INDOLE DERIVATIVES

LI*. INFLUENCE ON THE NATURE OF THE CATALYST ON THE YIELD OF THE PRODUCTS OF THE CYCLIZATION OF N-(β-HYDROXYETHYL) ANILINE AND N,N'-DIPHENYLETHYLENEDIAMINE

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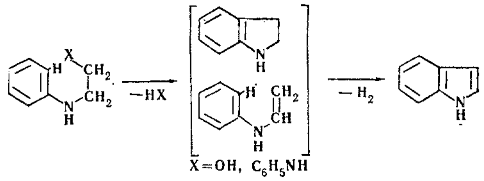
The influence of dehydrogenating dehydrating (deaminating) additives on the composition and yield on the products of the cyclization of N-(β-hydroxyethyl)aniline and N,N'-diphenylethylenediamine has been studied. The closure of the indole and pyrrole rings takes place through the dehydration and deamination, respectively, of the starting material on oxide catalysts. A reaction scheme explaining the formation of all the products observed has been suggested.

We have shown previously [1] that the catalytic cyclization of N-(β-hydroxyethyl)aniline and N,N'-diphenylethylenediamine at 350-470°C takes place with the formation of N-phenylpyrrole, indole, 1-methylindole, and 3-ethylindole. Alumina proved to have slight and approximate equal activities in cyclization of the two starting materials (yield of indole 6% and of phenyl pyrrole 10%), which can be explained by the poisoning of the surface of the catalyst by the reaction products water and aniline. However, silica gel, while being practically inactive in the cyclization of N-(β-hydroxyethyl)aniline (yield of indole 1-2%) proved to be more active in the cyclization of N,N'-diphenylethylenediamine (yield of indole 14.6%).

It may be assumed that the formation of the indole ring takes place through the dehydration (or deamination, as the case may be) of the initial product, and also by its dehydrocyclization [2, 3]:



In order to determine the way in which cyclization takes place, we have studied the influence of additives to the silica gel and alumina on the yield of cyclization products. Additions of dehydrogenating oxides (chromium oxide, cadmium oxide) had an adverse effect on the yield of indole in all cases. The yield of N-phenylpyrrole was also lower, as a rule. Apparently, the dehydrogenation of aniline derivatives leads not to bicyclic products but to vinylaniline or unstable derivatives of it, which are converted into resinous substances.

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*For Communication L see [1].

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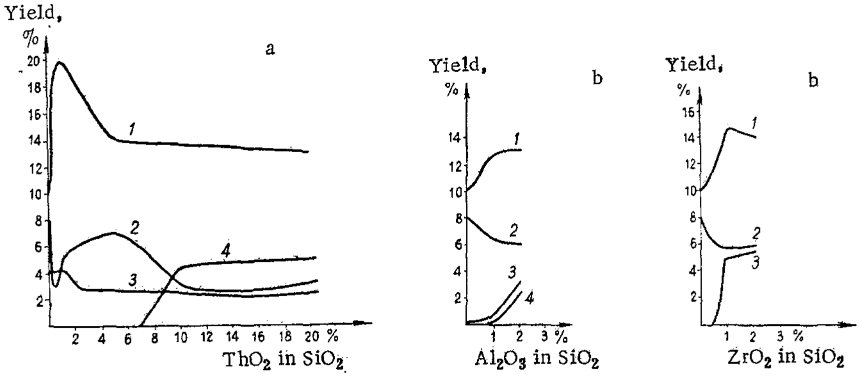
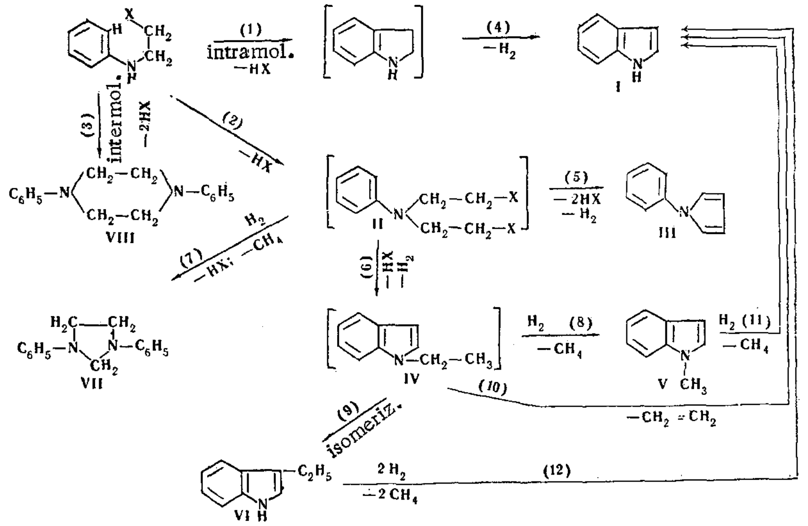


Fig. 1. Influence of additives to silica gel on the yield of the products of the cyclization of N,N'-diphenylethylenediamine at 400-430°C: 1) indole; 2) N-phenylpyrrole; 3) 1-methylindole; 4) 3-ethylindole.

