VINYLATION OF IMIDAZOLE AND BENZIMIDAZOLE

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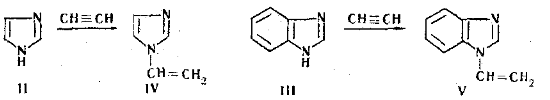
The reaction of imidazole and benzimidazole with acetylene under pressure in the presence of caustic potash has been studied. The corresponding N-vinyl derivatives have been obtained with yields of 80–86%.

In previous papers [1–3] we have reported the vinylation of indole (I) in the presence of alkaline catalysts. It appeared of interest to study the reaction of acetylene with heterocyclic compounds containing two nitrogen atoms in a five-membered ring, using imidazole (II) and benzimidazole (III) as examples. Only brief patent information is known concerning the vinylation of II and III in the presence of mixtures of the potassium salts of the starting materials, zinc oxide, and potassium hydroxide [4, 5]. The reaction includes the stage of the preliminary preparation of the catalyst and, moreover, is very lengthy (10–12 hr). In view of this, it appeared to us to be desirable to develop other methods for the synthesis of N-vinyl imidazole (IV) and N-vinyl benzimidazole (V) and to study some of their properties and compare them with N-vinyl indole. In contrast to that of I, the vinylation of II and III in the presence of alkali metals is accompanied by the charring and decomposition of the reaction mixture. Because of this, caustic potash was used as the catalyst.

We studied the dependence of the yields of IV and V on the amounts of KOH and water, and on the temperature and time of the reaction, and found optimum conditions for their synthesis. The reaction takes place best in aqueous dioxane in the presence of 20–30% of KOH according to the reactions:



An increase in the amount of KOH to 40–50% of the weight of the II had no appreciable effect on the yield of IV, while a decrease in the amount of potassium hydroxide to 10% led to a considerable fall in the yield.

The temperature for the vinylation of II may be as low as 160° C, as compared with 220° C for I. Under these temperature conditions, the yields of N-vinyl indole and of IV are similar, amounting to 70%. Raising the temperature to 190° C increased the yield of IV only to 78%. Above 200° C partial resinification of the reaction products was found. When the temperature was lowered to 140° C the reaction did not go to completion, and the starting material was recovered. Increasing the time of the process from 30 to 90 min raised the yield of IV to 86%. No thermal polymerization of the IV was observed under these conditions.

The vinylation of benzimidazole was found to take place similarly. However, the reaction of III with acetylene took somewhat longer than that of II. Using 30% KOH in aqueous dioxane at 160–180° C, the yield of V in 1 hr amounted to 77%.

The experimental results obtained show that the activities of imidazole and benzimidazole are greater than that of indole in the reaction with acetylene in the presence of caustic alkalis. This conclusion is in harmony with the ionization constants of the heterocycles considered. For II, $pK_a = 14.52$ [6], and for III $pK_a = 13.2$ [7]. There is no information in the literature on the ionization constant of I. This is apparently due to the greater stability of the N—H bond in indole.

The individuality of the N-vinyl derivatives IV and V synthesized was confirmed by thin-layer chromatography on alumina (Brockmann activity II). The calculated R_f values in the acetone–heptane–ethanol (5 : 5 : 2) and heptane–ethanol–chloroform (5 : 2 : 3) systems were 0.95 for IV and 0.59 for V.

The position of the vinyl group on the heteroatom is shown by hydrogenation and hydrolysis reactions and also by the IR spectra of the compounds. When the products of the vinylation of II and III were reduced with hydrogen in the presence of Raney nickel, the known N-ethyl imidazole (VI) and N-ethyl benzimidazole (VII) [8] were obtained.

The IR spectra of IV and V are characterized by strong absorption bands. Among them there is a band at 1645–1650 cm^{-1} due to the stretching vibrations of the terminal C=C double bond of the vinyl group, which disappears in the hydrogenation products. The latter are also characterized by the appearance of the vibrations of a methyl group at 2900, 2944, 2985 cm^{-1}. Bands at 1497, 1510, 3010, 3055, and 3110 cm^{-1} correspond to the imidazole ring [9]. There is no absorption in the 3300–3400 cm^{-1} region.

