B. The reaction mixture consists of 2 g (8 mmole) of bromide II, 3.07 g (33 mmole) of aniline, and 5 ml of DMFA. The mixture is stirred for 6 h at 50-60°C. After similar treatment, the following are isolated chromatographically: 0.98 g (48%) of azomethine XII, 0.25 g (12%) of amino derivative XI, and 0.14 g (5%) of compound XIII (mp 288-289°C).

C. A mixture of 0.5 g (2 mmole) of compound XI in 20 ml of DMFA is heated for 4 h at 160°C 160°C. After the DMFA has been distilled off, and the residue has been cleaned up, 0.38 g (76%) of azomethine XII is isolated in a chromatographic column with mp 132-133°C and R_f 0.7.

9-(N-β-Phenylethylimino)-4-azafluorene (XIV). A. The reaction mixture consists of 2 g (8 mmole) of bromide II, 2.87 g (24 mmole) of β-phenylethylamine, and 40 ml of DMFA. The mixture is stirred for 4 h at 50-60°C in a stream of nitrogen. After similar treatment, 2.2 g (52%) of azomethine XIV with mp 79-80°C (from hexane) and R_f 0.62 are isolated. PMR spectrum: 3.27 (2H, $-CH_2-Ph$); 4.42 ppm (2H, CH_2-N). Mass spectrum: 284 (1), 194 (1.3), 193 (100), 167 (3.8), 166 (1.5). Found: C, 84.3; H, 5.6; N, 9.7%. Calculated for $C_{20}H_{16}N_2$: C, 84.5; H, 5.6; N, 9.7%. Besides azomethine XIV, 0.28 g (10%) of XIII is isolated.

B. A solution of 1.2 g (7 mmole) of 4-azafluorenone (X) and 1.44 g (12 mmole) of β-phenylethylamine in 50 ml of toluene is boiled for 9 h with the removal of water from the reaction mixture. The toluene solution is treated with water and then with sodium carbonate and dried with potassium carbonate. The toluene is distilled off, and the residue is chromatographed. This results in the isolation of 1.46 g (78%) of azomethine XIV, mp 79-80°C, R_f 0.62.

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INVESTIGATIONS IN THE FIELD OF THE CHEMISTRY OF 2-HETARYLBENZIMIDAZOLES.

6.* SYNTHESIS AND PROPERTIES OF 1-METHYL-2-(2'-SELENIENYL)BENZIMIDAZOLE

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2-(2'-Selenienyl)benzimidazole has been synthesized by a Weidenhagen reaction and converted into the N-methylated derivative. Electrophilic-substitution reactions (nitration, sulfonation, bromination, chloromethylation, and acylation) in the selenophene ring have been studied. It has been shown that the substituent enters the α position of the selenophene ring in most cases. The bromination of 1-methyl-2-(2'-selenienyl)benzimidazole in acetic acid produces the 3',5'-dibromo derivative, whereas 1-methyl-5(or 6)-bromo-2-(3',5'-dibromo-2'-selenienyl)benzimidazole is obtained in polyphosphoric acid.

Continuing the study of the conversions of 2-hetarylbenzimidazoles [1, 2], we synthesized 2-(2'-selenienyl)benzimidazole (I) on the basis of 2-formylselenophene and o-phenylenediamine and converted it into the N-methylated derivative II. In comparison to other 2-hetarylbenzimidazoles [hetaryl = 2-furyl- (III) and 2-thienyl- (IV)], 2-(2'-selenienyl)benzimidazole undergoes methylation with difficulty. Compound II can be synthesized with an 81% yield without appreciable formation of the quaternary salt only with the use of a fourfold excess

*For Report 5, see [1].

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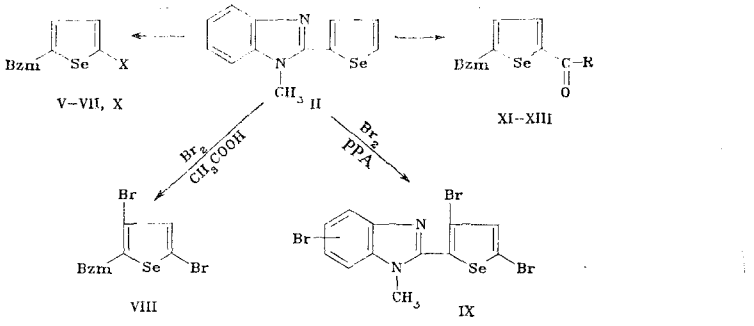
of methyl iodide and prolonged stirring at room temperature. The difficulty in the alkylation reaction in this case is apparently caused by the steric conditions, i.e., the significantly greater volume of the selenium atom in comparison to O and S.

