(Soret). Found: C 70.2; H 6.8; N 9.0%. $C_{54}H_{60}N_6O_8$. Calculated: C 70.4; H 6.6; N 9.1%.

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SYNTHESIS OF CARBAZOLE UNDER CONDITIONS FOR THE CATALYTIC DEHYDROGENATION OF CYCLOHEXYLAMINE

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The dehydrogenation of cyclohexylamine on platinum catalysts is investigated. In addition to aniline and diphenylamine, significant amounts of carbazole are formed. A possible mechanism for its formation is proposed.

Carbazole, I, is formed in small amounts as a by-product of such catalytic reactions as the preparation of diphenylamine by the deamination of aniline, as well as in the amination of phenol with aniline on oxide catalysts [1, 2], and the dehydrogenation of N-cyclohexylideneaniline on nickel/oxide catalysts [3]. In studying the deamination and dehydrogenation of cyclohexylamine on Ni/Al_2O_3 catalysts, we found that carbazole was formed in addition to the primary products, diphenylamine and aniline. The yield of carbazole increased significantly when aluminoplatinum catalysts were used.

The formation of carbazole in the dehydrogenation of diphenylamine and dicyclohexylamine was first observed by N. D. Zelinskii on Pt/carbon catalysts [4]. Despite the difference in the mechanisms of carbazole formation from the products named on acid-base type catalysts and of hydrogenation-dehydrogenation, a common step uniting these reactions is possible. The presence in the reaction mixtures of the same products through which the cyclization reaction probably occurs, is evidence in favor of this supposition. To elucidate the possible mechanism of formation of compound I from cyclohexylamine, we studied the transformation of the latter on platinum-containing catalysts under the conditions for dehydrogenation. The dependence of the percent yield of carbazole on the use of catalysts of aluminoplatinum and

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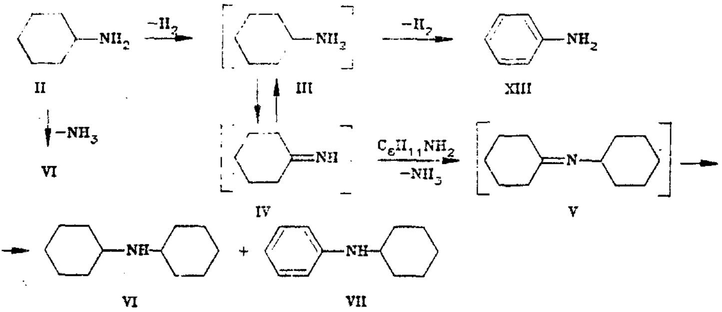
TABLE 1. Reaction Products of Dehydrogenation and Cyclization

Catalyst	Yield, %								
	I	VI	VII	VIII	X	XI	XII	XIII*	remainder
0,5% Pt/Al_2O_3	14.0	0,5	2.5	14,0	4.0	9,0	12,0	41,0	3,0
0,5% Pt/Al_2O_3+2,0% NaOH	3,6	2,0	5.0	36,0	—	—	6.2	45,0	2.2
0,5% Pt/SiO_2	2,0	1.0	3,0	39,0	—	—	1,0	53.0	1.0

*XIII — aniline.

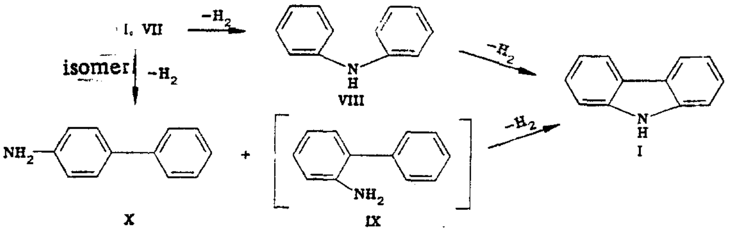
platinum on silicon oxide containing different amounts of the active metal was established:

