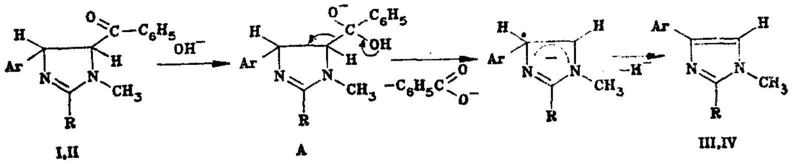
AROMATIZATION OF 1-METHYL-5-BENZOYL-2-IMIDAZOLINES TO IMIDAZOLES BY TREATMENT WITH ALCOHOLIC ALKALI

I. G. Tishchenko, O. N. Bubel',
and V. A. Konovalov

UDC 547.783.04

We have found that the readily-accessible 1-methyl-2-methyl(methylthio)-4-p-bromophenyl-5-benzoyl-2-imidazolines (I, II) [1] are converted on keeping in aqueous alcoholic caustic alkali for 3-4 days at room temperature into 1-methyl-2-methyl(methythio)-4-p-bromophenylimidazoles (III, IV).



I, III Ar=C_6H_4Br-p, R=CH_3; II, IV Ar=C_6H_4Br-p, R=SCH_3

In addition to the imidazoles (III) and (IV), potassium benzoate was also isolated from the reaction mixture.

It is likely that the leaving group in this reaction is either the benzoate anion, or benzaldehyde, which then disproportionates to benzyl alcohol and potassium benzoate. However, TLC and GLC failed to reveal the presence of either benzyl alcohol or of benzaldehyde in the reaction mixture during the course of the reaction. Furthermore, the amount of potassium benzoate formed was equimolar with the amounts of (III) and (IV) formed. It is therefore assumed that the leaving group is the benzoate anion. An ionic mechanism is therefore most likely for this reaction, involving the initial formation of the carbanion A, followed by cleavage of the benzoate anion and elimination of hydride ion in the presence of atmospheric oxygen. An ion-radical mechanism is, however, also possible.

The PMR spectra of the imidazoles (III) and (IV) contained signals for protons at 3.45 and 3.38 (s, 3H, N–CH_3), 2.20 (s, 3H, 2-CH_3), and 2.53 (s, 3H, S–CH_3), 6.97 and 6.90 (s, 1H, 5-H), 7.26-7.53 and 7.28-7.50 ppm (two d, arom. 4H, J = 8 Hz) respectively. The IR and mass spectra also supported the structures assigned to (III) and (IV), and the elemental analyses were in agreement with the calculated values.

To a solution of 0.02 mole of the 2-methyl-2-imidazolines (I) or 0.02 mole of the 2-methylthio-2-imidazole (II) in 100 ml of methanol was added a solution of 2.2 g (0.04 mole) of potassium hydroxide in 20 ml of water. The mixture was shaken and kept at room temperature for 60-80 h. The methanol was distilled off at reduced pressure, and the residue extracted with methylene chloride, dried over potassium carbonate, filtered, and the filtrate evaporated to give (III) [mp 157°C (ether–acetone), yield 86%], and (IV) [mp 93°C (ether–hexane), yield 71%].

LITERATURE CITED

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V. I. Lenin Belorussian State University, Minsk 220080, and the A. N. Sevchenko Research Institute for Problems in Applied Physics, Minsk 220106. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1570-1571, November, 1985. Original article submitted February 18, 1985.

0009-3122/85/2111-1296$09.50