FURAN COMPOUNDS

XXXIV. Reductive Amination of Furan Aldehydes with Monoethanolamine*

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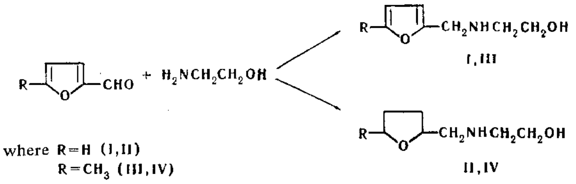
By reductive amination, starting from furfural, 5-methylfurfural, β-(2-furyl)acrolein, and monoethanolamine, we have obtained N-furfurylaminoethanol, N-(5-methyl-2-furfuryl)aminoethanol, and N-[1-(α-furyl)-3-propyl]aminoethanol. By reductive amination combined with the subsequent hydrogenation of the furan ring we have obtained N-tetrahydrofurfurylaminoethanol and N-(5-methyltetrahydro-2-furfuryl)aminoethanol.

Previously, one of us and his colleagues [2, 3] described a two-stage method of synthesizing N-furfurylaminoethanol (I) and N-tetrahydrofurfurylaminoethanol (II). I has also been obtained by the reaction of furfurylamine with ethylene oxide [4].

In view of the interest in I and II and also in N-(5-methyl-2-furfuryl)aminoethanol (IV) [5] and N-(5-methyltetrahydro-2-furfuryl)aminoethanol (IV) as intermediates for further organic synthesis, for example [4, 6, 7], we have developed a single-stage method for obtaining I–IV.



where R=H (I, II)
R=CH_3 (III, IV)

The reactions are carried out with equimolecular amounts of the reactants at 40–60° C for I and III and at 40° C and then 135° C for II and IV in methanol at an elevated pressure of hydrogen using Raney nickel as catalyst.

The absence of an excess of the amine component permits the process to be carried out at 40–60° C (with yields of I and III of 70–75%) while with an excess of ammonia [8] or an amine [9] the reaction takes place only at a higher temperature (80–100° C).

The stepwise performance of the reaction—first at 40–60° C (hydrogenation of the multiple bond in the side chain) and then at 135° C (to saturate the furan ring)—permits the preparative combination of reductive amination and the hydrogenation of the furan ring to a tetrahydrofuran ring. The yields of II and IV were 58 and 75%, respectively.

As was shown in the case of β-(2-furan)acrolein, in the reaction described furfural can be replaced by its vinylogs; thus, N-[1-(α-furyl)-3-propyl]aminoethanol (V) has been obtained in one stage with a yield of 54%.

EXPERIMENTAL

N-Furfurylaminoethanol (I). A solution of 96 g (1 mole) of freshly-distilled furfural in 150 ml of methanol was cooled and, with stirring, 61 g (1 mole) of monoethanolamine was added, after which the mixture was transferred to a rotating autoclave with a capacity of 610 ml Reductive amination was carried out at 40°–60° C in the presence of 10 g of Raney nickel. The hydrogen pressure was 90–100 atm. The calculated amount of hydrogen was absorbed in 1 hr. The hydrogenizate was discharged from the autoclave, the catalyst was filtered off, the solvent was distilled off on the water bath at reduced pressure, and the residue was distilled in vacuum. Yield 100 g (71%). Bp 99°–100° C (2 mm); n_D^{20} 1.5026 (according to the literature [3], Bp 99°–100° C (2 mm); n_D^{20} 1.5028). Found, %: C 59.36, 59.28; H 7.64, 7.91; N 10.12, 10.34. Calculated for $C_7H_{11}NO_2$, %: C 59.55; H 7.85, N 9.92.

N-(5-Methylfurfuryl)aminoethanol (III) was obtained in a similar manner to the preceding compound from 55 g (0.5 mole) of 5-methylfurfural dissolved in 120 ml of methanol and 31 g (0.5 mole) of monoethanolamine. Yield 51.3 g (75.5%). Bp 111°–113° C (4 mm); n_D^{20} 1.5030 d_4^{20} 1.077. Found, %: C 61.52, 61.85; H 8.72, 8.18; N 9.01, 8.79. Calculated for $C_8H_{13}NO_2$, %: C 61.90; H 8.45; N 8.98.

N-[1-(α-Furyl)-3-propyl]aminoethanol (V). A rotating autoclave with a capacity of 610 ml was charged with 61 g (0.5 mole) of β-(2-furyl)acrolein dissolved in 180 ml of methanol, 31 g (0.5 mole) of hydrogen was 80–100 atm. The temperature of the experiment was 60° C. After 1 hr, the calculated amount of hydrogen had been absorbed. The hydrogenizate was freed from catalyst and solvent and the residue was distilled in vacuum. Yield 45.5 g (54%). Bp 132°–135° C (4.5 mm); n_D^{20} 1.4970. Literature data [2], bp 134°–135° C (4.5 mm); n_D^{20} 1.4970.

N-(5-Methyltetrahydrofurfuryl)aminoethanol (IV). With cooling and stirring, 24.4 g (0.4 mole) of monoethanolamine was added to a solution of 44.0 g (0.4 mole) of freshly distilled 5-methylfurfural in 176 ml (5.5 mole) of methanol. The mixture was charged into a rotating autoclave with a capacity of 610 ml. Raney nickel (4 g) was used as catalyst. The pressure of hydrogen was 90–100 atm and the initial temperature 40°–60° C. After 1 hr, the temperature was raised to 135°–140° C. The reaction was complete after ~5 hr, when the calculated amount of the hydrogen had been absorbed. Then the hydrogenizate was treated as described above. Yield 47.6 g (74.8%). Bp 110° C (4 mm); d_4^{20} 1.016, n_D^{20} 1.4712. Found, %: C 59.87, 60.06; H 10.77, 10.46; N 8.92, 8.70. Calculated for $C_8H_{17}NO_2$, %: C 60.34; H 10.76; N 8.80; MR_D 43.71.

N-Tetrahydrofurfurylaminoethanol (II). was obtained similarly from 48.0 g (0.5 mole) of furfural in 192 ml (6 mole) of methanol and 31 g (0.5 mole) of monoethanolamine. Yield 41.9 g (57.8%). Bp 114°–115° C (5 mm); d_4^{20} 1.049, n_D^{20} 1.4765 (according to the literature [3, 10] bp 114°–115° C (5 mm); n_D^{20} 1.4780). Found, %: C 57.61, 57.75; H 10.63, 10.70; N 9.56, 9.64; MR_D 39.08. Calculated for $C_7H_{15}NO_2$, %: C 57.90; H 10.41; N 9.64; MR_D 39.09.

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*For part XXXIII, see [1].

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