

REACTION OF 2-VINYLPYRIDINE
WITH 2,5-DIMETHYL-4-PIPERIDONE

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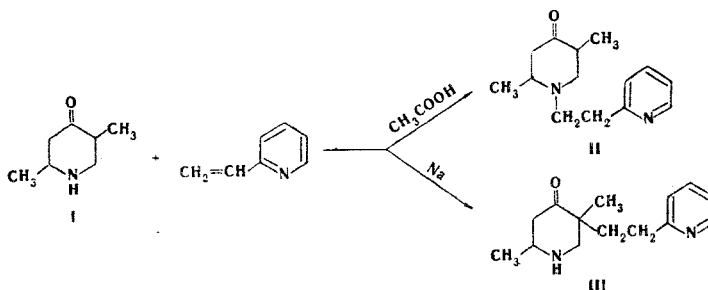
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2-Vinylpyridine adds to 2,5-dimethyl-4-piperidone in the 1 position in the presence of acetic acid and in the 5 position in the presence of sodium metal.

The pyridylethylation of diverse aliphatic and cyclic ketones has been quite adequately studied [1]. However, the literature contains no studies devoted to the investigation of the pyridylethylation of heterocyclic ketones.

We have carried out the reaction of 2-vinylpyridine with 2,5-dimethyl-4-piperidone (I), which was used in the form of a mixture of two spatial isomers. Owing to the presence of several labile hydrogen atoms in piperidone I, 2-vinylpyridine may undergo reaction in the 1, 5, and 3 positions.

Reaction of piperidone I with 2-vinylpyridine in the presence of acetic acid gives 1-[β -(2-pyridyl)ethyl]-2,5-dimethyl-4-piperidone (II)



When this reaction is carried out in the presence of sodium metal, 2-vinylpyridine reacts at the methylidyne group (the 5 position) rather than at the methylene group (the 3 position), inasmuch as in the reaction of α , ρ -unsaturated compounds with ketones the reaction proceeds initially at the methylidyne group, next at the methylene group, and finally at the methyl group [2, 3]. The imino group is not involved under the indicated conditions. The structures of the synthesized piperidones (II and III) are confirmed by the presence in the IR spectra of piperidone III of absorption bands of stretching vibrations of an N-H group at 3315-3330 cm^{-1} , which are absent in the IR spectra of piperidone II [4]. The signal of the methyl group attached to C-5 in the PMR spectrum of piperidone III is a singlet with δ 1.22 ppm, which attests to the absence of spin-spin coupling of the protons of the methyl group with the ring proton and, consequently, to location of the pyridylethyl group at the C-5 atom.

This dependence of the direction of pyridylethylation of 2,5-dimethyl-4-piperidone (I) on the catalyst used can be explained by the fact that a carbanion, the nucleophilicity of which is probably greater than the nucleophilicity of the imino group, is formed in the presence of sodium, as a consequence of which pyridylethylation proceeds at the methylidyne group. The carbanion is not formed in the presence of acetic acid, and the only nucleophilic agent is the imino group, which also adds to 2-vinylpyridine.

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EXPERIMENTAL METHOD

The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra of methylene chloride solutions of the compounds were recorded with a Perkin-Elmer R-12 spectrometer with tetramethylsilane as the standard.

1- $[\beta$ -(2-Pyridyl)ethyl]-2,5-dimethyl-4-piperidone (II). A mixture of 20 g (0.15 mole) of piperidone I, 8 g (0.075 mole) of 2-vinylpyridine, and 1 ml of glacial acetic acid was heated at 105-110° for 4 h. It was then cooled, 10 ml of water was added, and the mixture was treated with a saturated solution of potassium hydroxide and extracted with benzene. The benzene extracts were dried with potassium carbonate, the benzene was removed by distillation, and the residue was vacuum-fractionated to give 13 g (72%) of piperidone II with bp 159-160° (3 mm), n_D^{20} 1.5225, and d_4^{20} 1.0599. Found: C 72.3; H 8.9; N 11.9%; MR_D 66.90. $C_{14}H_{20}N_2O$. Calculated: C 72.4; H 8.6; N 12.1%; MR_D 68.14.

2,5-Dimethyl-5- $[\beta$ -(2-pyridyl)ethyl]-4-piperidone (III). A mixture of 26 g (0.2 mole) of piperidone I, 10.5 g (0.1 mole) of 2-vinylpyridine, and 0.3 g of sodium metal was stirred at 90-95° for 6 h. It was then cooled, and 30 ml of benzene and 15 ml of water were added successively. The benzene layer was separated, and the aqueous layer was extracted with benzene. The benzene extracts were combined, the benzene was removed by distillation, and the residue was vacuum-fractionated to give 18 g (77%) of piperidone III with bp 145-146° (1 mm), n_D^{20} 1.5305, and d_4^{20} 1.0696. Found: C 72.2; H 8.7; N 11.9%; MR_D 67.12, $C_{14}H_{20}N_2O$. Calculated: C 72.4; H 8.6; N 12.1%; MR_D 67.80.

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