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reaction scheme: 2-methyl-5-vinylpyridine is converted with Br_2 to dibromide I; with NaOH to bromovinyl compound V, which gives piperidylvinyl compound VI with piperidine and vinyl ether III with CH_3ONa ; alcoholic $\text{KOH}/\text{C}_2\text{H}_5\text{OH}$ gives vinyl ether III and ethynyl compound II; III and II are hydrolyzed with water/acid to acetyl compound IV.

Figure 1: reaction scheme: 2-methyl-5-vinylpyridine is converted with Br_2 to dibromide I; with NaOH to bromovinyl compound V, which gives piperidylvinyl compound VI with piperidine and vinyl ether III with CH_3ONa ; alcoholic $\text{KOH}/\text{C}_2\text{H}_5\text{OH}$ gives vinyl ether III and ethynyl compound II; III and II are hydrolyzed with water/acid to acetyl compound IV.

Abstract

Full Text

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PROPERTIES OF AN ACETYLENIC GROUP ATTACHED TO A PYRIDINE NUCLEUS

(Presented by Academician A. N. Nesmeyanov, 21 IX 1959)

The properties of ethynylpyridines have not been studied. The only representative of this class, 3-ethynylpyridine, has been characterized only by physical constants⁽¹⁾. It was to be expected, however, that in these compounds the reactivity of the triple bond and of the acetylenic hydrogen atom would be higher than in phenylacetylene.

We added a molecule of bromine to 2-methyl-5-vinylpyridine. On treatment of the resulting 2-methyl-5-(1,2-dibromoethyl)pyridine (I) with alcoholic alkali, 2-methyl-5-ethynylpyridine (II) was obtained, and, as a by-product of the reaction, the corresponding α -vinyl ether (III). The structure of this ether (III) is confirmed by the fact that on hydrolysis it is converted into the known 2-methyl-5-acetylpyridine (IV).

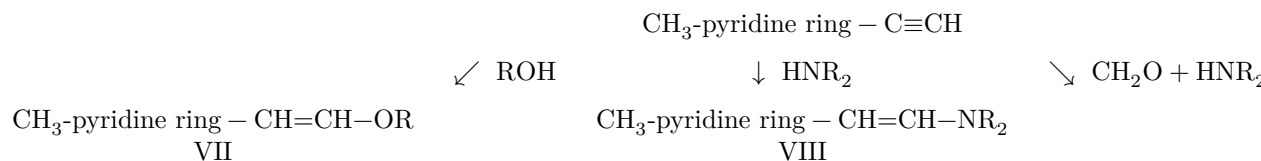
It may be assumed that, when alkali acts on dibromide I, the β -halogen atom is eliminated first, since under mild conditions from this dibromide we obtained 2-methyl-5-(1-bromovinyl)pyridine (V). It is interesting to note that this bromide readily replaces the bromine atom. Thus, on heating bromide V with sodium methoxide we obtained the vinyl ether (III) in 55% yield. Replacement of bromine by a piperidine residue likewise proceeded readily, with formation of 2-methyl-5-(1,N-piperidylvinyl)pyridine (VI). Thus, the influence of the pyridine nucleus considerably diminishes the passivating effect of the vinyl group on the carbon-halogen bond.

The 2-methyl-5-ethynylpyridine (II) obtained by us possesses all the properties

of monosubstituted acetylenes; namely, with ammoniacal solution of cuprous chloride forms the corresponding copper acetylide; hydration in dilute sulfuric acid in the presence of mercuric oxide salts leads to 2-methyl-5-acetylpyridine (IV); on heating to 180° with alcohols and secondary amines it forms, respectively, β -vinyl ethers (VII) and β -vinylamines (VIII).

The structure of the β -vinyl ethers (VII) follows from the fact that the constants of the 2-methyl-5-(2-methoxyvinyl)pyridine obtained (VII; $R = CH_3$) differ from the constants of the above-described 2-methyl-5-(1-methoxyvinyl)pyridine (III). In addition, if on hydrolysis of III ketone IV is formed, then on hydrolysis of VII a polymer is rapidly formed, which is characteristic of arylacetaldehydes.

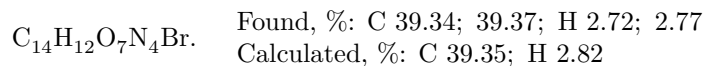
2-Methyl-5-ethynylpyridine enters the Mannich reaction fairly readily, with formation of the corresponding acetylenic amines (IX).



Data on the physiological action of the compounds obtained will be the subject of a separate communication.

Experimental Part

2-Methyl-5-(1-bromovinyl)pyridine (V). To a solution of 119 g of freshly distilled 2-methyl-5-vinylpyridine in 240 g of glacial acetic acid, with stirring and cooling (0°), 160 g of bromine was added; the mixture was stirred for 1 hour, 500 ml of water was added, it was neutralized with a 40% sodium hydroxide solution, and the resulting solution was distilled with steam. The condensate was extracted with ether, dried over magnesium sulfate, and the residue after removal of the ether was distilled in vacuo. Yield 107 g (54%), b.p. 103–104° at 10 mm, m.p. 8°, n_D^{20} 1.5820; d_4^{20} 1.4154. Picrate m.p. 167° (from alcohol).



