SYNTHESIS OF 2, 5-DIVINYLPYRIDINE BY THE MANNICH REACTION

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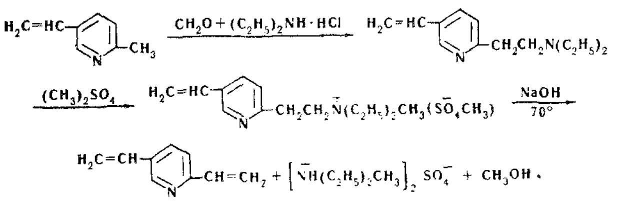
The Mannich reaction is used to obtain 2-(β-diethylaminoethyl)-5-vinylpyridine from 2-methyl-5-vinylpyridine. Decomposition of a quaternary salt of 2-(β-diethylaminoethyl)-5-vinylpyridine gives 2, 5-divinylpyridine.

If accessible, various applications could be found for 2, 5-divinylpyridine, but its preparation by catalytic dehydrogenation is described in only one patent [1], and the process is difficult to carry out.

The present paper describes the synthesis of 2, 5-divinylpyridine using the Mannich reaction, and starting from 2-methyl-5-vinylpyridine, which is made on an industrial scale. The 2- and 4-methyl derivatives of pyridine are known to undergo the Mannich reaction [2–4]. However, it has been found that 2-methyl-5-ethylpyridine and its N-oxide do not react when heated with formaldehyde and diethylamine for a long time at 100° C, at various pH.

2-Methyl-5-vinylpyridine reacts more easily. This is due to stabilization of the intermediate carbanion [5, 6] due to conjugation with the vinyl group. For the same reason quinaldine and lepidine undergo the Mannich reaction considerably more easily than the corresponding pyridine derivatives [7].

The synthesis of 2, 5-divinylpyridine was carried out as follows:



The quaternary salt of 2-(β-diethylaminoethyl)-5-vinylpyridine was more stable than the analogous salt of 2-(β-diethylaminoethyl)quinoline [7]. It was not decomposed by triethylamine, but treatment with sodium hydroxide gave 2, 5-divinylpyridine.

EXPERIMENTAL

2-(β-Diethylaminoethyl)-5-vinylpyridine. A mixture of 142.8 g (1.2 mole) 2-methyl-5-vinylpyridine (MVP), 48 g 38% formaldehyde (0.6 mole), 65.1 g (0.6 mole) $Et_2N \cdot HCl$, and 50 ml PrOH were heated together for 6 hr at 80° C. Then the reaction products were diluted with water and the unreacted MVP extracted with ether, 108.6 g being recovered. Steam distillation gave complete removal of MVP.

The aqueous layer was made alkaline, and extracted with ether, the ether extract dried over K_2CO_3, the ether taken off, and the residue vacuum distilled in a current of CH_4. The following cuts were obtained: 5.6 g MVP bp 52°–56° C (1 mm), 25.4 g 2-(β-diethylaminoethyl)-5-vinylpyridine, bp 116°–118° C (1 mm), n_D^{20} 1.521, and 3.4 g bp 157°–165° C (1 mm).

2-(β-Diethylaminoethyl)-5-vinylpyridine. Colorless oil, readily polymerizing on heating with a blowing agent. Found: C 76.4; H 9.8; N 13.8%, calculated for $C_{13}H_{20}N_2$: C 76.4; H 9.9; N 13.7%.

2, 5-Divinylpyridine. 6.6 g (0.0524 mole) Me_2SO_4 was added dropwise to 10.7 g (0.0524 mole) 2-(β-diethylaminoethyl)-5-vinylpyridine dissolved in 15 ml PrOH, and the mixture was stirred and cooled to keep the temperature under 40° C. The alcohol solution was diluted with water (70 ml), 3 g NaOH in 10 ml water added, and the whole steam distilled. The 2, 5-divinylpyridine was extracted from the distillate with ether, the extracts dried over K_2CO_3, and vacuum distilled in a current of inert gas. Yield of 2, 5-divinylpyridine 4.7 g (68%), bp 68°–70° C (1 mm); n_D^{20} 1.5900; d_4^{20} 0.9831. Found: C 82.5; H 7.2; N 10.5%; MR_D 44.95, calculated for C_9H_9N: C 82.4; H 6.9; N 10.7%; MR_D 43.46.

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