3) Cyclohexanone oxime (25 g), 12.5 g of KOH, and 200 ml of DMSO were placed in a flask equipped with a stirrer, reflux condenser, thermometer, and bubbler, the mixture was heated with stirring to 90-95°C, and acetylene was admitted at atmospheric pressure for 4-5 h (until cyclohexanone oxime disappeared on the chromatogram). Standard workup gave 28.9 g (90%) of II.

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BEHAVIOR OF N-ALKOXYBENZIMIDZOLES WITH RESPECT TO NUCLEOPHILIC REAGENTS. ATTEMPTS TO SYNTHESIZE N-HYDROXY-2-AMINOBENZIMIDAZOLES

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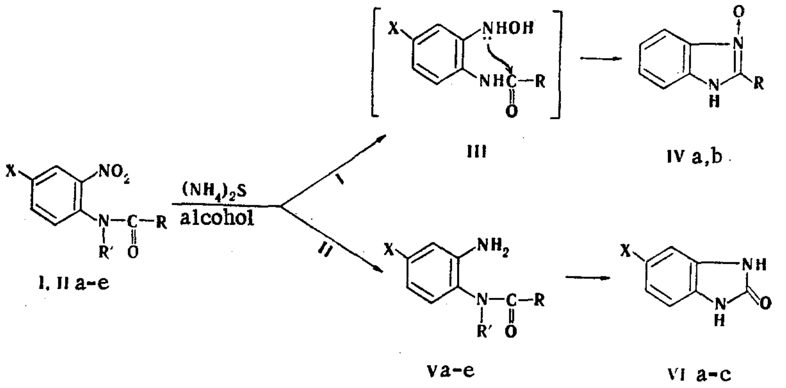
Various possibilities for the synthesis of N-hydroxy- and N-alkoxy derivatives of 2-aminobenzimidazoles — reductive cyclization of o-nitrophenylureas, the action of sodium amide on 1-alkoxybenzimidazoles, the ammonolysis of 1-alkoxy-2-iodobenzimidazoles, etc. — were investigated. Organometallic compounds of 1-alkoxybenzimidazoles were obtained for the first time, and their reactivities with respect to benzophenone, iodine, and 1-substituted benzimidazoles were studied. 2,2'-Dibenzimidazolyls that contain an alkoxy group in the 1 position were synthesized.

The present research was undertaken in order to synthesize N-oxides of 2-aminobenzimidazoles — a class of compounds that heretofore has not been described in the literature. Two approaches based on the cyclization of suitable o-phenylenediamine derivatives and on the direct incorporation of an amino group in N-hydroxybenzimidazoles were studied.



I R=H, Alk, Ar; R'=H; II **a** R=NH_2, X=H, R'=H; **b** R=NH_2, X=CH_3, R'=H; **c** R=NH_2, X=NO_2, R'=H; **d** R=NH_2, X=NO_2, R'=CH_3; **e** R=NH_2, X=CH_3, R'=CH_3; IV **a** R=H, Alk, Ar; **b** R=NH_2; V **a** X=H, R'=H, R=NH_2; **b** X=CH_3, R'=H, R=NH_2; **c** X=NH_2, R'=H, R=NH_2; **d** X=NH_2, R'=CH_3, R=NH_2; **e** X=CH_3, R'=CH_3, R=NH_2; VI **a** X=H; **b** X=CH_3; **c** X=NH_2

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It is known that the general method for the preparation of N-oxides of benzimidazole (IVa) is reduction of N-acyl derivatives of o-nitroaniline (I) with ammonium sulfide [1]; the N-hydroxyamino intermediates (III) undergo spontaneous cyclization to the final products.

