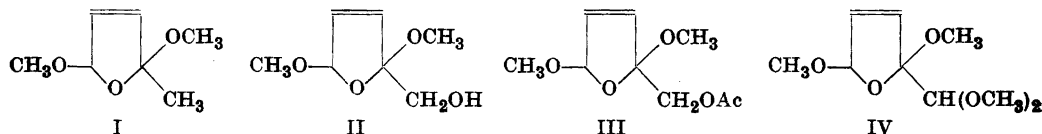


Electrolytic Methoxylation of Some α -Substituted Furans

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An electrolytic method of methoxylating furan has recently been described¹. Furan was mixed with a methanolic solution of ammonium bromide and the mixture electrolyzed. We have now methoxylated silvan, furfuryl alcohol, furfuryl acetate and furfural dimethyl acetal to the corresponding 2,5-dimethoxy-2,5-dihydrofurans (I-IV) in the same way. These compounds have all



been prepared previously, but the electrolytic method was in each case found more convenient than the old method of methoxylation.

EXPERIMENTAL

Microanalyses by Kirsten Glens

2,5-Dimethoxy-2,5-dihydrosilvan (I). 5.00 g of ammonium bromide (0.051 mole) is dissolved in 265 ml of methanol and 41.0 g of freshly distilled silvan (0.50 mole) (note 1) and the mixture (total volume about 310 ml) electrolyzed with the set-up used previously for the electrolytic methoxylation of furan¹.

Hours	Current (ampere)	Potential across the cell during electrolysis (volt)	Temperature in the cell	Ampere hours (per cent of theoretical amount)
0.2	3.3	4.4	- 16°	0.6 (2 %)
3.5	3.0	4.4	- 15°	11.3 (42 %)
6.1	2.8	4.5	- 15°	19.3 (72 %)
7.3	2.8	4.6	- 15°	22.8 (85 %)

After electrolysis the colourless liquid in the cell is poured into a solution of sodium methoxide (1.20 g of sodium (0.052 mole) in 20 ml of methanol) and the methanol containing the ammonia and the excess of silvan is distilled through a Vigreux column from a water-bath under atmospheric pressure. 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 distilled through a 5 cm column packed with glass helices.

Fraction (g)	B. p. $^{\circ}$ ₇₆₀	n_D^{25}	OCH ₃ Calc. 43.1
1 (0.2)	76–158 $^{\circ}$		
2 (10.7)	158 $^{\circ}$	1.4259	44.4
3 (23.2)	158–159 $^{\circ}$	1.4265	42.8
4 (13.7)	159 $^{\circ}$	1.4265	43.1
5 (1.9)	159 $^{\circ}$	1.4261	42.8
residue (3)			

All fractions show a negative Beilstein test for halogens. Yield (fractions 2–5) 49.5 g of dimethoxydihydrosilvan = 69 %; current efficiency 81 %.

Dimethoxydihydrosilvan has previously been prepared by methoxylation of silvan by Jones² (no experimental data) and by Clauson-Kaas and Limborg³ (yield 65 %, b.p.₈ = 46–56 $^{\circ}$).

2,5-Dimethoxy-2,5-dihydrofurfuryl alcohol (II). 5.00 g of ammonium bromide is dissolved in 265 ml of methanol and 39.2 g of freshly distilled furfuryl alcohol (0.40 mole) (note 2) and the mixture electrolyzed and poured (colourless liquid) into sodium methoxide as above.

Hours	Current (ampere)	Potential across the cell during electrolysis (volt)	Temperature in the cell	Ampere hours (per cent of theoretical amount)
0.3	3.3	4.7	– 14 $^{\circ}$	1.1 (5 %)
3.3	2.8	4.6	– 15 $^{\circ}$	10.0 (47 %)
5.9	2.6	4.8	– 15 $^{\circ}$	17.2 (80 %)
6.3	2.5	4.8	– 15 $^{\circ}$	18.3 (85 %)

The methanol and the ammonia are evaporated in vacuum from a water-bath and the clear yellowish-brown residue precipitated with 100 ml of ether. The precipitate of sodium bromide is removed by centrifugation and washed with a little ether. The supernatant liquid is then distilled in vacuum through a 5 cm column packed with glass helices.

Fraction (g)	B.p.-10-12	n_D^{25}	OCH ₃ Calc. 38.8 %
1 (7.3)	76-106°	1.4712	
2 (4.9)	106-109°	1.4567	36.7
3 (33.2)	109-110°	1.4568	38.4
4 (3.9)	109°	1.4568	38.3
residue (6)			

All fractions show a negative Beilstein test for halogens. Yield (fractions 2-4) 42.0 g of dimethoxydihydrofurfuryl alcohol = 66 %; current efficiency 77 %.

Dimethoxydihydrofurfuryl alcohol has previously been prepared by methoxylation of furfuryl alcohol by Meinel⁴ (yield 40 %; b.p._{0.4} = 86-87°; n_D^{25} = 1.4600). Meinel believed his product to be the 4,5-addition product, but it is almost certain that the methoxy groups add to the α -positions of furfuryl alcohol³.

