

## SYNTHESIS AND POLYMERIZATION OF N-VINYLINDOLE

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The reaction of indole with acetylene under pressure is investigated. It is shown that under the action of KOH in aqueous dioxane at 220° C, N-vinylindole  $C_{10}H_9N$  is formed in 66% yield, and that this compound undergoes free radical and cationic polymerization.

N-vinylindole (I) is synthesized, and investigation of its properties opens up new vistas in the practical use of nitrogen-containing pyrrole series monomers.

There is very limited information on the synthesis of I in the literature. Thus there are German patents which give only indirect indications regarding the possibility of preparing I similarly to vinylcarbazole and vinylpyrrole [1]. They do not give actual examples of conditions for vinylating indole under the action of potassium hydroxide. W. Reppe's review, dealing with ethynylation of heterocyclic imines, describes a synthesis of I by passing indole vapor mixed with acetylene over an iron catalyst at 300° C, but without stating the yield [2]. We have previously published a preliminary communication on the vinylation of indole in the presence of potassium hydroxide. A low yield, 13-15% of I, was obtained [3]. It was shown that the optimum vinylation conditions for indole are different from those for carbazole.

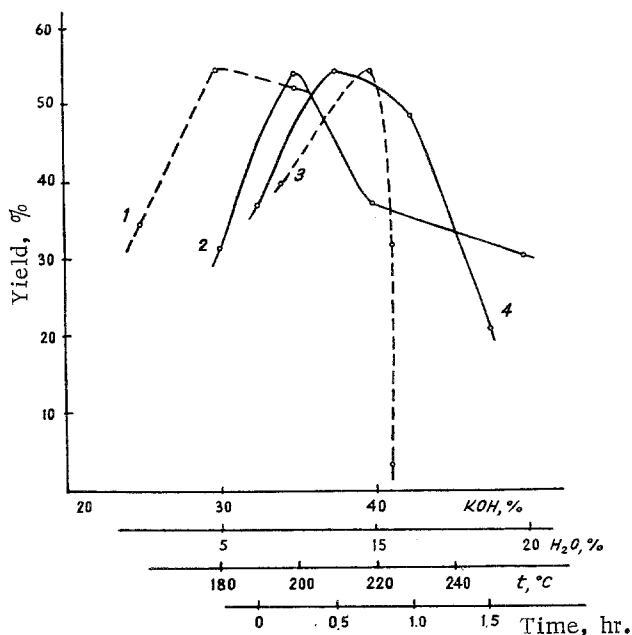


Fig. 1. N-vinylindole yield relationships: 1) as a function of the amount of catalyst (220° C, 30 min., 10% water); 2) as a function of the amount of water (30% KOH, 220° C, 30 min); 3) as a function of temperature (30% KOH, 30 min, 10% water); 4) as a function of time (30% KOH, 220° C, 10% water).

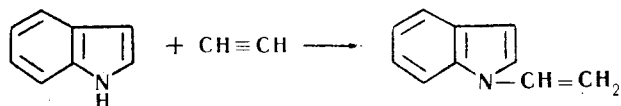
Consequently, the present work suitably included a more detailed study of the reaction of indole with acetylene under various reaction conditions.

The present research led to the yield of I being raised to 66%. An essential factor in this was carrying out the reaction in dioxane or toluene containing small quantities of water, without diluting the acetylene with nitrogen.

Figure 1 shows how the yield of I depends on alkali concentration, amount of water, reaction time, and temperature when indole is vinylated in toluene. Figure 1 shows that the best results are obtained by using 30% KOH based on the weight of indole. Further increase in the amount of potassium hydroxide did not appreciably affect the yield. Cutting it to 25% almost halved the yield.

Unlike the synthesis of vinylactams, the vinylation of indole was run in the presence of water. It was shown that the best yield of I was obtained by adding 10% water (curve 2) to the reactants. Study of how indole vinylation depended on temperature showed that raising this from 220° C to 230° C leads to a sharp drop in the yield of I due to thermal polymerization of the latter, to pentamer. It should be mentioned that use of dioxane in place of toluene as the solvent led to the yield of I being increased by 12–15%. When the potassium hydroxide was replaced by sodium hydroxide the course of the reaction was not markedly affected. Under the same conditions, the yield of indole vinylation products was still quite high, 50–60%.

Thus the optimum conditions for indole vinylation were found by repeated exploratory experiments. They were reacted with acetylene at 220° C in the presence of 30% KOH in water-dioxane for half an hour, the equation being:



The I which we obtained by vacuum-distillation was isolated in crystalline form for the first time; hitherto, it has not been mentioned in the literature. The structure of the synthetic I was proved by hydrolytic splitting, hydrogenation, and study of IR spectra. Dilute sulfuric acid effected quantitative hydrolysis of I with separation of acetaldehyde. Hydrogenation over nickel catalyst gave N-ethylindole, forming with picric acid orange-red crystals whose properties correspond with those given in the literature for N-ethylindole picrate [4].

