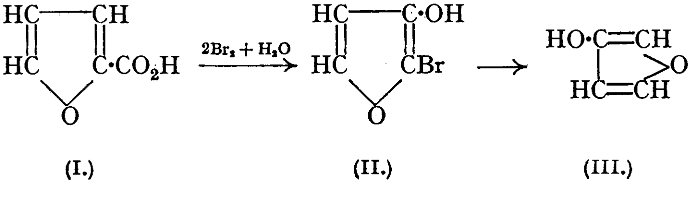
171. *Preparation of 2- and 3-Hydroxyfuran.*

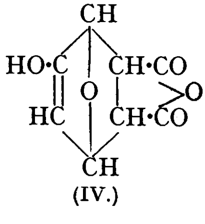
By Herbert H. Hodgson and R. Ronald Davies.

2-*Hydroxyfuran* has been prepared by heating 5-sulphofuroic acid with aqueous sodium hydroxide in the presence of a little potassium chlorate in an autoclave at 200°. The isomeric 3-*hydroxyfuran* has been prepared by the debromination of 2-*bromo*-3-*hydroxyfuran*, which was obtained by the action of bromine and water on furoic acid.

Limpricht (*Annalen*, 1873, **165**, 291) found that the reaction of bromine with a mixture of furoic acid (I) and water gave in very small yield a product $C_4H_3O_2Br$, which was debrominated by sodium amalgam to a substance $C_4H_4O_2$ that did not reduce ammoniacal silver nitrate. The last substance has now been shown to be 3-*hydroxyfuran* (III), and the bromo-compound is almost certainly 2-*bromo*-3-*hydroxyfuran* (II), since the attack of the hypo-



(I.) (II.) (III.)



(IV.)

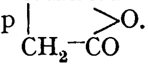
bromous acid should be at the 2 : 3-double bond. By the method of Diels and Alder (*Annalen*, 1931, **490**, 243) the 3-hydroxyfuran was condensed with maleic anhydride to give 4-*hydroxy*-3 : 6-end*oxo*-Δ^4-*tetrahydrophthalic anhydride* (IV), which on treatment with a saturated solution of hydrogen bromide in glacial acetic acid at 160° afforded 4-hydroxyphthalic acid. This acid was also prepared from naphthol-yellow S by the method of Bentley and Weizmann (J., 1907, **91**, 100) and gave *m*-hydroxybenzoic acid when heated with hydrochloric acid at 180°.

The action of bromine on furoic acid varies considerably with the amount of water in the medium employed, since dry bromine at 100° gives 3 : 5-dibromofuroic acid (Hill and Sanger, *Annalen*, 1885, **232**, 42), whereas the presence of excess of water tends to produce ring rupture, a reaction which is considerably enhanced by alkaline hypobromites. Since aldehydes result from ring rupture, this scission is readily detected. To prevent overbromination on the one hand and ring rupture on the other, the bromination was conducted in chloroform, and the amount of water present was the equivalent of that demanded by the above scheme. The bromo-compound, obtained in about 75% yield, was 2-bromo-3-hydroxyfuran, apparently identical with that recorded by Limpricht (*loc. cit.*). If the quantity of water used is gradually increased above one molecule, the yield is progressively lowered owing to ring rupture.

A modification of Limpricht's reduction procedure with sodium amalgam afforded an 89% yield of 3-hydroxyfuran from 2-bromo-3-hydroxyfuran, a reduction which is also effected by sodium and ethyl alcohol. The 3-hydroxyfuran so obtained differs from the oil described by Limpricht in that it is a crystalline solid (m. p. 58°). This difference is ascribed to the circumstance that Limpricht distilled his product under atmospheric pressure, and this procedure is now found to entail partial decomposition at *ca.* 120° with the production of water; unless 3-hydroxyfuran is thoroughly dry, it will not readily crystallise, and the crystals themselves become oily if exposed to a damp atmosphere.

2-*Hydroxyfuran* was prepared by the action of caustic alkali under pressure at 200° on 5-sulphofuroic acid (Hill and Palmer, *Amer. Chem. J.*, 1888, **10**, 373) in presence of a small quantity of potassium chlorate to prevent reduction. Its constitution follows from analysis and from its isomerism with 3-hydroxyfuran. Attempts to condense it with maleic anhydride did not give satisfactory results.

