Summary

1. The chlorination of 2-amino-*p*-xylene (acetyl derivative) at the freezing point of glacial acetic acid yields a monochloro derivative. The location of the chlorine atom at Position 5 was proved by converting the compound into 2,5-dichloro-terephthalic acid. The hydrochloride is described.

2. A dichloro derivative is obtained if the chlorination is carried out at a slightly higher temperature, 18–20°.

3. A series of new azo dyes was obtained by coupling the monochloroxylidine with: phenol, resorcinol, thymol, 1-naphthol, 2-naphthol, 2-naphthol-6-sulfonic acid, 1-naphthol-5-sulfonic acid and 1,8-dihydroxy-3,6-disulfonic acid.

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2-CHLOROMETHYL-FURAN FROM 2-FURANCARBINOL

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The number of known halogen derivatives of the simpler furan compounds is extremely small. In a large measure, this is due to the long-known sensitiveness of the furan nucleus to halogen acids. Because of the recent availability of furfural in large quantities and at a price that makes it the least expensive aldehyde, 2-furancarbinol ($C_4H_3OCH_2OH$) is now a readily accessible alcohol.[2]

By analogy with benzyl chloride, 2-chloromethyl-furan ($C_4H_3OCH_2Cl$) should be prepared from 2-furancarbinol. A series of studies has shown the correctness of this view despite the rather marked instability of the chloride. Apart from the actual synthesis of the compound, the problem may not be without some interest in an interpretation of the resinification of some furan derivatives and the scission of the furan ring by mineral acids.

Many workers have reported on the instability of 2-furancarbinol towards halogen acids, without considering the possibility of the intermediate formation of the halide. Limpricht,[3] working with an alcohol that was not entirely pure, found that it was decomposed readily by dil. hydrochloric acid and explosively by concd. hydrochloric acid. Baeyer[4] observed that the pure 2-furancarbinol gave a green color with alcoholic

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[1] This paper is an abstract of a thesis presented by Clarence C. Vernon in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

[2] Large quantities can be prepared in a single run from furfural by the Cannizzaro reaction in yields of over 80%.

[3] Limpricht, *Ann.*, **165**, 300 (1873).

[4] Baeyer, *Ber.*, **10**, 356 (1877).

hydrochloric acid. Wissell and Tollens[5] mention the formation of an intermediate colored oil prior to resinification when the alcohol is warmed with dil. hydrochloric acid. They include the similar although slower action of acetic and sulfurous acids. Erdmann[6] after confirming all the foregoing observations, noted briefly a significant experiment wherein dry hydrogen chloride caused no immediate turbidity or brown coloration when passed into an ether solution of the alcohol. Others[7,8] have had similar results, but the most recent and comprehensive study is one by Pummerer and Gump[9] on the splitting of 2-furancarbinol and the mechanism of levulinic acid formation from hexoses.

2-Bromomethyl-furan has recently been prepared. v. Braun and Köhler,[8] after remarking "...2-furancarbinol, as is known, resinifies with mineral acids and permits no exchange of the hydroxyl group by halogens," described the preparation of the bromide by indirect methods. Using v. Braun's well-known method, they synthesized the compound by treating furomethyl-methylethylamine $C_4H_3O.CH_2.N(CH_3)(C_2H_5))$ with bromocyanogen.

The bromide so obtained was found to be extraordinarily unstable. It quickly resinifies in the cold and attempts to distil the oil resulted in complete decomposition. They were contented with "the surprisingly favorable results that permitted the bromide to be kept for at least a few hours." The prophetic observation was made that the great instability of the bromide would probably show itself with the corresponding chloride.

Experiments have borne this out rather completely. They reëmphasize the surprising, relatively high stability of the furan ring towards mineral acids when both α-carbon atoms are substituted. 5-Bromomethyl-furfural has been prepared and used in many reactions under conditions which, at present, appear quite forbidden to mono α-substituted derivatives. Also, Hale, McNally and Pater[7] have shown that di α-dicarbinols are more stable towards mineral acids than are the corresponding mono-α-carbinols.

The 2-chloromethyl-furan was prepared by two general reactions from 2-furancarbinol. First, thionyl chloride was added to a dil. ethereal solution of the alcohol cooled by an ice-and-salt mixture which was kept well agitated by a mechanical stirrer. The yield was 10%, as determined by the quantity of the known ethyl ether of 2-furancarbinol obtained by adding an excess of sodium ethylate to the reaction mixture.

Second, dry hydrogen chloride was passed into an ether solution under conditions like those mentioned above. Water is formed in this reaction, and because aqueous mineral acids have a more harmful effect than the

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[5] Wissell and Tollens, *Ann.*, **272**, 291 (1892).

[6] Erdmann, *Ber.*, **35**, 1855 (1902).

[7] Hale, McNally and Pater, *Am. Chem. J.*, **35**, 68 (1906).

[8] v. Braun and Köhler, *Ber.*, **51**, 79 (1918).

[9] Pummerer and Gump, *Ber.*, **56**, 999 (1923).

corresponding dry acids it was found advantageous to use calcium carbide as a dehydrating agent. With this reagent, resinification was retarded and the yields improved.