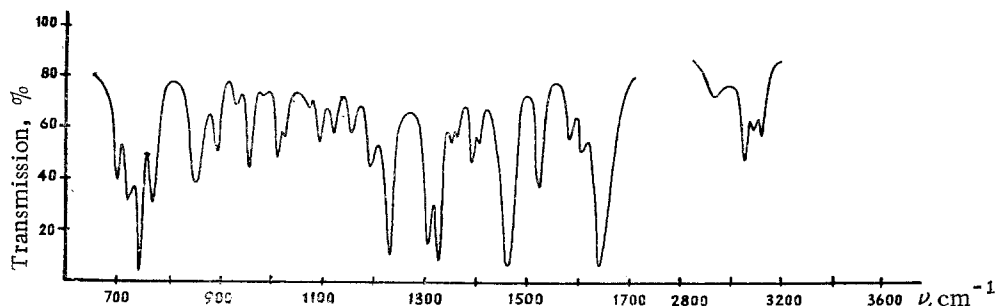
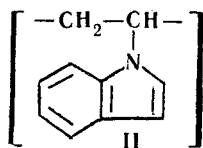


Fig. 2. N-Vinylindole IR spectra.

Figure 2 shows the IR spectrum of I in the 700–3600  $\text{cm}^{-1}$  region. It is characterized by numerous high-intensity absorption bands. Among them is a band at 1642  $\text{cm}^{-1}$ , connected with valence vibrations of C=C in the vinyl group. The end double bond adjacent to the hetero atom can also be identified by weak frequencies at 3136, 3116, and 3096  $\text{cm}^{-1}$  [5]. Strong bands at 958 and 1014  $\text{cm}^{-1}$  are evidently due to deformation vibrations of hydrogen atoms in the =CH<sub>2</sub> group. All of the above mentioned bands are absent from the IR spectra of the hydrogenation and polymerization products. In the C=C valence vibrations region there are two bands at 1575 and 1520  $\text{cm}^{-1}$ , corresponding to the pyrrole ring [6]. The absence of NH vibration frequencies from the spectrum of I confirms that the vinyl group is on the nitrogen. The homogeneity of I is also shown by gas-liquid chromatography.

To exhibit the reactivity of the double bond of the vinyl group, polymerization of I by cationic catalysts was investigated, the catalysts being boron trifluoride etherate, and the following metal chlorides: SnCl<sub>2</sub> · 2H<sub>2</sub>O, AlCl<sub>3</sub> · 6H<sub>2</sub>O, TiCl<sub>4</sub>, FeCl<sub>3</sub> · 6H<sub>2</sub>O; SnCl<sub>4</sub>, SnCl<sub>4</sub> · 5H<sub>2</sub>O. The most effective were BF<sub>3</sub> · OEt<sub>2</sub> and stannic chloride hydrate. It was found that at negative temperatures in range -20° C to -5° C, I is not polymerized cationically, and the starting monomer is recovered almost unchanged. However, at room temperature, there is 96–98% polymerization of I in 24 hr by 2% SnCl<sub>4</sub> · 5H<sub>2</sub>O. The polyvinylindole yield is halved by raising the temperature from 20° C to 90° C with simultaneous shift of the optimum catalyst concentration to 1–2%. Study of polymerization of I as affected by reaction time showed that when using 2% SnCl<sub>4</sub> · 5H<sub>2</sub>O at 18°–20° C a precipitate of polymer forms in the first 5–10 min. In half an hour the conversion was over 80%.



Polyvinylindole is a white powder, mp 180°–210° C, viscosity 0.032, soluble in acetone, benzene, toluene, dioxane, and insoluble in ethanol, diethyl ether, water. From the structural formula of polyvinylcarbazole, it can be assumed that II is the structure of the repeating unit of polyvinylindole.

The literature contains information about dimerization of indole by mineral acids [7]. In view of that information, it might have been expected that cationic catalysts would dimerize indole at positions 2,3 in addition to polymerizing it at the vinyl group. However, dimerization is improbable, since an attempt to polymerize indole itself with stannic chloride was unsuccessful. Furthermore, fractionation work with polyvinylindole indicates that polymerization of I involves the vinyl double bond. The method used was fractional precipitation of the polymer with ethanol from 1% acetone solution. Elementary analyses and IR spectra of all fractions were identical, while the molecular weights ranged from 700 to 1500.

A study of the polymerization of I by the free radical mechanism showed that its activity varied for different initiators. I was not polymerized by 0.5, 1.5, or 5% benzoyl peroxide. At the same time, hydrogen peroxide converted it quantitatively into solid polymer. With azaisobutyrodinitrile the same glass-like substance, molecular weight 1400, was formed after 100 hours. Thus it was shown that I is an active vinyl monomer susceptible to both ionic and radical polymerization.

