1-Methyl-2-(5'-hydroxymethyl-2'-selenienyl)benzimidazole (X). A mixture of 1.3 g (5 mmole) of II, 1.15 g (13 mmole) of paraform, and 10 ml of hydrochloric acid (d 1.19) is heated for 20 h at 70-80°C. Then the reaction mass is cooled and cautiously neutralized by a solution of potassium hydroxide. The reaction product is extracted by chloroform and chromatographed in a column with aluminum oxide, chloroform being used for its elution.

1-Methyl-2-(5'-formyl-2'-selenienyl)benzimidazole (XI). A mixture of 1.3 g (5 mmole) of compound II and 1.4 g (10 mmole) of urotropin in 20 g of polyphosphoric acid is stirred for 6 h at 70-80°C. Then the reaction mass is diluted with 100 ml and neutralized by a solution of ammonium. The reaction product is separated and recrystallized.

1-Methyl-2-(5'-acetyl-2'-selenienyl)benzimidazole (XII). A mixture of 1.3 g (5 mmole) of II and 0.9 g (15 mmole) of glacial acetic acid in 20 g of polyphosphoric acid is stirred at 100°C for 3 h. The reaction mass is diluted with 100 ml of water and neutralized by a solution of ammonia. Acetylated derivative XII is separated from the trimer in a column with aluminum oxide, the eluent being chloroform.

1-Methyl-2-(5'-benzoyl-2'-selenienyl)benzimidazole (XIII). A mixture of 1.3 g (5 mmole) of II and 1.8 g (15 mmole) of benzoic acid is stirred for 8 h at 150°C. The reaction product is separated precisely as in the case of compound XII.

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VINYLATION OF NAPHTHO[2,3-d]IMIDAZOLE

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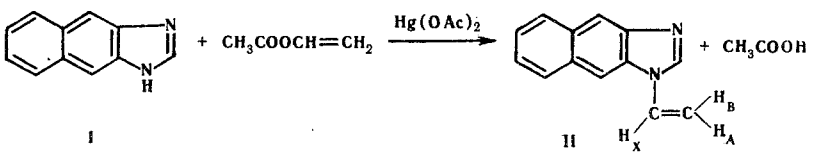
1-Vinylnaphtho[2,3-d]imidazole has been synthesized by reacting naphtho[2,3-d]-imidazole with vinyl acetate in the presence of mercuric acetate, as well as with acetylene under pressure in the presence of potassium hydroxide.

In the last few years investigators have shown increasing interest in N-vinylazoles, which have served as a basis for the synthesis of polymers with a set of valuable properties [1-5]. The present work was devoted to the synthesis and investigation of the properties of the previously unknown compound 1-vinylnaphtho[2,3-d]imidazole.

The reaction of naphtho[2,3-d]imidazole (I) with vinyl acetate in the presence of mercuric acetate results in the formation of 1-vinylnaphtho[2,3-d]imidazole (II) with a 66% yield



This is simple in execution; however, the application of a scarce, highly toxic mercury catalyst restricts its use on a large scale. Vinylnaphthoimidazole II has been obtained with

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TABLE 1. Conditions for the Vinylation of Naphtho[2,3-d]imidazole (I)

Experiment no.	Temperature, deg C	Pressure, atm	Reaction time, h	Yield, %
1	190	14	3,00	62
2	190	15	1,50	78
3	190	16	1,50	89
4	210	14	0,25	66
5	210	15	1,00	75
6	220	15	0,25	70
7	220	18	0,25	87
8	230	16	0,25	30
9	240	16	0,25	Resinification

a higher yield (87%) in the absence of a mercury catalyst by another method, viz., by reacting naphthoimidazole I with acetylene under pressure in the presence of potassium hydroxide. The reaction pressure and temperature have a significant influence on the yield of compound II (see Table 1). As is seen from the table, lowering the temperature and the pressure slows the reaction. At the same time, increasing the temperature above 220°C lowers the yield of the desired product due to the strong resinification of the reaction mass. The naphthoimidazole synthesized, II, is a crystalline substance, which is highly soluble in alcohols, acetone, dioxane, and dimethyl sulfoxide and is insoluble in water and carbon tetrachloride.

The structure of compound II was confirmed by the data from IR, PMR, and UV spectrodcopy, as well as by hydrogenation. The reduction of vinylation product II by hydrogen in the presence of Raney nickel, as well as the reaction of naphthoimidazole I with ethyl iodide, give 1-ethylnaphtho[2,3-d]imidazole (III).

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument in tablets with KBr, and the UV spectra were obtained on a Specord UV-VIS spectrophotometer in acetonitrile at 20°C. The PMR spectra were recorded on a Tesla BS-4878 spectrometer (80 MHz) in $CDCl_3$ with HMDS as an internal reference. Thin-layer chromatography was carried out on Silufol UV-254 plates in a 1:1 acetone–benzene system. The original naphtho[2,3-d]imidazole I was synthesized according to the method in [6].