2- and 3-Hydroxyfuran dissolve in aqueous alkalis to give solutions which rapidly darken. Neither compound reduces ammoniacal silver nitrate, indicating that the keto-structure is not readily assumed. In this respect the isomers differ from α- and β-angelica-lactones, crotonolactone, and the cardiac aglycones which contain the group



$$\begin{array}{l}\mathrm{CHR{:}CH}\\ |\qquad\;\; >\mathrm{O.}\\ \mathrm{CH_2{-}CO}\end{array}$$

EXPERIMENTAL.

Sulphonation of Furoic Acid.—Furoic acid (20 g.) was stirred into 30% oleum (100 g.) at 0° and after 24 hours the mixture was poured on ice (300 g.) and neutralised with lime. The filtered solution was treated with sodium carbonate and evaporated to dryness after removal of calcium carbonate. The disodium salt of 5-sulphofuroic acid was thus obtained as a waxy white solid (43 g.).

2-*Hydroxyfuran.*—The above disodium salt (20 g.) was heated with 30% aqueous sodium hydroxide (200 c.c.) and potassium chlorate (2 g.) in an autoclave at 200° for 15 hours. On cooling, a dark brown solution, mixed with a slight amount of resin, was obtained. The alkalinity to Titan (Clayton)-yellow paper was carefully removed by addition of hydrochloric acid to the externally ice-cooled mixture and, after filtration, the ice-cooled liquid was rendered just acid to litmus by hydrochloric acid, an amber-coloured flocculent precipitate being obtained with evolution of sulphur dioxide. An ethereal extract of the product was dried with calcium chloride and evaporated. The pale amber residue (4·8 g.) was distilled rapidly under reduced pressure, a small amount of 2-*hydroxyfuran* being obtained in colourless prisms, m. p. 80° (decomp. at 90°) [Found: C, 57·0; H, 4·6; O, estimated by Whitaker's process (private communication), 38·0. $C_4H_4O_2$ requires C, 57·2; H, 4·7; O, 38·1%]. The product had a pungent acrid odour very dissimilar from the benzene-like odour of 3-hydroxyfuran, turned brown on keeping, and resinified with great ease, especially during distillation with steam, in which it was volatile.

Preparation of 2-Bromo-3-hydroxyfuran.—(a) *In the absence of chloroform.* Furoic acid (10 g.), made into a paste with water (10 c.c.), was treated gradually below 30° with bromine (30 g.) with vigorous stirring; hydrogen bromide and carbon dioxide were evolved copiously and a yellow oil separated. The mixture was poured into water and steam-distilled, the distillate extracted with ether, the extract dried with anhydrous sodium sulphate, and the ether allowed to evaporate gradually; yellow needles of *2-bromo-3-hydroxyfuran* separated (1·3 g.), m. p. 85° (Found : C, 29·3; H, 1·7; Br, 48·9. $C_4H_3O_2Br$ requires C, 29·4; H, 1·8; Br, 49·1%). The product had a sharp characteristic odour, was slightly soluble in water, very volatile in steam, soluble in alkalis, alcohol, chloroform and ether, and did not reduce ammoniacal silver nitrate.

(b) *In the presence of chloroform.* Furoic acid (10 g.) was made into a paste first with water (4 c.c.) and then with chloroform (20 c.c.) and the mixture was treated below 30°, with vigorous stirring, with a solution of bromine (32 g.) in chloroform (20 c.c.), added during 1 hour. After 1 hour's stirring at 30°, the thick white paste obtained was mixed with water (100 c.c.) and the colourless needles of 2-bromo-3-hydroxyfuran were filtered off and washed free from hydrobromic acid with water. The product crystallised from hot water in colourless needles, m. p. and mixed m. p. with the product from (a) 85° (Found : Br, 48·9%); yield, 9 g. The chloroform (*ca.* 20 c.c.) in the filtrate was separated and washed with water, and the solvent distilled; 3 g. of 2-bromo-3-hydroxyfuran were thus obtained, making the total yield 75% of the theoretical.

Dehalogenation of 2-Bromo-3-hydroxyfuran.—(a) *By sodium amalgam.* 2-Bromo-3-hydroxyfuran (10 g.) was dissolved in a mixture of water (50 c.c.) and the amount of aqueous 30% sodium hydroxide necessary to effect dissolution. The solution was treated during 1 hour with 2·5% sodium amalgam (200 c.c.), and heated at 80° for 2 hours. The straw-coloured liquid, containing a few crystals, was separated from the mercury, acidified with sulphuric acid, and steam-distilled. An ethereal extract of the distillate was dried (anhydrous sodium sulphate) and allowed to evaporate gradually; *3-hydroxyfuran* crystallised in colourless needles, m. p. 58° (Found : C, 57·0; H, 4·8. $C_4H_4O_2$ requires C, 57·1; H, 4·8%); mixed m. p. with 2-hydroxyfuran, 33—37°.

