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

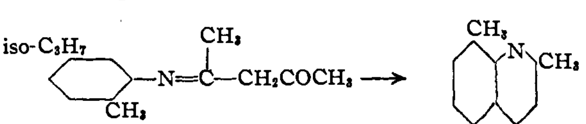
[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

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).