Additions of oxides catalyzing dehydration-deamination (alumina, thorium dioxide, zirconium dioxide) lead to an increase in the total yield of cyclization products, especially of indole (Fig. 1). The fact that the effect of additives to a silica-gel support is the greatest is possibly because silica gel itself is only a relatively inactive dehydration and deamination catalyst. (For the same reason, it is less subject to poisoning by a reaction product – aniline – than alumina). The optimum content of activating additives in the catalyst is 1-2%. A further increase in the amount of these additives leads to the appearance of 3-ethylindole in the catalysate (Figs. 1 and 2). In the cyclization of N,N'-diphenylethylenediamine on silica gel above 410°C 1-methylindole appears. All this, and also the qualitative composition of the gaseous products, suggests the following scheme of conversions:



Cyclization to form indole takes place through the intramolecular dehydration or deamination of the starting material by reactions (1) and (4). Intramolecular dehydration (deamination) leads to the formation of N-phenylpyrrole by directions (2) and (5). As is well known, an intermolecular reaction is found under milder conditions and an intramolecular reaction under more severe conditions. In agreement with this, in our experiments a more marked fall with the temperature of the yield of N-phenylpyrrole than of indole was found (Fig. 2); the formation of N,N'-diphenylpiperazine [route (3)] was observed under considerable milder conditions (about 350°C). Product II can also be subject to conversion in directions (6), (8), (9), and (10), as a result of which 1-methylindole and 3-ethylindole may be formed. Simultaneously with a rise in the yield of alkylated indoles the yield of N-phenylpyrrole falls considerably (Fig. 1). At the same time, no relationship of any kind is found between the yields of unsubstituted indole and its homologs. This permits the assumption of the parallel formation of alkylated indoles and N-phenylpyrrole from product II.

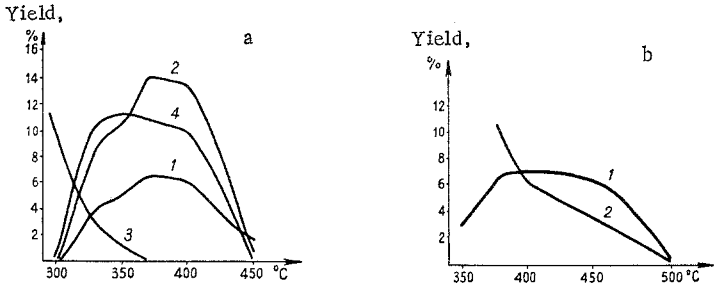


Fig. 2

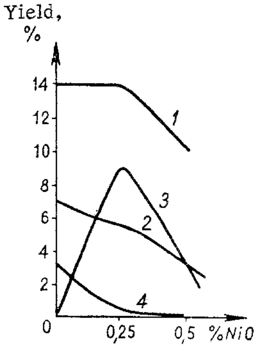


Fig. 3

Fig. 2. Influence of the temperature on the yield of the products of the catalytic cyclization on alumina of N-(β-hydroxyethyl)aniline (a) and N,N'-diphenylethylenediamine (b): 1) indole; 2) N-phenylpyrrole; 3) N,N'-diphenylpiperazine; 4) 3-ethylindole.

Fig. 3. Influence of additions of NiO to a ThO_2-SiO_2 catalyst (5% of ThO_2) on the yield of products of the cyclization of N,N'-diphenylethylenediamine at 400-430°C: 1) indole; 2) N-phenylpyrrole; 3) N-methylindole; 4) 3-ethylindole.

In actual fact, 3-ethylindole was found in the products of the cyclization of N-(β-hydroxyethyl)aniline on alumina and of N,N'-diphenylethylenediamine on silica gel with additions of alumina (above 2%) and of thorium dioxide (above 10%). As is well known, electrophilic rearrangements are catalyzed by acids; alumina is an acid catalyst which is active in various isomerization reactions. Thorium dioxide is also known as a catalyst of alkylation in the aromatic nucleus [4, 5].

The influence of additions of nickel oxide to a mixed ThO_2/SiO_2 catalyst is shown in Fig. 3. While reducing the yield of indole somewhat, small amounts (0.25-0.5%) of nickel oxide more considerably lower the yield of the byproducts of the cyclization process – mainly 1-methylindole and then 3-indole – which is apparently due to the dealkylating action of the metallic nickel formed through the reduction of the reaction products. According to the calculations, the cleavage of $C_{al}-N_{ar}$ bond takes place first and that of the $C_{al}-C_{ar}$ bond ($E_{12} > E_{11}$; $E_{12} - E_{11} = 15.5$ kcal/mole).[*] A similar sequence of bond cleavage was found in specially set-up experiments on the dealkylation of indole homologs under the action of hydrogen on nickel. The introduction of nickel additives into the catalyst decreased resin formation and increased the purity of the cyclization products. Obviously, on nickel the resinous substances are decomposed to form methane under the action of the hydrogen liberated in the main reaction and also as a result of reactions with the carbon dioxide used as carrier gas.

All the conversions shown in the scheme apart from directions (7) and, in part, (2) and (3) take place on the surface of the oxide catalysts, since the products to which these reactions lead are not formed by catalysis on carbon (the product of this reaction is N,N'-diphenylimidazolidine). Conversions in directions (2) and (3) may also take place on carbon. The pyrolitic decomposition of the starting materials was not observed below 500°C. Above 500°C the partial carbonization of the starting materials and their subsequent transformation on the carbon liberated take place.

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[*] A mean value of $Q_{C_{al}-N_{ar}}$ between $Q_{C=N_{ar}}$ and $Q_{C-N_{al}}$ was taken by analogy with the corresponding values of the energies of the C–C bond. The values of the energies were taken from the literature [6].