REFERENCES

1. Hideji Takamatsu, Shinsaku Minami, Akio Fujita, Katsuro Fujimoto, Masanao Shimizu, and Yoshiyuki Takase, C. A., **62**, 9, 10443a, 1965.
2. P. M. G. Bavin, J. Med. Chem., **9**, 788, 1966.
3. F. T. Pozharskii, V. Ts. Bukhaeva, and A. M. Simonov, KhGS [Chemistry of Heterocyclic Compounds], **3**, 910, 1967.

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BROMINE MOBILITY IN 2-ACETYL-3-BROMOFURAN

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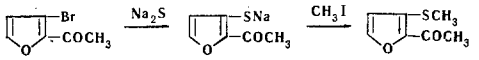
UDC 547.722.4.724:543.422.4

In preceding papers it was shown that the halogen atoms in the α-position of disubstituted furan derivatives readily undergo a nucleophilic substitution reaction with sodium sulfide [1], sodium thiosulfate [2], and mercaptides [3]. The mobility of the halogen atom in the β position of the furan ring has been studied only for monosubstituted halofurans. The investigations showed that halogen in the β position of furan is not active in substitution reactions.

Continuing investigations on the mobility of halogen in a furan ring, we have studied the substitution of the bromine in 2-acetyl-3-bromofuran (I) with sodium sulfide. The reaction takes place readily under conditions analogous for the replacement of the bromine in 5-acetyl-2-bromofuran:



Without being isolated, the resulting sodium salt of 2-acetyl-3-mercaptofuran was converted with methyl iodide into 2-acetyl-3-methylthiofuran (II), the structure of which was confirmed by its IR spectrum and the preparation of its oxime.

2-Acetyl-3-methylthiofuran (II). A mixture of 18.9 g of **I**, 24 g of sodium sulfide, and 100 ml of water was boiled for 4 hr. The dark solution formed was filtered and boiled for another 3 hr with 16 g of methyl iodide. The **II** that separated out was extracted with ether and crystallized from aqueous ethanol. Yield 46%. Mp 54° C. Found, %: C 53.36; H 5.03. Calculated for $C_7H_8O_2S$, %: C 53.44; H 5.13. **Oxime of II.** Mp 65.6–66° C. Found, %: N 8.01. Calculated for $C_7H_9NO_2S$, %: N 8.18.

REFERENCES

1. Z. N. Nazarova and Yu. A. Babaev, ZhOKh, **34**, 4010, 1964.
2. Z. N. Nazarova and G. F. Potemkin, ZhOKh, **34**, 157, 1964.
3. L. A. Boiko, Yu. A. Boiko, and Z. N. Nazarova, KhGS [Chemistry of Heterocyclic Compounds], **5**, 1969 (in press).

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OPENING OF THE IMIDAZOLE RING IN IMIDAZO[1,2-a]BENZIMIDAZOLES

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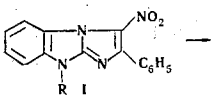
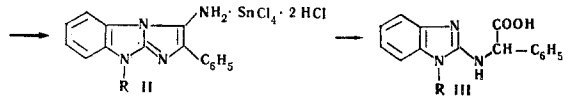
Reduction of 9-methyl-3-nitro-2-phenylimidazo[1,2-a]benzimidazole (**Ia**) [1] with stannous chloride leads to a complex of a tin salt and the amine (**IIa**) from which it is impossible to liberate the free amine. We have established that boiling the complex with highly dilute alcohol causes the opening of the imidazole ring attached to the benzimidazole nucleus at the bond 3-4 with the formation of 2-(α-carboxybenzylamino)-1-methylbenzimidazole (**IIIa**), which separated from the reaction mixture in the form of the hydrochloride with a yield of 94%. Similar conversions are observed for the 9-benzyl derivative (**Ib**) also. Thus, in present case the imidazole ring opens in a different manner from that in the molecule of 9-methyl-2-phenylimidazo[1,2-a]benzimidazole methiodide, where the C=N bond at the "guanidine" carbon atom is cleaved.





