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SYNTHESIS AND CATALYTIC HYDROGENATION OF 2-PHENYLETHYLENIMINE

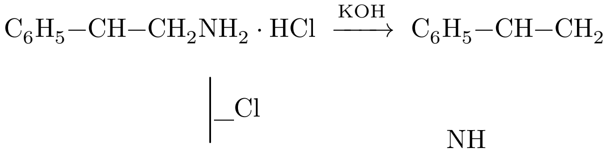
(Presented by Academician B. A. Kazanskii, 30 III 1965)

Recently we showed (^{8}) that the ethylenimine ring of N-phenylethylenimine is readily opened under mild conditions during catalytic hydrogenation in the presence of platinum and especially palladium.

This observation contradicts the data available in the literature (^{8}) on the stability of a substituted ethylenimine ring under hydrogenation conditions; it was therefore necessary, while maintaining the same reaction conditions, to check our data on ethylenimines of another structure.

As the object of the present investigation we chose a compound in which the substituent is attached to the carbon atom of the ethylenimine ring—2-phenylethylenimine. The synthesis of this compound presented considerable difficulties.

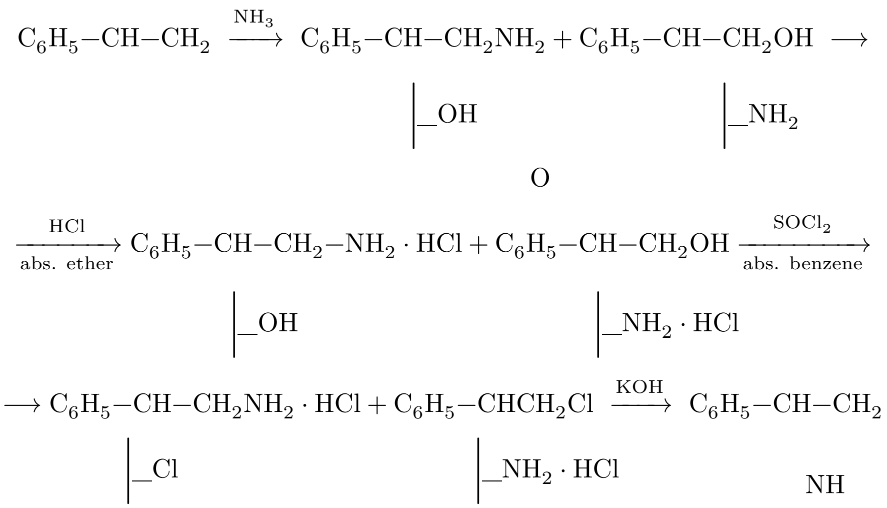
Until recently, cyclization of haloarylamine salts with alkali was considered the only method for obtaining C-aryl-substituted ethylenimines (arylaziridines). It was precisely by this route that Wolfheim (^{1}) first attempted to carry out the synthesis of 2-phenylethylenimine:



$$C_6H_5-\underset{|\_Cl}{CH}-CH_2NH_2\cdot HCl \xrightarrow{KOH} C_6H_5-\underbrace{CH-CH_2}_{NH}$$

The author succeeded in isolating the final product only in the form of the picrate, as a result of which the work gives no characteristics of 2-phenylethylenimine other than the melting point of the picrate. The synthesis of the starting compounds is also not reported in the work.

For the preparation of 2-phenylethylenimine (PEI) we used the following scheme:



$$C_6H_5-CH-CH_2 \xrightarrow{NH_3} C_6H_5-\underset{|\_OH}{CH}-CH_2NH_2 + C_6H_5-\underset{|\_NH_2}{CH}-CH_2OH \longrightarrow$$

O

$$\xrightarrow[\text{abs. ether}]{HCl} C_6H_5-\underset{|\_OH}{CH}-CH_2-NH_2 \cdot HCl + C_6H_5-\underset{|\_NH_2 \cdot HCl}{CH}-CH_2OH \xrightarrow[\text{abs. benzene}]{SOCl_2}$$

$$\longrightarrow C_6H_5-\underset{|\_Cl}{CH}-CH_2NH_2 \cdot HCl + C_6H_5-\underset{|\_NH_2 \cdot HCl}{CH}CH_2Cl \xrightarrow{KOH} C_6H_5-CH-CH_2 \quad NH$$

According to this scheme, styrene oxide gives a mixture of two isomeric amino alcohols (^{2}), which have very close boiling points. There is no need to separate this mixture, since ultimately the derivatives of both amino alcohols give one and the same product upon cyclization.

