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# RESEARCHES ON FURANS

## XLII. Electrolytic Methoxylation of Furan Amines and 2-Furylacetonitrile*

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Investigation of the possibility of methoxylating furan series amines electrolytically showed that, contrary to what is stated in the literature, such methoxylation occurs without prior acylation of the amines, to give 30-60% yields of the corresponding 2,5-dimethoxy-2,5-dihydrofurfurylamines. Electrolytic methoxylation of 2-furylacetonitrile gives 2,5-dimethoxy-2,5-dihydrofurylacetonitrile.

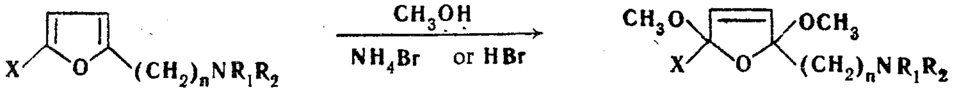
Previously, two of the present authors [2-4] obtained a number of mono- and bis(aminomethyl)furans, starting from mono- and bis(chloromethyl)furans. The present work investigates the possibility of methoxylating such amines electrolytically, to prepare 2,5-dialkoxy-2,5-dihydrofurfurylamines, and with a view to using the latter to synthesize other heterocyclic systems.

The literature states [5] that when an attempt was made to electrolytically methoxylate 2-furfurylamine to the corresponding dimethoxydihydrofurfurylamine, the yield was insignificant. To obtain the amine, previously acylated amine was methoxylated, and the acyl group subsequently removed.

Electrolytic methoxylation was applied to the following furan series monoamines: furfurylamine (Ia), 2(β-aminoethyl)furan (Ib), N-ethylfurfurylamine (Ic), N,N-dimethylfurfurylamine (Id), 2-methyl-5-(N,N-dimethylaminomethyl)furan (Ie), N,N-diethylfurfurylamine (If), and 2-(N-piperidinomethyl)furan (Ig); and to the following diamines: 2,5-bis(dimethylaminomethyl)furan (IIa), and 2,5-bis(N-piperidinomethyl)furan (IIb).

It has now been ascertained that monoamines Ia-e methoxylate electrolytically both in the presence of ammonium bromide, and of hydrobromic acid, to give 30-60% yields of 2,5-dimethoxy-2,5-dihydrofurfurylamines. Methoxylation of If and Ig gives complex mixtures of reduction products, from which no individual amine could be separated.

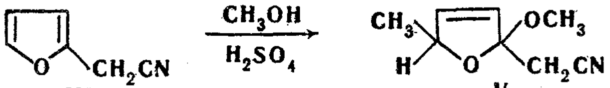
Unlike the monoamines, the diamines IIa and b did not react under the reaction conditions, and were recovered unchanged.



Ia-e　　IIIa-e

a $n=1$, $R_1=R_2=X=H$; b $n=2$, $R_1=R_2=X=H$;
c $n=1$, $R_1=X=H$, $R_2=C_2H_5$;
d $n=1$, $R_1=R_2=CH_3$, $X=H$; e $n=1$, $R_1=R_2=X=CH_3$.

Electrolytic methoxylation of 2-furylacetonitrile (IV) in the presence of sulfuric acid gave 2,5-dimethoxy-2,5-dihydrofurylacetonitrile (V) in 31% yield.



IV　　V

### Experimental

The electrolytic methoxylation was run in an electrolytic cell with a Ni cathode and graphite anode [6], using 24 V and current 3-5 amp. 0.1 mole compound was electrolyzed at −12° to −15° C until 5 amp-hr no longer passed through the solution. The purities of the dimethoxydihydrofurans were confirmed by non-stabilized thin layer chromatography on alumina.

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* For Part XLI see [1].

2, 5-Dimethoxy-2, 5-dihydrofurfurylamine (IIIa). A solution of 5 g Ia (bp 40–41° C (10 mm), $n_D^{20}$ 1.4895 [7] ) and 5 g $NH_4BR$ in 200 ml MeOH were placed in the electrolyzer, cooled to – 12° C, and electrolysis carried out. Then the products were poured into a Na methoxide solution (1.2 g Na in 30 ml MeOH), the MeOH vacuum-distilled off, 150 ml dry ether added to the residue, the NaBr precipitate filtered off, and repeatedly washed with ether. The solvent was distilled off, and the residue vacuum-distilled to give 3.2 g IIIa (40%), bp 98–99° C (14 mm), $n_D^{20}$ 1.4608, $d_4^{20}$ 1.0702. The literature gives [5] bp 95–96° (12 mm), $n_D^{25}$ 1.4589. Found: C 52.50, 52.50; H 8.02, 8.07%; $MR_D$ 40.47. Calculated for $C_{17}H_{13}NO_3$: C 52.79; H 8.23%; $MR_D$ 40.21.

