[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

High Molecular Weight Hydrocarbons. I. Eicosane, 1-Phenyleicosane and 3-Ethyloctadecane

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The recent report[1] of the synthesis of 1-phenyleicosane prompts us to submit our own results in a similar synthetic undertaking.[2]

Eicosane and 1-phenyleicosane were prepared by the reduction of the appropriate heptadecyl ketones which, in turn, were derived from highly purified stearic acid. The conventional synthesis through the nitrile[1] was abandoned after preliminary experiments led to significant amounts of a neutral by-product[3] which reduced the yield of ketone and complicated its isolation in the high state of purity desired in this work. The difficulty was circumvented by the use of an alternative approach through stearyl chloride and an appropriate dialkylcadmium derivative.[4] In this case the only by-product interfering with the direct isolation of the pure ketone is ethyl stearate, which arises from acid chloride–ether exchange. The latter reaction was minimized by application of the method of Cason and Prout,[5] and the undesired ester was removed completely by saponification.

The ketones were reduced by the Wolff–Kishner method in the presence of sodium butoxide and butyl alcohol. It appeared to us that the use of the butyl derivatives, rather than the commonly employed methyl and ethyl or isopropyl[1] analogs, offered the advantages of reduced pressures in the bomb-reaction and enhanced solubility for the high molecular weight reactant.

3-Ethyloctadecane was prepared according to the general method of Landa and Sliva.[6] 3-Ethyloctadecanol-3, from methyl palmitate and ethylmagnesium bromide, was easily dehydrated with anhydrous formic acid,[7] and hydrogenation of the resulting olefin gave the desired product.

Experimental

1-Phenyleicosanone-3.—Two moles (568 g.) of stearic acid[8] was dissolved in 2 liters of anhydrous C. P. benzene, and a total of 2.04 moles (425.5 g.) of phosphorus pentachloride was added in 70-g. portions. The smooth evolution of hydrogen chloride subsided after twelve hours at room temperature and two more hours at reflux temperature. Stearyl chloride, twice distilled at reduced pressure after removal of solvent and phosphorus chlorides in the initial fore-run, was obtained as a water-white oil, 424 g. (70%), b. p. 182° at 3 mm., m. p. 23°.

Considerable difficulty was encountered in the earlier distillations due to decomposition of the product, with the evolution of hydrogen chloride and the formation of tarry residues. This was particularly noticeable in the case of the crude material; the final product could be distilled at lower pressure with only slight residue. Best results were obtained by carrying out the distillations in batches of 300 g. or less, using a vacuum pump of high capacity. The use of thionyl chloride (Eastman, White Label) under a variety of conditions involved more of the same difficulties. No appreciable improvement resulted from the use of more highly purified thionyl chloride.[9]

A solution of β-phenylethylmagnesium bromide was prepared from 1.78 gram-atoms (42.7 g.) of magnesium and 1.755 moles (325 g.) of β-phenylethyl bromide[10] in anhydrous ether. Over a period of ten minutes, 0.936 mole (171.5 g.) of cadmium chloride was added to the well-stirred, ice-cold Grignard solution and the mixture was allowed to warm to room temperature. The solvent was removed on a steam-bath until the mixture was converted to a cream-colored, soupy, residual mass which resisted further action of the mechanical stirrer. At this point 1.5 liters of dry C. P. benzene was added[5] and the concentration process was repeated. A second portion of dry benzene was added and the mixture was vigorously stirred and refluxed until the hard residue was uniformly dispersed. A solution of 1.405 moles (400 g.) of stearyl chloride in 1 liter of dry C. P. benzene was added over a period of two hours to the well-stirred suspension. After refluxing for five hours, the cooled mixture was treated with ice and excess hydrochloric acid. The product was worked up for the neutral fraction after removal of a small amount of acidic material by extraction with sodium carbonate. The benzene was removed and the residue was saponified with excess alcoholic potassium hydroxide in the usual way. The desired product was isolated as the non-saponifiable fraction by extraction with benzene. After washing thoroughly with water and with a saturated solution of sodium chloride, and drying with anhydrous magnesium sulfate, the extract was freed from solvent and the residue was distilled from a Claisen flask at reduced pressure. Practically the entire distillate, 1-phenyleicosanone-3, (342 g., 65.5%, b. p. 219° at 1 mm.) was water-white and crystallized in the receiver. The melting point of 56° was unchanged by recrystallization from ethanol or from petroleum ether.