Then 1-methyl-2-(2'-selenienyl)benzimidazole was reacted with electrophilic reagents: acetyl nitrate, a mixture of sulfuric acid and polyphosphoric acid (PPA), bromine in carbon tetrachloride, acetic acid or PPA, paraform and concentrated hydrochloric acid, urotropic and PPA, and carboxylic acids in the presence of PPA.



V X=NO_2; VI X=SO_3H; VII X=Br; X X=CH_2OH; XI R=H; XII R=CH_3; XIII R=C_6H_5;
Bzm = 1-methyl-2-benzimidazolyl

As in the case of 2-hetarylbenzimidazoles III and IV, 1-methyl-(2'-selenienyl)benzimidazole (II) was found to be resistant to the action of the electrophilic reagents just cited under severe conditions: the reaction results in the formation of its 5'-substituted derivatives (V-VIII, XI-XIII), but, according to the data from the PMR spectrum, bromination in acetic acid gives the 3',5'-dibromo derivative VIII, and in PPA with a bromine excess the H atoms of the benzene ring in position 5 (or 6) are also involved in the substitution. The PMR spectrum of VIII contains a singlet at 7.2 ppm, which belongs to the 4'-H proton, in addition to the signals of the N-methyl group and the multiplet of the aromatic protons. The PMR spectrum of IX is similar to that of VIII; however, the aromatic protons are manifested in the form of a singlet at 7.5 and a doublet at 7.3 ppm.

The chloromethylation of benzimidazole II takes place with great difficulty and a low yield. The reaction product could be isolated after treatment with potassium hydroxide and identified only in the form of the hydroxymethylated derivative X due to its contamination by the original substance.

Although the acetylation of compound II was carried out at 100°C for 30 h, the yield of acetylated derivative XII amounted to 39%, and it was not possible to avoid the formation of the trimerization product (compare [1]).

The nitration, sulfonation, formylation, and benzoylation of II takes place smoothly and with high yields.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in chloroform or liquid petrolatum, and the PMR spectra were recorded on a Tesla BS-467 instrument (60 MHz) in trifluoroacetic acid with HMDS as an internal reference.

2-(2'-Selenienyl)benzimidazole (I). A mixture of 4.32 g (40 mmole) of o-phenylenediamine in 75 ml of isopropanol, 16 g (80 mmole) of cupric acetate in 200 ml water, and 6.36 g (40 mmole) of selenophene-2-carboxaldehyde is heated at 80-90°C for 2 h. The reaction mass is cooled, and the precipitate of the copper salt is separated and suspended in 75 ml of dimethylformamide. This method made it possible to sharply increase the yield, since compound I is difficultly soluble in alcohols. Hydrogen sulfide is passed through the suspension for 1 h. Cupric sulfide is separated, and the filtrate is diluted with water. The precipitate of compound I formed is filtered out and washed with water. The yield is 8.5 g (96%) of colorless crystals with mp 347-348°C (from ethanol). Found: N, 11.5%. Calculated for $C_{11}H_8N_2Se$: N, 11.3%. The compound was previously obtained by reacting sodium hypochlorite with N-phenylselenophenecarboxamidine hydroiodide [3], mp > 300°C.

1-Methyl-2-(2'-selenienyl)benzimidazole (II). A 2.47-g portion (10 mmole) of compound I is introduced into a solution of 1.12 g (20 mmole) of potassium hydroxide in 20 ml of etha-

TABLE 1. 1-Methyl-2-(5'-R-2'-Selenienyl)benzimidazoles

Compound	R	mp, deg C (from methanol)	Found, %			Empirical formula	Calculated, %			IR spectrum, cm^{-1} (CO)	Yield, %
			C	H	N		C	H	N		
II	H	85—86	55,6	4,2	10,6	$C_{12}H_{10}N_2Se$	55,2	3,9	10,7	—	81
V	NO_2	305—306 (DMFA)	47,4	3,2	13,9	$C_{12}H_9N_3O_2Se$	47,1	3,0	13,7	1360	100
VI	SO_3H	>330 (water)	42,5	3,2	8,3	$C_{12}H_{10}N_2O_3SSe$	42,2	2,9	8,2	1280	77
VII	Br	174—175	42,6	2,8	7,9	$C_{12}H_9BrN_2Se$	42,4	2,7	8,2	—	75
X	CH_2OH	187—188	53,2	4,3	9,9	$C_{13}H_{12}N_2OSe$	53,6	4,2	9,6	3220	31
XI	CHO	149—150	54,3	3,1	9,8	$C_{13}H_{10}N_2OSe$	54,0	3,5	9,7	1680	84
XII	$COCH_3$	191—192	55,7	4,2	9,4	$C_{14}H_{12}N_2OSe$	55,5	4,0	9,2	1670	29
XIII	COC_6H_5	201—202	62,1	4,1	7,6	$C_{19}H_{14}N_2OSe$	62,5	3,9	7,7	1680	81

