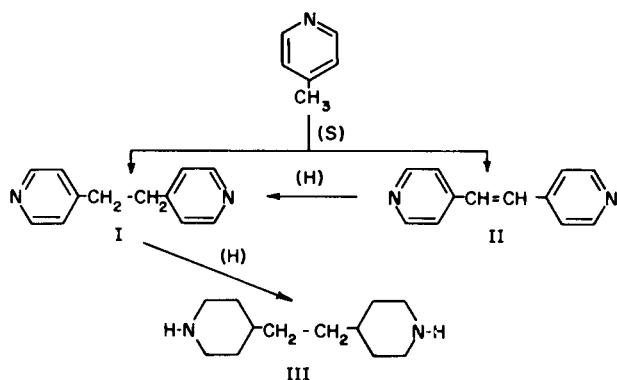


A Convenient Preparation of 1,2-Bis(4-piperidyl)ethane (I)

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The diamine, 1,2-bis(4-piperidyl)ethane, has proved to be an excellent monomer for the preparation of polyamides (3,4) which are not subject to secondary cross-linking reactions through amide hydrogen. However, its practical usefulness as an intermediate has been limited by a time-consuming and somewhat awkward synthesis. The most attractive method to date (5) involves dehydrodimerization of 4-picoline to yield a mixture of 1,2-bis(4-pyridyl)ethane (I) and 1,2-bis(4-pyridyl)ethylene (II), followed by isolation and hydrogenation of I to give the subject diamine (III); see figure. It has been shown (6)



that II can be quantitatively reduced to I using a charcoal-supported palladium (5%) catalyst, but this has not been used as an alternate preparative route except as a means of confirming structural identity.

We wish to report an improved, more convenient synthesis which capitalizes on the ease of reducing II and eliminates the need to separate the mixed bases. We have found that mixtures of I and II obtained from the action of sulfur on 4-picoline can be completely hydrogenated to III using a ruthenium dioxide catalyst at temperatures below 150°. Reduction of the heterocyclic rings of I and II and the ethylenic group of II is effected concurrently.

EXPERIMENTAL

Mixtures of 1,2-Bis(4-pyridyl)ethane (I) and 1,2-Bis(4-pyridyl)ethylene (II).

The procedure for the preparation of the mixed pyridyl bases I and II was adapted from that reported by Thayer and Carson (5). A mixture of 770 g. of freshly distilled 4-picoline (b.p. 142-143°) and 265 g. of sulfur was heated at gentle reflux for 10 hours in a

2-liter, 3-necked, round-bottomed flask fitted with a thermometer, mechanical stirrer, and reflux condenser. Pot temperature gradually increased from 140° to 160° during this period.

After being cooled and filtered to remove most of the unreacted sulfur, the reaction mixture was taken up in 50 percent aqueous sulfuric acid, refiltered, and neutralized with aqueous sodium hydroxide to give two layers. These were separated, and the aqueous layer was extracted three times with benzene. After the combined benzene extracts and organic layer were washed twice with small portions of water, the benzene was stripped off and the residue was distilled through a short column at 1 mm pressure with a maximum head temperature of 195°. To prevent possible poisoning of the ruthenium oxide catalyst by sulfur the distillate was redistilled once over zinc dust and twice over Raney cobalt. A total of 413 g. of mixed amine (I and II) was obtained from three preparations using a combined charge of 2,390 g. of 4-picoline. Unreacted 4-picoline was recovered and recycled.

It was shown in other preparations that limiting the pot temperature to 140° (5) during the reflux period merely resulted in a lower yield of crude product.

1,2-Bis(4-piperidyl)ethane (III).

The 413 g. mixture of I and II was placed with 415 ml. methanol, 100 g. ammonia, and 10 g. ruthenium dioxide catalyst in a 1400 ml. Aminco rocker bomb and hydrogenated under 1400-4600 psi hydrogen pressure at a maximum temperature of 132°. Hydrogenation began at 65-98°, became more rapid as the temperature increased, and was essentially complete after 3 hours. When after about 4 hours, hydrogen uptake had virtually stopped, the bomb was cooled and the contents were filtered through a mat of Celite filter-aid. The filtrate was treated with charcoal to remove color and stripped free of methanol. Recrystallization of the residue twice from ethylene glycol dimethyl ether gave 285 g. (64 percent of theory) of III, m.p. 110-111.6° (7); lit. (5) m.p. 113-114°. A second crop of crystals weighing 34.5 g. was collected but proved to be off-color.

Anal. Calcd. for C₁₂H₂₄N₂: N, 14.27. Found: N, 14.33, 14.44.

Infrared and ultraviolet spectra showed no trace of the precursor amines (6,8) and were consistent with the structure shown for III. No resonance signals were detected in the NMR spectrum in the region of 2-6 τ , indicating the absence of unsaturation in III.

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