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Higher Hydrocarbons.[1] III.[2] The Wolff–Kishner Reaction

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The method of converting aldehydes and ketones to the corresponding hydrocarbons by heating their hydrazones or semicarbazones to 180–200° with sodium ethoxide and alcohol has been the subject of a number of publications.[5,6,7,8,9] It is known as the Wolff–Kishner reaction. A modification of this reaction, employing commercially-available sodium methylate,[10] excess hydrazine hydrate,[11,12] and absolute ethanol or isopropanol in a high pressure hydrogenation bomb,[13] has been used in the preparation from ketone intermediates of four hydrocarbons of high molecular weight. The hydrocarbons are *n*-hexacosane, 1-phenyleicosane, 1-cyclohexyleicosane and 1-cyclopentylheneicosane. The ketone intermediates were synthesized by the reaction of stearonitrile[14] with the appropriate Grignard reagent.[15]

Only one intermediate, 1-bromo-3-cyclopentylpropane, presented any serious problem. The preparation of this new compound required two distinct steps. First, allylcyclopentane was prepared by a modification[16] of the Piaux and Bourguel[17] method of coupling cyclopentylmagnesium bromide with allyl bromide. The reverse addition of hydrogen bromide to allylcyclopentane in the presence of benzoyl peroxide gave the desired bromide.

With the exception of *n*-hexacosane[18] the compounds in this paper have never been reported. German workers synthesized this hydrocarbon by electrolyzing potassium myristate and the properties of their preparation agree well with those reported here.

Table I is a summary of the important properties of these hydrocarbons. The methods used in the measurements are the same as those given for the earlier series of hydrocarbons.[2]

Experimental

Intermediates.—The greatest of care has been taken to obtain pure intermediates, all of which (excepting stearonitrile and the ketones) were distilled through fractionating columns[19] having efficiencies of 30–35 theoretical plates. The stearonitrile was purified by distillation through a special high vacuum column,[19] rated at 9–10 theoretical plates. The boiling points and melting points of the intermediates are uncorrected. The constants given are for the constant boiling point, constant refractive index fractions, and only such material was used in the preparations.

(a) ***n*-Octyl Bromide.**—Prepared by passing hydrogen bromide (from the direct combustion of bromine and hydrogen) into technical *n*-octanol at 110°. The product was washed with cold (0–5°), concentrated sulfuric acid,

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[1] American Petroleum Institute Project No. 42—Advisory Committee: L. C. Beard, Jr. (Chairman), George Calingaert, L. M. Henderson and L. A. Mikeska. Presented before the Organic Division, American Chemical Society, Cleveland, 1944.

[2] Whitmore, Sutherland and Cosby, THIS JOURNAL, **64**, 1360 (1942); Whitmore, Cosby, Sloatman and Clarke, *ibid.*, **64**, 1801 (1942).

[3] Present address, Rohm and Haas Co., Philadelphia, Pa.

[4] Present address, Interchemical Corp., New York, N. Y.

[5] Staudinger and Kupfer, *Ber.*, **44**, 2197 (1911).

[6] Knorr and Hess, *ibid.*, **44**, 2760 (1911).

[7] Wolff, *Ann.*, **394**, 86 (1912).

[8] Kishner, *J. Russ. Phys.-Chem. Soc.*, **43**, 582 (1911); **43**, 1398 (1911); **44**, 165 (1912); **45**, 1779 (1913); *Chem. Zentr.*, **82**, II, 363 (1911); **83**, I, 1622 (1912); **83**, II, 1925 (1912); **84**, I, 1497 (1913).

[9] Thielepape, *Ber.*, **55B**, 136 (1922); **55**, 2929 (1922).

[10] Supplied by Mathieson Alkali Works, Inc., Niagara Falls, N. Y.

[11] Dutcher and Wintersteiner, THIS JOURNAL, **61**, 1992 (1939).

[12] Supplied by the Edwal Laboratories, Chicago, Ill.

[13] Supplied by the American Instrument Co., Silver Spring, Md.

[14] Supplied by Armour and Co., Chicago, Ill.

[15] The relatively low yields of ketones (about 50–70%) have led to an investigation of the side products, now in progress.

[16] The extensive research on this coupling reaction will be the subject of a later publication.

[17] Piaux and Bourguel, *Ann. chim.*, [11] **4**, 147 (1935).

[18] Schmidt, Schoeller and Eberlein, *Ber.*, **74B**, 1313 (1941).