We also developed a similar scheme for the synthesis of 2-aminobenzimidazole N-oxides (IVb), with the difference that we used o-nitrophenylureas (IIa-e) as the starting compounds instead of o-nitroaniline derivatives. Reduction of IIa-e with ammonium sulfide in alcohol gave high-melting colorless substances, which, according to the results of elementary analysis, IR spectral data, and the positive tests with a solution of $FeCl_3$ (red coloration), correspond to the desired 2-aminobenzimidazole N-oxides. However, it was found that the azomethines of the compounds obtained contain a carbonyl group, according to the IR spectroscopic data. This compelled us to assume that the products are actually o-aminophenylureas (V) rather than 2-aminobenzimidazole N-oxides. This assumption was confirmed by alternative synthesis of o-aminophenyl ureas V by the action of potassium cyanate on aqueous solutions of the corresponding o-phenylenediamines and their hydrochlorides. All of the properties of the compounds obtained by the two methods were identical. It is interesting to note that the two nitro groups are reduced immediately to give Vc in the case of the reaction of ammonium sulfide with IIc, although it is known that primarily the o-nitro group is reduced in 2,4-dinitroanilines under these conditions [2].

A characteristic feature of o-aminophenylureas is their easy conversion to benzimidazolones. This reaction takes place when they are heated in acids and alkalis and also during simple thermolysis. Compounds V initially melt with gas (ammonia) evolution, after which they solidify and remelt at the melting point of the corresponding benzimidazolone (VI).

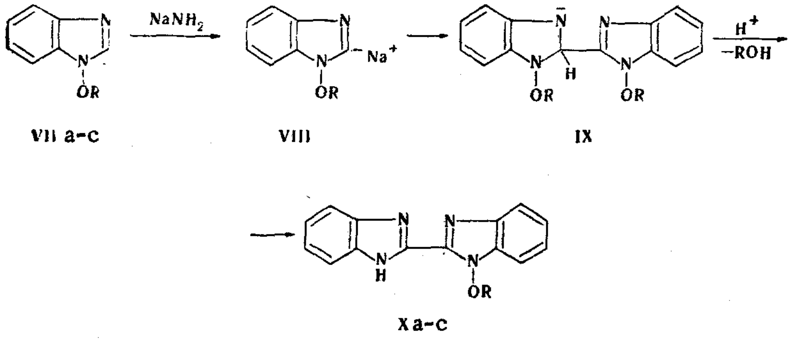
The failure to obtain 2-aminobenzimidazole N-oxides from o-nitrophenylureas is evidently explained by the low rate of intramolecular cyclization to the corresponding hydroxyaminophenylureas (III, R = NH_2), owing to which further reduction to an amino group occurs. In view of this, methods for the incorporation of an amino group in N-hydroxy- and N-alkoxybenzimidazoles were studied.

There are no indications in the literature [3] regarding the successful Chichibabin amination of heteroaromatic N-oxides. The attempts by various researchers to accomplish this reaction with N-oxides were probably unsuccessful. We also were unable to thoroughly aminate the N-oxides of 1-methyl-, 1-ethyl-, and 1-benzylbenzimidazoles with sodium or potassium amide in xylene, dimethylaniline, or liquid ammonia. In all cases we observed pronounced destruction of the N-oxides to give six to eight difficult-to-separate and unstable substances, and the reaction mixture had a strong isocyanide odor.

The reaction of 1-alkoxybenzimidazoles with metal amides proceeds in an interesting manner. As demonstrated by Takahashi and Kano [4], 1-ethoxybenzimidazole (VIIb) is converted to 1-ethoxy-2,2'-dibenzimidazolyl (Xb) by the action of $NaNH_2$ in dimethylaniline. We confirmed these results for VIIb and also extended them to 1-methoxy- and 1-benzyloxybenzimidazoles.

