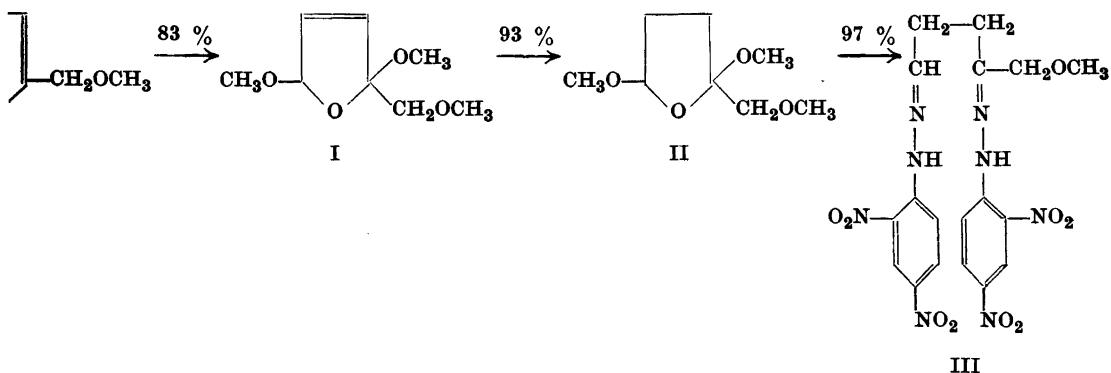


## Preparation of 2,5-Dimethoxy-2,5-dihydrofurfuryl Methyl Ether and 2,5-Dimethoxytetrahydrofurfuryl Methyl Ether

NIELS CLAUSON-KAAS

*Centrallaboratoriet, Sadolin & Holmblad A/S, Copenhagen, Denmark*

A new electrolytic method for the methoxylation of furans has recently been described<sup>1-3</sup>. This method has now been used to methoxylate furfuryl methyl ether to dimethoxydihydrofurfuryl methyl ether, which is a new compound. Catalytic hydrogenation of dimethoxydihydrofurfuryl methyl ether gave the expected dimethoxytetrahydrofurfuryl methyl ether, which also is new. Dimethoxytetrahydrofurfuryl methyl ether gave, with dinitrophenylhydrazine in methanol, a bis-dinitrophenylhydrazone with the formula  $C_{17}H_{15}O_8N_8(OCH_3)$ . This proves that the methoxy groups in both dimethoxy compounds are in the 2,5-positions (formulas I and II)<sup>cf. 3</sup>.



The bis-dinitrophenylhydrazone (structure III) is a derivative of  $\delta$ -methoxy-levulinaldehyde. Pummerer *et al.*<sup>4,5</sup> report having prepared the dimethyl acetal of  $\delta$ -methoxylevulinaldehyde by acid methanolysis of furfuryl alcohol or furfuryl methyl ether. They obtained from their product a bis-dinitro-

phenylhydrazone with the formula  $C_{18}H_{18}O_9N_8$ . The bis-dinitrophenylhydrazone of Pummerer *et al.* is reported to melt at  $192^\circ$  and to be easily soluble in benzene, while the bis-dinitrophenylhydrazone from dimethoxytetrahydrofurfuryl methyl ether melts at  $248-249^\circ$  and is almost insoluble in benzene. The two hydrazones are thus apparently not identical. Since the hydrazone from dimethoxytetrahydrofurfuryl methyl ether is prepared in high yield by a series of well-known reactions it is almost certainly a bis-dinitrophenylhydrazone of  $\delta$ -methoxylevulinaldehyde. The structure proposed by Pummerer *et al.* for their hydrazone should therefore not be accepted without further experimental evidence.

## EXPERIMENTAL

Microanalyses by Franz Limborg and Kirsten Glens

*2,5-Dimethoxy-2,5-dihydrofurfuryl methyl ether (I)*. 5.00 g of ammonium bromide (0.051 mole) is dissolved in 270 ml of methanol and 39.2 g of furfuryl methyl ether (0.35 mole) (note 1) and the mixture electrolyzed with the set-up used previously for the electrolytic methoxylation of furan<sup>1</sup>.

