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Benzofuran from Saccharic Acid

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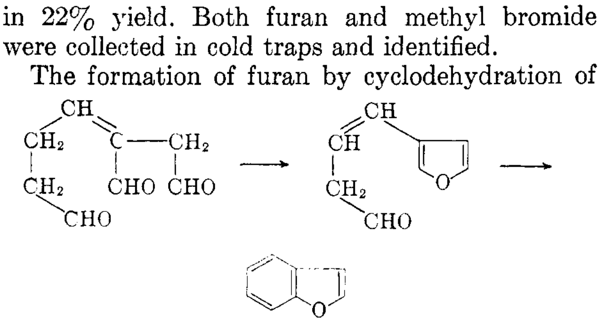
2,5-Furandicarboxylic acid commonly is prepared by heating potassium acid saccharate with very concentrated hydrobromic acid (53–60% by weight) for periods of 16 to 36 hours.[1,2] Yields by this procedure, originally described by Phelps and Hale, are 55–56%. In varying this procedure by use of commercial 48% hydrobromic acid and removing the water formed by continuous distillation, it was noted that a water-insoluble liquid separated from the distillate. This liquid has been identified as benzofuran (coumarone), and evidence has been obtained that it is formed from succinaldehyde, produced as a by-product by degradation of saccharic acid.

The yields of 2,5-furandicarboxylic acid obtained with 48% hydrobromic acid and continuous distillation for periods of 8 to 27 hours were 45–50%. Benzofuran was isolated from the distillate in 9.6–11.2% yield by extraction with ether and distillation. Furan also was isolated in one instance in 2.0% yield.

The most probable intermediate in the formation of benzofuran and furan appeared to be succinaldehyde, which might be formed from saccharic acid by loss of carbon dioxide and water. Evidence that succinaldehyde was in fact a very likely intermediate in the formation of benzofuran and furan was obtained by adding 2,5-dimethoxytetrahydrofuran (an acetal that forms succinaldehyde and methanol on hydrolysis) to slowly distilling hydrobromic acid. Benzofuran was isolated from the distillate in 22% yield. Both furan and methyl bromide were collected in cold traps and identified.

The formation of furan by cyclodehydration of succinaldehyde has been reported previously.[3] The formation of benzofuran can be interpreted as occurring by an aldol condensation of succinaldehyde, followed by successive dehydrations, as shown in the following equation.



EXPERIMENTAL[4]

Products from saccharic acid and hydrobromic acid. Potassium acid saccharate (353 g.) and 1 l. of 48% hydrobromic acid were heated in a 2-l. flask attached to a Claisen head connected to a receiver, which in turn was connected to an ice-cooled trap, two traps cooled with Dry Ice and acetone, and a water bubbler. The mixture was heated so that the vapor temperature was 100–120° and slow distillation occurred. Carbon dioxide was liberated continuously, in decreasing amount toward the end of the period of heating (8–27 hours).

2,5-Furandicarboxylic acid was isolated from the residue by the procedure of Phelps and Hale[1] in yields of 45–50% in five preparations.

Benzofuran was isolated from the contents of the receiver by extraction with 200 ml. of ether. The extract was dried over potassium carbonate and distilled, the yield of benzofuran being 9.4 g. (11%), b.p. 97–98° (73 mm.), n_{D}^{25} 1.5610–1.5635. In four similar preparations the yields were 9.6–11.2%. A pure redistilled sample of the benzofuran had n_{D}^{25} 1.5641, and was identified by comparison of its infrared and ultraviolet spectra with the spectra of an authentic sample prepared by the decarboxylation of coumarilic acid,[5] and by the identity of its picrate, m.p. 103–104.5°, with an authentic sample[5] (mixture m.p.).

Furan was isolated from the first trap cooled with Dry Ice by distillation in a yield of 1.9 g. (2.0%), b.p. 31.5–33°, and identified as the maleic anhydride adduct (mixture m.p. with an authentic sample).[6]

Products from 2,5-dimethoxytetrahydrofuran and hydrobromic acid. A solution of 102 g. of 2,5-dimethoxytetrahydrofuran in 300 ml. of water was added during a period of 45 minutes to a slowly distilling mixture of 1370 g. of 48% (by weight) hydrobromic acid in an apparatus similar to the one described above for the treatment of saccharic acid with hydrobromic acid. The 2,5-dimethoxytetrahydrofuran was added through a dropping-funnel with a 12-mm. tube extending about 5 cm. below the surface of the liquid. Slow distillation at 95–105° was continued for 30 minutes after addition of the acetal was completed. The receiver was heated in a bath at 40–50°. The bubbler at the end of the system indicated no gas evolution.

Benzofuran was isolated by the procedure described above in a yield of 9.8 g. (22%), b.p. 103–104° (90 mm.), n_{D}^{25} 1.5630–1.5642. Succinaldehyde was identified as a fore-run in the distillation of the benzofuran by conversion to the bis-2,4-dinitrophenylhydrazone, m.p. 267–268° (dec.). Furan was identified as the higher-boiling component of the condensate in the Dry Ice cooled trap by conversion to the maleic anhydride adduct,[6] while the lower boiling component was identified as methyl bromide.

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[1] I. K. Phelps and W. J. Hale, *Am. Chem. J.*, **25**, 445 (1901).

[2] W. N. Haworth, W. G. M. Jones, and L. F. Wiggins, *J. Chem. Soc.*, 1 (1945).

[3] C. Harries, *Ber.*, **34**, 1488 (1901); H. Metzner and D. Vorländer, *Ber.*, **31**, 1885 (1898).

[4] Melting points are corrected and boiling points are uncorrected.

[5] S. Tanaka, *J. Am. Chem. Soc.*, **73**, 872 (1951).

[6] O. Diels and K. Alder, *Ber.*, **62**, 554 (1929).