[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Preparation of Aldehydes from Alkenes by the Addition of Carbon Monoxide and Hydrogen with Cobalt Carbonyls as Intermediates

BY HOMER ADKINS AND GEORGE KRSEK

A U. S. patent issued to Otto Roelen[1] discloses a most interesting and rather surprising reaction, *i.e.*

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[125\text{–}200 \text{ atm.}]{90\text{–}200°} RCH_2CH_2CHO$$

In the examples given in the patent the reaction is applied to ethylene, to oil of turpentine and to a lubricating oil. The catalysts specified contained cobalt, thorium oxide, kieselguhr and sometimes copper. The liquid product from ethylene was reported as made up of "40% propionaldehyde, 20% diethyl ketone and 40% higher boiling aldehydes and ketones or other oxygenated products." The results of inquiries made in Germany in 1945–1946 indicated the practicality of this so called "oxo process," particularly for the preparation of primary alcohols from alkenes through the reduction of the aldehydes first formed.

Apart from the merits of the process for commercial utilization, the Roelen reaction is obviously of considerable potential value in organic syntheses. We were interested in working out the best conditions for carrying out the reaction in standard steel equipment in the laboratory, and in ascertaining the yields of aldehyde from various unsaturated compounds. There are limitations to the reaction as, for example, two aldehydes might be obtained by the addition of carbon monoxide and hydrogen to an alkene $RCH{=}CH_2$, *i.e.*, RCH_2CH_2CHO and $RCH(CH_3)CHO$ as well as ketones where two molecules of the alkene and one of carbon monoxide reacted. Other reactions which may occur under the conditions used are the reduction of the alkene or the reduction or condensation of the carbonyl compounds.

In view of the well-known variation in the reactivity of alkenes, depending upon their structure, it seemed improbable that all compounds containing a carbon to carbon double bond would add carbon monoxide and hydrogen. However, it has been possible to produce aldehydes in the indicated yield from unsaturated compounds having as diverse structures as pentene-2 (75%), styrene (30%), methyl undecylenate (75%), ethyl crotonate (36%), diethyl fumarate (51%), allyl alcohol (18%) and allyl acetate (70%).

The range of conditions specified in the Roelen patent are, as might be expected, rather wide. However, after a considerable number of experiments, conditions were found under which the reaction has proceeded well with several unsaturated compounds. For example, 25 g. of commercial pentene-2 in 60 ml. of ether, with 0.6 g. of a reduced cobalt on kieselguhr catalyst, was placed in a steel reaction vessel having a 270-ml. void. The vessel was charged with carbon monoxide to a pressure of 2400 p.s.i. and hydrogen was added until the total pressure was 3600 p.s.i. The bomb was then shaken and heated to 150° when the pressure was 4300 p.s.i. During three hours the pressure dropped to 2200 p.s.i. The pressure drop was 96% of that required for the absorption of one mole of carbon monoxide and one mole of hydrogen per mole of pentene. The bomb was allowed to cool to room temperature, opened and the catalyst separated by centrifugation. The ether was removed by distillation and the product distilled under reduced pressure. The yield of aldehydes amounted to 75% of the theoretical. The boiling range of the product indicated that the aldehydes were those which would be produced by the alternate possible adducts of pentene-2, *i.e.*, $CH_3CH_2CH_2CH(CH_3)CHO$ and $CH_3CH_2CH(C_2H_5)CHO$.

Another representative synthesis was with 21.5 g. of methyl undecylenate in 80 ml. of ether under the same condition of temperature, pressure and catalyst as given for pentene-2. There was an incubation period of about twenty minutes after the reaction mixture reached 150°. However, 100% of the theoretical amount of carbon monoxide and hydrogen was then taken up within 140 minutes. Methyl 11-aldehydo-undecanoate was obtained in yield of 75% of the theoretical by distillation under reduced pressure.

While carrying out experiments of the type described above we began to suspect that we were not primarily concerned with a reaction in heterogenous catalysis where the reaction occurs at the surface of a solid, as in catalytic hydrogenation. The reaction mixture in successful syntheses was always colored, whereas in the failures it was colorless. In order to test the hypothesis that the catalyst was soluble in ether, the reactions were carried out in two stages. In the first stage an ether soluble cobalt compound, dicobalt octacarbonyl, was prepared by reaction of cobalt and carbon monoxide. The ether solution so obtained was used as the catalyst for the reaction of an alkene with carbon monoxide and hydrogen. The reaction, in the presence of the preformed dicobalt octacarbonyl, proceeded to completion within a few minutes at a temperature 25° lower than was necessary where a soluble cobalt compound was not used.

