It appeared slightly yellow (probably due to impurities), melted at 2–4° and absorbed 3.99 mmol. of bromine per g. (theoretical, 4.00, on the assumption that such a triple bond will take up only one mole of bromine).

Anal. Calcd. for $C_{18}H_{34}$: C, 86.30; H, 13.69. Found: C, 85.51; H, 13.87.

Although the acetylene appeared to be selectively hydrogenated by the Raney catalyst according to the method of Dupont,⁶ a product having the proper analyses for 9-octadecene was not obtained.

Nonyloin.—This compound was prepared by the method of Hansley.⁷ It was found advantageous to use butyl

pelargonate instead of the methyl ester and also to increase the amount of xylene by 2 to 3 times. The yield of nonyloin, m. p. 45°, was 70–90% of the theoretical.

9,10-Octadecane-diol.—Twenty-gram portions of nonyloin were dissolved in 20–30 times their weight of absolute alcohol and hydrogenated using 0.15 g. of platinum oxide as catalyst. The diol was obtained by filtering off the catalyst, and removing about two-thirds of the alcohol by distillation. Upon cooling the remaining solution, the diol separated as a white crystalline material. After a second crystallization, the diol melted at 127°. The product contained 7.03 mmol. of hydroxyl group per g. (theoretical, 6.99 mmol. per g.) by the acetyl value method of West, Hoagland and Curtis.¹¹

Anal. Calcd. for $C_{18}H_{38}O_2$: C, 75.48; H, 13.38. Found: C, 75.64; H, 13.45.

9-Octadecanone.—Forty grams of 3% sodium amalgam was added to a solution of 5 g. of nonyloin in 200 cc. of absolute ethanol. After refluxing on a hot-plate for twenty-four hours, water was added to the solution until precipitation was complete. The product was taken up in ether and washed with dilute hydrochloric acid and water. After evaporation of the ether the product was recrystallized 8 times from ethanol to give colorless plates (3.2 g.) melting at 47°. The compound contained a functional group which reacted with 1 mole of methylmagnesium iodide but no active hydrogen. Acetyl determinations showed no hydroxyl or epoxy groups.

Anal. Calcd. for $C_{18}H_{36}O$: C, 80.51; H, 13.55. Found: C, 80.63; H, 13.50.

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Summary

The syntheses and some properties of *cis*-9-octadecene, 9-octadecyne and 9,10-octadecane-diol have been described.

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(9) Yasuda, *J. Biol. Chem.*, **94**, 401 (1931–32).

(10) Wilson and Lucas, *THIS JOURNAL*, **58**, 2396 (1936); Young and Lucas, *ibid.*, **52**, 1964 (1930).

(11) West, Hoagland and Curtis, *J. Biol. Chem.*, **104**, 627 (1934).