In preliminary experiments, stearyl chloride from stearic acid[11] and thionyl chloride, was converted to the amide by saturation of an ethereal solution with dry ammonia. After exhaustive recrystallization from 95% ethanol, the product (280 g., m. p. 108°), was converted to the nitrile by treatment with excess thionyl chloride in the usual way. Distillation under reduced pressure gave 248 g. (95%) of stearonitrile, b. p. 170–173° at 1.5 mm., m. p. 41–42°. Treatment of the nitrile according to the usual procedure with an ethereal solution of excess β-phenylethylmagne-

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[1] Whitmore, Herr, Clarke, Rowland and Schiessler, THIS JOURNAL, 67, 2059 (1945).

[2] This work is being carried out in the Chemical Laboratory at Smith College in coöperation with the Technical and Research Division of The Texas Company.

[3] The identity of this substance is being investigated.

[4] Gilman and Nelson, *Rec. trav. chim.*, 55, 518 (1936).

[5] Cason and Prout, THIS JOURNAL, 66, 46 (1944).

[6] Landa and Sliva, *Coll. Czechoslov. Chem. Commun.*, 4, 538 (1932); *C. A.*, 27, 1611 (1933).

[7] Difficulty due to incomplete elimination of water in the earlier methods, ref. 6, was not encountered with this reagent.

[8] Furnished by the Research Laboratory of The Texas Company at Beacon, N. Y. The product was exhaustively purified by repeated fractional crystallization, m. p. 70.2–70.7°.

[9] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, 1941, p. 381.

[10] The halides used were the best samples obtained by fractionation of the Eastman White Label product through a Fenske column with an efficiency of approximately twenty plates. Only those fractions of the distillate which had a constant boiling point and a constant index of refraction (±0.0001) were accepted.

[11] The Eastman White Label product was used without further purification.

sium bromide (from 280 g. (1.51 moles) of β-phenylethyl bromide[11] and 37.0 g. (1.52 gram-atoms) of magnesium) gave 148 g. (49%) of 1-phenyleicosanone-3, m. p. 55–56°, after a tedious separation from a crystalline by-product[3] (60 g., m. p. 122–123°), purification by extraction, fractional crystallization and distillation at reduced pressure.

1-Phenyleicosane.—In a typical batch preparation, 70.4 g. (0.189 mole) of 1-phenyleicosanone-3 and 16 ml. (0.32 mole) of 100% hydrazine hydrate[12] were heated in a 1-liter steel bomb with a sodium butoxide solution previously prepared from 18.4 g. (0.8 gram-atom) of sodium and 400 ml. of C. P. *n*-butyl alcohol. After a period of twenty-four to thirty-six hours at 200–215°, the cooled reaction mixture was distributed between benzene and water. The benzene layer was washed with dilute hydrochloric acid until the washings gave a negative test for hydrazine with a solution of potassium permanganate, and finally washed thoroughly with water and dried. Removal of benzene and butyl alcohol at reduced pressure and crystallization of the residue from 95% ethanol gave the colorless hydrocarbon. One recrystallization from the same solvent gave material whose melting point, 42–43°, was unchanged by further recrystallization. In several such batch operations[13] a total of 312 g. (0.84 mole) of the pure ketone was converted to 195.8 g., 0.545 mole (65.4%) of 1-phenyleicosane.

One hundred and seventy-six grams of this product, by distillation over sodium at reduced pressure, gave 170 g. of the hydrocarbon; b. p. 213° at 0.8 mm., m. p. 43°. A solution of the distillate in 1 liter of anhydrous C. P. benzene was passed through a 4-ft. column of silica gel,[14] and the column washed until the higher hydrocarbon was practically all eluted.[15] After removal of solvent, the residue, m. p. 43°, was fractionated at 0.03 mm. through a special column (five theoretical plates) designed for a very low pressure drop. The entire product distilled between 175 and 177°, and the central fractions, 141 g., comprising 90% of the total distillate, had a constant boiling point (177° at 0.03 mm.), a constant refractive index (n^{58}D 1.4656, ± 0.0001) and a constant melting point (43.5°).

We noted that the pure hydrocarbon seems to exhibit two solid phases. The slowly cooled liquid first changes to a translucent waxy solid which gradually reverts to the opaque brittle crystalline material.