It appears that the synthesis may be considered to involve at least four reactions which may be outlined as

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(1) Otto Roelen, U. S. Patent 2,327,066 (1943). The patent was vested in the Alien Property Custodian.

$$2Co + 8CO \xrightleftharpoons[150^\circ]{} [Co(CO)_4]_2 \qquad (1)$$

$$[Co(CO)_4]_2 \xrightleftharpoons[125^\circ]{H_2} 2Co(CO)_3COH \qquad (2)$$

$$4Co(CO)_3COH + 4CH_2{=}CH_2 \xrightarrow[125^\circ]{H_2} 4CH_3CH_2CHO + [Co(CO)_3]_4 \qquad (3)$$

$$[Co(CO)_3]_4 + 4CO \xrightleftharpoons[125^\circ]{} 2[Co(CO)_4]_2 \qquad (4)$$

In the first stage metallic cobalt is converted to dicobalt octacarbonyl (as in 1), a reaction which requires a higher temperature than the subsequent steps and even so goes more slowly. Dicobalt octacarbonyl is then reduced to cobalt tetracarbonyl hydride as indicated in (2). We suggest that a hydride is the reagent effective in the synthesis as shown in 3. The tetracobalt dodecacarbonyl $[Co(CO)_3]_4$, postulated as formed in 3, would be converted to dicobaltoctacarbonyl $[Co(CO)_4]_2$ by reaction with carbon monoxide as indicated in 4. The transformations involved are perhaps more clearly seen if the brackets in the formulas, indicating polymeric forms, are disregarded. The chemistry of the cobalt carbonyls, except that suggested in reaction 3, is covered in recent publications.[2,3]

The direct preparation of dicobalt octacarbonyl[4] from cobalt and carbon monoxide was carried out as follows: Raney cobalt (4 to 8 g.) was placed with 145 ml. of ether under carbon monoxide at 3200 p.s.i. and heated with shaking for five or six hours at 150°, after which the reaction vessel was allowed to cool. The pressure during the period of heating dropped from 4900 to 4300 p.s.i. and then to 2200 p.s.i. when the bomb was cooled to room temperature. The insoluble portion of the reaction mixture was removed by centrifugation. The dark reddish brown clear solution of 160 ml., including ether used in the transfers, contained 8.9 g. of dicobalt octacarbonyl. This compound was found to be soluble in ether to the extent of approximately 7.5 g. per 100 ml. of solution. The Raney cobalt has been specified above but the metal obtained by reduction of the Harshaw cobalt on kieselguhr catalyst, "Co-100 powder," has also been used.

Our practice has been to place the ether solution of dicobalt octacarbonyl as obtained from the reaction of cobalt and carbon monoxide in a 250 ml. Pyrex centrifuge bottle held in a wire guard, such as is used in hydrogenation at 2 or 3 atm. pressure. The bottle was provided with a rubber stopper held in place by a clamp. One leg of an inverted glass U tube extended through the stopper to the bottom of the flask. The other leg of the tube carried a stopcock. The container was kept in a refrigerator until a quantity of the catalyst solution was needed. The bottle was then allowed to warm up to room temperature or a little higher. Sufficient pressure was thus developed in the bottle so that the ether solution would flow through the U tube into a graduate when the stopcock was opened. The pressure developed over the solution at 30° was less than 0.5 atmosphere and was largely due to the vapor pressure of the ether.

