HIGH-TEMPERATURE SYNTHESIS OF 5,10-DIHYDROPHENAZINE

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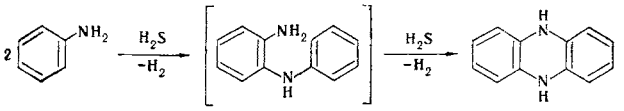
We have established that aniline at 720-750°C in a hydrogen sulfide atmosphere undergoes pyrolytic dehydrodimerization to give 5,10-dihydrophenazine (II) in 50% yield:



I II

This reaction is the simplest and most convenient method for the synthesis of the previously difficult-to-obtain 5,10-dihydrophenazine.

When hydrogen sulfide is absent, aniline is thermally converted mainly to carbazole [1]. The role of the hydrogen sulfide evidently reduces to initiation of the formation of $C_6H_5\dot{N}H$ radicals. It is well known that hydrogen sulfide at temperatures above 400° dissociates to give sulfhydryl and hydrogen radicals, which also react with aniline via the schemes

$$C_6H_5NH_2 + HS^{\cdot} \longrightarrow C_6H_5\dot{N}H + H_2S\ ;\quad C_6H_5NH_2 + H^{\cdot} \longrightarrow C_6H_5\dot{N}H + H_2$$

Hydrogen was detected in the gaseous reaction products. The $C_6H_5\dot{N}H$ radicals subsequently react with aniline to give 2-aminodiphenylamine (I), which is also dehydrogenated to 5,10-dihydrophenazine.

The pyrolysis of aniline in hydrogen sulfide was accomplished in a recirculation system in an empty quartz tube (length 520 mm, diameter 30 mm) with repeated recycling of aniline through the reaction zone. The contact time was 5 sec. A total of 27.5 g (50% based on the converted aniline) of 5,10-dihydrophenazine was obtained from 70 g of aniline after 7.5 h. The contact time in a flow system (with a 660-mm long quartz tube with a diameter of 30 mm) was 40-50 sec. The conversion of aniline to 5,10-dihydrophenazine per pass was 33%.

Dihydrophenazine II was isolated by vacuum distillation [bp 200-220° (1 mm)] and was purified by recrystallization from toluene to give a product with mp 238° (mp 212 [2, 3], 255, 315-316° [4]. Found: C 79.19; H 5.23; N 15.03%. $C_{12}H_{10}N_2$. Calculated: C 79.11; H 5.52; N 15.38%. The product is soluble only in dimethyl sulfoxide (DMSO) and hot benzene and toluene. The IR spectrum of II over the entire wave number range is completely identical to the spectrum described for 5,10-dihydrophenazine [5], in which, in contrast to the IR spectrum of phenazine, one observes the presence of stretching vibrations of an N–H bond (3410 cm^{-1}). The PMR spectrum (in DMSO) has signals of NH group protons at weak field (singlet, 10.7 ppm) and of an aromatic system (multiplet, 7.3 ppm). The mass spectrum of the compound confirms its structure: 182 (M^+ 100), 181 (84), 168 (30.7), 167 (56), 166 (56), 166 (40), 155 (22.7), 154 (46.6), 153 (20).

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