

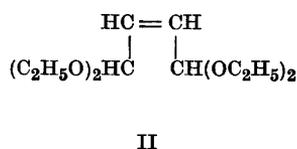
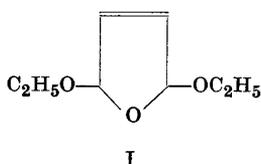
## Electrolytic Ethoxylation of Furan

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A new electrolytic method for the alkoxylation of furans with methanol, ethanol and the propanols has been described in a patent<sup>1</sup> and detailed directions were then worked out for the *methoxylation*, on a laboratory scale, of a number of the simple furans<sup>2-5</sup>. It has now been found that electrolytic *ethoxylation* of furans may be carried out with the same set-up as was used for the methoxylations and in this communication the preparation of 2,5-diethoxy-2,5-dihydrofuran I by electrolysis is given as an example. Diethoxydihydrofuran has been prepared previously, but the electrolytic method is more convenient than the known methods of alkoxylation.

In preparing diethoxydihydrofuran a small amount of a higher boiling liquid was formed. This has been found to consist mainly of malealdehyde tetraethyl acetal II<sup>Cf. 2</sup>.



## EXPERIMENTAL

Microanalyses by G. Cornali and K. Glens

*2,5-Diethoxy-2,5-dihydrofuran (I)*. 4.00 g of ammonium bromide (0.041 mole) is dissolved in 255 ml of absolute ethanol and 47.6 g of furan (0.70 mole) (all materials were technical products) and the mixture electrolyzed with the set-up used for the electrolytic methoxylation of furan<sup>2</sup>.

After electrolysis the light-brown liquid in the cell is poured into a solution of sodium methoxide (0.96 g of sodium (0.042 mole) in 15 ml of methanol) and the diethoxydihydrofuran isolated as described for the preparation of dimethoxydihydrofuran<sup>2</sup>.

Hours	Current (ampere)	Potential across the cell during electrolysis (volt)	Temperature in the cell	Ampere hours (per cent of theoretical amount)
0.5	2.5	11.0	- 9°	1.4 (4 %)
3.2	2.4	11.0	- 8°	7.9 (21 %)
14.8	1.4	11.2	- 11°	30.0 (80 %)
16.0	1.3	11.2	- 11°	31.7 (85 %)

Fraction (g)	B. p. <sub>760</sub>	$n_D^{25}$	OC <sub>2</sub> H <sub>5</sub> Calc. 57.0 %
1 (9.7)	184°	1.4303	56.2
2 (55.2)	184-185°	1.4306	56.4
3 (4.6)	185-186°	1.4305	56.5
residue (14)			

All fractions show a negative Beilstein test for halogens. Yield 69.5 g of diethoxydihydrofuran = 63 %; current efficiency = 74 %.

Diethoxydihydrofuran has previously been prepared by ethoxylation of furan by Clauson-Kaas <sup>6</sup> (cf. Clauson-Kaas, Limborg and Fakstorp <sup>7</sup>) (yield 56 %, b. p.<sub>12</sub> = 71-73°,  $n_D^{25}$  = 1.4309) and by Fakstorp, Raleigh and Schniepp <sup>8</sup> (yield 79 %, b. p.<sub>1</sub> = 50-53°,  $n_D^{25}$  = 1.4310).

*Identification of malealdehyde tetraethyl acetal (II).* By fractional distillation of the residue from an electrolytic preparation of diethoxydihydrofuran about 7 g of a higher boiling liquid could be isolated. One sample (b. p.<sub>11</sub> = 112-118°,  $n_D^{25}$  = 1.4243,  $d^{23}$  = 0.932), which gave a weak positive Beilstein test for halogens, was analyzed. The microhydrogenation was performed in 2 ml of ethanol using 36 mg of substance and 30 mg of Adams platinum oxide catalyst.

C<sub>4</sub>H<sub>4</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (232.3) Calc. C 62.0 H 10.4 OC<sub>2</sub>H<sub>5</sub> 77.6  $\bar{r}$  1.00  
Found » 61.7 » 10.5 » 77.9 » 0.96

84 mg of the sample was left standing for 1 hour at room temperature with 0.25 ml of phenylhydrazine in 12 ml of 32 % aqueous acetic acid. A precipitate of malealdehyde

bis-phenylhydrazone was formed and isolated in the usual way<sup>2</sup>. Yield of crystallized product 47 mg = 49 %; m. p. 169–170° (Kofler stage, corr.); previously<sup>9</sup> found 171°.

C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> (264.3)	Calc.	N	21.2
	Found	»	21.3

The above evidence shows that the higher boiling product is rather pure malealdehyde tetraethyl acetal. Wohl and Mylo<sup>10</sup> previously found b. p.<sub>11</sub> = 112° and  $d^{23} = 0.926$  for this compound.

#### SUMMARY

Directions are given for the preparation of 2,5-diethoxy-2,5-dihydrofuran (I) by electrolysis. Malealdehyde tetraethyl acetal (II) was isolated as a by-product of the reaction.

#### REFERENCES

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