The synthesis was carried out by placing 50 g. of allyl acetate, 40 ml. of the ether solution containing 2.2 g. of dicobalt octacarbonyl and 40 ml. of ether in a steel reaction vessel. Carbon monoxide was introduced to a pressure of 3200 p.s.i. and hydrogen added to a pressure of 4800 p.s.i. The pressure dropped to 4250 p.s.i. when the mixture was shaken and then rose to a maximum of 5050 p.s.i. when it was heated up to 115°. The bomb was then heated more slowly so that the temperature did not exceed 125°, by which time the pressure had already fallen to 4000 p.s.i. Within less than nine minutes the pressure had fallen to 3100 p.s.i. and the reaction was considered complete. The pressure in the bomb, when it had cooled to room temperature, was 2000 p.s.i. The drop in pressure during the reaction corresponded to the absorption of approximately 1 mole of each gas per mole of allyl acetate. When the product was worked up in the usual way γ-acetoxybutyraldehyde was obtained in 69% yield.

Hazards

The use of carbon monoxide under pressure with the highly poisonous cobalt carbonyls is not without danger. The ill effect of breathing carbon monoxide is sufficiently well known so that a warning is perhaps not necessary. According to Gilmont and Blanchard[2] "the odor of cobalt tetracarbonyl hydride is so intolerable that the danger from inhaling it is much less than from nickel tetracarbonyl. However, it is probably equally poisonous, and the same precautions should be taken as with nickel tetracarbonyl." The hydride decomposes even at room temperature, so that it will disappear rapidly from reaction mixtures held at atmospheric pressure, with the formation of dicobalt octacarbonyl. Fortunately this latter compound has a low vapor pressure and so may be handled with much less hazard than nickel tetracarbonyl. The dicobalt octacarbonyl also decomposes slowly in an open vessel to give carbon monoxide at room temperature. However, in an ether solution in a closed Pyrex bottle there is no development of pressure or appreciable decomposition at room temperature.

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(2) For a brief summary and references see Gilmont and Blanchard, "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., New York, N. Y., 1946, p. 238.

(3) Hieber, Schulten and Marin, *Z. anorg. allgem. Chem.*, **240**, 261-272 (1939).

(4) Apparently the preferred procedure for preparing dicobalt octacarbonyl has been that described by Gilmont and Blanchard.[2] Their procedure involves a series of reactions from cobalt nitrate to a potassium cobaltocyanide, to a potassium salt of cobalt tetracarbonyl hydride, to the hydride and then to the desired product. The process seems rather long and laborious, and while the weight of product is not stated it is apparently of the order of 2 g. The availability of steel reaction vessels and carbon monoxide under pressure makes the preparation of dicobalt octacarbonyl an easy and Simple process.

First class steel equipment in good condition and in the hands of a competent operator are essential if accidents are to be avoided. There should be no leaks of any kind in the equipment. All transfers of material and washing of the reaction vessel should be carried out in a hood with rapid ventilation. The residual gas from the reaction vessel, which contains carbon monoxide and probably volatile cobalt compounds, should be burned in a Bunsen burner or slowly vented in the hood. The exit gas from all distillations or filtrations should be taken care of by large quantities of running water. Residues after distillation should be similarly disposed of, *all* operations being carried out under a hood.

It is said that the presence of traces of volatile cobalt or nickel compounds in the air may be detected by the color of the flame of a burner. The U. S. Bureau of Standards has developed a tube with a filler which we have found useful in detecting carbon monoxide in air. In some laboratories canaries are used as detectors for carbon monoxide.

Pressures higher than necessary probably were used. This was done so that a quantity of carbon monoxide and hydrogen, sufficient to react with the desired quantity of alkene, could be placed in the bomb. The ratio of carbon monoxide to hydrogen was probably higher than necessary. Incidentally it may be noted that successful hydrogenations, with nickel or copper chromium oxide, usually cannot be carried out for some time after a bomb has been used with carbon monoxide.

Experimental Details

Cobalt Catalysts.—The cobalt on kieselguhr catalyst was "Co-100 powder" as supplied by the Harshaw Chemical Co. of Cleveland, Ohio. According to the supplier the "Co-100 powder" would give 50% of its weight of cobalt when reduced. In our experience the reduced catalyst contained 12 to 15% metallic cobalt after treatment with hydrogen at 425° for four hours. Raney cobalt was made from the Raney 40% cobalt–60% aluminum alloy, by the procedure used for preparing Raney nickel.[5]

Isolation and Characterization of Products.—The products (27 g.) from pentene-2 (25 g.) distilled at 40–50° (12 mm.) A titration by the hydroxylamine method[6] with methyl orange as the indicator, showed that the aldehyde content, calculated for $C_5H_{11}CHO$, was 88%. Fractional distillation gave a fraction, b.p. 28–29° (10 mm.), n^{25}D 1.4009, which was 95% aldehyde. The 2,4-dinitrophenylhydrazones melted over the range 90–120°. The boiling points of the two aldehydes[7,8] which would be produced from pentene-2 are too close together to make their separation feasible.

