

ARYL REARRANGEMENT OF 4-AROYL-1H-PYRAZOLO[3,4-d]PYRIMIDINES

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When a solution of 4-aryl-1-phenyl-1H-pyrazolo[3,4-d]pyrimidines (1) and aqueous sodium hydroxide in dimethyl sulfoxide (DMSO) was allowed to stir for few hours at room-temperature, rearrangement of aryl group to the 4-position occurred, resulting 4-aryl-4,5-dihydro-1-phenyl-1H-pyrazolo[3,4-d]pyrimidine-4-carboxylic acids (2) in good yields.

Thus, 4-benzoyl- (1-1), 4-(p-methoxybenzoyl)- (1-2), and 4-(p-bromobenzoyl)-1-phenyl-1H-pyrazolo[3,4-d]pyrimidines (1-3) gave the corresponding 4-phenyl- (2-1), 4-(p-methoxyphenyl)- (2-2), and 4-(p-bromophenyl)-4,5-dihydro-1-phenyl-1H-pyrazolo[3,4-d]pyrimidine-4-carboxylic acids (2-3), respectively. But p-nitrobenzoyl derivative (1-4) did not give the corresponding carboxylic acid (2-4), and resulted in the formation of 4-(p-nitrophenyl)-1-phenyl-1H-pyrazolo[3,4-d]pyrimidine (3-4) in 22 % yield with 6-anilino-4-(p-nitrophenyl)-5-pyrimidinecarbonitrile (4-4) which was formed by ring fission of pyrazole ring of the resulting 3-4.

Potassium ferricyanide oxidized the carboxylic acids (2-1 to 2-3), thus obtained, to the corresponding 4-aryl-1-phenyl-1H-pyrazolo[3,4-d]pyrimidines (3-1 to 3-3) in high yields with elimination of carbon dioxide.

Mechanism for the rearrangement of aryl group in 1, similar to that for benzilic acid rearrangement, is proposed.

