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CATALYTIC HYDROGENATION OF AROMATIC AMINES AT ATMOSPHERIC PRESSURE IN WATER

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Rhodium on alumina (5% Rh) has been found to be a good catalyst for the hydrogenation of aromatic amines *under atmospheric pressure at room temperature in water.*

Catalytic hydrogenation of aromatic compounds is frequently used in the synthesis of cyclohexane derivatives. This reaction can be achieved by using heterogeneous catalysts at high pressure and at temperatures between 100 and 200 °C. Homogeneous catalysts as well as phase transfer catalysts allow milder reaction conditions.[1]

In connection with our interest in (arene)tricarbonylchromium complexes[2] we had a need for chiral amines which should *not* contain an aromatic substructure. Among other methods of their preparation we considered a hydrogenation of some easily available aromatic amines. We found that commercially available rhodium on alumina (5%) allows this reaction under surprisingly mild reaction conditions, namely at 20 °C and at atmospheric pressure in water. We note that this catalyst has been used for hydrogenation at 4 atm. pressure.[3] Although even more active catalysts are known,[4] we believe that the reaction at atmospheric pressure and room

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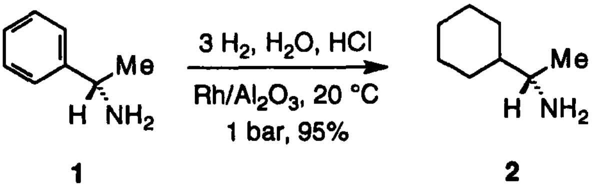
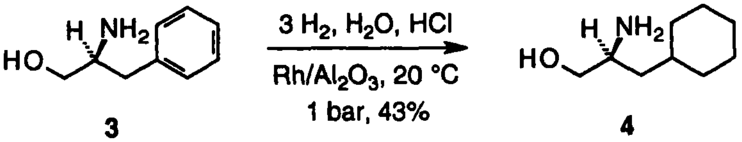
temperature in water is useful for laboratory hydrogenations, because no catalyst preparation nor special equipment for maintaining certain pressure or temperature is necessary.

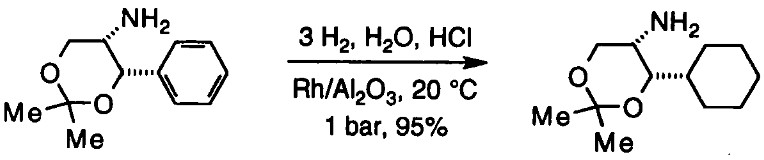
In order to prevent the amines from poisoning the catalyst and to increase solubility in water, they were used in the form of their hydrochlorides. Thus, (*S*)-1-phenylethylamine (**1**) was hydrogenated in aqueous HCl over Rh/Al_2O_3 by stirring the solution for 7 d at 20 °C under 1 atm. H_2 to give (*S*)-1-cyclohexylethylamine (**2**)[5,6] in 95% yield.



The reduction tolerates an alcohol functionality as was shown by the hydrogenolysis of L-phenylalaninol (**3**), which gave (*S*)-2-amino-3-cyclohexyl-1-propanol (**4**)[7,8] in 47% yield after 3 d. The lower yield presumably results from the more difficult isolation of the hydrophilic product from the aqueous phase.



Finally, aminoacetal **5** was tested, which is a side product in the synthesis of chloroamphenicol. The reaction worked under the mild conditions and gave the highly functionalized cyclohexane **6** in 95% yield.



5 6

Typical experimental procedure: 20.7 g (100 mmol) of (+)-(4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane (**5**) is suspended in 100 mL of water. Hydrochloric acid is added to p*H* ≈ 1 with dissolution of the amine. After addition of 1.0 g of of rhodium on alumina (5% Rh) the mixture is stirred for 28 d in an atmosphere of H_2 (1 bar). After filtration 0.1 N NaOH is added to p*H* ≈ 12, and the solution is extracted with diethyl ether. After drying of the collected organic layers over K_2CO_3, filtration and solvent removal 20.32 g (95.4 mmol, 95%) of (+)-(4*S*,5*S*)-5-amino-4-cyclohexyl-2,2-dimethyl-1,3-dioxane (**6**) is isolated as an air sensitive, colorless solid (m. p. 45 °C). IR ($CHCl_3$): $\tilde{\nu}$ = 3628 cm^{-1} (w, Amin), 2984 (m), 2958 (s), 2852 (m), 1448 (m), 1380 (m), 1244 (m), 1152 (w), 1100 (w), 1080 (w), 1040 (m), 872 (w), 824 (m). - ^1H-NMR (400.1 MHz, $CDCl_3$): δ = 0.78-1.50 (m, 5H), 1.37 (s, 3H, 7-H or 8-H), 1.39 (s, 3H, 7-H or 8-H), 1.54-2.10 (m, 5H), 2.91-3.92 (m, 5H), 3.16 (s, br, 2H, Amin). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, APT): δ = 26.6 (+, C-11 or C-12 or C-13), 26.7 (+, C-11 or C-12 or C-13), 27.0 (+, C-11 or C-12 or C-13), 28.6 (–, C-7 or C-8), 28.9 (–, C-7 or C-8), 29.8 (+, C-10 or C-14), 29.9 (+, C-10 or C-14), 42.7 (–, C-9), 63.3 (–, C-5), 63.7 (+, C-6), 83.3 (–, C-4), 94.6 (+, C-2). - MS (70 eV, 20 °C): *m/z* (%) = 199 (10), 198 (70) [M^+–CH_3], 183 (13), 182 (100) [M^+–CH_3–NH_2], 168 (4), 131 (3), 130 (35) [M^+–C_6H_{11}], 126 (27), 121 (30), 102 (16), 101 (50), 100 (36), 83 (24) [$C_6H_{11}^+$]. - MS-FAB: *m/z* (%) = 214 (65) [M^++1], 213 (13) [M^+]. - HRMS ($C_{11}H_{20}NO_2$): calcd. 198.149404; found 198.149414. - $C_{11}H_{20}NO_2$ (213.32): calcd. C 67.57, H 10.87, N 6.57; found C 66.19, H 10.90, N 6.70. - $[\alpha]_D^{20}$ = –9.2, (c = 1, THF).

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