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2-AMINO-3-(BENZIMIDAZOL-2-YL)BENZO[b]FURANS

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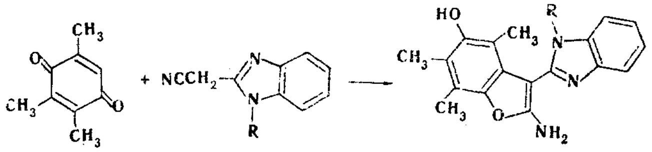
The corresponding 2-amino-3-(benzimidazol-2-yl)benzo[b]furans were obtained by reaction of 2,3,5-trimethyl-1,4-benzoquinone with 2-cyanomethylbenzimidazoles. It is shown that new benzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazole polynuclear heterocyclic systems (bases and quaternary salts) are formed in the reaction of these products with acylating agents.

We have previously shown that the corresponding 2-amino-3-(benzimidazol-2-yl)benzo[b]furan is formed in the reaction of 2-methyl-5-isopropyl-1,4-benzoquinone with 2-cyanomethylbenzimidazole (IIa) [1]. During a study of the general character of this reaction we found that 2,3,5-trimethyl-1,4-benzoquinone (I) reacts similarly with nitrile IIa to give 2-amino-3-(benzimidazol-2-yl)-5-hydroxy-4,6,7-trimethylbenzo[b]furan (IIIa). It is interesting that the compound forms a monosolvate with dimethylformamide (DMF), in which form it was also isolated from the reaction mixture. This is confirmed by the results of elementary analysis and the PMR spectrum, in which signals of the exchanged protons of amino and hydroxy groups at 6.85 ppm, signals of five methyl groups at 2.18-2.87 ppm, a multiplet of aromatic protons of the benzimidazole ring (7.27 ppm), and a singlet of the CH proton of DMF at 7.89 ppm are observed. A band of a keto group at 1658 cm^{-1} is present in the IR spectrum of IIIa. The complex does not decompose when it is recrystallized or heated in vacuo, and derivatives of the previously described [1] benzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazole system (IV) (Table 1) are formed and decomposition of the solvate is observed only when it is treated with acylating agents (acid anhydrides and chlorides and ortho esters).



I IIa,b IIIa,b

II, IIIa R=H; b R=CH_3

Benzoquinone I also reacts with 1-methyl-2-cyanomethylbenzimidazole (IIb) to give N-methyl derivative IIIb. The properties of IIIb differ from those of unsubstituted analog IIIa. In particular, acetic anhydride acylates only the amino and hydroxy groups of IIIb to give the corresponding V. Whereas the IR spectrum of IVb does not contain absorption above

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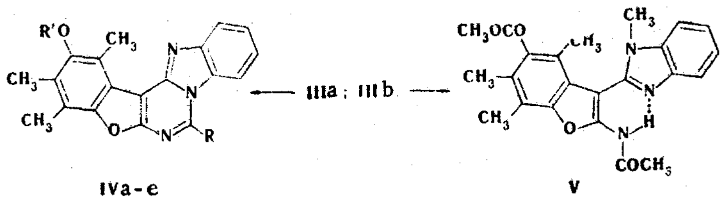
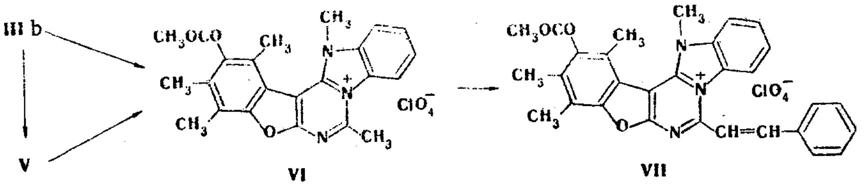


IVa-e V

IV a R=R'=H; b R=CH_3, R'=$COCH_3$, c R=C_2H_5, R'=COC_2H_5; d R=n-C_3H_7, R'=n-COC_3H_7; e R=C_6H_5, R'=COC_6H_5

3000 cm^{-1}, and the absorption band of only one ester group (CH_3COO) at 1750 cm^{-1} is observed, the IR spectrum of V is characterized by the presence of absorption bands of both ester and amide carbonyl groups at 1745 and 1698 cm^{-1}, respectively. The somewhat elevated value of the latter can be ascribed to chelation of the hydrogen atom of the NH group by the benzimidazole heteroatom. This is also confirmed by the shift of the NH band of V to 3050-3120 cm^{-1}.

