## THE VINYLATION OF BENZOTRIAZOLE

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The reaction of benzotriazole with acetylene under pressure in the presence of potassium hydroxide and cuprous chloride has been examined. 1-Vinylbenzotriazole was obtained in 75% yield.

In continuation of investigations into the vinylation of nitrogenous heterocycles [1, 2], we have examined the condensation of acetylene with benzotriazole (I). It is known from the patent literature that 1-vinylbenzotriazole may be obtained by vinylation of I in toluene in the presence of its potassium salt [3]. This process, however, requires the preliminary preparation of the catalyst, is lengthy, and gives a yield of only 10.3%.

The present paper describes attempts to vinylate I directly in the presence of KOH, by analogy with the preparation of N-vinylindole (III) [1]. These attempts resulted in an increase in the yield of II to 37%. The reaction proceeds in dioxane, in the presence of 30% of KOH and 10% of water at  $160^{\circ}$  for 30-40 min. When the amount of catalyst was increased to 50%, the main product was the stable potassium salt of I, identified by its mp. On increasing the temperature to  $200^{\circ}$ , and prolonging the reaction time, no thermal polymerization was observed. On using cuprous chloride (1-3%) for the first time as catalyst, in dioxane at  $165-170^{\circ}$ , the yields of II were increased to 75-80%. When the amount of catalyst was reduced to 0.5% and the temperature was reduced to  $150^{\circ}$ , the yield of II fell substantially. Other copper salts of mineral acids were active as catalysts in the vinylation of I. Table 1 shows the effect of the nature of the catalyst on the yield of II under the same conditions (180°, 1h).

It is interesting that indole does not react with acetylene in the presence of CuCl, but benzimidazole, like I, is vinylated under these conditions. These results show that, in all probability, different mechanisms of vinylation are operative in the heterocycles mentioned. It has been shown previously that the vinylation of indole proceeds for the most part by an ionic mechanism [4]. The vinylation of I apparently proceeds via an acetylene  $\pi$ -complex, which undergoes intramolecular conversion to a  $\sigma$ -metalloorganic compound [5]. This reacts with I to give II.

Catalyat	Amount	Yield of II.		
	weight, %	moles/mole 1	70	
CuCl <sub>2</sub> CuCl Complex $1 \cdot CuCl$ CuSO <sub>4</sub> KOH* HC=CNa Cd (CH <sub>3</sub> COO) <sub>2</sub> · 2H <sub>2</sub> O	$\begin{array}{c c} 2 \\ 1,5 \\ 2 \\ 30 \\ 1,5 \\ 18 \end{array}$	0,003 0,004 0,001 0,002 0,05 0,01 0,01	76 72 50 50 37 Traces 0	

TABLE 1.	Vinvlation	of	Benzotriazole	I	with	Various	Catalysts
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\* With the addition of 10% of  $H_2O_{\bullet}$ 

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TABLE 2. Vinylation of Benzotriazole

КОН*		Temp, Time,		Yield	CuCl		Temp,	Time,	Yield
%	moles	•C	min	of II, %	%	moles	•C	min	of II, %
30 30 30 30 50 20	0,05 0,05 0,05 0,05 0,09 0,037	200 180 200 160 200 180	30 30 60 60 30 60	36 36 36 36 30 6	0,5 1,1 3,0 5,0 1,5 1,5	0,0015 0.0033 0,009 0,015 0,0045 0,0045	180 170 180 150 150	60 60 40 60 120 180	12 65 69 56 23 39

\*With the addition of 10% of  $H_2O_{\bullet}$ .

The purity of the II obtained was shown by thin-layer chromatography, IR spectra, and hydrogenation. The IR spectra (obtained on a UR-10 spectrometer) showed strong absorptions at 3110, 1650, and 960 cm<sup>-1</sup>, indicative of the presence of a terminal vinyl group. Reduction of II with hydrogen in the presence of Raney nickel gave the known 1-ethylbenzotriazole [6].

## EXPERIMENTAL

"Pure" grade benzotriazole was used as starting material, mp 98°.

<u>1-Vinylbenzotriazole (II)</u>. <u>A)</u> In a rotating autoclave of 1 liter capacity was placed 30 g (0.25 mole) of I, 0.45 g (1.5%; 0.004 mole) of cuprous chloride, and 100 ml of drydioxane, and acetylene was introduced to a pressure of 15 atm. After heating at 165-170° for 40 min, the vinylation reaction mixture was cooled, and the dioxane was removed under reduced pressure. Distillation of the residue in vacuo gave 26 g (72%) of a clear oil, bp 96-98° (2 mm), which crystallized on standing, mp 30°,  $n_D^{20}$  1.6100,  $d_4^{20}$  1.575. Found: C 66.2; H 5.0; N 28.8%; MR<sub>D</sub> 42.64.  $C_8H_7N_3$ . Calculated: C 66.2; H 4.9; N 28.8%; MR<sub>D</sub> 42.51. R<sub>f</sub> 0.66 (benzene – hexane – chloroform, 2:1:2, on grade II Brockman alumina, without binder). II dissolved readily in most organic solvents.

<u>B)</u> On heating a mixture of 10 g (0.09 mole) of I, 3.3 g (0.05 mole) of KOH, and 10 ml of water in 60 ml of dioxane in an autoclave at 160° for 30 min, there was obtained 4.9 g (37%) of II.

The results of the vinylation of I with KOH and CuCl under other conditions are given in Table 2.

<u>1-Ethylbenzotriazole</u>. 5 g (0.034 mole) of II in 30 ml of ethanol was hydrogenated over Raney nickel until uptake of hydrogen ceased. There was obtained 4.5 g (88%) of 1-ethylbenzotriazole, bp 119-120° (3 mm), nD<sup>20</sup> 1.5680, d4<sup>20</sup> 1.1259 [7]. Found: MR<sub>D</sub> 42.353. C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>. Calculated: MR<sub>D</sub> 42.96. R<sub>f</sub> 0.51 (ether-hexane, 5:1).

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