REDUCTIVE CYCLIZATION OF 3-(2-NITROPHENYLAMINO)PROPIONIC ACID HYDRAZIDE

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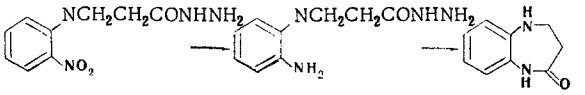
We have demonstrated that reductive cyclization to form 2,3,4,5-tetrahydro-1H-1,5-benzo-2-diazepinone (II) occurs in the reduction of 3-(2-nitrophenylamino)propionic acid hydrazide (I) with hydrogen during isolation. It might have been assumed that the intermediate product in this process is 3-(2-aminophenylamino)propionic acid hydrazide (III). To confirm this, I was reduced under milder conditions (with hydrogen on a Raney nickel catalyst at room temperature), and aminohydrazide III was isolated in a yield of 90%. The cyclization of III in the presence of an acid catalyst gives the known [1] 1,5-benzo-2-diazepinone.



I III II

EXPERIMENTAL

2,3,4,5-Tetrahydro-1H-1,5-benzo-2-diazepinone (II). A) A 4-g sample of zinc dust was added in small portions in the course of 30 min to 2.24 g (0.01 mole) of I, 30 ml of methanol, and 18 ml of concentrated hydrochloric acid. The reaction mixture was refluxed for 5 h, neutralized with sodium bicarbonate solution, and evaporated to dryness on a water bath. The dry residue was extracted with a Soxhlet apparatus with 100 ml of benzene for 5 h. The benzene was removed by distillation to give 1.0 g (62%) of II with mp 141-142°. Found: C 66.5; H 6.0; N 17.0%. $C_9H_{10}N_2O$. Calculated: C 66.7; H 6.2; N 17.2%.

B) A mixture of 2.24 g (0.01 mole) of hydrazide I, 100 ml of absolute alcohol, and 3 g of a Raney nickel paste was shaken for 3 h until the calculated amount of hydrogen had been absorbed. The nickel was removed by filtration, and the filtrate was refluxed for 3 h with 20 ml of dilute sulfuric acid. The mixture was neutralized with sodium bicarbonate solution and evaporated to dryness, and residue was extracted with benzene to give 0.42 g (55%) of II.

3-(2-Aminophenylamino)propionic Acid Hydrazide (III). A mixture of 2.24 g (0.01 mole) of hydrazide I, 100 ml of absolute alcohol, and 3 g of a Raney nickel paste was shaken until the calculated amount of hydrogen had been absorbed. The solution was filtered, the alcohol was removed by vacuum distillation in a stream of nitrogen, and the residue was crystallized from benzene to give 1.74 g (90%) of a product with mp 118-119°. Found: C 55.4; H 7.6; N 28.6%. $C_9H_{13}N_3O$. Calculated: C 55.7; H 7.7; N 28.9%.

LITERATURE CITED

1. G. B. Bachman and L. V. Heisey, J. Am. Chem. Soc., 71, 1985 (1949).

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