I-III a $R=CH_3$; b $R=C_6H_5CH_2$

The structure of III was shown by means of a series of reactions (methylation with diazomethane, decarboxylation, conversion into the 2,2'-azo derivative of benzimidazole under the action of sodium hypochlorite [2]) and was confirmed by IR spectra. The spectrum of the methyl ester of **IIIa** has the band of carbonyl absorption (1739 cm^{-1}) in the spectrum of free **IIIa** this is strongly shifted in the low-frequency direction (1655 and 1352 cm^{-1}), which shows the possibility of a betaine structure [3].

2-(α-Carboxybenzylamino)-1-methylbenzimidazole (IIIa). Small needles with mp 220° C (decomp., water), soluble in dilute alkalies and DMFA. Found, %: C 68.12; H 5.32; N 15.05. Calculated for $C_{16}H_{15}N_3O_2$, %: C 68.31; H 5.38; N 14.94. **Methyl ester of IIIa.** Needles with mp 150–151° C. Found, %: C 68.94; H 5.52; N 14.40. Calculated for $C_{17}H_{17}N_3O_2$, %: C 69.14; H 5.80; N 14.23.

2-(α-Carboxybenzylamino-2-benzylbenzimidazole (IIIb). Mp 246° C((DMFA and water). Found, %: C 73.68; H 5.60; N 11.83. Calculated for $C_{22}H_{19}N_3O_2$, %: C 73.93; H 5.36; N 11.76. **Methyl ester of IIIb.** Mp 166–167° C (from butanol). Found, %: C 74.48; H 5.80; N 11.47. Calculated for $C_{23}H_{21}N_3O_2$, %: C 74.36; H 5.70; N 11.32.

REFERENCES

1. A. M. Simonov and V. A. Anisimova, KhGS [Chemistry of Heterocyclic Compounds], **4**, 1102, 1968.

2. A. F. Pozharskii, E. A. Zvezdina, and A. M. Simonov, KhGS [Chemistry of Heterocyclic Compounds], **3**, 185, 1967.

3. S. Takahashi and H. Kano, J. Org. Chem., **30**, 1118, 1965.

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Rostov-on-Don State University

SYNTHESIS OF ALKYL-SUBSTITUTED PORPHYRINOGENS

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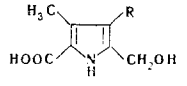
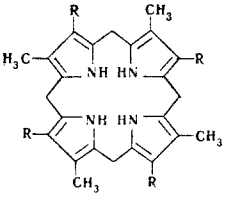
Porphyrinogens are hexahydroporphyrins in which the four pyrrole rings are connected by methylene bridges. They are intermediate in the biosynthesis of heme and chlorophyll [1, 2]. One of the methods of synthesis of the simple porphyrins with alkyl substituents, in broad outline analogous to the polymerization of porphobilinogen, is the condensation in an acid medium of 5-carboxy-2-hydroxymethylpyrroles [3]. We have shown that the heating of the pyrroles **I** and **II** in the dark at 50–60° C in a mixture of methanol and acetic acid for 15–20 min and in methanol with a small amount of HCl, HBr, or CF_3COOH for 1.5–2 min in an atmosphere of argon, leads to the porphyrinogens **III** and **IV** respectively, which are isolated from the solution in the form of large faintly colored prismatic needles. Octamethylporphyrinogen (yield 57%) does not melt below 250° C and is sparingly soluble in organic solvents. Found, %: C 78.32; H 8.80; N 13.35. Calculated for $C_{28}H_{36}N_4$, %: C 78.50; H 8.41; N 13.09. Etioporphyrinogen (yield 92%) decomposes on being heated above 100° C. Found, %: C 79.21; H 9.38; N 11.80. Calculated for $C_{32}H_{44}N_4$, %: C 79.33; H 9.1; N 11.57.



I $R=CH_3$; II $R=C_2H_5$



III $R=CH_3$; IV $R=C_2H_5$

In the crystalline state, the porphyrinogens are stable in the air for several days, and in ethanolic solution in the dark they do not decompose nor undergo transition into porphyrins during several hours. By the photooxidation of the porphyrinogens in various solvents and using metal acetates, we have obtained porphyrins and the corresponding metal complexes with high yields.

REFERENCES

1. D. Mauzerall and S. Granick, J. Biol. Chem., **232**, 1141, 1958.

2. D. Mauzerall, J. Am. Chem. Soc., **82**, 2601, 1960.

3. W. Siedel and F. Winkler, Ann., **554**, 162, 1943.

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