# THE MANNICH REACTION WITH 2-METHYL-5-VINYLPYRIDINE

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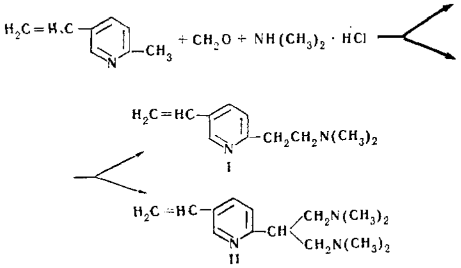
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, pp. 1066–1067, 1968

UDC 547.822:542.953.4:543.422.4

1,3-Bis(dimethylamino)-2-(5'-vinyl-2'-pyridyl)propane and 2-(β-dimethylaminoethyl)-5-vinylpyridine were prepared by the aminomethylation of 2-methyl-5-vinylpyridine. These Mannich bases have been transformed into 1-dimethylamino-2-(5'-vinyl-2'-pyridyl)-1-propene and 2,5-divinylpyridine by the decomposition of their quaternary salts.

Monomers prepared by the Mannich reaction from 2-methyl-5-vinylpyridine (MVP), which is produced on an industrial scale at the present time, may find wide use for the production of anion-exchange resins, for the modification of polymers, etc.

In the present work we studied the aminomethylation of MVP with formaldehyde and dimethylammonium chloride and some reactions of the Mannich bases so obtained:

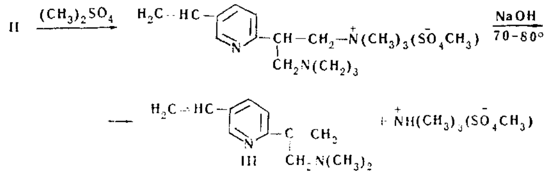


If the reaction is performed with diethylammonium chloride, the main product is 2-(β-diethylaminoethyl)-5-vinylpyridine [1]. Dimethylammonium chloride is more active in this reaction, as in many other examples of Mannich reactions [2,3,4], and when it is used, a mixture of bases I and II, in which II predominates, is obtained.

The structures of I and II were confirmed by a study of their IR spectra and by transforming them into the corresponding divinyl compounds. The spectra of I and II have strong absorption bonds characteristic of terminal vinyl groups in the 1634 $cm^{-1}$ ($\nu_{C=C}$), and 991 and 909 $cm^{-1}$ ($\gamma_{CH}$) regions. Weak bands at 1309 and 1424 $cm^{-1}$ may be assigned to planar deformation vibrations of the vinyl CH bond. Compounds I and II readily polymerize on being heated at 70° C in the presence of azobisisobutyronitrile.

Depending on the reaction conditions, 49–90% of MVP is recovered unchanged from the reaction mixture. This is connected with the fact that dimethylammonium chloride reacts with formaldehyde to form bis(dimethylamino)methylene [6]. The latter is not an aminomethylating agent in the given conditions. The formation of bis(dimethylamino)methylene is a reversible reaction and in acid media it decomposes completely into the starting compounds. Increasing the concentration of acid in the initial mixture causes an increased conversion of the MVP and an increase in the amount of II in the products. The preferential formation of II is linked with the increased reactivity of MVP following protonation of the nitrogen atom of the pyridine ring [3, 5].

Mannich bases I and II were converted into the corresponding vinyl derivatives according to the following equation:



The preparation of 2,5-divinylpyridine IV from I is analogous. All these compounds, except 2,5-divinylpyridine [1], are here described for the first time.

## EXPERIMENTAL

**1,3-Bis(dimethylamino)-2-(5'-vinyl-2'-pyridyl)propane (II) and 2-(β-dimethylaminoethyl)-5-vinylpyridine (I).** 119 g (1 mole) of freshly distilled 2-methyl-5-vinylpyridine (MVP), stabilized with metol, 172 g of 35% formalin (2 mole), 164 g (2 mole) of dimethylammonium chloride, 10.2 ml of conc Hcl (d 1.19, 0.125 mole), and 100–150 ml of alcohol were mixed and heated at 85–90° C for 8 hr. When the reaction was completed, the methanol and most of the unchanged MVP (38 g) were steam-distilled off. The residue was made alkaline with caustic soda and the mixture of bases that separated out was extracted with ether. It was necessary to saturate the mother liquor with sodium sulfate in order to achieve complete extraction. The ether extract was dried with calcined sodium sulfate and the ether was distilled off. The residue was fractionally distilled in vacuum through a column 15 cm high. The following fractions were collected: MVP, 20 g, bp 65–66° C (6 mm), $n_D^{20}$ 1.5420; I, 10 g, bp 123–124° C (6 mm), $n_D^{20}$ 1.5345; and II, 75 g, bp 135–137° C (6 mm), 115–116° C (1 mm), $n_D^{20}$ 1.5250.

**I)** Colorless liquid miscible with water. Found, %: C 74.64; H 9.20; N 16.10. Calculated for $C_{11}H_{16}N_2$, %: C 74.95; H 9.15; N 15.90.

**II)** Colorless liquid miscible with water. Found, %: C 71.73; H 10.1; N 18.09. Calculated for $C_{14}H_{23}N_3$, %: C 72.06; H 9.93; N 18.01. The purity of the products obtained was checked by thin-layer chromatography on alumina. The solvent system was dichloroethane–petroleum ether-ethanol (9 : 10 : 1). Compound I, $R_f$ 0.79; compound II, $R_f$ 0.45. Yield of mixed bases, 85 g (75% calculated on the MVP that reacted).

When the synthesis was carried out in the same conditions but using different molar proportions of the reactants, the following results were obtained: MVP–dimethylammonium chloride–formaldehyde–acid 1 : 0.5 : 0.5 : 0; recovered MVP 107 g; yield of I, 6.2 g; II, 10.1 g; total yield 71.5%; 1 : 0.5 : 0.5 : 0.25; recovered MVP 99 g; yield of I, 4.5 g; yield of II, 21.4 g; total yield 69.5%.

**3-Dimethylamino-2-(5'-vinyl-2'-pyridyl)-1-propene (III).** 11.7 g (0.05 mole) of II was dissolved in 15 ml of methanol and 6.3 g (0.05 mole) of dimethyl sulfate was added in small portions, the temperature not being allowed to rise above 60° C. The resulting solution of quaternary salt was diluted with 70 ml water, treated with 3 g of NaOH, and heated at 80° C for 1 hr. The III that separated out was extracted with ether, and the extract was dried over anhydrous $Na_2SO_4$. After evaporation of the ether, the product was vacuum-distilled, bp 127–130° C (6 mm), $n_D^{20}$ 1.5570, yield 6.3 g (67%). Found, %: C 76.23;

H 8.61; N 15.12. Calculated for $C_{12}H_{16}N_2$, %: C 76.55; H 8.57; N 14.88.

**2, 5-Divinylpyridine.** I was alkylated as described above. The quaternary salt was diluted with water, caustic soda was added, and the 2, 5-divinylpyridine was steam-distilled off. The distillate was extracted with ether and the extract was dried with anhydrous sodium sulfate. The ether was distilled off and the residue vacuum-distilled, bp 80° C (6 mm), $n_D^{20}$ 1.5920, yield 70.7%.

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14 September 1966

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