1-Vinylnaphtho[2,3-d]imidazole (II). A. A 68-g portion (0.79 mole) of vinyl acetate is given an addition of 1.08 g (3 mmole) of mercuric acetate, a dropwise addition of 1 ml of anhydrous sulfuric acid, and an addition of 20 g (0.12 mole) of I, and the mixture is boiled for 28 h with a reflux condenser. At the conclusion of the reaction, 6.7 g of sodium acetate and 5.2 g of anhydrous sodium carbonate are added to the mixture, and the precipitate is filtered off. The reaction product remaining after the removal of the excess vinyl acetate from the filtrate is vacuum-distilled in a stream of argon, bp 211-212°C (8 kPa). The yield is 15.2 g (66%). IR spectrum: 960, 1648 (δ_{CH}, $\nu_{C=C}$ in $CH{-}CH_2$, respectively), 760, 3040 cm^{-1} (δ_{CH}, ν_{CH} in naphthoimidazole). PMR spectrum: 5.09 (H_A, d. d, J = 1.0, 8.0 Hz); 5.59 (H_B, d. d, J = 1.0, 15.0 Hz); 7.06 (H_X, d. d, J = 8.0, 15.0 Hz); 7.24-8.06 ppm (7H in naphthoimidazone, m). UV spectrum (in acetonitrile), λ_{max} (log ε): 264 (4.2), 305 (3.4), 3.8 (3.5), 334 (3.4), 348 nm (3.5). Found: C, 78.8; H, 5.0; N, 13.8%. Calculated for $C_{13}H_{10}N_2$: C, 80.4; H, 5.1; N, 14.4%. R_f 0.73.

B. A rotating 0.5-liter steel autoclave is charged with 10 g (0.06 mole) of naphthoimidazole I, 2 g (0.04 mole) of KOH, and 10 ml of dioxane. Acetylene under a pressure of 16 atm is admitted. The reaction mixture is heated and held at 190°C for 1 h 30 min. After the autoclave has cooled, the solvent is removed from the reaction mixture, and 8.9 g (89%) of compound II are recovered by vacuum distillation at bp 211-212°C (8 hPa). Found: C, 80.8; H, 5.2; N, 14.1%. Calculated from $C_{13}H_{10}N_2$: C, 80.4; H, 5.1; N, 14.4%. R_f 0.73.

1-Ethylnaphtho 2,3-d imidazole (III). A. A mixture of 2 g (0.01 mole) of compound II, 15 ml of absolute ethanol, and 0.8 g of Raney nickel is placed in a rotating 0.25-liter steel autoclave, hydrogen is admitted under a pressure of 50 atm, and the mixture is heated for 1 h at 50°C. At the conclusion of the process, the liquid layer is separated from the catalyst by filtration, the alcohol is removed, and the residue is sublimated in a vacuum at a sublimation temperature of 101°C (1.33 hPa). The yield is 1.98 g (98%), and the mp is 70-72°C. Found: C, 78.7; H, 5.4; N, 15.4%. Calculated for $C_{13}H_{12}N_2$: C, 79.5; H, 6.1; N, 14.3%. R_f 0.62.

B. A misture of 5.00 g (0.06 mole) of compound I and 9.5 g (0.12 mole) of ethyl iodide is added to a solution of 2.5 g (0.09 mole) of potassium hydroxide in 18 ml of absolute ethanol, and the mixture is bioled for 15 min. After the reaction mixture has cooled, the potassium iodide precipitate is filtered out. The solvent is distilled off from the filtrate, and the precipitate formed is washed with 100 ml of diethyl ether and sublimated at a sublimation temperature of 101°C (1.33 hPa). The yield is 4.2 g (85%), and the mp is 70-72°C. Found: C, 78.6, H, 6.6; N, 14.3%. Calculated from $C_{13}H_{12}N_2$: C, 79.6; H, 6.1; N, 14.3%. R_f 0.62.

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3-ARYL- AND 3-(ARYLOXY)PHTHALIC ACIDS IN THE SYNTHESIS OF FLUORENONES AND XANTHONES

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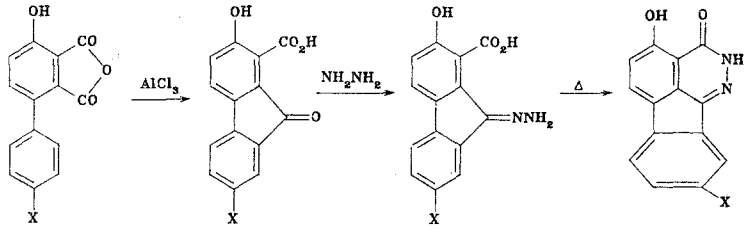
Aryl- and aryloxyfurans can serve as the starting compounds in the synthesis of fluorenones, xanthones, and diazafluoranthenes.

3-Aryl(or aryloxy)-6-hydroxyphthalic acids can easily be obtained from aryl and aryloxyfurans with the aid of a Diels–Alder reaction [1]. In the present work the derivatives of diphenyl and diphenyl ether synthesized in this manner (I, V) served as the starting compounds in the synthesis of condensed aromatic and heterocyclic systems, i.e., fluorenones (II) and xanthones (VI).

The presence of antiviral preparations [2, 3] among the derivatives of fluorenone called for a search for new ways of synthesizing the derivatives of this series. We synthesized hitherto unknown 1-carboxy-2-hydroxyfluorenones of type II by cyclization of 3-aryl-6-hydroxyphthalic anhydrides under the action of aluminum chloride (the yield was 87%):



I a, b — II a, b — III a, b — IV a, b

Ia—IVa X=CH_3; Ib X=OCH_3; II—IVb X=OH*

*Under the conditions for cyclization of Ib, demethylation of the latter occurred.

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