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REACTION OF 2-AMINOBENZIMIDAZOLE WITH ACETYLENE

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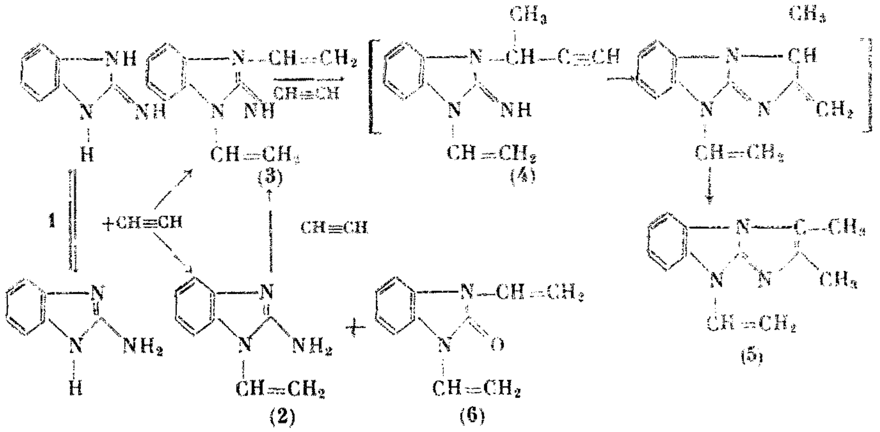
The reaction of 2-aminobenzimidazole (1) with acetylene under pressure proceeds with the formation of vinyl monomers, corresponding to amine and imine forms, 1-vinyl-2-amino- and 1,3-divinyl-2-iminobenzimidazoles, depending on the reaction conditions. 1,3-Divinyl-2-benzimidazolone was also isolated in aqueous dioxane in addition to the monovinyl derivative of 1. Cyclization of the divinyl derivative of 1 with acetylene proceeds to give 9-vinyl-1,2-dimethylimidazo[1,2-a]-benzimidazole.

Keywords: *2-aminobenzimidazole, acetylene, vinyl monomers.*

Among the many functional derivatives of N-vinylbenzimidazole, no data have been reported on vinyl monomers of 2-aminobenzimidazole, whose synthesis might open a pathway to obtain monomers and polymers with valuable properties. A considerable number of aminoheterocycles have been found to possess high pharmacological activity [1-3].

In the present work, we studied the direction of the nucleophilic addition of acetylene to 2-aminobenzimidazole (**1**). Independently of the nature of the catalyst and reaction temperature, previously unreported vinyl monomers are formed corresponding both to the amine and imine tautomeric forms of **1** [4]: 1-vinyl-2-amino- (**2**) and 1,3-divinyl-2-iminobenzimidazoles (**3**). The vinylation in the presence of KOH at 140-180°C is accompanied by considerable tar formation and vinyl derivatives **2** and **3** were isolated in yields not exceeding 10%. CuCl and $Cd(OAc)_2$ are the most efficient catalysts in this reaction. The reaction of benzimidazole (**1**) with acetylene in the presence of CuCl at 180°C over 2 h gives divinyl derivative **3** in 50% yield and 1-vinyl-2-aminobenzimidazole in 12% yield. Reduction of the reaction temperature to 160°C leads to a reduction of the total yield of vinyl monomers **2** and **3** (to 50%); the fraction of monovinyl derivative **2** increases to 75% relative to **3**.

The use of $Cd(OAc)_2$ as the catalyst at 160°C leads to an increased total yield of the vinyl monomers to 75%; the **2**:**3** ratio was 4:1. However, when the reaction was carried out at 180°C, **2** was formed in 30% yield and tarry products of the vinyl derivatives of benzimidazole **1** were formed in 65% yield.