Styrene (18 g.) reacted as did the other unsaturated compounds giving a product (9.3 g.) boiling 78–120° (10 mm.) which analyzed[6] for 80% aldehyde. After fractionation hydrotropaldehyde, b.p. 76–77° (0.08 mm.), n^{25}D 1.5148, was obtained 95% pure.[9] It gave a semicarbazone,[10] m.p. 153–154°.

Diethyl fumarate (17.2 g.) reacted with carbon monoxide and hydrogen as did methyl undecenylate. The product (14.3 g.) distilled at 85-120° (1 mm.) and was 70% pure by titration.[6] After fractionation the diethyl α-formyl-succinate[11] had a b.p. 104–105° (0.04 mm.), n^{25}D 1.4486, and was 95% pure. It gave a semicarbazone, m.p. 124–125°, and a *p*-nitrophenylhydrazone, m.p. 100–101°.

The product (18 g.) from methyl undecylenate (21.5 g.) distilled at 125–150° at less than 1 mm. pressure, was 90% methyl 11-aldehydo-undecanoate according to hydroxylamine titration.[6] After fractionation the aldehyde, b.p. 144–147° (0.1 mm.), n^{25}D 1.4432, was 97% pure.[12] The 2,4-dinitrophenylhydrazone had the m.p. 69–70°. Oxidation with air at 60° followed by saponification to dodecanedioic acid $(CH_2)_{10}(CO_2H)_2$, m.p. 122–124°, showed the aldehyde to be methyl 11-aldehydo-undecanoate,[13] $CHO(CH_2)_{10}CO_2CH_3$.

Allyl alcohol (29 g.) in ether reacted with carbon monoxide and hydrogen in the presence of 2.2 g. of dicobalt octacarbonyl, as has been described for allyl acetate. The product (16 g.) distilled at 80–100° (28 mm.) and was found to be 55% pure. After fractionation γ-hydroxybutyraldehyde, 96% pure, b.p. 98–99° (35 mm.), n^{25}D 1.4384, gave a 2,4-dinitrophenyl-hydrazone, m.p. 178–179°. The aldehyde was oxidized with air at 60° and lactonized to give an 80% yield of butyrolactone,[14] b.p. 90–91° (25 mm.), n^{25}D 1.4345, having a saponification equivalent of 85.

The product (46 g.) from the reaction as described above of allyl acetate (50 g.) distilled at 60–90° (10 mm.) and was 92% pure by titration. After fractionation the γ-acetoxybutyraldehyde, b.p. 59–60° (1 mm.), n^{25}D 1.4245, was 94% pure and gave a 2,4-dinitrophenylhydrazone, m.p. 180–181°. The aldehyde was oxidized with air at 60° in 97% yield to give γ-acetoxybutyric acid, b.p. 112–113° (1 mm.), n^{25}D 1.4343, which was by titration 99% pure. The acid was hydrolyzed and lactonized to butyrolactone. *Anal.* Calcd. for γ-acetoxybutyraldehyde $C_6H_{10}O_3$: C, 55.4; H, 7.8, Found: C, 55.4; H, 8.0. *Anal.* Calcd. for γ-acetoxybutyric acid $C_6H_{10}O_4$: C, 49.3; H, 6.7. Found: C, 49.3; H, 7.1.

Ethyl crotonate (29 g.) in ether reacted with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl (2.2 g.) as described for allyl acetate. The product (19.1 g.), b.p. 96–100° (35 mm.), was 96% pure by titration. The ethyl β-formylbutyrate distilled at 58–59° (0.01 mm.), had n^{25}D 1.4236 and gave a 2,4-dinitrophenylhydrazone, m.p. 87–88°.

Anal. Calcd. for $C_7H_{11}O_3$: C, 58.3; H, 8.4. Found: C, 58.5; H, 8.5.