Picrate: mp 138–138.5° C (ex MeOH). Found: C 40.01, 40.23; H 4.13, 4.16%; Calculated for $C_7H_{13}NO_3 \cdot C_6H_2(NO_2)_3OH$; C 40.21; H 4.15%.

2, 5-Dimethoxy-2, 5-dihydro-2-(β-aminoethyl) furan (IIIb). 7.5 g Ib (bp 54° (12 mm), $n_D^{20}$ 1.4835 [8] ) and 5 ml 47% HBr in 200 ml MeOH were electrolyzed, Na methoxide solution (1.2 g Na in 30 ml MeOH) added, and the products worked up as described above. After distilling off the solvent there remained 4.3 g (35%), bp 106–107° C (9 mm), $n_D^{20}$ 1.4675, $d_4^{20}$ 1.0782. Found: C 55.34, 55.46; H 8.64, 8.60%; $MR_D$ 44.61. Calculated for $C_8H_{15}NO_3$: C 55.49; H 8.73%; $MR_D$ 44.82.

Picrate: (ex dry ether), mp 90–91° C (washed with ether). Found: C 42.04, 41.98; H 4.79, 4.69%. Calculated for $C_8H_{15}NO_3 \cdot C_6H_2(NO_2)_3OH$: C 41.79; H.4.51%.

2, 5-Dimethoxy-2, 5-dihydro-2-(ethylaminomethyl) furan (IIIc). 7.5 g Ic (bp 58–60° (15 mm), $n_D^{20}$ 1.4692* and 5 g $NH_4Br$ in 200 ml MeOH when electrolyzed as described above gave 6.5 g (58%), bp 101–102° C (15 mm), $n_D^{20}$ 1.4475, $d_4^{20}$ 1.0272. Found: C 57.62, 57.94; H 8.92, 8.93%; $MR_D$ 48.75. Calculated for $C_9H_{17}NO_3$: C 57.75; H 9.16%; $MR_D$ 49.63.

Picrate: (ex dry ether), mp 100–101° C (ex petrol ether + benzene). Found: C 43.34, 43.11; H 4.72, 4.72%. Calculated for $C_9H_{17}NO_3 \cdot C_6H_2(NO_2)_3OH$: C 43.36; H 4.84%.

2, 5-Dimethoxy-2, 5-dihydro-2-(dimethylaminomethyl) furan (IIId). 12.5 g Id bp 143–145° (758 mm) and 10 ml 47% HBr in 200 ml MeOH was electrolyzed as described above, to give 3.2 unchanged amine, and 6.9 g IIId (45% on the reacted amine); bp 87–87.5° C (13 mm), $n_D^{20}$ 1.4485, $d_4^{20}$ 1.0142. Found: C 57.26, 57.24; H 8.93, 8.86%; $MR_D$ 49.48. Calculated for $C_9H_{17}NO_3$: C 57.75; H 9.15%; $MR_D$ 49.96.

Methiodide: mp 126–127° C (ex dry EtOAc + EtOH). Found: C 36.53, 36.78; H 6.53, 6.44%. Calculated for $C_9H_{17}NO_3 \cdot CH_3I$: C 36.72; H 6.16%.

2, 5-Dimethoxy-2, 5-dihydro-2-methyl-5-(dimethylaminomethyl) furan (IIIe). Prepared as described, from 7 g Ie (bp 68°–70° (25 mm), $n_D^{20}$ 1.4633 [11]) and 5 ml 47% HBr in 200 ml MeOH, yield 5.7 g (57%); bp 93°–95° C (15 mm), $n_D^{20}$ 1.4468, $d_4^{20}$ 0.9998. Found: C 59.73, 59.70; H 9.32, 9.37%; $MR_D$ 53.76. Calculated for $C_{10}H_{19}NO_3$: C 59.67; H 9.51%; $MR_D$ 54.58.

Methiodide: mp 140.5–141° C (ex dry AcOEt+ EtOH). Found: C 38.87, 38.96; H 6.29, 6.49%. Calculated for $C_{10}H_{19}NO_3 \cdot CH_3I$: C 38.50; H 6.46%.

2, 5-Dimethoxy-2, 5-dihydrofurylacetonitrile (V). Prepared by electrolyzing 22 g IV (bp 66–68° (8 mm), $n_D^{20}$ 1.4705 [4]), 2 ml concentrated $H_2SO_4$ and 200 ml MeOH, yield 10.5 g (31%); bp 118–119° C (8 mm), $n_D^{20}$ 1.4567, $d_4^{20}$ 1.1152. Found: C 56.51, 56.52; H 6.81, 6.80%; $MR_D$ 41.31. Calculated for $C_8H_{11}NO_3$: C 56.79; H 6.56%; $MR_D$ 41.22.

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* Ic was prepared from 2-chloromethylfuran and ethylamine. The literature gives [9] 63–65° C (17–18 mm), $n_D^{20}$ 1.4688.

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