The absence of a hydrogen atom attached to the nitrogen atom of the benzimidazole ring makes it impossible for amide V to undergo cyclization. The necessary conditions are realized by the addition of a strong acid to V. Thus cyclization accompanied by splitting out of water and the formation of perchlorate VI occurs when V is refluxed in acetic anhydride in the presence of $HClO_4$; the band of an amide carbonyl group vanishes in the IR spectrum of VI, whereas the band at 1750 cm^{-1} is retained in this case. Compound VI can be obtained by treatment of amine IIIb with a mixture of acetic anhydride with perchloric acid, but the yield is lower (up to 20%). Another confirmation of the polycyclic structure of product VI is the presence of an active methyl group in the 6 position of the heteroring, which is also conjugated with the quaternary nitrogen atom. Dye VII is formed in the reaction of salt VI with p-dimethylaminobenzaldehyde. The relatively low wavelength of its color [λ_{max} (log ε) = 520 nm (4.45)] makes it possible to assume that of all of the mesomeric structures, structure VII with the shortest chromophore makes the greatest contribution.



VI VII

EXPERIMENTAL

The PMR spectrum of a 0.2 M solution of IIIa in $(CD_3)_2CO$ was recorded with a Tesla BS-478B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of KBR pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectrum of a solution of VII in DMF was recorded with an SF-10 spectrophotometer.

2-Amino-3-(benzimidazol-2-yl)-5-hydroxy-4,6,7-trimethylbenzo[b]furan (IIIa). A 1-ml sample of piperidine was added with stirring to a mixture of 7.5 g (0.05 mole) of I and 7.85 g (0.05 mole) of IIa in 8 ml of DMF, and the mixture was allowed to stand overnight at 20°C. The resulting crystals were removed by filtration and washed with toluene and isopropyl

TABLE 1. Physical Constants of IV

Compound	mp, °C	IR spectrum, ν_{OR}'', cm^{-1}	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
IVa	>300[a]	3210	72,1	4,9	13,1	$C_{19}H_{15}N_3O_2$	71,9	4,7	13,2	98
IVb	300—301[b]	1750	70,8	5,3	11,3	$C_{22}H_{19}N_3O_3$	70,8	5,1	11,3	98
IVc	266—267[b]	1745	71,9	5,7	10,6	$C_{24}H_{23}N_3O_3$	71,8	5,7	10,5	87
IVd	235—236[b]	1735	72,6	6,2	9,7	$C_{26}H_{27}N_3O_3$	72,7	6,3	9,8	97
IVe	>300[a]	1720	76,9	4,8	8,6	$C_{32}H_{23}N_3O_3$	77,3	4,6	8,4	96

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[a] From dimethylformamide. [b] From chlorobenzene.

alcohol to give 12.25 g (64.5%) of IIIa (in the form of a monosolvate with DMF). The white crystalline powder had mp 215-216°C (dec., from propanol). Found, %: C 66.3; H 6.5; N 14.7. $C_{18}H_{17}N_3O_2\cdot C_3H_7NO$. Calculated, %: C 66.3; H 6.3; N 14.7.

2-Amino-3-(1-methylbenzimidazol-2-yl)-5-hydroxy-4,6,7-trimethylbenzo[b]furan (IIIb). A 1.2-ml sample of piperidine was added with stirring and cooling to a mixture of 2 g (0.013 mole) of I and 2.3 g (0.013 mole) of IIb in 2.5 ml of DMF, and the mixture was maintained at 20°C for 3 days. The resulting IIIb was removed by filtration and washed with propanol and ether to give 2.61 g (61%) of a white crystalline product with mp 230-231°C (from propanol). IR spectrum: 3455 (OH) and 3360 cm^{-1} (NH_2). Found, %: C 70.7; H 6.1; N 13.0. $C_{19}H_{19}N_3O_2$. Calculated, %: C 71.0; H 5.9; N 13.1.

