

The residue was warmed with 20% aqueous potassium hydroxide, cooled, filtered off, washed and dried. Extracting the mother liquor with ether gave more of the product. The quinoline-4-methanol was purified by distilling *in vacuo*, b. p. 145° at 0.2 mm., and crystallizing from benzene; yield 50–60%, m. p. 96–97° (uncor.).

Anal. Calcd. for $C_{10}H_9NO$: C, 75.43; H, 5.70; N, 8.81. Found: C, 75.43, 75.68; H, 5.89, 5.88; N, 9.05, 8.89.

Heating under certain conditions converted the product into a higher melting substance.

Phenylurethan of 4-Quinolinemethanol.—From the components at 100°, crystallized from alcohol, m. p. 159.5–160.5° (uncor.).

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: N, 10.06. Found: N, 9.86, 10.02.

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Preparation of Benzaldehyde from Benzene

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In previous reports from this Laboratory,^{1,2} the use of sodium cyanide instead of hydrogen cyanide in the Gattermann synthesis of aldehydes has been shown to be applicable to aromatic hydrocarbons.

In an extension of this investigation it has now been found that contrary to the statements in the literature³ sodium cyanide can be used satisfactorily to replace hydrogen cyanide even for the preparation of benzaldehyde from benzene. A maximum yield of 14% benzaldehyde has been obtained. Additional quantities of aluminum chloride did not increase the yield of aldehyde beyond this percentage. Augmenting the proportionate amount of sodium cyanide caused the yield of benzaldehyde to drop.

Procedure.—Into a mixture of 400 g. (3 moles) of anhydrous aluminum chloride and 50 g. (1 mole) of sodium cyanide in 200 cc. (2.25 moles) of benzene in a 3-necked flask with a mercury-sealed stirrer and an efficient reflux condenser, dry hydrogen chloride was passed for twenty minutes. The mixture was then boiled on a water-bath and the boiling, stirring and introduction of the hydrogen chloride continued for eleven hours.

At the end of this period, the reaction mixture was cooled and poured on a large amount of ice and hydrochloric acid contained in a three-liter, round-bottom flask. The mixture was refluxed under the hood for about an hour to expel excess hydrogen cyanide and to complete the hydrolysis of the phenylmethyleneformamidine hydrochloride.⁴ It was then steam-distilled for two to three hours and the distillate extracted with ether, the extract being dried with anhydrous sodium sulfate. The ether was then distilled off and the residue fractionated. The first fraction, mostly benzene, was collected at 75–100°, the second at 100–160°, the third at 160–185°.

The third fraction was rectified and 20 g. of a liquid boiling at 176–180° was obtained. This compound was characterized by its semicarbazone, m. p. 222° (cor.).

Anal. (benzaldehyde). Calcd.: C, 79.24; H, 5.66. Found: C, 79.07; H, 5.86.

(1) Niedzielski and Nord, *THIS JOURNAL*, **63**, 1462 (1941).

(2) Niedzielski and Nord, *J. Org. Chem.*, **8**, 147 (1943).

(3) J. E. Jones, "Synthetic Organic Chemicals," (Eastman Kodak Company) 15, No. 2 (1943).

(4) Hinkel, Ayling and Morgan, *J. Chem. Soc.*, 339 (1936).

The first fraction (75–100°) was about 30 cc. Assuming this to be mostly benzene, then subtracting this amount from 200 cc., we found that 170 cc. (149 g.) of benzene underwent reaction from which 20 g. of the aldehyde was obtained. On this basis the yield was about 14%.

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The Purification of Acetone by the Shipsey-Werner Method

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The Shipsey-Werner¹ method of purifying acetone, which involves the formation of the solvate, $NaI \cdot 3C_3H_6O$, is commonly used for small scale laboratory purifications. This method (which was quoted in 1935 by Weissberger and Proskauer²) was published before the detailed data on the solubility of NaI and $NaI \cdot 3C_3H_6O$ in acetone^{3,4,5} were available. In light of the latter information, the procedure can be improved in respect both to yield and to convenience. The following outline has been tested and proved to be satisfactory.

Saturate acetone with dry sodium iodide at about 25° (between 25 and 30°). Decant the solution from the excess solid. Cool the solution to as low a temperature as can be conveniently maintained during filtration, etc. With ordinary equipment a temperature of about –10° is satisfactory. Filter off the mother liquor on a Buchner or sintered glass filter. Transfer the cold salt to a flask and warm to about 30° (>26°). Decant the liquid into a distilling flask, distill, rejecting the last 10%.

Saturating the acetone with sodium iodide at approximately room temperature (25 to 30°), rather than at the boiling point of the solvent (2), has two advantages. First, it is more convenient; and, second, it results in an increase in the theoretical yield of purified acetone from about 23 to about 35%. The step of warming the solvated salt above its transition point and decanting the liquid into the distilling flask, is introduced largely to avoid the awkward transfer of a moist solid; but it has the additional advantage that the salt cake, remaining in the flask after distillation, is reduced by about 40%.

Precautions: Contamination of the salt, solvent or vessels by acids or by salt of heavy metals (such as iron or copper) should be avoided. Manipulation of the chilled solvent should be planned to

(1) K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

(2) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, 1935, p. 142.

(3) R. Macy and E. W. Thomas, *THIS JOURNAL*, **48**, 1547 (1926).

(4) A. E. Wadsworth and H. M. Dawson, *J. Chem. Soc.*, **129**, 2784 (1926).

(5) W. R. G. Gell, C. B. Rowlands, I. J. Bamford and W. J. Jones, *ibid.*, 1930 (1927).