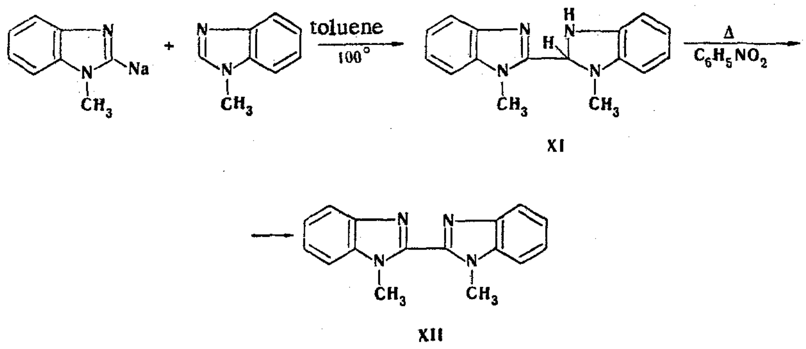
This reaction proceeds exothermically at room temperature in both dimethylaniline and xylene (however, it does not take place in liquid ammonia). Dimers X are formed in xylene in 60-80% yield. The yield of dimers is somewhat lower in dimethylaniline. The structures of dimers X are in good agreement with the data from the IR and PMR spectra. The PMR spectra contain signals of corresponding integral intensity of an NH group at 5.0 ppm (this signal vanishes after deuteration) and of an alkoxy group. An interesting feature of the PMR spectra of dimers X is a pronounced paramagnetic shift of the protons of the alkoxy group in trifluoroacetic acid. Thus the signal of a CH_2 group appears in the spectrum of Xc in d_5-pyridine at 5.6 ppm, whereas it appears at 3.7 ppm in CF_3COOH. In addition to a band of stretching vibrations of free NH groups at 3450 cm^{-1}, the IR spectra of the dimers in $CHCl_3$ solution contain a strong broad band at 2500-3300 cm^{-1}, which corresponds to associated NH groups and is evidently due to the formation of an intramolecular hydrogen bond. The spectra of crystalline samples of the dimers do not contain bands of free NH groups, and only a broad band at 2550-3300 cm^{-1} is present.

We assume that the mechanism of the dimerization includes the intermediate formation of 2-sodio compound VIII, which adds to the C=N bond of a molecule of the starting 1-alkoxybenzimidazole with subsequent aromatization of adduct IX by splitting out of a molecule of alcohol:



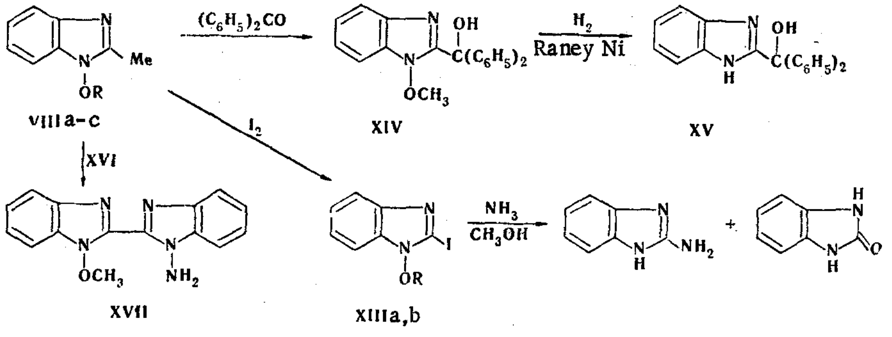
VII a $R{=}CH_3$; b $R{=}C_2H_5$; c $R{=}C_6H_5CH_2$; X a $R{=}CH_3$; b $R{=}C_2H_5$; c $R{=}C_6H_5CH_2$

In conformity with our assumption regarding the mechanism of dimerization we found that a genuine sample of 1-methoxy-2-sodiobenzimidazole (VIIIa) obtained by means of metallation gives dimer Xa in 80% yield when it is heated with 1-methoxybenzimidazole in toluene at 100°C. Since no examples of such dimerization in the imidazole series have been previously noted, we extended this reaction also to 1-methyl-2-sodiobenzimidazole. We found that the latter gives 2,3-dihydro-1,1'-dimethyl-2,2'-dibenzimidazolyl (XI) in 77% yield when it is heated with 1-methylbenzimidazole. Dihydro derivative XI was obtained in two forms – a low-melting form (mp 155°C) and a high-melting form (mp 208°C). Judging from the results of elementary analysis, the low-melting form is a crystal hydrate containing one molecule of water. Both forms are converted in quantitative yield to aromatized dimer XII when they are heated briefly in nitrobenzene. They have very similar IR and UV spectra; the only difference is that the ν_{NH} band at 3370 cm^{-1} in the spectrum of the crystal hydrate is somewhat broader and that residual absorption in the UV spectrum is observed up to 400 mm.



