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.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Wolff–Kishner Reaction at Atmospheric Pressure

BY C. H. HERR,[1] FRANK C. WHITMORE AND ROBERT W. SCHIESSLER

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.

In the reduction of diisopropyl ketone the yield was doubled by varying the method of bringing the alkaline catalyst and crude hydrazone together. By dropwise addition of the hydrazone–triethylene glycol solution to a triethylene glycol solution of sodium methylate held at 190–200°, the yield was raised from 17 to 36%. Although this method of adding the hydrazone to the heated solution of alcoholate did not improve appreciably the yield in the reduction of methyl cyclopropyl ketone, from an experimental standpoint it is very advantageous, particularly for large runs, since the rate of nitrogen evolution can be conveniently controlled by the rate of addition of the hydrazone solution to the hot alkali. Probably the improvement in yield with this modification will only be experienced with highly hindered ketones such as diisopropyl ketone.

Experimental

General Procedure. (a) **Hydrazone Preparation.**—A mixture of 1.0 mole of ketone, 120 g. (2 moles) of 85% hydrazine hydrate,[4] 180–200 ml. of triethylene glycol[9] and 5 ml. of glacial acetic acid is heated under a fractional distillation column[5] to 130–180°. Two layers form in the column take-off reservoir, the stopcock being adjusted to remove only the aqueous lower layer. The progress of the reaction is followed by weighing the quantity of water and excess hydrazine hydrate so removed. The distillation temperature usually is maintained below 125°, and distillation is discontinued when the theoretical amount of water and hydrazine hydrate is collected. The flask is cooled rapidly. The product is not isolated, the solution of crude hydrazone in the still being employed in the next step.

(b) **The Wolff–Kishner Reaction.**—A solution of 27 g. (0.5 mole) of commercial sodium methylate[3] in 200 ml. of triethylene glycol is added[6] to the cold hydrazone mixture, and the resulting solution heated rapidly to 170°, then more slowly to 190–200°, under the same column[5] employed in the hydrazone formation. A Dry Ice–acetone trap is included in the gas exit line from the column, followed by a gas-bubbler or gas collection bottle for following the course of the nitrogen evolution. A somewhat vigorous reaction occurs at 190–200°, the hydrocarbon formed distilling over if it boils below 190°. For a one-mole run the decomposition is complete in one-half to one and one-half hours, and about 80–85% of the theoretical nitrogen is evolved.

The distillate and trap contents are combined, extracted twice with 1/1 hydrochloric acid, followed by a dilute carbonate wash. The hydrocarbon is then dried over anhydrous potassium carbonate and fractionally distilled. Passage through a column of activated silica gel is advantageous for the removal of traces of polar impurities prior to distillation.

Carbonyl Compounds.—Care was taken to obtain pure aldehydes and ketones. Fractional distillation columns with efficiencies of 15 to 30 theoretical plates have been used in all preparations. The boiling points of the carbonyl compounds and the final hydrocarbons are uncorrected. The constants given are those of the constant boiling point, constant index refraction fractions. Only this material was used.

(a) **2,3,3-Trimethyl-4-pentanone.**—Prepared by treating tetramethylethylene with acetic anhydride in the presence of zinc chloride. The resulting unsaturated ketone[7] was hydrogenated over Raney nickel at room temperature,[8] and the product distilled through an all-glass 25-plate column: b. p. 159° (735 mm.), 101° (152 mm.); n^{20}_{D} 1.4229.

(b) **2-Octanone.**—Material synthesized by students in a preparation course was carefully fractionated: b. p. 171° (734 mm.), n^{20}_{D} 1.4154.

(c) **Butyrophenone.**—The ketone made by students in a preparation course was carefully fractionated: b. p. 130° (34 mm.), n^{20}_{D} 1.5204.

(d) **Cyclohexanone.**—Eastman Kodak Co. practical grade cyclohexanone was carefully fractionated: b. p. 154° (727 mm.), n^{20}_{D} 1.4500.

(e) ***n*-Heptaldehyde.**—Eastman Kodak Co. White Label *n*-heptaldehyde was dried over anhydrous calcium chloride, passed through a column of silica gel and fractionated: b. p. 151° (734 mm.), n^{20}_{D} 1.4121.

(f) **Diisopropyl Ketone.**—Du Pont de Nemours and Co. technical diisopropyl ketone was carefully fractionated: b. p. 122° (730 mm.), n^{20}_{D} 1.4002.

(g) **Methyl Cyclopropyl Ketone.**—U. S. Industrial Chemicals methyl cyclopropyl ketone was carefully fractionated: b. p. 111° (737 mm.), n^{20}_{D} 1.4250.

Solvents.—The commercially available solvents studied included "technical octanol" (2-ethylhexanol),[9] ethylene glycol,[10] and triethylene glycol.[9] One run was also made using *n*-octanol.[11] The commercial grade solvents were not purified for these studies.