Summary

Several aldehydes, *i.e.*, hexaldehydes, hydratropaldehyde, diethyl α-formylsuccinate, methyl 11-aldehydoundecanoate, γ-hydroxybutyraldehyde, γ-acetoxybutyraldehyde and ethyl β-formylbutyrate, have been prepared in an average yield of 50% by the addition of carbon monoxide and hydrogen to the alkene linkage in pentene-2, styrene, diethyl fumarate, methyl undecylenate, allyl alcohol, allyl acetate or ethyl crotonate.[15]

The first step in the catalysis of the reaction appears to be the formation of an ether-soluble cobalt compound, dicobalt octacarbonyl. While the conversion of the alkene to the aldehyde may be brought about at 150° in the presence of cobalt

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(5) Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

(6) Alexander Halasz, *Ann. Chim.*, **14**, 336 (1940).

(7) Stoermer, *Ber.*, **39**, 2297 (1906).

(8) Skita, *ibid.*, **48**, 1491 (1915).

(9) Wooten, *J. Chem. Soc.*, **97**, 409 (1910).

(10) Claisen, *Ber.*, **38**, 705 (1905).

(11) Schtschukena and Preobrashenski, *Ber.*, **68B**, 1991 (1935).

(12) Adams, THIS JOURNAL, **49**, 522 (1927).

(13) Noerdlinger, *Ber.*, **23**, 2357 (1890).

(14) Sircar, *J. Chem. Soc.*, 898 (1928).

(15) Succindialdehyde-1,1-diacetate and γ-carbethoxypropionaldehyde were prepared in 74–75% yields from 50 g. of allylidene diacetate and of ethyl acrylate, respectively, with 0.6 g. of dicobalt octacarbonyl as a catalyst in benzene at 125° and 1200 to 4000 p. s. i. (Added in proof, January 5, 1948.)

on a support, it appears advantageous to use preformed dicobalt octacarbonyl in ether or other solvent for the catalysis of the synthetic reaction. The dicobalt octacarbonyl is readily made at 150° by the direct reaction of cobalt and carbon monoxide, and may be kept in ether for use as needed as a catalyst. The addition of carbon monoxide and hydrogen to an alkene goes very rapidly at 125° or lower in the presence of dicobalt octacarbonyl. The reactions may be carried out at 100 to 300 atm. pressure in the steel reaction vessels ordinarily used for hydrogenation.

The poisonous properties of carbon monoxide and of the cobalt carbonyls suggest that considerable care be exercised in carrying out the syntheses of aldehydes for alkenes by the method outlined.

MADISON, WISCONSIN RECEIVED SEPTEMBER 6, 1947

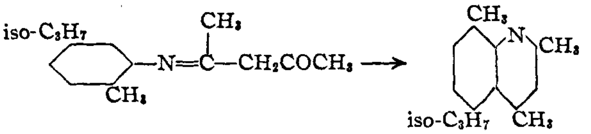
[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Some Quinoline Derivatives of 2-Amino-*p*-cymene[1]

BY ALVIN SAWYER WHEELER AND JOSEPH NISBET LECONTE

Introduction

This paper records a study of several methyl homologs of 5-isopropylquinoline. The 8-methyl derivative was prepared by the method of Cohn and Gustavson,[2] and the 2,4,8-trimethyl compound was obtained by cyclizing, according to Bulow and Issler,[3] the compound I obtained by condensing 2-amino-*p*-cymene with acetylacetone.



The 8-methyl derivative and the 2,8-dimethyl compound of Phillips and Goss[4] on reduction with sodium and absolute ethanol yielded py-tetrahydroquinolines.

Experimental

Temperatures are in °C., uncorrected.

5-Isopropyl-8-methylquinoline.—2-Amino-*p*-cymene (59.6 g.), 2-nitro-*p*-cymene (35.8 g.), 80% acetic acid (60 cc.), 95% sulfuric acid (54 cc.) and glycerol (100 g.) were treated in the manner of Cohn and Gustavson[2] to yield 20 g. (27%) of the quinoline which is a pale yellow oil with the characteristic quinoline-like odor; b. p. 175° (35 mm.); $d^{26.2}_{4}$ 1.0287; n^{27}_{D} 1.5798. *Anal.* Calcd. for $C_{13}H_{15}N$: N, 7.56. Found: N, 7.43. Chloroplatinate, m. p. 212° (shrinks at 160°). *Anal.* Calcd. for $C_{13}H_{17}NCl_6Pt$: Pt, 24.82. Found: Pt, 24.90. Picrate, m. p. 166–168°. *Anal.* Calcd. for $C_{19}H_{18}N_4O_7$: N, 13.52. Found: N, 13.44.