1-Alkoxybenzimidazoles also readily form organomagnesium compounds (VIIIb, c) under the influence of dibutylmagnesium. The latter were converted to 1-alkoxy-2-iodobenzimidazoles (XIII) by the action of iodine. Under the influence of benzophenone, metal derivatives VIII readily form carbinol XIV, which as a result of hydrogenolysis over Raney nickel, loses a methoxy group to give the previously described diphenyl-2-benzimidazolylcarbinol (XV).

In conclusion, we attempted to obtain 1-alkoxy-2-aminobenzimidazoles by means of direct amination of 1-alkoxy-2-iodobenzimidazoles XIII and organometallic compounds VIII. In addi-



VIII a $R{=}CH_3$, $Me{=}Na$; b $R{=}CH_3$, $Me{=}MgBr$; c $R{=}C_6H_5CH_2$, $Me{=}MgBr$; XIII a $R{=}CH_3$; b $R{=}C_6H_5CH_2$

TABLE 1. Synthesized II and V

Compound	mp, °C (from butanol)	$\nu_{C=O}$, cm^{-1} (mineral oil)	Found, %			Empirical formula	Calculated, %			Yield, % (after crystallization)
			C	H	N		C	H	N	
IIb	216—217	1670	48,7	4,2	22,1	$C_8H_9N_3O_3$	49,2	4,5	21,5	35
IId	181—182	1660	40,5	3,3	22,9	$C_8H_8N_4O_5$	40,0	3,4	23,3	30
IIe	134—135	1674	51,9	5,3	20,0	$C_9H_{11}N_3O_3$	51,8	5,3	20,1	33
Vb	286—287	1640	55,7	6,4	24,6	$C_8H_{11}N_3O \cdot {}^1/_2H_2O$	55,2	6,9	24,1	64
Vd	175—176	1640	48,4	6,9	32,2	$C_7H_{10}N_4O \cdot {}^1/_2H_2O$	48,0	6,3	32,0	23
Ve	175—176*	1650	55,1	7,2	21,4	$C_9H_{13}N_3O \cdot H_2O$	54,8	7,7	21,8	33

*From water.

tion to replacement of iodine by an amino group under the influence of a methanol solution of ammonia on VIIIa, we also observed splitting out of a methoxy group to give 2-aminobenzimidazole (67%) along with a small amount of benzimidazolone.

The electrophilic amination of 1-methoxy-2-sodiobenzimidazole (VIIIa) by means of O-mesitylenylsulfoxylhydroxylamine (XVI) in toluene gave a compound (in 36% yield), which, according to the results of elementary analysis and the IR and PMR spectral data, is N-aminated dimer XVII. A characteristic feature of all the 2,2'-dibenzimidazolyls is the very low intensity of the bands of the stretching vibrations of the aromatic C$\cdots$C and C$\cdots$N bonds at 1550-1650 cm^{-1}. This peculiarity is observed in the spectrum of XVII.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in methanol were measured with an SF-4a spectrophotometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

Compounds IIa and IIc were synthesized by the methods in [5, 6].

3-Nitro-4-ureidotoluene (IIb). A 169-ml (3.2 moles) sample of H_2SO_4 was added dropwise with stirring to a suspension of 90 g (0.6 mole) of p-tolylurea [7, 8] in 500 ml of CCl_4 as such a rate that the temperature of the reaction mixture did not rise above 40°C. The mixture was then cooled, and 30 ml of HNO_3 (sp. gr. 1.5) was added dropwise at such a rate that the temperature of the mixture did not rise above 0°C. After all of the HNO_3 had been added, the mixture was stirred with cooling for 30 min. The solvent and excess acid were decanted, and the residual oil was poured off in a fine stream into ice water with vigorous stirring. The resulting precipitate was removed by filtration, washed with water to pH 7, and triturated with acetone to give 41 g of IIb (see Table 1).

