SUBSTITUTED PYRIDINES. DEHYDROGENATION, DESAMINATION, AND N-DESMETHYLATION OF 4-AMINO-1,2,5-TRIMETHYLPIPERIDINE AND (1,2,5-TRIMETHYL-4-PIPERIDYL)BENZYLIDENEAMINE

N. S. Prostakov, N. N. Mikheeva, and S. K. Banerdzhi

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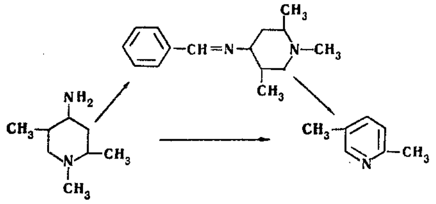
4-Amino-1, 2, 5-trimethylpiperidine and (1, 2, 5-trimethyl-4-piperidyl)-benzylideneamine are partially converted into α, β'-lutidine as a result of dehydrogenation, desamination, and N-desalkylation over a type K-12 dehydrogenating catalyst.

It has previously been established that 4-alkyl(aryl, alkaryl)-N-methyl(benzyl)-2,5(3,5)-dimethyl-Δ^4-piperideines are converted on a type K-12 dehydrogenating catalyst at 400–410° C into 4-alkyl(aryl, alkaryl)-2,5(3,5)-dimethylpyridines in up to 90% yield [1–3]. It appeared of interest to investigate the reactions taking place on the same catalyst in the case of an amino-substituted piperidine. In view of this, as the subject of study, we used 4-amino-1, 2, 5-trimethylpiperidine [4].

At 400° C, this aminopiperidine undergoes far-reaching changes. One of the directions of these changes is its dehydrogenation, N-desmethylation, and desamination. As a result, α,β'-lutidine is formed with a yield of up to 24%. These reactions were carried out in benzene and nitrobenzene as solvents. In the latter case it was assumed that the nitrobenzene would perform the role of acceptor of the hydrogen liberated in the dehydrogenation stage which would possibly lead to a limitation of the desamination reaction. However, in this case the same reactions took place and α,β'-lutidine was formed in approximately the same amount.



We have previously studied conversions on the same catalyst with the Schiff's base obtained from 1,2,5-trimethyl-4-piperidone and aromatic amines as examples. In particular, it was found that 1,2,5-trimethyl-4-piperidylideneaniline was partially converted into 2,5-dimethyl-4-pyridylaniline [5]. Somewhat different from this Schiff's base is (1,2,5-trimethyl-4-piperidyl)benzylideneamine, which was obtained from 4-amino-1,2,5-trimethylpiperidine and benzaldehyde. At 400° C on the K-12 catalyst, this Schiff's base also undergoes far-reaching changes. But in this case the main product is α,β'-lutidine. Its yield amounts to about 66%. α,β'-Lutidine has previously been obtained similarly from 1,2,5-trimethyl-Δ^4-piperideine with a yield of 70% [6].

EXPERIMENTAL

Conversions of 4-amino-1, 2, 5-trimethylpiperidine on type K-12 dehydrogenating catalyst. a) A solution of 19 g of 4-amino-1, 2, 5-trimethylpiperidine [bp 52–54° C (2 mm)] in 50 ml of benzene was passed at a constant rate during 4 hr over type K-12 catalyst (130 ml). The temperature in the catalyst zone was 400° C, 6.3 *l* of gas (22° C, 723 mm) was collected. The residue after the distillation of the benzene from the catalyzate amounted to 12.7 g and its distillation yielded 3.4 g of α, β'-lutidine [bp 52–62° C (12 mm); picrate mp 167–168° C (from ethanol)].

b) After the regeneration of the catalyst (2 hr, 500° C, slow current of air), a solution of 15 g of 4-amino-1, 2, 5-trimethylpiperidine in 50 ml of freshly distilled nitrobenzene was passed at a constant rate for 3 hr at 400° C. 1.4 *l* of gas (23° C, 724 mm) was collected. The catalyzate was made acid to Congo Red with hydrochloric acid (1 : 1). The nitrobenzene and the neutral substances were extracted with ether. The acid layer was made alkaline with potassium hydroxide and extracted with ether to give 2.8 g of α, β'-lutidine [bp 60–67° C (19 mm); picrate mp 167–168° C].

(1, 2, 5-Trimethyl-4-piperidyl)benzylideneamine and its conversions on type K-12 catalyst. A mixture of 25 g of freshly distilled 4-amino-1, 2, 5-trimethylpiperidine, 28 ml of benzaldehyde, 30 ml of anhydrous toluene, and 1 ml of acetic acid was boiled for 2 1/2 hr with the continuous elimination of water. 4.15 ml of water was collected. The toluene and the excess of benzaldehyde were distilled off and the residue was distilled in vacuum, to give 28.25 g of (1, 2, 5-trimethyl-4-piperidyl)benzylideneamine, bp 132–134° C (1 mm); n_D^{21} 1.5375. Found, %: N 12.17, 12.05. Calculated for $C_{15}H_{22}N_2$, %: N 12.17.

A solution of 15 g of (1, 2, 5-trimethyl-4-piperidyl)benzylideneamine in 50 ml of anhydrous benzene was passed over type K-12 catalyst (130 ml) during 3 hr. The temperature in the catalyst zone was 400° C. 3.7 *l* of gas (23° C, 718 mm) was collected. After the benzene had been eliminated from the catalyst, and the reaction products had been distilled, 4.6 g of α, β'-lutidine was obtained (bp 154–155° C, picrate mp 167–168° C).

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Patrice Lumumba University of
People's Friendship, Moscow