Reduction of this quinoline with sodium and absolute ethanol yielded py-tetrahydro-5-isopropyl-8-methylquinoline, b. p. 165–167° (27 mm.). *Anal.* Calcd. for $C_{13}H_{19}N$: N, 7.40. Found: N, 7.39. Chloroplatinate, m. p. 198°. *Anal.* Calcd. for $C_{13}H_{21}NCl_6Pt$: Pt, 24.22. Found: Pt, 24.37.

2,8-Dimethyl-5-isopropylquinoline was prepared in the manner formerly employed by Phillips and Goss.[4] Chloroplatinate, m. p. 226° (shrinks 212°). *Anal.* Calcd. for $C_{14}H_{19}NCl_6Pt$: Pt, 23.62. Found: Pt, 23.80. Picrate, m. p. 142°. *Anal.* Calcd. for $C_{20}H_{20}N_4O_7$: N, 14.52. Found: N, 14.60.

Reduction of this quinoline with sodium and absolute ethanol yielded py-tetrahydro-2,8-dimethyl-5-isopropylquinoline, m. p. 65°. *Anal.* Calcd. for $C_{14}H_{21}N$: N, 6.89. Found: N, 6.78. Chloroplatinate, m. p. 202° (shrinks 199°). *Anal.* Calcd. for $C_{14}H_{23}NCl_6Pt$: Pt, 23.39. Found: Pt, 23.80.

Compound I.—A mixture of 2-amino-*p*-cymene (15.05 g.) and acetylacetone (10 g.) was refluxed on a steam-bath for three hours, during which water appeared in the mixture and the mixture became dark red in color. Distillation of the mixture under reduced pressure yielded 11.8 g. of a pale yellow oil, b. p. 184–185° (22 mm.), $d^{27.5}$ 0.9827, insoluble in water, easily soluble in alcohol and ether, blood-red color with ferric chloride, and no reaction with the Hinsberg reagent. *Anal.* Calcd. for $C_{15}H_{21}ON$: N, 6.06. Found: N, 5.89. Chloroplatinate, m. p. 177°. *Anal.* Calcd. for $C_{15}H_{23}ONCl_6Pt$: Pt, 21.93. Found: Pt, 22.04.

2,4,8-Trimethyl-5-isopropylquinoline.—Ninety-five per cent. sulfuric acid (60 cc.) was cooled to 0° and 19.5 g. of compound I was cautiously added. The mixture was allowed to stand ten minutes, heated on a steam-bath for one hour, poured into a mixture of ice (100 g.) and water (60 cc.), made basic with ammonium hydroxide, saturated with sodium chloride and extracted with ether. Distillation of the dried ether solution under reduced pressure yielded 5 g. of a pale yellow oil, b. p. 170–178° (22 mm.) (boiling mostly at 177–178°). *Anal.* Calcd. for $C_{15}H_{19}N$: N, 6.57. Found: N, 6.70. Chloroplatinate, m. p. 213–216°. *Anal.* Calcd. for $C_{15}H_{21}NCl_6Pt$: Pt, 22.85. Found: Pt, 22.89. Picrate, m. p. 181–183°. *Anal.* Calcd. for $C_{21}H_{22}N_4O_7$: N, 12.67. Found: N, 12.58.

Summary

1. Some methyl homologs of 5-isopropylquinoline have been prepared.

2. 8-Methyl and 2,8-dimethyl-5-isopropylquinolines were reduced to their corresponding py-tetrahydroquinolines.

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(1) This paper is a portion of a thesis submitted by Joseph N. LeConte in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry, University of North Carolina. Doctor Wheeler is now deceased.

(2) Cohn and Gustavson, THIS JOURNAL, **50**, 2709 (1928).

(3) Bulow and Isler, *Ber.*, **36**, 2448 (1903); **36**, 4013 (1903).

(4) Phillips and Goss, THIS JOURNAL, **48**, 823 (1926).