1-Methyl-1-(2',4'-dinitrophenyl)urea (IId). A 182-ml (3.4 moles) sample of concentrated H_2SO_4 was added with stirring in the course of 20-30 min to a suspension of 50.3 g (0.34 mole) of N-methyl-N-phenylurea [7, 9-11] in 150 ml of refluxing methylene chloride, after which the mixture was cooled to 0°C, and 31.5 ml of HNO_3 (sp. gr. 1.5) was added at such a rate that the temperature of the mixture did not rise above 7°C. After all of the HNO_3 had been added, the cooling bath was removed, and the temperature of the mixture was allowed to rise gradually to 22°C, at which temperature the mixture was allowed to stand for 30 min. The solvent was then removed by distillation, and the residue was poured in portions over finely crushed ice in such a way that the temperature did not rise above 20°C. The resulting precipitate was removed by filtration and was washed successively with water, a saturated solution of sodium bicarbonate, and water to pH 7. The yield was 24 g.

3-Nitro-4-(1'-methylureido)toluene (IIe). A 1.6-ml sample of HNO_3 (sp. gr. 1.5) was added dropwise to a mixture of 5 g (0.032 mole) of N-methyl-N-p-tolylurea [7], 9.1 ml (0.17 mole) of concentrated H_2SO_4, and 25 ml of methylene chloride at such a rate that the temperature did not rise above 7°C. The methylene chloride and acids were decanted, and the residue was treated with a saturated solution of sodium bicarbonate (up to pH 7). Benzene (25 ml) was added, and the precipitated IIe was removed by filtration. The yield was 2 g.

General Method for the Synthesis of Va-e. Alcohol (50 ml) saturated with ammonia at −20°C was added to a suspension of II (0.04 mole) in 100 ml of alcohol, after which a stream of H_2S was passed through the mixture until a red-brown solution formed. The solution was allowed to stand at room temperature for 24 h, after which it was evaporated to a volume of 75 ml, and the precipitated sulfur was removed by filtration. Removal of all of the solvent by distillation gave V.

General Method for the Synthesis of p-Nitrobenzylidene Derivatives of V. Hot alcohol solutions of the appropriate o-aminophenylureas V (4 mmole) and p-nitrobenzaldehyde (7 mmole) were mixed, three drops of 20% aqueous NaOH solution were added, and the mixture was refluxed for 1.5 h. The precipitated orange crystals of the azomethine were removed by filtration.

1-(p-Nitrobenzylideneamino)-2-ureidobenzene. This compound, with mp 185-186°C (dec., from butanol), was obtained in 53% yield. Found: C 58.8; H 4.1; N 19.6%. $C_{14}N_{12}N_4O_3$. Calculated: C 59.2; H 4.3; N 19.7%.

3-(p-Nitrobenzylideneamino)-4-ureidotoluene. This compound, with mp 322°C (dec., from DMF), was obtained in 66% yield. Found: C 57.8; H 4.0; N 19.8%. $C_{21}H_{16}N_6O_5$. Calculated: C 58.3; H 3.7; N 19.4%.

3-(p-Nitrobenzylideneamino)-4-ureidoaniline. This compound, with mp 200-201°C (dec., from butanol), was obtained in 40% yield. Found: C 58.8; H 5.3; N 17.9%. $C_{15}H_{14}N_4O_3 \cdot 1/2H_2O$. Calculated: C 58.6; H 4.9; N 18.2%.

Acid Hydrolysis of V. A mixture of 2 mmole of the appropriate o-aminophenylurea (V) and 6 ml of 5% HCl was refluxed for 2 h, and the precipitated benzimidazolone VI was removed by filtration and washed with water (to pH 7) to give the product in 74-77% yield. The melting points of the resulting benzimidazolones were in agreement with the data in [17], and no melting-point depressions were observed for mixtures with authentic samples.