[19] Described in a separate publication to be submitted to the *Analytical Edition of Industrial and Engineering Chemistry.*

TABLE I

Name	Structure	Empirical formula	M. p., °C.	B. p., °C. (1.0 mm.)	n^{20}D	d^{20}	Molecular refraction Found	Molecular refraction Calcd.	Viscosity, 20° (centip.)
n-Hexacosane	$CH_3(CH_2)_{24}CH_3$	$C_{26}H_{54}$	56.2	205.0	1.4497[a]	0.8040[c]	122.5[c]	122.3	16.1[c]
1-Phenyleicosane	$C_6H_5—(CH_2)_{19}CH_3$	$C_{26}H_{46}$	42.3	212.0	1.4802[b]	.8542[c]	119.3[b]	118.7	17.5[c]
1-Cyclohexyleicosane	Cyclo-$C_6H_{11}—(CH_2)_{19}CH_3$	$C_{26}H_{52}$	47.9	212.0	1.4623[b]	.8320[c]	120.6[b]	120.1	25.8[c]
1-Cyclopentylheneicosane	Cyclo-$C_5H_9—(CH_2)_{20}CH_3$	$C_{26}H_{52}$	45.2	210.5	1.4604[a]	.8290[c]	120.6[c]	120.1	20.7[c]

[a] Calculated refractive index. [b] Calculated from $\Delta n = 0.6\ \Delta d$ [Ward and Kurtz, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 559 (1939)]. [c] Extrapolated values, or from extrapolated values.

ammoniacal methanol and pure methanol. After drying over anhydrous calcium chloride and anhydrous potassium carbonate, the bromide was distilled through an all-glass 35-plate column. Yield of pure bromide was 90%: b. p. 106° (39 mm.); n^{20}D 1.4527.

(b) **β-Phenylethyl Bromide.**—Prepared from 610 g. (5 moles) of β-phenylethyl alcohol (Eastman Kodak Co. White Label) and hydrogen bromide gas as in (a). After separation of the water layer the crude product was washed with 3 300-cc. portions of water, dried over anhydrous potassium carbonate, and fractionally distilled. Yield of pure bromide was 92%: b. p. 99° (15 mm.); n^{20}D 1.5572.

(c) **1-Bromo-3-cyclopentylpropane.**—Cyclopentylmagnesium bromide was prepared from 915 g. (6.15 moles) of cyclopentyl bromide[2] (b. p. 137° (737 mm.); n^{20}D 1.4890), with an equimolar quantity of magnesium in dry ether. Titration of a sample of the Grignard solution indicated a yield of 95%. After filtering, the Grignard reagent was added to 745 g. (6.15 moles) of redistilled allyl bromide[19] (b. p. 71° at 733 mm., n^{20}D 1.4695) in 2.5 liters of anhydrous ether over a period of six hours with stirring, while the mixture was cooled in a water-bath to about 15–20°. The excess Grignard reagent was decomposed by pouring over crushed ice. Several such runs were made, and the allylcyclopentane distilled through 35-plate columns; yield 510 g., 75%; b. p. 125.8° (739 mm.), 95.4° (298 mm.) (both Cottrell); d^{20} 0.7940; n^{20}D 1.4410. Allylcyclopentane (196 g., 1.78 moles) was treated with dry hydrogen bromide in the presence of 0.5 mole per cent. of benzoyl peroxide[20] at temperatures ranging from 0 to 40° until the theoretical weight of hydrogen bromide had been absorbed. The crude product was washed with water and dilute sodium carbonate, dried over anhydrous sodium carbonate, and the product was distilled through an all-glass 35-plate column. Yield of pure bromide was 253 g., 74%; b. p. 145° (124 mm.), 103.8° (26 mm.) (Cottrell); d^{20} 1.223; n^{20}D 1.4841. For structural proof the bromide was converted to the Grignard reagent, which was oxidized to give the alcohol. The phenylurethan (recrystallized from ligroin) melted at 56–57°. The phenylurethan of 3-cyclopentylpropanol prepared from cyclopentylmagnesium bromide and trimethylene oxide by Noller and Adams[21] melted at 55.0–55.4°.

(d) **Stearonitrile.**[14]—Purified by fractional distillation through the high vacuum column,[19] and constant freezing point fractions combined: b. p. 142° (0.45 mm.); f. p. 40.6–40.8°.

***n*-Hexacosane.**[22]—A Grignard reagent was prepared from 772 g. (4 moles) of *n*-octyl bromide in the usual manner. To this was added rapidly 755.5 g. (2.83 moles) of stearonitrile dissolved in 3 liters of anhydrous ether. After standing for a week the mixture was hydrolyzed with ice and a slight excess of sulfuric acid. After separation and ether extraction, the ether was removed by distillation and the residue recrystallized from methanol. Due to traces of inorganic impurity the crude ketone was refluxed overnight with sulfuric acid and excess methanol. Upon recrystallization from methanol, 920 g. (1.918 moles) of 9-hexacosanone[23] having constant melting point was obtained: yield 69%; m. p. 67–68°; oxime m. p. 40–41°.