Catalysts.—J. T. Baker C. P. glacial acetic and concd. hydrochloric acids were used as catalysts for the preparation of the hydrazones.

2,3,3-Trimethylpentane.—Following are the quantities of reactants employed in a typical run: The crude hydrazone was prepared as in the above General Procedure from 128 g. (1.0 mole) of 2,3,3-trimethyl-4-pentanone, 120 g. (2 moles) of 85% hydrazine hydrate,[4] 200 ml. of technical 2-ethylhexanol[9] and 5 ml. of glacial acetic acid. The Wolff–Kishner decomposition, conducted as described in the General Procedure, was made with the crude hydrazone and a solution of 34.5 g. (1.5 moles) of sodium in 300 ml. of 2-ethylhexanol. Reaction was complete in one and one-half hours, 21 liters of nitrogen being evolved. The product was purified as described above. Yield[12] of pure 2,3,3-trimethylpentane was 62%; b. p. 113°, n^{20}_{D} 1.4074.[13] A total of six experiments were conducted, four of which were successful. The unsuccessful reactions involved attempts to use ethylene glycol as a solvent with either sodium methylate[3] or sodium ethylene glycolate. The other experiments employed octanol with sodium octylate (yielding 72% pure hydrocarbon) or 2-ethylhexanol with sodium 2-ethylhexylate. Yields varied from 53 to 72%.

***n*-Octane.**—From a typical run, the hydrazone of 128 g. (1.0 mole) of 2-octanone was prepared with 120 g. (2.0 moles) of 85% hydrazine hydrate[4] in 440 ml. of triethylene glycol and 6 ml. of gl. acetic acid by the method described above. To the solution of crude hydrazone was added 27 g. (0.5 mole) of powdered sodium methylate,[3] and the decomposition and purification conducted as directed in the General Procedure. Yield[12] of fractionated *n*-octane was 66%: b. p. 124.0–124.5°; n^{20}_{D} 1.3977.[14]

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(4) Supplied by Edwal Laboratories, Chicago, Ill.

(5) An 18-inch, 11-mm. i. d., total condensation, partial take-off column containing no packing was employed to facilitate the removal of water and excess hydrazine hydrate. The column was jacketed but not heated externally.

(6) The following procedure is recommended for large scale preparations or highly hindered ketones such as diisopropyl ketone: the sodium methylate solution is heated to 190–200°, and the solution of crude hydrazone slowly added from a dropping funnel. The rate of nitrogen evolution can thus be controlled conveniently.

(7) Byrns and Doumani, *Ind. Eng. Chem.*, **35**, 349 (1943).

(8) The authors thank J. A. Krimmel for the pure ketone used in this work.

(9) Supplied by Carbide and Carbon Chemicals Corporation, 30 East 42nd St., New York, N. Y.

(10) Practical grade, Eastman Kodak Co., Rochester, N. Y.

(11) Du Pont de Nemours and Co., Wilmington, Del.

(12) All yields are based on the quantity of ketone employed.

(13) B. p. 114.6°, n^{20}_{D} 1.4072: Hoog, "Second World Petroleum Congress," Paris, 1937, Vol. II, p. 494.

(14) B. p. 125.6°; n^{20}_{D} 1.3976; Boord and Henne, A. C. S. Meeting, Detroit, Sept. 9, 1940.

A total of five preparations of *n*-octane from 2-octanone were made successfully, employing 2-ethylhexanol as solvent with sodium 2-ethylhexylate as catalyst and triethylene glycol with sodium methylate or sodium triethylene glycolate. The yields[12] of pure *n*-octane were consistently 65–68%, and the quantity of nitrogen evolved was nearly theoretical in each case.

Butylbenzene.[15]—The hydrazone was prepared in three hours from 148 g. (1.0 mole) of butyrophenone. It was decomposed at 170–210° in the usual manner, evolving 22 liters of nitrogen. The yield[12] was 66%; b. p. 180°; $n^{20}\text{D}$ 1.4890.[16]

Cyclohexane.[15]—The hydrazone was prepared from 98 g. (1.0 mole) of cyclohexanone in one and one-half hours. A vigorous evolution of gas occurred at 203° during the Wolff–Kishner decomposition, which was complete in forty-five minutes. Yield of pure cyclohexane was 63%; b. p. 80.5°; $n^{20}\text{D}$ 1.4261.[17]

***n*-Heptane.**[15]—A hydrazone was prepared from 114 g. (1.0 mole) of *n*-heptaldehyde in the usual manner. Gas evolution during the decomposition began at 108°, a lower temperature than experienced with any of the ketones. At 180°, the decomposition rate was very rapid, as evidenced by the nitrogen evolution rate. Yield of pure *n*-heptane was 54%; b. p. 98.0°; $n^{20}\text{D}$ 1.3877.[18]

2,4-Dimethylheptane.[6,15]—Although diisopropyl ketone proved insoluble in triethylene glycol, the hydrazone preparation was made using 114 g. (1.0 mole) of ketone. Two layers were observed in the flask until a temperature of 110–120° was reached, at which point a vigorous reaction occurred with the formation of one liquid phase. The rest of the experiment proceeded smoothly except that only 10 liters of nitrogen were evolved in the decomposition. Two preparations were conducted in this manner, yielding only 16–17% of pure 2,4-dimethylheptane in each case.