Hours	Current (ampere)	Potential across the cell during electrolysis (volt)	Temperature in the cell	Ampere hours (per cent of theoretical amount)
0.5	2.9	4.5	$-14^\circ$	1.6 (8 %)
2.2	2.8	4.5	$-15^\circ$	6.5 (35 %)
6.3	2.3	4.8	$-15^\circ$	17.4 (93 %)
7.0	1.9	4.9	$-15^\circ$	18.8 (100 %)

After electrolysis the liquid in the cell is colourless in the upper part of the cell and slightly yellow from unreacted bromine near the bottom. The liquid is poured into a solution of sodium methoxide (1.20 g of sodium (0.052 mole) in 15 ml of methanol) and the methanol and the ammonia evaporated in vacuum from a water-bath. The residue is filtered and the precipitate of sodium bromide washed with a little ether. The filtrate is distilled through a 5 cm column packed with glass helices (see p. 553).

All fractions show a negative Beilstein test for halogens. Yield (fractions 2-4) 50.8 g of dimethoxydihydrofurfuryl methyl ether = 83 %; current efficiency 83 %.

Fraction 3 was further analyzed for carbon and hydrogen.

$C_5H_5O(OCH_3)_3$ (174.2)	Calc.	C	55.2	H	8.1
	Found	»	55.2	»	8.2

Fraction (g)	B. p. <sub>10</sub>	$n_D^{25}$	OCH <sub>3</sub> Calc. 53.5 %
1 (0.4)	67–84°		
2 (37.8)	84–85°	1.4384	53.3
3 (8.0)	85°	1.4383	53.6
4 (5.0)	85°	1.4384	54.1
residue (2)			

*2,5-Dimethoxytetrahydrofurfuryl methyl ether (II)*. 30.0 g of dimethoxydihydrofurfuryl methyl ether and 50 ml of anhydrous methanol are shaken with 4.0 g of Raney nickel under 100 atmospheres of hydrogen for 4 hours. After filtration the methanol is evaporated in vacuum and the residue distilled further in vacuum.

Fraction (g)	B. p. <sub>12</sub>	$n_D^{25}$	OCH <sub>3</sub> Calc. 52.8 %
1 (3)	< 42°		
2 (7.8)	80–82°	1.4285	53.2
3 (7.2)	81–82°	1.4283	52.3
4 (9.0)	81–82°	1.4289	52.3
5 (4.2)	82–83°	1.4285	52.7
no residue			

Yield (fractions 2–5) 28.2 g of dimethoxytetrahydrofurfuryl methyl ether = 93 %.  
 Fraction 4 was further analyzed for carbon and hydrogen.

$C_5H_7O(OCH_3)_3$  (176.2) Calc. C 54.5 H 9.2  
 Found » 54.5 » 9.2

*Bis-dinitrophenylhydrazone of  $\delta$ -methoxylevulinic aldehyde (III)*. 176 mg of dimethoxytetrahydrofurfuryl methyl ether in 5 ml of anhydrous methanol was added to a solution of 495 mg of dinitrophenylhydrazine in 10 ml of methanol and 1 ml of concentrated sulfuric acid. The yellow hydrazone, which precipitated immediately, was filtered off after 1 hour, washed thoroughly with methanol and dried (sulfuric acid, 0.1 mm, 80°,

1 hour). Yield 477 mg of bis-dinitrophenylhydrazone = 97 %; m. p. (Hershberg apparatus, corr.) 227–229° (destruction).

$C_{17}H_{15}O_8N_8(OCH_3)$  (490.4) Calc. C 44.1 H 3.7 N 22.9  $OCH_3$  6.3  
Found » 44.3 » 3.9 » 22.5 » 6.4

The hydrazone is almost insoluble in benzene and very slightly soluble in acetone. It crystallizes well from nitromethane. 50 mg gave 40 mg of recrystallized product; m. p. 249–250°. Recrystallization gave 30 mg; m. p. 248–249°. This product was dried (sulfuric acid, 0.01 mm, 80°, 16 hours) and analyzed.

Found C 44.3 H 3.8 N 22.2  $OCH_3$  6.3

Note 1. Analytical grades of ammonium bromide and of methanol were used. The furfuryl methyl ether was prepared after Pummerer *et al.*<sup>4</sup> (b. p.<sub>760</sub> = 136°,  $n_D^{25}$  = 1.4511).

#### SUMMARY

2,5-Dimethoxy-2,5-dihydrofurfuryl methyl ether has been prepared by electrolytic methoxylation of furfuryl methyl ether. Catalytic hydrogenation gave 2,5-dimethoxytetrahydrofurfuryl methyl ether. Both compounds are new.

#### REFERENCES

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