When the azide was taken up in ether, a sparingly soluble by-product separated crystalline from benzene, m. p. 220–222°. A second by-product (140–160°) is found in the crude oily urethan. (4) The urethan yields 96% of 2-[γ-amino-*n*-propyl]-dibenzofuran hydrochloride, m. p. 228–231°, corr. (M. and K., 219–220°).

One gram of 2-[γ-amino-*n*-propyl]-dibenzofuran hydrochloride, 1 g. of 99–100% formic acid, and 10 g. of 37% aqueous formaldehyde were heated in a sealed tube for fifteen hours at 130–160°. After treatment of the basic reaction products with benzene sulfonyl chloride, 0.45 g. of the hydrochloride of 2-[γ-(dimethylamino)-*n*-propyl]-dibenzofuran, m. p. 190–193° was obtained, and purified by repeated crystallization.

Summary

1. The synthesis of benzofuro-[3,2-g]-quinoline and benzofuro-[2,3-f]-quinoline from 3-aminodibenzofuran is described.

2. The tetrahydro and N-methyltetrahydro compounds of the benzofuroquinolines were prepared.

3. The constitution of the benzofuro-quinolines has been proved through the Emde degradation products of the N-methyltetrahydrobenzofuro-quinolines.

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The Preparation of Aromatic Alcohols by the Crossed Cannizzaro Reaction with Formaldehyde

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Introduction

The conversion of aldehydes to esters or their hydrolytic products (Cannizzaro reaction) may be brought about by alkalies (hydroxides or alkoxides).[1,2,3,4,5,6,7]

$$RCHO + RCHO \longrightarrow RCH_2OCOR \xrightarrow{H_2O} RCH_2OH + RCOOH$$

Nord and others have shown that aluminum ethoxide effects a crossed Cannizzaro reaction, converting binary mixtures of anhydrous aldehydes into unsymmetrical esters.[8] Crossed Cannizzaro reactions may also be assumed to occur in the formation of polyhydric alcohols by the action of alkalies on mixtures of aliphatic aldehydes; *e. g.*, the production of pentaerythritol from a mixture of acetaldehyde and formaldehyde.[9]

The action of alkali on mixtures of aromatic aldehydes and formaldehyde does not appear to have been studied previously.[10] It has now been found that a crossed Cannizzaro reaction occurs which leads to the formation of formic acid and the aromatic alcohol

$$RCHO + CH_2O + H_2O \longrightarrow RCH_2OH + HCOOH$$

This offers a particularly convenient method of preparing certain aromatic alcohols, such as anisyl, piperonyl, and veratryl alcohols, of which the corresponding aldehydes are readily available.

(1) Wöhler and Liebig, *Ann.*, **3**, 254 (1832).
(2) Cannizzaro, *ibid.*, **88**, 129 (1853).
(3) Kohn and Trantom, *J. Chem. Soc.*, **75**, 1158 (1899).
(4) Lachman, THIS JOURNAL, **45**, 2356 (1923).
(5) Elderfield, *J. Chem. Ed.*, **7**, 594 (1930).
(6) Tischtschenko, *Chem. Zentr.*, **77**, II, 1309, 1554, 1556 (1906).
(7) Child and Adkins, THIS JOURNAL, **47**, 799 (1925).
(8) (a) Nord, *Biochem. Z.*, **106**, 275 (1920); (b) *Beiträge Physiol.*, **2**, 301 (1924); (c) Nakai, *Biochem. Z.*, **152**, 258 (1924); (d) Chusetsu Endoh, *Rec. trav. chim.*, **44**, 866 (1925); (e) Orloff, *Bull. soc. chim.*, [4] **35**, 360 (1924).
(9) "Organic Syntheses," Coll. Vol. I, 1932, p. 417.
(10) Van Marle and Tollens, *Ber.*, **36**, 1347 (1903), reported that no solids were formed by the action of barium or calcium hydroxides on mixtures of benzaldehyde and formaldehyde.

Experimental

Into a 2-liter three-necked flask equipped with dropping funnel, efficient mercury-sealed mechanical stirrer, and reflux condenser are introduced one mol of aromatic aldehyde, 200 cc. of methanol, and 100 cc. (1.3 mols) of formalin. The mixture is heated to 65° and then surrounded by cold water while a solution of 120 g. (3 mols) of sodium hydroxide (or 168 g. of potassium hydroxide) in 120 cc. of water is added rapidly through the dropping funnel, the internal temperature being maintained between 65 and 75°. The reaction mixture is then heated at 70° for 40 minutes and finally refluxed for 20 minutes. The product is isolated by cooling the reaction mixture, diluting with 300 cc. of water, separating the oil, extracting the aqueous layer four times with 150-cc. portions of benzene, washing the combined oil and extracts with water, clearing the benzene solution with sodium sulfate, and distilling in vacuum; yield, 85–90%.

About 2–5% of the aromatic acid may be recovered from the aqueous layer by blowing out the benzene and acidifying with hydrochloric acid.

Summary

The action of alkali on mixtures of aromatic aldehydes and formaldehyde results in the practically complete conversion of the aromatic aldehydes to the corresponding alcohols.

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