Two further runs were made, using the modified procedure[6] and yields of 35–36% pure 2,4-dimethylheptane were realized: b. p. 78–80°; $n^{20}\text{D}$ 1.3815.[19]

Ethylcyclopropane.[15]—A hydrazone was prepared from 84 g. (1.0 mole) of methyl cyclopropyl ketone in the usual manner. The decomposition was carried out after mixing the crude hydrazone and sodium methylate, yielding 57% of pure ethylcyclopropane. A second preparation, employing the modification whereby the hydrazone solution is added slowly to the hot alkali.[6] resulted in a 60% yield of ethylcyclopropane: b. p. 36.0°; $n^{20}\text{D}$ 1.3784.[20]

Summary

The Wolff–Kishner reaction has been successfully employed in reducing one aldehyde and six ketones of various types to the corresponding low molecular weight hydrocarbons without any pressure equipment. Utilizing readily available solvents and catalysts, this reaction at atmospheric pressure was found to yield pure hydrocarbons in good yields and in reasonable time without any operation dangers. No evidence of rearrangement was noted.

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[15] Using 120 g. of 85% hydrazine hydrate, 440 ml. triethylene glycol and 6 ml. gl. acetic acid in preparation of the hydrazone. Sodium methylate (0.5 mole, 27 g.) was the decomposition catalyst. Refer to the General Procedure for details of operation.

[16] B. p. 182.1–183.1°; $n^{20}\text{D}$ 1.4880: Evans, *J. Inst. Petroleum Tech.*, **24**, 537 (1938).

[17] B. p. 80.8°; $n^{20}\text{D}$ 1.4262: Wibaut, *Rec. trav. chim.*, **58**, 329 (1939); **59**, 1220 (1940).

[18] B. p. 98.4°; $n^{20}\text{D}$ 1.3877: Brooks, *J. Research Nat. Bur. Standards*, **24**, 44 (1940); see also ref. 17.

[19] B. p. 80.6°; $n^{20}\text{D}$ 1.3815: Smittenberg, Hoog, Moerbeek and Zijden, *J. Inst. Petroleum Tech.*, **26**, 294 (1940); see also ref. 17.

[20] B. p. 35.8°; $n^{20}\text{D}$ 1.3789: Lespieaux, *Bull. soc. chim.*, [4] **47**, 847 (1930).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Radical Chain Processes in Vinyl and Diene Reactions

BY HUGH S. TAYLOR AND ARTHUR V. TOBOLSKY

The polymerization of vinyl and diene derivatives occurs in many cases by a radical chain mechanism, the chain being initiated by addition of a free radical to the double bond of the substrate.

In addition to linear growth, various other important reactions occur both during the polymerization process and after the apparent completion of polymerization. These include branching, cross-linking, depolymerization or scission, cyclization and autoxidation of the long chain molecules. These competing reactions which we shall term subsidiary reactions, also are radical chain reactions, and it is the purpose of this paper to bring out the fundamental similarities in chemical mechanism underlying all of these apparently diverse phenomena.

The subsidiary reactions profoundly affect the physical properties of vinyl and diene plastics maintained at elevated temperatures, and these changes are collectively known as "aging." Oxygen and peroxides play a fundamental part in the natural or accelerated aging of these substances. Several new experimental techniques have been developed which allow a separation of the effects of these simultaneously occurring reactions and by means of these methods the kinetics of the reactions can be studied.

Polymerization.—The commonly accepted version of the nature of vinyl and diene polymerization was formulated through the efforts of Staudinger,[1] Mark,[2] Schulz[3] and many others. Also earlier work had established the possibility of polymerization of ethylene through the introduction of free radicals.[4,5] The most important processes occurring under the conditions of polymerization are chain initiation, chain growth and chain termination.

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[1] H. Staudinger, "Die Hochmolekularen organischen Verbindungen," Springer, Berlin, 1932.

[2] H. Dostal and H. Mark, *Z. physik. Chem.*, **B29**, 299 (1935).

[3] G. V. Schulz and E. Husemann, *ibid.*, **B34**, 187 (1936); **B36**, 184 (1937); **B39**, 246 (1938).

[4] H. S. Taylor, *Proc. Am. Phil. Soc.*, **65**, 90 (1926).

[5] H. S. Taylor and W. H. Jones, THIS JOURNAL, **52**, 1111 (1930).