A 1300-cc. high pressure bomb was charged with 100 g. (0.265 mole) of 9-hexacosanone, 108 g. (2 moles) of sodium methylate,[10] 31.2 g. (0.53 mole) of 85% hydrazine hydrate[12] and 700 cc. of absolute ethanol. The autoclave was shaken for eighteen hours at 200°. After removing the product, the bomb was washed with ligroin and water. The product plus extract was extracted with water and then ligroin, after which the ligroin was removed by distillation, leaving 83 g. of crude hydrocarbon. A second identical run was made, and the combined products from the two reactions recrystallized several times and then fractionally distilled through the high-vacuum column[19] at 0.5 mm. pressure. Yield of hydrocarbon having constant viscosity at 98.9° and constant freezing point was 51% (based on ketone).

Several successful runs were made at 195–210°, replacing the absolute ethanol with absolute isopropanol, obtaining an average 57% yield of pure, fractionally-distilled hydrocarbon. In one experiment the reaction time was decreased to twelve hours with no effect on the yield. An attempt to replace the hydrazine hydrate with hydrazine sulfate resulted in less than 10% conversion to *n*-hexacosane.

To insure complete removal of minute quantities of ketonic impurities, the constant melting fractions were dissolved in distilled pentane fraction and passed through silica gel. The solvent was removed on the steam-bath at 15 mm., followed by heating to 150° at 12 mm. for forty-five minutes.

1-Phenyleicosane.[22]—A Grignard solution was prepared from 420 g. (2.27 moles) of β-phenylethyl bromide and 57.5 g. (2.27 atoms) of magnesium in the usual manner. Titration of a sample of the Grignard solution indicated a yield of 95%. To the Grignard solution, maintained at 45–50°, was added 530 g. (2.0 moles) of stearonitrile dissolved in 800 cc. of dry toluene over a period of eleven hours. After stirring overnight and standing for two days the Gilman test for unreacted organomagnesium halide was negative, and the solution was poured onto an ice–ammonium sulfate solution mixture. After standing, the ether layer was separated and washed with warm water. The ether and toluene were removed by distillation through an indented column. Distillation through a modified Claisen flask at 1–2 mm. of the crude products indicated a 53% yield[15] of 1-phenyl-3-eicosanone (394 g., 1.06 moles); b. p. 232° (1–2 mm.); m. p. 54–56°; oxime m. p. 40–41°.

The reduction of 111 g. (0.3 mole) of 1-phenyl-3-eicosanone was performed in a 2760-ml. autoclave. After mixing the ketone with 2.3 moles of sodium methylate, 0.62 mole of 85% hydrazine hydrate and 850 ml. of ethanol, the mixture was heated to 200° with shaking for eighteen hours. The gaseous reaction products were allowed to escape, the products removed while warm and the bomb washed with three 300-ml. portions of ligroin and two 600 ml. portions of water, the latter to dissolve the excess solid sodium methylate lining the walls. The water wash solution was heated on the steam-bath, neutralized with dilute hydrochloric acid, and extracted with two 300-cc. portions of ligroin, adding the extracts to the original organic material. The alcohol and most of the ligroin were removed by distillation. The crude hydrocarbon was then washed with 600 cc. of 1:1 hydrochloric acid followed by three 500-cc. portions of warm water. The layers were separated and the solvent removed from the organic layer on the steam-bath. The product was fractionally distilled through the high vacuum column[19]

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[20] Kharasch, *et al.*, THIS JOURNAL, **56**, 244 (1934).

[21] Noller and Adams, *ibid.*, **48**, 1080 (1926).

[22] See Table I for properties.

[23] Mikeska's modification of the Clemmensen method [*J. Org. Chem.*, **2**, 499 (1938)] was unsuccessfully attempted, less than 10% hexacosane being obtained without recycling.

at 0.42 mm. Eighty-two per cent. of the distillate had a constant melting point, a 67% yield.

Three more preparations were made, in each case using a mixture of 0.5 mole of 1-phenyl-3-eicosanone, 4 moles of sodium methylate, 1 mole of 85% hydrazine hydrate and 1300 cc. of absolute ethanol. The only modification of the above procedure was the passage of a ligroin solution of the crude hydrocarbon through activated silica gel prior to fractional distillation. Yields of 67-70% of pure 1-phenyleicosane were obtained.

