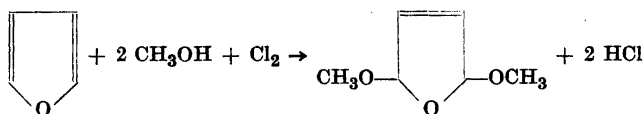


Electrolytic Methoxylation of Furan

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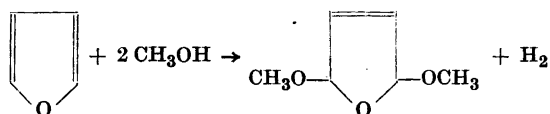
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When furan is treated with a methanolic solution of bromine or chlorine it adds two methoxy groups whereby 2,5-dimethoxy-2,5-dihydrofuran and two moles of hydrogen halide are formed. Since dimethoxydihydrofuran is sensitive to acids, the reaction is carried out in the presence of sodium



carbonate¹ or potassium acetate^{2,3}. We have found that dimethoxydihydrofuran prepared by this method is often contaminated with a small amount of some halogen-containing impurity, which may cause the formation of hydrogen halide and therefore greatly influence the stability of the acid sensitive dimethoxydihydrofuran.

We have now developed a methoxylation method, which is simpler and cheaper than the one above, and which gives a halogen-free reaction product⁴. Furan is mixed with a methanolic solution of ammonium bromide and the mixture electrolyzed. At the cathode, hydrogen and ammonia, at the anode bromine are formed. The bromine reacts immediately with furan and methanol to give dimethoxydihydrofuran and hydrogen bromide. The hydrogen bromide and the ammonia from the cathode then regenerate the ammonium bromide. The net equation for the process is:



The yield of dimethoxydihydrofuran is 73 per cent and the current efficiency 86 per cent. As the boiling point and the refractive index of the product rise

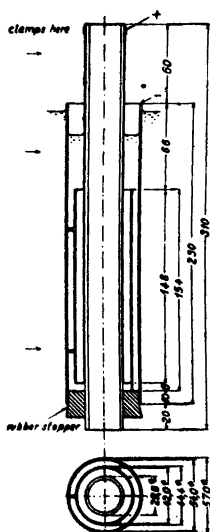
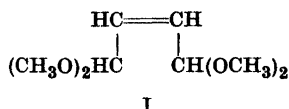


Fig. 1. Cell for electrolytic alkoxylation.

slightly during distillation, we believe that the dimethoxydihydrofuran is a mixture of the *cis* and the *trans* isomer.

A small amount of a higher boiling liquid is also formed by the electrolysis. This has been found to consist mainly of malealdehyde tetramethyl acetal (I).



EXPERIMENTAL

Apparatus. Fig. 1 gives a detailed design of the cell used for the electrolysis. The cathode consists of two brass cylinders electroplated with nickel, while the anode is a porcelain tube covered with sheet platinum (note 1). During electrolysis the electrolyte circulates continuously owing to the evolution of hydrogen at the inner surface of the inner cathode.

The cell is fed from a storage battery or from a rectifier and connected with an ammeter and a coulometer of the ordinary domestic type.

Procedure. 5.00 g of ammonium bromide (0.051 mole) is dissolved in a mixture of 230 ml of methanol (5.7 moles) and 68.0 g of freshly distilled furan (1.00 mole) (note 2) and the solution (total volume about 310 ml) poured into the cell. The cell is placed in a cooling-bath kept at -22° and the voltage applied after some minutes. The data of the electrolysis are given below.

Hours	Current (ampere)	Potential across the cell during electrolysis (volt)	Temperature in the cell	Ampere hours (per cent of theoretical amount)
0.3	3.0	4.6	-14°	1.0 (2 %)
5.8	3.0	4.8	-14°	10.9 (20 %)
7.9	3.0	4.8	-14°	23.6 (44 %)
15.5	2.4	5.2	-14°	44.7 (83 %)
15.9	2.3	5.3	-14°	45.6 (85 %)

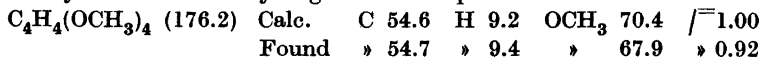
After 45.6 ampere hours have passed through the cell (85 % of the theoretical amount), the electrolysis is stopped. The volume of the liquid in the cell has diminished 35 ml mainly due to contraction (note 3). The liquid, which is colourless in the upper part of the cell, but slightly yellow from unreacted bromine near the bottom, is poured into a solution of sodium methoxide (1.20 g of sodium (0.052 mole) in 20 ml of methanol) and the mixture distilled through a *Vigreux* column from a water-bath under atmospheric pressure. About 160 ml of distillate, containing ammonia and the excess of furan, is collected. The residue consists of a clear yellowish-brown liquid and a precipitate of sodium bromide, which is filtered off and washed with a little ether. The filtrate is then distilled through a 5 cm column packed with glass helices.

Fraction (g)	B. p.-760	n_D^{25}	OCH ₃ Calc. 47.7 %
1 (2)	80—160°		
2 (26.4)	160°	1.4321	47.8
3 (25.4)	160—161°	1.4323	47.1
4 (24.3)	161°	1.4322	47.5
5 (19.3)	161—162°	1.4326	46.9
residue (5)			

All fractions show a negative Beilstein test for halogens. Yield (fractions 2—5) 95.5 g of dimethoxydihydrofuran = 73 %; current efficiency 86 %.

Dimethoxydihydrofuran has previously been prepared by methoxylation of furan by Jones¹ (yield 48 %, $n_D^{20} = 1.4353$) and by Clauson-Kaas, Limborg and Fækstorp³ (yield 65 %, $n_D^{20} = 1.4328$).

Identification of malealdehyde tetramethyl acetal (I). By fractional distillation of the residue from an electrolytic preparation of dimethoxydihydrofuran about 2 g of a higher boiling liquid may be isolated. One sample boiling at 200—201° (760 mm), $n_D^{25} = 1.4247$, was analyzed. The microhydrogenation was performed in 2 ml of ethanol using 32 mg of



Found » 54.7 » 9.4 » 67.9 » 0.92

substance and 30 mg of Adams platinum oxide catalyst. The hydrogen uptake was complete after about 2 hours.

65 mg of the same sample was left standing for 1 hour at room temperature with 0.25 ml of phenylhydrazine in 12 ml of 32 % aqueous acetic acid. The precipitate was then filtered off, washed with dilute acetic acid and water and dried. The crude product was crystallized from acetone-ligroin. Yield 65 mg of malealdehyde bis-phenylhydrazine = 63 %; m.p. 171° (Kofler stage, corr.); previously found⁵ 171°.

$C_{16}H_{16}N_4$ (264.3)	Calc.	N	21.2
	Found	»	21.2

The above evidence shows, that the higher boiling product is rather pure malealdehyde tetramethyl acetal. This compound has previously been prepared by Wohl and Bernreuther ⁶ (b.p.₇₆₀ = 198.0–198.5°, n_D^{25} = 1.4282).

Note 1. Graphite may also be used as an anode.

Note 2. The ammonium bromide and the furan were technical products. The methanol was an analytical grade in this particular experiment, but it was found in other experiments that a good technical grade may equally well be used. It is not essential, that the methanol is perfectly dry.

Note 3. The contraction of the mixture due to the reaction is about 33 ml, while about 1 ml of methanol and 1 ml of furan are lost by evaporation owing to the liberation of hydrogen.

SUMMARY

Directions are given for the preparation of 2,5-dimethoxy-2,5-dihydrofuran by electrolysis. Malealdehyde tetramethyl acetal was isolated as a by-product of the reaction.

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