2,5-Dimethoxy-2,5-dihydrofurfuryl acetate (III). 5.00 g of ammonium bromide is dissolved in 260 ml of methanol and 42.0 g of furfuryl acetate (0.30 mole) (note 3) and the mixture electrolyzed and worked up as described for the preparation of dimethoxydihydrofurfuryl alcohol.

Hours	Current (ampere)	Potential across the cell during electrolysis (volt)	Temperature in the cell	Ampere hours (per cent of theoretical amount)
0.5	3.4	4.3	- 12°	1.8 (11 %)
1.5	3.2	4.3	- 13°	5.3 (33 %)
4.1	2.9	4.6	- 15°	13.4 (83 %)
5.2	2.3	5.0	- 15°	16.3 (101 %)

The final product is distilled without a column. Yield 45 g of a colourless liquid; b.p.₁₂ about 100–120° (note 4). 50 ml of acetic anhydride and 50 ml of pyridine are added and the mixture, which gets hot, left standing at room temperature for 20 hours. The low-boiling products are distilled in vacuum from a water-bath and the residue distilled further through a 5 cm column packed with glass helices.

Fraction (g)	B.p. ₁₂	n_D^{25}	OCH ₃ Calc. 30.7 %	OCCH ₃ Calc. 21.3 %
1 (8.7)	117°			
2 (8.7)	117–119°	1.4431	30.2	21.2
3 (39.2)	119°	1.4433	30.5	20.9
4 (4.7)	119°	1.4433	30.2	20.8
residue (< 1)				

All fractions show a negative Beilstein test for halogens. Yield (fractions 2–4) 52.6 g of dimethoxydihydrofurfuryl acetate = 87 %; current efficiency = 86 %.

Dimethoxydihydrofurfuryl acetate has previously been prepared by methoxylation of furfuryl acetate by Clauson-Kaas and Limborg³ (yield 66 %, b.p.₂₀ = 131°).

2,5-Dimethoxy-2,5-dihydrofurfural dimethyl acetal (IV). 5.00 g of ammonium bromide is dissolved in 270 ml of methanol and 35.5 g of furfural dimethyl acetal (0.25 mole) (note 5) and the mixture electrolyzed and worked up as described for the preparation of dimethoxydihydrofurfuryl alcohol.

Hours	Current (ampere)	Potential across the cell during electrolysis (volt)	Temperature in the cell	Ampere hours (per cent of theoretical amount)
0.5	3.1	4.7	– 13°	1.5 (11 %)
2.1	2.9	4.7	– 14°	6.6 (49 %)
4.8	2.2	5.2	– 16°	14.0 (104 %)

Fraction (g)	B.p. ₁₃	n_D^{25}	OCH ₃ Calc. 60.8 %
1 (1.8)	60–107°	1.4467	
2 (0.8)	107°	1.4429	59.0
3 (30.8)	107–110°	1.4428	60.0
4 (10.2)	110°	1.4431	59.5
residue (1)			

All fractions show a negative Beilstein test for halogens. Yield (fractions 2–4) 41.8 g of dimethoxydihydrofurfural dimethyl acetal = 82 %; current efficiency 79 %.

Dimethoxydihydrofurfural dimethyl acetal has previously been prepared by Meinel ⁴ by methoxylation of furfural (yield 50 %; b.p._{0.3} = 80–81°, n_D^{20} = 1.4451).

Note 1. All materials were technical products.

Note 2. All materials were technical products.

Note 3. The ammonium bromide and the methanol were technical products. The furfuryl acetate was prepared after directions given by Blatt, A. H. *Organic Synthesis, Collective Volume 1* (1941) 285. New York: John Wiley & Sons Inc.

Note 4. This product contains 30–50 % of dimethoxydihydrofurfuryl alcohol, apparently formed by methanolysis during electrolysis. It is therefore acetylated in order to get pure dimethoxydihydrofurfuryl acetate.

Note 5. The ammonium bromide and the methanol were technical products. The methanol was dried with magnesium. Furfural dimethyl acetal was prepared from furfural and methyl orthoformate after Claisen. Yield 90 %; b.p.₁₄ = 57–58°; n_D^{25} = 1.4486. Previously found ⁵ b.p.₇₆₀ = 178°.

C ₅ H ₄ O(OCH ₃) ₂ (142.2)	Calc.	C	59.1	H	7.1	OCH ₃	43.7
	Found	•	59.4	•	7.6	•	42.9

SUMMARY

Directions are given for the preparation of 2,5-dimethoxy-2,5-dihydro-*silvan*, 2,5-dimethoxy-2,5-dihydrofurfuryl alcohol, 2,5-dimethoxy-2,5-dihydrofurfuryl acetate and 2,5-dimethoxy-2,5-dihydrofurfural dimethyl acetal by electrolytic methoxylation of the corresponding furans.

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