1-Cyclohexyleicosane.—Half of the previously prepared 1-phenyleicosane, 225 g., 0.6 mole, was dissolved in "olefin-free" ligroin and completely hydrogenated over 12 g. of nickel catalyst[24] at 185° and 1200-2000 lb./sq. in. pressure of hydrogen in four hours. The product was filtered through a tube of silica gel to remove the nickel and any remaining aromatic compounds, and distilled through the vacuum column at 0.25 mm. Ninety-four per cent. of the distillate had a constant freezing point and constant viscosity at 98.9°.

1-Cyclopentylheneicosane.—A Grignard solution was prepared from 440 g. (2.3 moles) of 1-bromo-3-cyclopentylpropane and 56 g. (2.3 atoms) of magnesium in the usual manner. To this was added 531 g. (2 moles) of stearonitrile dissolved in 750 cc. of anhydrous ether. The reaction mixture was decomposed by pouring over ice and concd. sulfuric acid. Distillation at 1-2 mm. in a modified Claisen flask of the crude product indicated a 49% yield[15] of 1-cyclopentyl-4-heneicosanone (371 g., 0.98 mole); b. p. 235° (1-2 mm.); m. p. 53-54°; oxime m. p. 40-1°.

The ketone was reduced in two half-mole portions in the same manner as the 1-phenyl-3-eicosanone. Fractionation of the resulting hydrocarbon through the vacuum column at 0.30 mm. indicated 79% yield. Eighty-five per cent. of the distillate had a constant freezing point. Two fluorescing fractions were treated with silica gel and the impurity causing the fluorescence removed satisfactorily.

Summary

1. The Wolff-Kishner method of converting a carbonyl group to a methylene group has been simplified and modified so that large reductions may be carried out with ease.

2. The preparations and five important properties are given for four 26-carbon hydrocarbons.

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[24] Supplied by the Universal Oil Products Co., Chicago, Ill.

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The Wolff-Kishner Reaction at Atmospheric Pressure

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In the first paper on the Wolff-Kishner reaction[2] special emphasis was placed on its utilization in the synthesis of high molecular weight hydrocarbons. Even with the simplified procedure described in that paper, the necessity of using pressure equipment remained.

The use of autoclaves, especially in the preparation of appreciable quantities of low molecular weight hydrocarbons from carbonyl compounds, is a distinct drawback. For this reason a modification was sought which would function satisfactorily at atmospheric pressure. It was evident that high temperature (190-200°) was needed for the Wolff-Kishner decomposition, and that pressure was probably unnecessary. Hence the substitution of a high-boiling solvent for the ethanol or isopropanol should permit reaction at atmospheric pressure.

Several different solvents and catalysts were tried, namely, *n*-octanol with sodium octylate, 2-ethylhexanol with sodium 2-ethylhexylate, ethylene glycol with sodium ethylene glycolate or commercial sodium methylate,[3] and triethylene glycol with sodium triethylene glycolate or sodium methylate.[3] The solvent of choice for atmospheric work was found to be triethylene glycol, using sodium methylate as the catalyst. The other combinations all have one or more drawbacks: *n*-octanol and 2-ethylhexanol are very poor solvents for sodium methylate, necessitating tedious preparation of their sodium alkoxides; ethylene glycol proved too low-boiling to permit the decomposition reaction at 190-200°, the hydrazone co-distilling with the glycol before this temperature was reached.

In general, yields of constant refractive index, fractionally distilled hydrocarbon were 60-65% depending somewhat on the structure of the carbonyl compound.

The method itself is divided into two parts. First the hydrazone is prepared in the high boiling solvent, then the decomposition reaction is run on this crude reaction mixture. The split was made in order that the hydrazone formation could be carried out under acidic conditions. This was felt desirable since with a reagent such as anhydrous potassium hydroxide it is possible to convert hydrazine hydrate into hydrazine. Since the latter has the disadvantage of tending to explode, it seemed advisable to avoid conditions under which it was possible to obtain free hydrazine. Therefore, in all hydrazone preparations using acid catalysts, the water and excess hydrazine hydrate were removed by fractional distillation prior to the addition of the alkaline Wolff-Kishner catalyst.

The minimum necessary quantities of solvent and sodium alcoholate were not determined. For one mole of aldehyde or ketone 400-450 ml. of solvent and 0.5 mole of sodium alcoholate proved quite satisfactory. Increasing the quantity of glacial acetic acid catalyst (for hydrazone preparation) had no appreciable effect on the yield.

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[1] Du Pont Fellow in Chemistry, 1943-1944.

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

[3] Supplied by Mathieson Alkali Works, Inc., Niagara Falls, N. Y.