### Experimental

**Indole vinylation.** The starting material used was a "pure" indole, mp 52° C, from a Khar'kov coal tar chemicals factory. A 2 l rotating autoclave was charged with 60 g (0.53 mole) indole, 18 g (0.32 mole) KOH, 6 g (0.33 mole) water, 200 ml dioxane (previously freed from peroxides by 12 hr refluxing over KOH followed by distillation over Na). The acetylene was charged in from a cylinder, starting pressure 17 atm. Then the autoclave was heated at 220° C for 30 min, when the acetylene pressure fell to 9 atm. The product removed from the autoclave was a mobile brown liquid which was vacuum-distilled in nitrogen, to give the solvent and I as a dark blue liquid bp 120°–133° C (8 mm),  $n_D^{20}$  1.6243, yield 48.81 g (66.6%). 37.6 g of the product was washed with KOH solution and dried over solid KOH, then over  $K_2CO_3$ , and finally over Na, after which it was distilled in a current of  $N_2$  under reduced pressure, through a column rated at 20 theoretical plates, to give a main fraction (28.8 g) corresponding to I, with the following properties: mp 29°–30° C, bp 71°–72° C (1 mm),  $d_4^{20}$  1.0658,  $n_D^{20}$  1.6300. Found: C 83.65, 83.72; H 6.27, 6.15; N 9.45, 9.63%;  $MR_D$  47.74. Calculated for:  $C_{10}H_9N$ : C 83.87; H 6.33; N 9.79%;  $MR_D$  46.99. Gas-liquid chromatography showed it was 97.5% pure. Pure I could be stored for a long time as a colorless liquid, which mechanical action causes to crystallize. It was readily soluble in EtOH,  $Me_2CO$ ,  $CCl_4$ , dioxane, toluene.

From the products of vinylating indole, a solid was isolated by decanting off the liquid. Solution in  $Me_2CO$  and precipitation with EtOH gave 11 g polyvinylindole forming a light brown powder mp 282°–317° C. Found: N 9.26, 9.38%; M 704.9 (cryoscopic in benzene). Calculated for:  $(C_{10}H_9N)_n$ : N 9.79%.

Indole was vinylated in toluene and the product worked up similarly. The results are shown in Table 1.

**Hydrogenation of N-vinylindole.** A long-necked hydrogenation flask was charged with 3.17 g (0.022 mole) N-vinylindole, 15 ml EtOH, and Raney Ni catalyst. Hydrogenation was effected at 20° C, using constant stirring; a total of 0.49 l  $H_2$  was absorbed, the theoretical amount being 0.5 l. At the end of the reaction, the catalyst was filtered off, the EtOH distilled off on a water bath and the hydrogenation product vacuum-distilled to give 2.64 g N-ethylindole, as a colorless liquid, bp 85°–87° (1 mm);  $d_4^{20}$  1.0253;  $n_D^{20}$  1.5878. Found:  $MR_D$  47.57. Calculated for  $C_{10}H_{11}N$ :  $MR_D$  47.45.

The N-ethylindole thus prepared reacted with picric acid to give an orange-red picrate mp 100°–102° C, literature [4] mp 105° C. IR spectrum: 3048, 2980, 2940, 2884  $cm^{-1}$  ( $CH_2-CH_3$ ); 1516, 1462, 1316, 1223, 742  $cm^{-1}$ .

**Cationic polymerization.** In a glass ampul were placed 0.56 g (0.0039 mole) freshly distilled vinylindole and 0.01 g  $SnCl_4 \cdot 5H_2O$  in 1 ml dry ether, the air displaced by  $N_2$ , and the ampul kept in a thermostat at 20° C for 24 hr. It was then emptied and the contents dissolved in 3 ml dry acetone. The polymer was precipitated by adding 20 ml dry EtOH to the acetone solution, then repeatedly washed with EtOH to remove residual catalyst and monomer. The solid was centrifuged and dried to constant weight in a vacuum-desiccator. Yield 0.54 g (96.3%) polyvinylindole, a white powder mp 169°–177° C. Found: C 83.43, 83.15; H 6.28, 6.21; N 9.77, 9.72%; M 730. Calculated for  $(C_{10}H_9N)_n$ : C 83.91; H 6.29; N 9.79%.

IR spectrum: 3040, 2960, 2864, 1603, 1544, 1450, 1332, 1296, 1204, 1100, 1008, 730  $cm^{-1}$ .

**Radical polymerization.** 0.02 g azoisobutyrodinitrile was added to 0.5 g (0.0035 mole) freshly distilled vinylindole in an ampul, which was then sealed and thermostatted at 60° C. After 100 hr the glassy solid formed was freed from monomer and catalyst by dissolving it in benzene, and precipitating with 10 ml dry EtOH: it was centrifuged off, and dried to constant weight in a vacuum-desiccator. Yield 0.46 g (92.8%) N-polyvinylindole mp 130°–143° C.

Found: N 10.54, 10.19%. Calculated for (C<sub>10</sub>H<sub>9</sub>N)<sub>n</sub>: N 9.79%.

The IR spectrum of I was measured with a UR-10 double beam spectrophotometer, using NaCl and LiF prisms, over the ranges 1800–600 cm<sup>-1</sup> and 3600–2800 cm<sup>-1</sup>, using either liquids (thin capillary layer between NaCl and LiF plates) or solids (pressed with KBr into plates).

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