Alkaline Hydrolysis of V. A mixture of 2 mmole of o-aminophenylurea V and 6 ml of 5% NaOH solution was refluxed for 1.5 h, after which it was acidified with concentrated HCl, and the corresponding benzimidazole VI was removed by filtration. The products were obtained in 50-74% yields. The alkaline hydrolysis of azomethine of o-aminophenylureas also gave benzimidazolone.

1-Alkoxybenzimidazoles (VII). 1-Methoxy- [1] and 1-ethoxybenzimidazoles were synthesized by the methods in [4].

1-Benzyloxybenzimidazole (VIIc). A mixture of 8.7 g (0.065 mole) of benzimidazole N-oxide, 2.6 g (0.065 mole) of NaOH, 3 ml of water, 80 ml of ethanol, and 8 ml (0.065 mole) of benzyl chloride was heated at 50°C for 3-4 h, after which the solution was evaporated, and VIIc was extracted from the residue with ether and purified by chromatography with a column filled with Al_2O_3 (elution with chloroform). The yield was 14.5 g (quantitative). The colorless oil had bp 195-200°C (3 mm). PMR spectrum (in CF_3COOH): 5.07 (2H, s, OCH_2-); 6.9 and 7.32 (9H, m); 8.15 ppm (1H, s, H_2). Found: C 75.2; H 5.3; N 12.4%. $C_{14}H_{12}N_2O$. Calculated: C 75.0; H 5.4; N 12.5%. The picrate was obtained as yellow crystals with mp 155-156°C (from acetic acid). Found: C 52.5; H 3.5; N 15.3%. $C_{14}H_{12}N_2O \cdot C_6H_3N_3O_7$. Calculated: C 53.0; H 3.3; N 15.4%.

General Method for the Reaction of 1-Alkoxybenzimidazoles with Sodium Amide. A 1.56-g (0.04 mole) sample of finely ground sodium amide was added to a solution of 0.02 mole of the appropriate 1-alkoxybenzimidazole in 20 ml of absolute xylene. Vigorous gas evolution (100 ml in 15-20 min) was observed at room temperature. After gas evolution had ceased, the mixture was heated at 100°C for 1 h, cooled and treated with 5 ml of water. The precipitated crystals of dimer X were removed by filtration, washed with ether, and triturated with petroleum ether. The product was purified by chromatography with a column filled with Al_2O_3 (elution with chloroform).

1-Methoxy-2,2'-dibenzimidazolyl (Xa). This compound was obtained as colorless crystals with mp 169-170°C (from aqueous alcohol). The yield was 2.12 g (80%). IR spectrum ($CHCl_3$): 3420 cm^{-1} (NH). PMR spectrum (in d_5-pyridine): 4.3 (3H, s, OCH_3); 4.95 (1H, m, N−H); 7.3 and 7.82 ppm (8H, m). Found: C 67.8; H 4.8; N 21.6%. $C_{15}H_{12}N_4O$. Calculated: C 68.2; H 4.6; N 21.2%.

1-Benzyloxy-2,2'-dibenzimidazolyl (Xc). This compound was obtained as colorless crystals with mp 152-153°C (from aqueous acetone). The yield was 60%. IR spectrum ($CHCl_3$): 3430 cm^{-1}

(NH). PMR spectrum (in d_5-pyridine): 5.02 (1H, m, NH); 5.62 (2H, s, O-CH_2–); 7.2 and 7.5 ppm (13H, m). Found: C 73.0; H 5.3; N 16.0%. $C_{22}H_{16}N_4O \cdot 1/2H_2O$. Calculated: C 72.5; H 4.9; N 16.4%.