3-Hydroxy-1,2,4-trimethylbenzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazole (IVa). One drop of concentrated sulfuric acid was added to a mixture of 1 g (3 mmole) of IIIa and 5 ml (0.03 mole) of ethyl orthoformate, and the mixture was refluxed for 10 min. The product was then removed by filtration and washed with alcohol to give a white crystalline powder. The yields, physical constants, and results of elementary analysis of IV are presented in Table 1.

3-Acetoxyl-1,2,4,11-tetramethylbenzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazole (IVb). A mixture of 2 g (5 mmole) of IIIa, 4 ml (0.04 mole) of acetic anhydride, and 4 ml of pyridine was refluxed for 1 h, and the product was removed by filtration and washed with isopropyl alcohol to give white needles.

3-Propionyloxy-1,2,4-trimethyl-11-ethylbenzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazole (IVc). This compound was similarly obtained as a white crystalline powder from 1 g (3 mmole) of IIIa and 2 ml (0.02 mole) of propionic anhydride in 2 ml of pyridine.

3-Butyryloxy-1,2,4-trimethyl-11-propylbenzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazole (IVd). This compound was similarly obtained as slightly yellowish needles from 1 g (3 mmole) of IIIa and 2 ml (0.01 mole) of butyric anhydride in 2 ml of pyridine.

3-Benzoxy-1,2,4-trimethyl-11-phenylbenzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazole (IVe). A 0.8-ml (7 mmole) sample of benzoyl chloride was added gradually with stirring to a solution of 0.4 g (1 mmole) of IIIa in 4 ml of pyridine, and the mixture was maintained at 20°C for 1 h. Water (15 ml) and 8 ml of 25% ammonium hydroxide was added, and the product that formed after 0.5 h was removed by filtration and washed with water and methanol to give a slightly yellowish crystalline powder.

2-Acetamido-5-acetoxy-3-(1-methylbenzimidazol-2-yl)-4,6,7-trimethylbenzo[b]furan (V). A solution of 0.8 g (2 mmole) of IIIb in 5 ml (0.05 mole) of acetic anhydride and 5 ml of pyridine was maintained at 20°C for 24 h, after which it was decomposed with excess water. The resulting oil crystallized on standing. The product was removed by filtration and washed with water to give 0.92 g (91.4%) of a white crystalline powder with mp 279-280°C. (From ethanol). Found, %: C 68.2; H. 5.7; N 10.3. $C_{23}H_{23}N_3O_4$. Calculated, %: C 68.2; H 5.7; N 10.4.

3-Acetoxy-1,2,4,5,11-pentamethylbenzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazolium Perchlorate (VI). A solution of 0.2 g (0.5 mmole) of V and 0.08 ml (0.5 mmole) of 70% $HClO_4$ in 2 ml of acetic anhydride was refluxed for 5 h, after which product was removed by filtration and washed with acetone and methanol to give 0.18 g (74.7%) of VI. The product was isolated from the reaction mixture in analytically pure form. The white crystalline product melted above 300°C. Found, %: C 56.7; H 4.5; N 8.6. $C_{23}H_{22}N_3O_7Cl$. Calculated, %: C 56.6; H 4.5; N 8.6.

3-Acetoxy-1,2,4,5-tetramethyl-11-(4'-dimethylaminostyryl)benzo[b]furo[2',3':4,5]pyrimido[1,6-a]benzimidazolium Perchlorate (VII). A mixture of 0.15 g (0.3 mmole) of VI and 0.06 g (0.4 mmole) of p-dimethylaminobenzaldehyde in 2 ml of acetic anhydride was refluxed for 7 h, after which it was cooled, and the product was removed by filtration and washed with acetone and methanol to give 0.13 g (69.3%) of a dark-red crystalline powder with mp > 300°C (from acetic anhydride). IR spectrum: 1755 cm^{-1} ($OCOCH_3$). Found, %: C 62.2; H 5.4. $C_{32}H_{31}N_4O_7Cl$. Calculated, %: C 62.1; H 5.0.

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