

216. *Nitrosation and Nitration of 2- and 3-Hydroxyfuran.*

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Nitrosation and nitration of 2-hydroxyfuran give 5-nitroso-2-hydroxyfuran and 5-nitro-2-hydroxyfuran respectively; both compounds yield 5-amino-2-hydroxyfuran on reduction. 3-Hydroxyfuran similarly gives 2-nitroso- and 2-nitro-3-hydroxyfuran, both reducible to 2-amino-3-hydroxyfuran.

NITROSATION of 2- and of 3-hydroxyfuran produces a single mononitroso-derivative in each case, both of which are readily oxidised by alkaline potassium ferricyanide to the respective mononitro-compounds, also obtainable by direct mononitration of 2- and 3-hydroxyfuran. The nitro-derivative from 2-hydroxyfuran is non-volatile, and that from 3-hydroxyfuran is volatile, in steam. It appears reasonable, therefore, to conclude from analogy and the laws of substitution that the former compound is *5-nitro-2-hydroxyfuran* and the latter *2-nitro-3-hydroxyfuran*, and that the nitrosation products are *5-nitroso-2-hydroxyfuran* and *2-nitroso-3-hydroxyfuran* respectively (compare Gilman and Burtner, *J. Amer. Chem. Soc.*, 1933, **55**, 2907). Supporting evidence appears to be afforded by the facts that the melting points of the 5-substituted compounds are much higher and the colours much less pronounced than those of the 2-substituted isomerides. The latter, being *o*-derivatives, are probably chelated as indicated by their bright yellow colours.

In each case reduction of the nitroso- and the nitro-derivative affords the same amine, indicating that nitrosation and nitration take place in the same positions in the respective hydroxyfurans.

EXPERIMENTAL.

5-Nitroso-2-hydroxyfuran.—2-Hydroxyfuran (5 g.) was dissolved in water (100 c.c.) by addition of the requisite quantity of 10% aqueous sodium hydroxide, sodium nitrite (6 g.) added, and the solution run during 30 minutes into well-stirred dilute hydrochloric acid (20 c.c. of acid, *d* 1.16, and 200 c.c. of water) kept at 0°. The precipitate formed was collected next day (3 g.), dried at 50°, and crystallised from ether, *5-nitroso-2-hydroxyfuran* forming pale yellow prisms, m. p. 176° (Found : N, 12.35. $C_4H_3O_3N$ requires N, 12.4%), which gave Liebermann's nitroso-reaction.

5-Nitro-2-hydroxyfuran.—A solution of 5-nitroso-2-hydroxyfuran (1 g.) in 10% aqueous potassium hydroxide (20 c.c.) was heated with potassium ferricyanide (22 g.) at 80° for 6 hours, then diluted with water to 200 c.c., filtered, acidified with dilute sulphuric acid, and extracted with ether; slow evaporation of the dried extract gave *5-nitro-2-hydroxyfuran* (0.6 g.) in yellow plates, m. p. 92° (Found : N, 10.8. $C_4H_3O_4N$ requires N, 10.85%).

Nitration of 2-Hydroxyfuran.—2-Hydroxyfuran (2.5 g.) was dissolved in concentrated sulphuric acid (10 g.) below 10°, and the stirred solution treated gradually at 0° with nitric acid (5 g., *d* 1.4), kept for 2 hours with continuous agitation, and then poured on ice. A dried ethereal extract of the solution afforded 5-nitro-2-hydroxyfuran (1.2 g.) in yellow plates, m. p. and mixed m. p. with the previous product 92° (Found : N, 10.7%). No compound volatile in steam was produced by the nitration.

5-Amino-2-hydroxyfuran.—5-Nitroso-2-hydroxyfuran (1 g.) and also 5-nitro-2-hydroxyfuran (1 g.) were dissolved each in water (10 c.c.) by addition of the necessary quantity of 10% aqueous sodium hydroxide, the solutions added to hot dilute hydrochloric acid (2 c.c. of acid, *d* 1.16, and 10 c.c. of water), and zinc dust (5 g.) introduced. The two mixtures were boiled under reflux for 1 hour, acidity to Congo-red paper being just maintained by further additions of hydrochloric acid, and the straw-coloured solutions were filtered hot from inorganic solids. Dried ethereal extracts on slow evaporation gave colourless prisms of *5-amino-2-hydroxyfuran*, m. p.'s and mixed m. p. 185° (Found : N, 14.2. $C_4H_5O_2N$ requires N, 14.1%).

2-Nitroso-3-hydroxyfuran.—3-Hydroxyfuran (5 g.), nitrosated in the same way as the 2-hydroxy-isomeride, afforded *2-nitroso-3-hydroxyfuran* (3 g.), which crystallised from ether in bright yellow plates (much yellower than 5-nitroso-2-hydroxyfuran), m. p. 151° (Found : N, 12.3. $C_4H_3O_3N$ requires N, 12.4%), and gave Liebermann's nitroso-reaction. On oxidation with alkaline potassium ferricyanide as above, *2-nitro-3-hydroxyfuran* was obtained, which crystallised from ether in yellow prisms (yellower than 5-nitro-2-hydroxyfuran), m. p. 76° (Found : N, 10.9. $C_4H_3O_4N$ requires N, 10.85%).

Nitration of 3-Hydroxyfuran.—(a) *In concentrated sulphuric acid solution.* 3-Hydroxyfuran (5 g.), when nitrated in the same way as 2-hydroxyfuran, afforded 2-nitro-3-hydroxyfuran (3.5 g.), which crystallised from ether in bright yellow prisms, m. p. and mixed m. p. with the previous product 76° (Found : N, 10.9%).

(b) *In acetic anhydride solution.* 3-Hydroxyfuran (1 g.), dissolved in acetic anhydride (20 c.c.), was treated gradually at 0° with a solution of nitric acid (3 c.c., *d* 1.4) in acetic anhydride (10 c.c.) during 15 minutes. The solution was then agitated at 0–5° for 1 hour, allowed to attain room temperature, and poured on ice, and the mixture extracted with ether. After removal of the ether from the dried extract, the residue was treated with pyridine (16 c.c.) at 50° for 30 minutes, the mixture diluted with water, rendered just acid to Congo-red with dilute sulphuric acid, and ether-extracted, and the dried extract allowed to evaporate slowly; bright yellow prisms (0.06 g.) of 2-nitro-3-hydroxyfuran were deposited, m. p. and mixed m. p. 76° (Found : N, 10.9%). *2-Amino-3-hydroxyfuran*, obtained by reduction of 2-nitroso- or 2-nitro-3-hydroxyfuran with zinc dust as described above, crystallised from ether in colourless needles, m. p. and mixed m. p. 92° (Found : N, 14.0. $C_4H_5O_2N$ requires N, 14.1%).

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