It should be noted that reproduction of the final stage of the above-mentioned Wolffheim procedure showed that it is unsuitable for the synthesis of 2-phenylethylenimine, since the latter polymerizes during distillation with steam. Only the first drops of the distillate contained traces of 2-phenylethylenimine, which can indeed be detected with picric acid.

We developed another procedure for carrying out the cyclization, in which the reaction was conducted in absolute ethyl alcohol and in an atmosphere of nitrogen, since it is known that compounds of the ethylenimine series are very unstable in the presence of water, carbon dioxide, and oxygen. In this way 2-phenylethylenimine was obtained by us in a yield of 66% of theory.

Recently 2-phenylethylenimine was synthesized by Brois by another route (^{3}), by the action of sulfuric acid on the corresponding amino alcohol, followed by cyclization of the resulting compound with alkali. It should be noted that, before the appearance of this work, it was considered that this method–the Wenker method (^{4})–was not applicable to the synthesis of arylaziridines, since the interaction of amino alcohols with sulfuric acid usually leads to vinylamines (^{5}). Brois succeeded in avoiding this by employing milder reaction conditions.

In Brois' s work the boiling point of 2-phenylethylenimine and its refractive index are given, differing somewhat from those obtained by us. Therefore, to prove the structure of the compound obtained by us, we turned to its spectral characteristics.*

The results of the study of its vibrational spectra confirmed the proposed structure of the compound. Thus, in the Raman spectrum all the characteristic lines of monosubstituted benzenes are present, as well as a very intense line near 3000 cm^{-1}, indicating the presence of a three-membered ring. The NH group appears as an intense broad band in the region of 3310 cm^{-1} in the Raman and infrared absorption spectra. Substitution at the carbon atom, and not at nitrogen, is also indicated by the relatively low value of the frequency of the totally symmetric vibration of the ethylenimine ring, 1230 cm^{-1}, whereas in N-substituted ethylenimines the frequency of this vibration is much higher (1250–1320 cm^{-1}).

Catalytic hydrogenation of 2-phenylethylenimine showed that in this case also the ethylenimine ring is unstable and, under mild conditions, readily undergoes hydrogenolysis in the presence of platinum and palladium blacks. In the example of this compound, the difference in hydrogenation rate depending on the catalyst used is especially sharply manifested. Thus, with identical charges of 2-phenylethylenimine, in the presence of palladium the reaction ends with absorption of one mole of hydrogen in 15 min, whereas in the presence of platinum it takes 7–8 h.

Hydrogenation of 2-phenylethylenimine was carried out by us under the same conditions as the previously described hydrogenation of 1-phenylethylenimine (^{8}). This enabled us, by comparing the rates of hydrogen uptake, to estimate the ease of opening of the ethylenimine ring for these two compounds, which differ only in the position of the phenyl substituent. It turned out that in the presence of palladium 2-phenylethylenimine is hydrogenated approximately 4 times faster than 1-phenylethylenimine. This indicates the lower stability, under these conditions, of the ethylenimine ring substituted at carbon.

In the present work we were interested in the ease with which the substituted ethylenimine ring undergoes hydrogenolysis; therefore, catalytic was analyzed only qualitatively, with the aid of IR spectra; β-phenylethylamine was detected in it.

$$C_6H_5{-}CH{-}CH_2 \xrightarrow[Pt,Pd]{H_2} C_6H_5{-}CH_2{-}CH_2NH_2$$

Thus, rupture of the ring of 2-phenylethylenimine, as was to be expected, proceeds mainly at the C—N bond adjacent to the substituent.

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* The spectroscopic study of 2-phenylethylenimine was carried out in the Spectroscopy Commission of the Academy of Sciences of the USSR by V. T. Aleksanyan, to whom the authors express their gratitude. The complete spectrum of 2-phenylethylenimine will be presented in subsequent publications.

