CHARACTERISTIC FEATURES OF DIAZOTIZATION OF 5,4- AND 4,5-AMINONITROPYRAZOLES AND REDUCTION OF 5-ARYLAZO-1-METHYL-4-NITROPYRAZOLES

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It is known that in several cases, the behavior of 4,5-disubstituted 1-methylpyrazoles in chemical reactions differs sharply from the 4,3-isomers: in contrast to 3-halo-4-nitropyrazoles, 5-halo-1-methyl-4-nitropyrazoles react with nucleophiles under fairly mild conditions [1], 4-bromo-1-methyl-3-nitropyrazole-5-carboxylic acid decarboxylates on heating in aqueous ammonia [2], and nitrodecarboxylates under nitration conditions [3].

We found new characteristic features of the course of the reactions of 4,5-disubstituted 1-methylpyrazole. In the diazotization of 5-amino-1,3-dimethyl-4-nitropyrazole (I) in hydrochloric acid, the diazo group is rapidly replaced by chlorine to form 1,3-dimethyl-4-nitro-5-chloropyrazole (II), while 5-bromo-1,3-dimethyl-4-nitropyrazole (III) is obtained in hydrobromic acid. Under similar conditions, 3-amino-1,5-dimethyl-4-nitropyrazole is diazotized without any complications. When the diazotization of aminonitrophrazole I was carried out in hydrochloric acid in the presence of an equimolar amount of phenol, 1,3-dimethyl-4-nitro-5-(4-hydroxyphenylazo)pyrazole (IV) was obtained. When this is reduced by sodium hydrosulfite, it is not the nitro group but the azo group that is reduced with the formation of compound I and p-aminophenol. Under the similar conditions, the benzene analog of compound IV, 2-(4-hydroxyphenylazo)nitrobenzene is converted into 2-(4-hydroxyphenyl)-2H-benzotriazole N-oxide.

In the diazotization of 4-amino-1-methyl-5-nitropyrazole (V) in hydrochloric acid, in the diazo compound synthesized the nitro group is replaced by chlorine atom, and on subsequent combination with phenol in an alkaline medium, only 1-methyl-4-(4-hydroxyphenylazo)-5-chloropyrazole (VI) is formed. Compound II: yield 70%, mp 65-66°C (from isopropanol); PMR spectrum (DMSO-D_6): 2.38 (3H, s, 3-CH_3), 3.76 ppm (3H, s, 1-CH_3). Compound III was obtained in a 39% yield, and was identified by comparison with an authentic sample. Compound IV: yield 80%, mp 199-201°C; PMR spectrum (DMSO-D_6): 2.32 (3H,s, 3-CH_3); 3.78 (3H, s, 1-CH_3); 6.78-7.22 (4H, m, C_6H_4); 10.8 ppm (1H, s, OH). Compound VI: yield 98%, mp 213-215°C; mass spectrum: M^+ 236, 238; PMR spectrum (DMSO-D_6): 3.81 (3H, s, 1-CH_3); 6.88-7.64 (4H, m, C_6H_4); 7.80 ppm (1H, s, 3-H). Data of elemental analysis correspond to the calculated values.

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