Eicosanone-3.—This synthesis was carried out as described for the synthesis of the phenyl derivative. Ethyl magnesium bromide, from 14.8 g. (0.0795 mole) of purified[10] ethyl bromide and 2.0 g. (0.082 gram-atom) of magnesium, was treated with 7.7 g. (0.043 mole) of anhydrous cadmium chloride, and the cadmium derivative was mixed as before with 18.0 g. (0.0595 mole) of pure stearyl chloride. After three hours at reflux temperature and isolation of the product as the neutral unsaponifiable fraction, two recrystallizations from 95% ethanol gave 10.7 g. (62%) of constant-melting eicosanone-3, m. p. 61°.[16]

***n*-Eicosane.**—Ten grams (0.034 mole) of pure eicosanone-3 was reduced by the method previously described, using 2.7 ml. (0.054 mole) of 100% hydrazine hydrate and a sodium butoxide solution prepared from 3.1 g. (0.135 gram-atom) of sodium and 75 ml. of *n*-butanol. Two recrystallizations from ethanol gave the hydrocarbon. 7.0 g. (73%), m. p. 37°. Distillation of this material over sodium and redistillation, both at reduced pressure, gave 4.0 g. of pure *n*-eicosane,[17] b. p. 153° at 1.8 mm., which melted sharply at 37.5°. The melting point was not changed by further recrystallization.

In preliminary experiments the same product was obtained from stearonitrile by the methods described for the similar preparation of 1-phenyleicosane, but in lower yields than those obtained in the synthesis outlined above.

3-Ethyloctadecane.—A solution of 37 g. (0.1 mole) of methyl palmitate[11] in 200 ml. of dry ether was treated in the usual way with an ethyl Grignard reagent prepared from 0.5 mole of starting materials[11] and 150 ml. of ether. After decomposition with a cold saturated solution of ammonium chloride containing a crystal of sodium thiosulfate, and washing and drying as usual, removal of the ether at reduced pressure left 38.0 g. (96%) of 3-ethyloctadecanol-3 as a white waxy residue, m. p. 31–33.5°. The pure material, m. p. 36.5–37.5°,[18] was obtained from a small sample, recrystallized twice from methanol at −50°.

Twenty-five grams of the whole carbinol above, recrystallized once from methanol (m. p. 34.5–36°) was shaken with 90 ml. of anhydrous formic acid and the mixture, after two days at room temperature, was refluxed for one hour. After the addition of water and excess sodium hydroxide solution, the oily unsaturated hydrocarbon was extracted with petroleum ether, freed from solvent, and distilled over sodium at reduced pressure in an atmosphere of nitrogen. **3-Ethyloctadecene** was obtained in quantitative yield as a water-white liquid, b. p. 146–147° at 1.3 mm., m. p. −7 to −6°.[19] The product instantly decolorized a solution of bromine in carbon tetrachloride.

A mixture of 15.2 g. (0.0543 mole) of the olefin, 75 ml. of acetic acid, 20 ml. of ethyl acetate, 20 ml. of absolute ethanol and 0.06 g. of Adams catalyst, absorbed the theoretical amount of hydrogen in eleven minutes at 1.5 atmospheres pressure. The platinum was removed after the immiscible liquid phases were converted to a homogeneous solution by the addition of 60 ml. of 35–60° petroleum ether. Water and excess dilute aqueous alkali were added, and the washed and dried neutral fraction, freed from solvent, was distilled over sodium at reduced pressure. The entire product, **3-ethyloctadecane** distilled without residue as a water-white oil, 13.8 g. (90%), b. p. 145° at 1.8 mm., m. p. 2–3°,[20] and gave negative tests for unsaturation.

Summary

n-Eicosane and 1-phenyleicosane were prepared in a high state of purity by the reduction of the ketones obtained by the action of stearyl chloride on the appropriate dialkylcadmium derivative. Some alternative syntheses of the intermediates, and an improved synthesis of 3-ethyloctadecane, are described.

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RECEIVED AUGUST 25, 1945

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[12] Edwal Laboratories, Chicago, Illinois.

[13] An improved general method which permits large-scale reduction at atmospheric pressure was subsequently developed (Soffer, Soffer and Sherk, THIS JOURNAL, **67**, 1453 (1945).

[14] Silica Gel Dept., Davidson Chemical Corp.

[15] Preliminary experiments with hydrocarbon–ketone mixtures showed that the selective elution of the hydrocarbon by this procedure was quantitative. See, also, Mair and Forziati, *J. Research Natl. Bur. Standards*, **32**, 165 (1944).

[16] The recorded melting points (Heilbron, 1943) are 60–61° and 57°.

[17] The accepted melting point is 36–37° (*ibid.*).

[18] Ryan and Dillon [*J. Chem. Soc.*, **104**, I, 583 (1913)] reported the melting point as 34–35° (from petroleum ether).

[19] The previous workers, ref. 6, reported only the boiling point (199–202° at 10 mm.). There are three theoretical dehydration products of the foregoing carbinol (the Δ^2-, and the *cis*- and *trans*-Δ^3 olefins). The sharp melting point may support their view that the product is mainly one isomer (ref. 6).

[20] Landa and Sliva, ref. 6, reported the b. p. 202° at 12 mm. and m. p. −3°.