All efforts to distil the chloride were futile. Complete decomposition set in while the ether was being removed in a vacuum and when the temperature of the water-bath did not exceed 30°. However, the ether solution could be kept essentially unchanged for two days in an ice chest. This assures the reasonable probability of carrying out a number of reactions with the chloride in ether solution.

Several unsuccessful experiments were made to reduce furfural to the corresponding 2-methylfuran by the Clemmensen[10] reaction. An equal lack of success was experienced in an attempt to prepare 2-furomethyl pyromucate from furfural and calcium carbide.[11] This method has given excellent yields of benzyl benzoate from benzaldehyde. We have here apparently one of the very few striking illustrations of a breakdown in the fairly complete analogy between benzaldehyde and furfural.

Experimental Part

Preparation of 2-Furancarbinol.—The method of Erdmann[6] was found to work very satisfactorily. In later preparations, four times the quantity of materials he used in a single run gave comparable yields. By foregoing an ether extraction subsequent to steam distillation, less than 5% of carbinol was lost. The average yield of many runs, exclusive of the ether extraction, was about 80%. A series of experiments under varying conditions showed that calcium hydroxide could not successfully replace sodium hydroxide. When mixtures of calcium hydroxide and sodium hydroxide were used, the yields appeared to be proportional to the quantity of sodium hydroxide.

The Reaction between 2-Furancarbinol and Thionyl Chloride.—Preliminary experiments showed that the slow addition of undiluted thionyl chloride to the pure carbinol at room temperature caused a very vigorous reaction with immediate charring. Almost the same phenomena were observed when the thionyl chloride, diluted with two volumes of dry benzene, was added to the carbinol cooled to 0°. The reaction is more satisfactorily controlled when the carbinol is also diluted with benzene; however, to get a lower temperature dry ether was used as the medium.

Accordingly, 0.3 mole of thionyl chloride was added slowly to a well-stirred solution of 0.35 mole of the carbinol in 200 cc. of ether, cooled by a freezing mixture of ice and salt. The contents of the flask, at first light yellow, became a characteristic very dark green. The absence of solid material indicated that but slight charring had occurred.

Several attempts were made to distil the reaction product under diminished pressure.

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[10] Clemmensen, *Ber.*, **47**, 681 (1914).

[11] Bast, "Action of calcium carbide on benzaldehyde and some other organic compounds." *Thesis*, **1918**, Catholic University of America, Washington, D. C.

In each case, after some 80 to 90% of the ether had been distilled at reduced pressure, the contents of the flask suddenly and violently decomposed into a hard, intractable tar. The temperature of the water-bath in which the flask was immersed did not exceed 30°. In all these attempted distillations rigorous precautions were observed to exclude moisture.

The Reaction between 2-Chloromethyl-furan and Sodium Ethylate.— To prepare a derivative of the chloride and at the same time to get an approximate estimation of its yield, three equivalents of sodium ethylate in ether were added to one of the typical runs as described above.

The sodium ethylate was slowly added to the cold ether solution of chloride, stirring being continued for one hour. No evidence of decomposition was noted.

The ether solution was separated after filtration, dried with potassium carbonate, and vacuum-distilled. The fraction boiling at 67° (2 mm.) was redistilled at atmospheric pressure and found to boil at 148–150°; d_4^{20}, 0.9888; n^{20}, 1.4316.

The boiling point and density agree with the constants of the ethyl ether of 2-furancarbinol previously determined by Wissell and Tollens.[5] They, however, did not determine the refractive index. The yield, based on 2-furancarbinol, was 10%. Like results were obtained in two other runs. A blank run, in which the thionyl chloride was not added, gave no ethyl ether of 2-furancarbinol. The ether has a highly characteristic pleasant odor, and on standing for several days undergoes slight decomposition.

The Reaction between 2-Furancarbinol and Hydrogen Chloride.— Dry hydrogen chloride when passed into the carbinol cooled to 0° and containing calcium carbide, first gives the characteristic green color which becomes black within an hour. It is surprising to note that even when the hydrogen chloride was bubbled at a moderate rate for one hour into 0.25 mole of the carbinol, some of the carbinol was recovered.

A mixture of 0.25 mole of the carbinol in 100 cc. of dry ether with 0.3 mole of finely powdered calcium carbide was placed in a reaction flask, provided with a stirrer and cooled to —15°. Dry hydrogen chloride was passed in for one hour at a rate of two bubbles per second and was completely absorbed. The reaction mixture became green, but there was no evidence of charring or resinification. When the mixture was stoppered and kept in an ice box, no charring took place for two days. All efforts to distil the chloride prepared in this manner were without success. The compound was identified, as in the thionyl chloride runs, by conversion into the ethyl ether of 2-furancarbinol. The yield in a one-mole run of carbinol in 125 cc. of ether, using one mole of calcium carbide and but two moles of sodium ethylate, was 5%.

Calcium carbide is not indispensable to the preparation of the chloride. The yield in a comparable run, in which calcium carbide was not used, was about 4%. However, in this run the reaction mixture blackened soon after the hydrogen chloride was admitted and then charred considerably.

In one experiment acetic anhydride was used as the dehydrating agent, but it appeared to be less satisfactory than calcium carbide.

The authors wish to express their appreciation to the Miner Laboratories of Chicago for ample supplies of furfural.

Summary

2-Chloromethyl-furan has been prepared from 2-furancarbinol by the reaction with thionyl chloride and with hydrogen chloride.

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