Reaction of 1-Methoxy-2-sodiobenzimidazole with 1-Methoxybenzimidazole. A solution of 1.48 g (0.01 mole) of 1-methoxybenzimidazole in 3 ml of absolute toluene was added at −10 to −15°C to a suspension of 0.018 mole of phenylsodium [12] in 30 ml of absolute toluene, and the mixture was stirred for 1.5 h. Another 1.48 g (0.01 mole) of VIIa in 3 ml of absolute toluene was then added, and the mixture was stirred at 100°C for 3 h. It was then cooled, 30 ml of water, was added, and the mixture was filtered to give 0.6 g of 1-methoxy-2,2'-dibenzimidazolyl. The filtrate was treated with excess concentrated HCl, and the hydrochloric acid solution was separated, neutralized with ammonia, and extracted with chloroform to give an additional 1.5 g of dimer Xa. The overall yield of Xa was 2.1 g (80%). The colorless needles and mp 115°C (from aqueous alcohol). IR spectrum ($CHCl_3$): 3450 cm^{-1} (NH). PMR spectrum (in d_5-pyridine): 4.3 (3H, s, OCH_3); 4.95 (1H, m, N–H); 7.3 and 7.82 ppm (8H, m). Found: C 64.0; H 4.8; N 20.1%. $C_{22}H_{16}N_4O \cdot 1/2H_2O$. Calculated: C 63.8; H 5.0; N 20.0%.

Reaction of 1-Methyl-2-sodiobenzimidazole with 1-Methylbenzimidazole. A solution of 0.01 mole of 1-methylbenzimidazole in 3 ml of toluene was added in an atmosphere of dry nitrogen to a suspension of 0.01 mole of 1-methyl-2-sodiobenzimidazole in 15 ml of absolute toluene, and the mixture was heated at 100°C for 3 h. It was then cooled and treated with 15 ml of water, and the mixture was allowed to stand overnight in a refrigerator. Workup gave 0.9 g of yellowish crystals of 1,1'-dimethyl-2,3-dihydro-2,2'-dibenzimidazolyl (precipitate A) with mp 207°C (from benzene). UV spectrum, λ_{max} (log ε): 250 (4.2), 277 (3.97) , 302 nm (3.72) IR spectrum ($CHCl_3$): 3365 cm^{-1} (NH). Found: C 72.7; H 6.7; N 21.6%. $C_{16}H_{16}N_4$. Calculated: C 72.7; H 6.1; N 21.2%. Brief heating of XI in nibrobenzene gave 1,1'-dimethyl-2,2'-dibenzimidazolyl (XII), with mp 210°C (in agreement with the data in [13]), in quantitative yield.

The filtrate remaining after separation of precipitate A was evaporated in vacuo at room temperature, during which pink crystals of 1,1'-dimethyl-2,3-dihydro-2,2'-dibenzimidazolyl monohydrate, with mp 154-155°C (from alcohol), precipitated. The yield was 1.1 g. UV spectrum, λ_{max} (log ε): 250 (4.45), 277 (4.35), 287 (4.38), 303 (3.85), 353 (3.27), 385 (3.22) and 397 nm (3.08). IR spectrum ($CHCl_3$): 3370 cm^{-1} (NH). Found: C 68.2; H 6.4; N 20.4%. $C_{16}H_{16}N_4 \cdot H_2O$ Calculated: C 68.2; H 6.4; N 19.5%. The overall yield of the dimerization product was 77%.

Diphenyl(1-methoxy-2-benzimidazolyl)carbinol (XIV) and 1-Methoxy-2,2'-dibenzimidazolyl (Xa). A solution of 0.02 mole of benzophenone in 10 ml of toluene was added in an atmosphere of dry nitrogen to a suspension of 0.01 mole of 1-methoxy-2-sodiobenzimidazole in 15 ml of toluene, after which the temperature of the mixture was raised to room temperature, and 10 ml of water was added. The precipitated XIV was removed by filtration and washed with water to give colorless crystals with mp 182-183°C (from benzene) in 51% yield. Found: C 76.6; H 5.7; N 8.6%. $C_{21}N_{18}N_2O_2$. Calculated: 76.3; H 5.5; N 8.5%.