Under the action of dilute sulfuric acid, IV and V decompose with the liberation of acetaldehyde. Their hydrolysis takes place under considerably more severe conditions than that of N-vinyl indole and N-vinyl pyrrole. Under similar temperature conditions of hydrolysis, N-vinyl indole readily forms a homopolymer.

The investigation of the reactivity of the N-vinyl imidazole is continuing.

EXPERIMENTAL

The starting materials used were imidazole (imported, purity 99%) with mp 89–90° C and benzimidazole with mp 169° C.

N-Vinyl imidazole (IV). A 1-liter rotating autoclave was charged with 10 g (0.15 mole) of **II**, 3 g (0.051 mole) of KOH, 1.5 g (0.083 mole) of water, and 100 ml of absolute dioxane. Acetylene was fed in from a cylinder to an initial pressure of 17 atm. Then the reaction mixture was heated at 160° C for 1.5 hr. The product discharged from the cooled autoclave consisted of a mobile brown oil, which was subjected to vacuum distillation in an atmosphere of nitrogen. After the removal of the solvent, 11.9 g of (IV) was obtained in the form of a dark blue liquid with bp 78–85° C (10 mm), n_D^{20} 1.5210. After drying over solid KOH, redistillation gave pure **IV** with bp 80° C (10 mm); d_4^{20} 1.0382; n_D^{20} 1.5338. Found, %: C 63.60; H 6.57; N 30.34%; MR_D 28.16. Calculated for $C_5H_6N_2$, %: C 63.80; H 6.42; N 29.87; MR_D 28.43. Compound IV is readily soluble in water and in the majority of organic solvents.

N-Vinyl benzimidazole (V). Acetylene was passed into a mixture of 30 g (0.25 mole) of **IV**, 6 g (0.1 mole) of KOH, 3 g (0.16 mole) of water, and 100 ml of dioxane at an initial pressure of 16 atm. The autoclave was heated at 180° C for 1 hr. Vacuum distillation yielded a fraction with bp 130–139° C (5 mm); n_D^{20} 1.6230, 28.04 g (76.6%), which was dried over KOH. After redistillation in vacuum, V was obtained with bp 130° C (3 mm); d_4^{20} 1.1297; n_D^{20} 1.6260. Found, %: C 74.88; H 5.87; N 19.76; MR_D 45.04. Calculated for $C_9H_8N_2$, %: C 74.97; H 5.59; N 19.43; MR_D 44.43. Compound V is soluble in acetone, ethanol, and benzene, but insoluble in water.

Hydrogenation of N-vinyl imidazole (IV) and N-vinyl benzimidazole (V). The reduction of IV and V in the presence of Raney Ni by the method described previously [2] yielded N-ethyl imidazole **(VI)** and N-ethyl benzimidazole **(VII)**. Found for **VI:** bp 73–75° C (3 mm); d_4^{20} 0.9990; n_D^{20} 1.4978; MR_D 28.19; picrate, mp 172.5° C (from ethanol). Calculated for $C_5H_8N_2$: MR_D 28.90. According to the literature [8], bp 206° C (760 mm); d_4^{20} 0.999; picrate, mp 173° C.

Found for **VII:** bp 135° C (2 mm); picrate, mp 218.5° C (from ethanol). Calculated for $C_9H_{10}N_2$; d_4^{20} 1.0980; n_D^{20} 1.5918; MR_D 44.94 MR_D 44.90. According to the literature [8]: bp 160–162° C (12 mm); picrate, mp 219–220° C.

Hydrolysis of N-vinyl imidazole (IV). A 100-ml sealed tube containing 0.354 of **IV** and 20 ml of 15% H_2SO_4 was kept in a thermostat at 100 ± 0.5° C for 30 hr. Then the contents of the tube were transferred quantitatively into a measuring flask. The amount of acetaldehyde was determined by Ripper's method [10], the excess of bisulfite being back-titrated with 0.1 N iodine solution. The yield of acetaldehyde was 27.2%. The degree of hydrolysis of **V** with 4% H_2SO_4 after 30 hr at 60° C was 30.7%.

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