(b) *With sodium and ethyl alcohol.* 2-Bromo-3-hydroxyfuran (10 g.), dissolved in ethyl alcohol (200 c.c.), was treated gradually under reflux with sodium (7 g.), the mixture refluxed for 2 hours, and the brown solution just acidified to litmus by the addition of a solution of sulphuric acid in ethyl alcohol. After filtration, and removal of the alcohol by distillation, the residue was washed with hot water, the separated oil dissolved in ether, the solution dried (anhydrous sodium sulphate) and filtered, and the ether gradually removed by evaporation; needles of 3-hydroxyfuran separated, m. p. and mixed m. p. with the product from (a) 58° (Found : C, 56·9; H, 4·7%).

4-Sulphophthalic Anhydride (cf. Bentley and Weizmann, J., 1907, **91**, 100).—A mixture of 2 : 4-dinitronaphthol-7-sulphonic acid (naphthol-yellow S) (50 g.) and nitric acid (150 g., 63%) was evaporated to dryness, and the pale yellow, crystalline mass extracted with hot water; the solution was treated with just sufficient barium chloride to precipitate the unchanged naphthol-yellow S. The liquid was filtered, freed from barium by addition of sulphuric acid, and evaporated to dryness after filtration. The yield of 4-sulphophthalic anhydride was 30 g.

4-Hydroxyphthalic Acid.—A mixture of potassium hydroxide (100 g.), sodium hydroxide (50 g.), and water (20 c.c.) was heated in an iron pot to 150°, 4-sulphophthalic anhydride (20 g.) added during 15 minutes, and the temperature gradually raised to 180—190°. After 4 hours, the melt was poured on ice. The solution (300 c.c.) was just acidified to Titan (Clayton)-yellow paper with hydrochloric acid, filtered from inorganic matter, made acid to phenolphthalein by addition of more hydrochloric acid, and filtered at 80° from a trace of *m*-hydroxybenzoic acid. The cooled filtrate was ether-extracted, and the ether removed from the dried extract (calcium chloride); the 4-hydroxyphthalic acid obtained was recrystallised from hot water; m. p. 204° (lit., 204° to 205°).

4-Hydroxy-3 : 6-endo*xo-*Δ^4*-tetrahydrophthalic Anhydride* (cf. Diels and Alder, *Annalen*, 1931, **490**, 243; *Ber.*, 1929, **62**, 554).—A solution of 3-hydroxyfuran (4·2 g.) in anhydrous ether (100 c.c.) was added to one of maleic anhydride (4·9 g.) in dry ether (70 c.c.). The mixture was heated to 40° to initiate reaction, and kept for 48 hours in a closed flask; brown needles had then separated, m. p. 132° (decomp.) (Found : C, 52·5; H, 3·1. $C_8H_6O_5$ requires C, 52·7; H, 3·3%). Further keeping resulted in fresh crops. Total yield, 5·5 g.

Transformation of 4-Hydroxy-3 : 6-endo*xo-*Δ^4*-tetrahydrophthalic Anhydride into 4-Hydroxyphthalic Acid and* m*-Hydroxybenzoic Acid.*—The anhydride (3 g.) was heated in a sealed glass tube for 12 hours at 100° with glacial acetic acid saturated with hydrogen bromide (20 c.c.).

The greenish-brown solution, on cooling, deposited grey prisms, which were filtered off and refluxed with 15% aqueous sodium hydroxide for an hour. The alkaline solution was acidified with hydrochloric acid and ether-extracted. The dried extract on evaporation yielded colourless rhombs of 4-hydroxyphthalic acid, which were recrystallised from hot water; m. p. and mixed m. p. with the specimen prepared above, 204°. Yield, 1·5 g. This product (0·5 g.), when heated with hydrochloric acid (10 c.c., *d* 1·16) in a sealed tube at 180° for 6 hours, gave, after dilution with water and extraction with ether, *m*-hydroxybenzoic acid, m. p. and mixed m. p. with an authentic specimen 200°.

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THE TECHNICAL COLLEGE, HUDDERSFIELD.

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