The filtrate after separation of XIV was treated with 10 ml of 20% hydrochloric acid, during which 1-methoxy-2,2'-dibenzimidazolyl hydrochloride precipitated; the latter is evidently formed in the step involving the production of the organosodium compound. The hydrochloride was converted to base Xa, with mp 171-172°C (from alcohol), by the action of 20% ammonium hydroxide.

Diphenyl(2-benzimidazolyl)carbinol (XV). A solution of 1.65 g (5 mmole) of XIV in 10 ml of methanol was subjected to hydrogenolysis over Raney nickel by the method in [4]. Workup gave 1 g (67%) of a product that was identical to the carbinol described in [14].

1-Methoxy-2-iodobenzimidazole (XIIIa). A solution of 2.96 g (0.02 mole) of VIIa in 5 ml of ether was added to a suspension of dibutylmagnesium [15] obtained from 1.3 g (0.054 mole) of powdered magnesium and 6 ml (0.057 mole) of n-butyl bromide in 50 ml of absolute ether and 10 ml of absolute dioxane, and the mixture was refluxed for 1 h. A solution of 10.24 g (0.04 mole) of iodine in 100 ml of ether was then added with vigorous stirring, 30 min after which, 10 ml of saturated solution of sodium bisulfite and 30 ml of water were added, and the ether layer was separated and treated with 20 ml of 20% hydrochloric acid. The precipitated hydrochloride was removed by filtration, washed with acetone, suspended in 30 ml of chloroform, and treated with 10 ml of concentrated NH_4OH. After extraction, the chloroform layer was separated, and the solvent was removed by evaporation to give white crystals of XIIIa with mp 133-134°C. The yield of XIIIa after crystallization from benzene was 1.5 g (30%). Found: C 34.7; H 2.9; I 45.8; N 9.8%. $C_8H_7IN_2O$. Calculated: C 34.8; H 3.3; I 46.0; N 10.2%.

1-Benzyloxy-2-iodobenzimidazole (XIIIb). Compound XIIIb was obtained in 46% yield by the method described above. The colorless crystals had mp 103-104°C (from acetone). Found: C 48.4; H 3.6; I 36.0; N 8.1%. $C_{14}H_{11}IN_2O$. Calculated: C 48.0; H 3.2; I 36.2; N 8.0%.

Ammonolysis of 1-Methoxy-2-iodobenzimidazole. Ammonolysis was carried out in an autoclave at 150-160°C for 40 h with a saturated (at −21°C) methanol solution of ammonia, after which the methanol was removed by distillation, and the residue was treated with 10 ml of a 10% solution of NH_4OH and extracted repeatedly with ethyl acetate. The ethyl acetate was removed by evaporation, and the residue was treated with a 10% solution of HCl. The benzimidazolone (in 7% yield) was removed by filtration, and the hydrochloric acid solution was made alkaline with concentrated NH_4OH and again extracted repeatedly with ethyl acetate. The yield of 2-aminobenzimidazole was 67%. It was identified by chromatography, IR spectroscopy, and a mixed-melting-point determination.

1-Methoxy-1'-amino-2,2'-dibenzimidazolyl (XVII). A solution of 0.03 mole of o-mesitylenylsulfonylamine (XVI) [16] in 40 ml of toluene was added in an atmosphere of dry nitrogen to a suspension of 0.01 mole of 1-methoxy-2-sodiobenzimidazole, obtained by the method indicated above, and the mixture was stirred at 0°C for 20 min and at room temperature for 1 h. Water (30 ml) was added, the toluene solution was separated, and the aqueous layer was extracted with 50 ml of concentrated HCl to give 0.5 g (36%) of XVII as colorless needles with mp 184-185°C (from alcohol). IR spectrum ($CHCl_3$): 3060, 3150, and 3340 cm^{-1} ($N-NH_2$). PMR spectrum (in d_5-pyridine): 4.27 (3H, s, OCH_3); 4.92 (2H, s, $N-NH_2$); 7.20 and 7.88 ppm (8H, m).

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