2-Methyl-5-ethynylpyridine (II). To a solution of 119 g of 2-methyl-5-vinylpyridine in 400 ml of methyl alcohol, with cooling and stirring, 160 g of bromine was added. After 1 hour, a solution of 160 g of caustic potash in 200 ml of methyl alcohol was added, and the mixture was boiled for 2 hours. The excess alcohol was distilled off in vacuo, the mixture was treated with water, extracted with ether, the extract was dried, the ether was removed, and the

residue was distilled in vacuo. This gave 66.5 g (57%) of white crystals with b.p. 64-66° at 5 mm, m.p. 51-52° (from petroleum ether).

C_8H_7N . Found, %: C 82.20; 82.20; H 6.19; 5.96; N 11.86; 12.01
Calculated, %: C 82.02; H 6.02; N 11.96

In addition, 56.8 g (38.8%) of III was isolated, b.p. 94-96° at 4 mm, n_D^{20} 1.5376, d_4^{20} 1.0320.

$C_9H_{11}ON$, Found, %: N 9.04; 9.02
Calculated, %: N 9.38

Hydration of 2-methyl-5-ethynylpyridine. A solution of 11.7 g of II and 0.05 g of mercuric chloride in 40 ml of 50% sulfuric acid was boiled

5 h, made alkaline, extracted with ether, dried with magnesium sulfate, the solvent was removed, and the residue was distilled in vacuo. Obtained 11.5 g (86%) of IV, b.p. 107-108° at 10 mm, n_D^{20} 1.5308, d_4^{20} 1.0660. The oxime had m.p. 184° from alcohol, which corresponds to the literature data (2).

2-Methyl-5-(2-methoxyvinyl)pyridine (VII, R = CH₃). A solution of 11.7 g of II in 16 g of methyl alcohol was heated in an ampoule for 5 h at 180°; the excess alcohol was distilled off, and the residue was distilled in vacuo. Yield 6.8 g (46%), b.p. 118-120° at 10 mm, n_D^{20} 1.5600.

$C_9H_{11}ON$. Found %: N 9.36; 9.42
Calculated %: N 9.39.

2-Methyl-5-(2-(2-diethylaminoethoxy)vinyl)pyridine (VII, R = CH₂-CH₂-N(C₂H₅)). Obtained analogously from 5.9 g of 2-methyl-5-vinylpyridine and 11.8 g of 2-diethylaminoethanol. Yield 5.9 g (60%), b.p. 182-189° at 12 mm, n_D^{20} 1.5270.

$C_{14}H_{22}ON_2$. Found %: N 11.59; 11.65
Calculated %: N 11.96.

2-Methyl-5-(2-N-morpholyvinyl)pyridine. Obtained analogously from 9 g of II and 13 g of morpholine (8 h, 165°). Yield 4.6 g (40%), b.p. 193-195° at 7 mm, m.p. 65-66° (from acetone).

$C_{12}H_{16}ON_2$. Found %: N 13.59; 13.67
Calculated %: N 13.72.

2-Methyl-5-(2-N-piperidylvinyl)pyridine. Also obtained from 5.8 g of II and 8.5 g of piperidine. Yield 7.1 g (70%), b.p. 185-190° at 10 mm, m.p. 32° (from acetone).

$C_{13}H_{18}N_2$. Found %: C 76.50; 76.85; H 9.04; 8.99
Calculated %: C 77.18; H 8.97.

Picrate, m.p. 154-156° (from alcohol).

2-Methyl-5-(1-N-piperidylvinyl)pyridine. A mixture of 9.5 g of V and 8.5 g of piperidine was boiled in a flask with a reflux condenser for 5 h, made alkaline with 2 N caustic potash solution, extracted with ether, the extract was dried with magnesium sulfate, the ether was removed, and, after distillation in vacuo, 5.8 g (57.5%) of VI was obtained, b.p. 194-195° at 10 mm, n_D^{20} 1.5675.

$C_{13}H_{18}N_2$. Found %: N 13.68; 13.58
Calculated %: N 13.85.

Picrate, m.p. 128-130° (from alcohol).

2-Methyl-5-(3-N-morpholypropyn-1-yl)pyridine. A mixture of 5.9 g of II, 4.8 g of morpholine, and 1.6 g of paraform was boiled in 10 ml of dioxane for 8 h; 4 g of solid caustic potash was added, and the mixture was distilled in vacuo. Yield 3.8 g (51%), b.p. 196-198° at 12 mm, n_D^{20} 1.5540. Picrate m.p. 183-185° (from alcohol).

$C_{19}H_{20}O_8N_5$. Found %: N 15.63; 15.92
Calculated %: N 15.73.

2-Methyl-5-(3-N-piperidylpropyn-1-yl)pyridine. Obtained analogously from 5.9 g of II, 4.5 g of piperidine, and 1.8 g of paraform. Yield 9.1 g (92%), b.p. 182-183° at 11 mm, n_D^{20} 1.5550.

$C_{14}H_{18}N_2$. Found %: N 12.73; 12.88
Calculated %: N 13.07.

Picrate, m.p. 179-181° (from alcohol).

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named after M. V. Lomonosov

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.

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