

Hydrogenation of Furfurylamine to 2,5-Dipropylpiperazine and Piperidine

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The transformation of furfurylamine into piperidine by catalytic hydrogenation has been reported twice in the literature.

Schmidt, Blaser and Manchen¹ obtained piperidine in good yields (yields not specified) when heating furfurylamine with hydrogen, ammonia, and various catalysts under pressures above 50 atmospheres and at temperatures above 200°. Wilson,² under similar conditions, using Raney nickel, but no ammonia, obtained a 9% yield of piperidine together with 43% of *N*-tetrahydrofurfurylpiperidine.

We have hydrogenated furfurylamine catalytically under 100 atmospheres at 300° and obtained piperidine (11%) and 2,5-dipropylpiperazine (24%). Our reaction does not proceed *via* tetrahydrofurfurylamine, since this compound was recovered unchanged after treatment under the same reaction conditions.

2,5-Dipropylpiperazine is new. Its structure was proved by analysis and comparison with a sample prepared by hydrogenation of 3,6-dipropyl-2,5-piperazinedione (*cf.* Ref. 3).

Experimental. Hydrogenation of furfurylamine. Furfurylamine (30.0 g, 0.31 mole) and copper-chromium oxide (2.00 g) (catalyst G22 from Girdler-Südchemie Katalysator GmbH, München, Germany) were shaken under hydrogen (100 atm.) in a 500 ml glass-lined autoclave at 300° for one hour. The quantity of hydrogen absorbed was 0.84 mole. After being cooled to zero the reaction mixture (odour of ammonia) was filtered. The filtrate was mixed with a filtrate from an identical experiment and the mixture distilled through a short 10-plate column under atmospheric pressure. 20 ml of distillate, b.p. 80–99°, was collected.

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The residue from the distillation crystallized on cooling. The crystals were isolated by filtration, washed with cold petroleum ether and dried. 2,5-Dipropylpiperazine (12.61 g, 24%) was hereby obtained as white hygroscopic crystals, m.p. 84° (Hershberg app., corr.) Crystallization from petroleum ether (60 ml) gave 9.45 g, m.p. 87–88°. Further crystallization did not change the melting point. [Found: C 70.7; H 13.0; N 16.3. Calc. for C₁₀H₂₂N₂ (170.2): C 70.6; H 13.0; N 16.5]. The product was in every respect identical with a sample prepared by hydrogenation of 3,6-dipropyl-2,5-piperazinedione.³

The 20 ml portion of the distillate was dried with solid potassium hydroxide and redistilled. Piperidine (5.88 g, 11%), b.p. 90–105° (main portion 104°), was hereby collected. The product was further characterized by its toluenesulfonamide derivative and by gas chromatographic analysis.

2,5-Dipropylpiperazine dihydrochloride was prepared in the usual way. [Found: C 49.5; H 10.0; Cl (ionic) 29.4; N 11.5. Calc. for C₁₀H₂₄Cl₂N₂ (243.1): C 49.3; H 10.0; Cl 29.2; N 11.5].

- Schmidt, W., Blaser, B. and Manchen, F. *Ger. Pat. 695,472* (1940).
- Wilson, C. L. *J. Am. Chem. Soc.* **67** (1945) 693.
- McElvain, S. M. and Pryde, E. H. *J. Am. Chem. Soc.* **71** (1949) 326.

Received January 25, 1966.

Kinetic Equations Assuming two Sets of Active Sites on a Catalyst

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Recently Shah and Davidson¹ published an article exploring the possibility that it may be necessary to assume more than one rate determining step in the kinetic equations of the Hougen-Watson type² for a heterogeneously catalyzed gas phase reaction. An equation taking into account that both surface reaction and desorption