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9-Vinyl-1,2-dimethylimidazo[1,2-*a*]benzimidazole (**5**) was isolated in 8-12% yield when the reaction was carried out at 195-210°C independently of the nature of the catalyst. As in the case of aliphatic secondary amines [5], the reaction may proceed through the formation of butyl derivative **4**, which cyclizes at the amino group. Such cyclization of divinyl derivative **2** upon the reaction of azoles with acetylene has not been reported.

The vinylation of benzimidazole **1** in the presence of 10-20% water catalyzed by either $Cd(OAc)_2$ or CuCl at 180°C over 2 h leads to the formation of 1,3-divinyl-2-benzimidazolone (**6**) [6] in addition to vinyl derivative **2**. Apparently, this reaction involves the hydrolysis of the amino group of divinyl derivative **3**. The yield of vinyl monomers is reduced in the presence of water to 40-50% in the case of cadmium acetate and 20% in the case of cuprous chloride. Independently of the nature of the catalyst, **6** comprises up to 70-80% of the vinylation products.

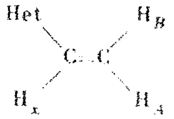
The structures of **3-6** were supported by elemental analysis and IR and PMR spectroscopy.

EXPERIMENTAL

1-Vinyl-2-aminobenzimidazole (2) and 1,3-divinyl-2-iminobenzimidazole (3). A mixture of 10 g **1**, 0.15 g (1.5%) CuCl, and 100 ml dioxane was placed into an autoclave and acetylene was introduced at a pressure of 13-15 atm. The reaction mixture was maintained for 2 h at 180°C and the solvent was distilled off. Vacuum distillation gave 7.6 g divinyl derivative **3** in 49% yield, bp 156-158°C (2 mm Hg) and monovinyl derivative **2** in 12% yield, bp 194-196°C (2 mm Hg). Mp of **3** (from hexane): 80-82°C. Found, %: C, 71.57; H, 6.03; N, 22.49. $C_{11}H_{11}N_3$. Calculated, %: C, 71.35; H, 5.95; N, 22.70. PMR spectrum (δ, ppm): 5.14 (H_A), 5.49 (H_B), 6.87 (H_X), 6.98-7.25 (H_{NH}). Mp of **2** (from acetone): 115-117°C. Found, %: C, 69.03; H, 5.89; N, 27.21. $C_9H_9N_3$. Calculated, %: C, 68.92; H, 5.66; N, 26.92. PMR spectrum (δ, ppm): 5.26 (H_A), 5.50 (H_B), 6.89 (H_X), 4.90 (H_{NH_2}).

9-Vinyl-1,2-dimethylimidazo[1,2-*a*]benzimidazole (5) was obtained upon separation of the mixture of vinyl derivatives on a chromatographic column packed with L 100/250 silica gel using ethanol as the eluent. Found, %: C, 73.45; H, 6.26; N, 19.41%. $C_{13}H_{13}N_3$. Calculated, %: C 73.93; H, 6.16; N, 19.91. PMR spectrum (δ, ppm): 4.99 (H_A), 5.99 (H_B), 7.06 (H_X), 2.30 (H_{CH_3}), 2.51 (H_{CH_3}).

1,3-Divinyl-2-benzimidazolone (6) was synthesized under analogous conditions from 15 g **1**, 1.2 g (8%) $Cd(OAc)_2$, 100 ml dioxane, and 10 ml water at 180°C over 2 h. Vacuum distillation at 150-169°C (3 mm Hg) gave a mixture of vinyl derivatives **2** and **6** in 50% yield (6.7 g). Preparative gas-liquid chromatography gave 4.7 g (70%) **6** and 2 g (30%) **2**. We also obtained 1,3-divinyl-2-benzimidazolone (**6**), bp 148-151°C (2 mm Hg). Found, %: C, 70.83; H, 5.41; N, 15.25. $C_{11}H_{10}N_2O$. Calculated, %: C, 70.97; H, 6.38; N, 15.05. PMR spectrum (δ, ppm): 5.03 (H_A), 5.63 (H_B), 6.97 (H_X)



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