1.0% Pt/Al_2O_3	25.0	1.0% Pt/Al_2O_3 + 2.0% NaOH	5.5
3.0% Pt/Al_2O_3	30.0	1.0% Pt/SiO_2	4.0



The process of formation of carbazole must include the following steps: the autocondensation of cyclohexylamine II, dehydrogenation, and cyclization with the formation of the five-membered heterocycle. The condensation of two molecules of compound II can occur via the deamination reaction with the participation of the acid centers of the substrate [5, 6] and via an imine mechanism with the participation of the dehydrogenation centers [7]. The imine mechanism presupposes the participation in the reaction of enamine III, formed in the first step of the dehydrogenation of II. The enamine III/imine IV tautomer readily undergoes condensation with amines, a reaction known as "imine exchange" [8]. N-Cyclohexylidenecyclohexylamine, V, was not found in the reaction mixtures. This is apparently to be explained as the result of a catalytic disproportionation (Zelinskii reaction), which is also characteristic for compounds with an exocyclic multiple bond [9].

The dicyclohexylamine, VI, and N-cyclohexylaniline, VII, obtained here were reliably identified in all cases (Table 1). Compound I can be subsequently formed by two methods: the cyclization of diphenylamine, VIII, the product of the dehydrogenation of compounds VI and VII with the direct formation of a C—C bond (the possibility of such a reaction was shown in [10] in the case of the dehydrocyclization of diethylamine to pyrrole) and the cyclization of 2-aminodiphenyl, IX, the product of an intermediate isomerization. It is known [11] that the isomerization of VII, accompanied by dehydrogenation, occurs on acidic catalysts containing a dehydrogenating component (Pt, Pd) with the formation primarily of 2- and 4-aminodiphenyl (IX, X). Product IX is further cyclized to I. The ease with which such a reaction takes place has been shown in [12].



The formation of carbazole I from intermediate X is not possible, in as much as compound X is constantly present in small amounts in the reaction products. Some of it undergoes further conversion to diphenyl, XI, and benzene, XII (Table 1). The possibility of the breakdown of compound IX into XI and XII is not precluded. For confirmation of the isomerization scheme, the reaction was studied on catalysts that had no acid properties. In the first case, after deposition of the platinum and calcination, the catalyst was treated with base in order to poison the acid centers. In the second, silicon oxide was used as a non-acidic support. The suppression of the isomerization function of the catalysts, which was confirmed by the absence of compounds X, XI, and XII in the reaction products, leads to a significant lowering of the carbazole yield (see Table 1). Thus, a basic contribution to heterocyclization is made by a synthetic method that involves the isomerization of secondary amines.

EXPERIMENTAL

The cyclohexylamine used in the reaction had the following properties: T_{bp} = 134°C, n_D^{20} = 1.4595. The catalysts were prepared by saturating industrial, grade A-1 aluminum oxide with aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$. The samples were dried at 120°C and calcined at 400°C for four hours. The experiments were run in a flow-type, quartz reactor (d = 18 mm) at atmospheric pressure. The catalysts (10 cm^3, 1.5-2.6 mm fraction) were first reduced in a steady stream of hydrogen at 400°C for three hours. Using a 0.5% Pt/Al_2O_3 catalyst we determined the optimum conditions for the synthesis of carbazole. T_{react} = 400°C, space rate of feed of starting compound = 0.3 h^{-1}. The conversion of the cyclohexylamine under the chosen conditions was complete. The quantitative and qualitative analyses of the reaction products were done chromatographically with the use of an LKhM-8MD chromatograph on a column (2 m × 4 mm) filled with Chromasorb-W (60-80 mesh), treated with 5% KOH in ethanol, and saturated with Apieson K (12%) at 210°C. The cyclization products were analyzed on a column (1 m × 4 mm) filled with 5% Silikone XE-60 on Chromaton-AW (0.20-0.25 mm) at 220°C.

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