SYNTHESES OF 1-METHYLIMIDAZOLE-4 & 5-CARBOXYLIC ACIDS AND THEIR DERIVATIVES

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Methylation at 1-position of imidazole-4(5)-carbanilide and methyl imidazole-4(5)-carboxylate was investigated on their reaction with methyl iodide, diazomethane and dimethyl sulfate in methanol, respectively. In case of the anilide as the substrate, it was converted exclusively to 1-methylimidazole-4-carbanilide, whereas the methyl ester gave methyl 1-methylimidazole-5-carboxylate except the case with methyl iodide which resulted in a mixture of 4-methyl ester and 5-methyl ester. Particularly the methylation of the methyl ester with diazomethane gave 5-methyl ester in a good yield. Such difference is discussed on the reaction mechanism.

Alternative path to prepare the derivatives of 1-methylimidazole-4 and 5-carboxylic acids was studied. While decarboxylation of 1-methylimidazole-4,5-dicarboxylic acid in boiling aniline gave 1-methylimidazole-4-carbanilide, the treatment of the same dicarboxylic acid in hot acetic anhydride was found to decarboxylate, resulting in 1-methylimidazole-5-carboxylic acid in an excellent yield. This selectivity is discussed on the basis of the adjacent chage effect.