Alkoxylation and Acetoxylation of Furan

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IN their Communication on some anodic reactions of furans, Baggaley and Brettle[1] described the anodic methoxylation and acetoxylation of furan under basic conditions. We reported[2,3] these reactions in 1953, and now give further details of them.

We have found that the methoxylation of furan gives a 50% yield of 2,5-dimethoxy-2,5-dihydrofuran at theoretical current using a graphite anode when NaOMe, KOH, NaOH, NaBr, LiCl, or NH_4Br is used as electrolyte. The use of halide salts gives some (less than 10%) malealdehyde tetramethyl acetal as by-product. Under basic conditions the nature of the anode is important, the yields with various anode materials being as follows: platinum, 51%; graphite, 49%; silver, 14%; iron, 14%; nickel, 6%; and copper, 5%. Maximum yields of product (about 70%) are

obtained at 150% of theoretical current. Current density has little effect on yield. While ethoxylation is also possible under basic conditions, the oxidation of the ethoxy-radical to carbonate greatly lowers the efficiency of the reaction.

Electrolysis of furan in sodium acetate and acetic acid gives 2,5-diacetoxy-2,5-dihydrofuran in good yield only at a platinum anode. An increase in current density from 0·01 to 0·015 amp/cm.[2] lowers the yield at theoretical current from 45 to 20%. Work is under way to determine whether or not this is a result of the diffusion rate of furan to the anode.

The first reported electrolytic preparation of 2,5-dimethoxy-2,5-dihydrofuran was by Clausen-Kaas *et al.*[4] They electrolyzed a solution of furan in methanol with NH_4Br as electrolyte. Under these acidic conditions changing the anode material from graphite to various metals produced no marked difference in yield.[5] This would seem to indicate that with the halides the reaction is probably an initial addition of halogen to furan followed by methanolysis. Under basic conditions the reaction probably involves direct addition of the alkoxy- or acetoxy-radicals to the furan molecule.

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[1] A. J. Baggaley and R. Brettle, *Chem. Comm.*, 1966, 108.
[2] C. L. Wilson and K. E. Kolb, 124th Meeting of the American Chemical Society, Chicago, Illinois, Sept. 1953, Abstracts of Papers, No. 111, p. 640.
[3] K. E. Kolb, *Diss. Abs.* 1959, **20**, 86.
[4] N. Clausen-Kaas, F. Limborg, and K. Glens, *Acta Chem. Scand.*, 1952, **6**, 531.
[5] N. Clausen-Kaas, private communication.