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## BROMINE MOBILITY IN 2-ACETYL-3-BROMOFURAN

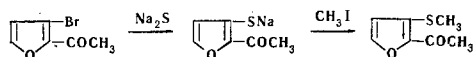
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In preceding papers it was shown that the halogen atoms in the  $\alpha$ -position of disubstituted furan derivatives readily undergo a nucleophilic substitution reaction with sodium sulfide [1], sodium thiosulfate [2], and mercaptides [3]. The mobility of the halogen atom in the  $\beta$  position of the furan ring has been studied only for monosubstituted halofurans. The investigations showed that halogen in the  $\beta$  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  $\text{C}_7\text{H}_8\text{O}_2\text{S}$ , %: C 53.44; H 5.13. **Oxime of II.** Mp 65.6–66° C. Found, %: N 8.01. Calculated for  $\text{C}_7\text{H}_9\text{NO}_2\text{S}$ , %: N 8.18.

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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-( $\alpha$ -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.