Experimental Part

I. Synthesis: styrene oxide was obtained by the reaction of styrene with N-bromosuccinimide in water, followed by treatment of the resulting bromohydrin with alkali (6). Yield 85% of theory. The product obtained had b.p. 65.0° (5 mm); n_D^{20} 1.5348. Lit. (6): b.p. 65° (5 mm), n_D^{20} 1.534.

α-Phenyl-β-aminoethanol and β-phenyl-β-aminoethanol were obtained by the action of ammonia on styrene oxide (2). On distillation from a Favorskii flask, a fraction 135–145° (6 mm) was collected, which contained mainly α-phenyl-β-aminoethanol and a small amount of β-phenyl-β-aminoethanol. Yield of the mixture 50% of theory. Lit. (2): b.p. of α-phenyl-β-aminoethanol 136–137° (5 mm), β-phenyl-β-aminoethanol 135–140° (6 mm).

Hydrochloride salts of phenylaminoethanols were obtained by the reaction of dry hydrogen chloride with the above-described mixture of amino alcohols in abs. ether. Yield 80% of theory. M.p. 165–170°. Lit. (2): α-phenyl-β-aminoethanol hydrochloride has m.p. 176–177°, β-phenyl-β-aminoethanol hydrochloride m.p. 149.1–150.0°.

Found, %: C 55.30; H 6.99; Cl 20.43; N 8.11
$C_8H_{12}ClNO$. Calculated, %: C 55.33; H 6.97; Cl 20.42; N 8.07

Hydrochloride salts of α-phenyl-β-chloroethylamine and β-phenyl-β-chloroethylamine (7). In a round-bottomed flask with a stirrer were placed 30 g (0.17 mole) of the mixture of hydrochlorides of the amino alcohols and 40–50 ml of absolute benzene; with good stirring, 20 ml (0.17 mole) of thionyl chloride was rapidly added to the reaction mass from a dropping funnel. After one hour of stirring, all volatile products were distilled off in vacuo while heating the flask on a water bath to 50°. The dry residue was dissolved in alcohol and the mixture of hydrochlorides of phenylchloroethylamines was precipitated with ether. After two recrystallizations from ethyl alcohol and drying in a vacuum desiccator, the m.p. of the reaction product was 154–156°. Yield 86% of theory. Lit. (7): m.p. of β-phenyl-β-chloroethylamine hydrochloride 157–158°.

Found, %: C 50.01; H 5.77; Cl 37.02
$C_8H_{11}Cl_2N$. Calculated, %: C 50.02; H 5.77; Cl 36.91

2-Phenylethylenimine. 20 g (0.104 mole) of the mixture of hydrochloride salts of phenylchloroethylamines was dissolved in a minimum amount of absolute alcohol (~200 ml), and to this solution, with stirring in a nitrogen atmosphere, a solution of 30 g KOH in ethanol was added dropwise. A precipitate of KCl formed. Stirring was continued for another 30 min, after which the alcohol was evaporated in vacuo in a stream of dry nitrogen without heating. The residue was extracted with ether, and the ethereal extracts were dried with granular KOH. After distillation of the ether, the residue was distilled—

in vacuo under a stream of dry nitrogen. 10 g of 2-phenylethylenimine was obtained. Yield 66% of theory; b.p. 73.0° (5 mm), n_D^{20} 1.5564; d_4^{20} 1.0246. Lit.

(3): b.p. 94–95° (10 mm), n_D^{20} 1.5588.

2-Phenylethylenimine is a colorless liquid with an amine odor; it polymerizes readily in the presence of water and CO_2. It is readily soluble in alcohol and ether.

II. **Catalytic hydrogenation** was carried out by the method described previously (8). Several parallel experiments were performed; in each, 0.12 g (0.001 mol) of 2-phenylethylenimine, 0.02 g of catalyst (platinum or palladium black), and 25 ml of *n*-heptane were taken. In all cases, at 20° approximately 24 ml of hydrogen (0.001 mol) was absorbed. In the presence of palladium the reaction proceeded vigorously and was complete after 15 min, whereas in the presence of platinum it was complete after 7–8 hr. In all cases, β-phenylethylamine was detected in the catalyzate by the IR spectra method.

The results of a comparative hydrogenation of 2-phenylethylenimine and 1-phenylethylenimine in the presence of palladium black, obtained under identical conditions, are presented in Fig. 1.

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