TABLE 2. Proton-Magnetic-Resonance Spectra of 2-Hetarylbenzimidazoles

Compound	PMR spectrum, ppm (CF_3COOH)
II	3,8 (s, 3H, N—CH_3); 7,1 (t, 1H, 4'-H); 7,3 (m, 4H, arom.); 7,7 (d, 1H, 3'-H); 8,3 (d, 1H, 5'-H)
VII	3,8 (s, 3H, N—CH_3); 7,2 (d, 1H, 4'-H); 7,3 (m, 4H, arom.); 7,7 (d, 1H, 3'-H)
VIII	3,7 (s, 3H, N—CH_3); 7,2 (s, 1H, 4'-H); 7,3 (m, 4H, arom.)
IX	3,7 (s, 3H, N—CH_3); 7,1 (s, 1H, 4'-H); 7,3 (d, 2H, arom.); 7,5 (s, 1H, arom.)
XI	3,8 (s, 3H, N—CH_3); 7,3 (m, 4H, arom); 7,7 (d, 1H, 3'-H); 7,8 (d, 1H, 4'-H); 9,7 (s, 1H, CHO)
XII	2,3 (s, 3H, $COCH_3$); 3,9 (s, 3H, N—CH_3); 7,3 (m, 4H, arom.); 7,7 (d, 1H, 3'H); 7,6 (d, 1H, 4'-H)

nol. The mixture is given a dropwise addition of 5.68 g (40 mmole) of methyl iodide and stirred at room temperature for 6 h. The potassium iodide precipitated is filtered out, and the reaction product is isolated by adding water.

1-Methyl-2-(5'-nitro-2'-selenienyl)benzimidazole (V). A 5-g portion of nitric acid (d 1.5) is added at 0°C to 7.5 g of freshly distilled acetic anhydride at 0°C. Then 1.3 g (5 mmole) of compound II are introduced. The reaction mixture is stirred for 2 h at 0°C and 1 h at room temperature and diluted with 100 ml of water, and the yellow crystals are filtered out.

1-Methyl-2-(5'-sulfo-2'-selenienyl)benzimidazole (VI). A mixture of 1.3 g (5 mmole) of II, 0.98 g (10 mmole) of sulfuric acid (d 1.84), and 20 g of polyphosphoric acid is heated at 120°C for 3 h. The reaction mass is cooled and diluted with 50 ml of water, and the precipitated sulfonic acid is filtered out.

1-Methyl-2-(5'-bromo-2'-selenienyl)benzimidazole (VII). A solution of 0.8 g (5 mmole) of bromine in 10 ml of carbon tetrachloride is gradually added at room temperature to a solution of 1.3 g (5 mmole) of II in 20 ml of carbon tetrachloride. At the conclusion of the addition, the mixture is boiled for 30 min. The precipitate of VII is separated and converted into the base.

1-Methyl-2-(3',5'-dibromo-2'-selenienyl)benzimidazole (VIII). A solution of 1.3 g (5 mmole) of II in 20 ml of acetic acid is given an addition of 3.2 g (20 mmole) of bromine. The mixture is heated to boiling for 10 h. The reaction product is isolated in analogy to compound VII. The yield is 1.1 g (53%), and the mp 145-146°C (from ethanol). Found: Br, 38.5; N, 7.0%. Calculated for $C_{12}H_8Br_2N_2Se$: Br, 38.1; N, 6.7%.

1-Methyl-2(or 6)-bromo-2-(3',5'-dibromo-2'-selenienyl)benzimidazole (IX). A mixture of 1.3 g (5 mmole) of II with 3.2 g (20 mmole) of bromine in 20 g of polyphosphoric acid is stirred at 80-90°C for 10 h. The reaction mass is cooled, diluted with 75 m of water, and neutralized by an ammonium solution. The reaction product precipitated is separated. The yield is 1.4 g (55%), and the mp is 209-210°C (from ethanol). Found: C, 29.3; H, 1.6; Br, 47.9%. Calculated for $C_{12}H_7Br_3N_2Se$: C, 28.9; H, 1.4; Br, 48.1%.

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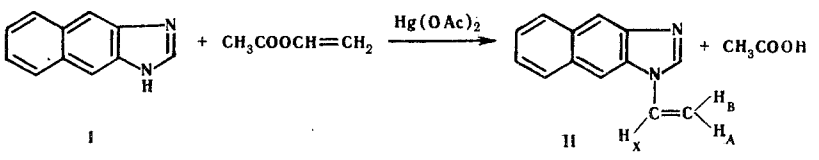
1-Vinylnaphtho[2,3-d]imidazole has been synthesized by reacting naphtho[2,3-d]-imidazole with vinyl acetate in the presence of mercuric acetate, as well as with acetylene under pressure in the presence of potassium hydroxide.

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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