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NOVEL VARIANT OF RECYCLIZATION OF N-ARYLMALEIMIDES WHEN REACTED WITH AMINOAZOLES

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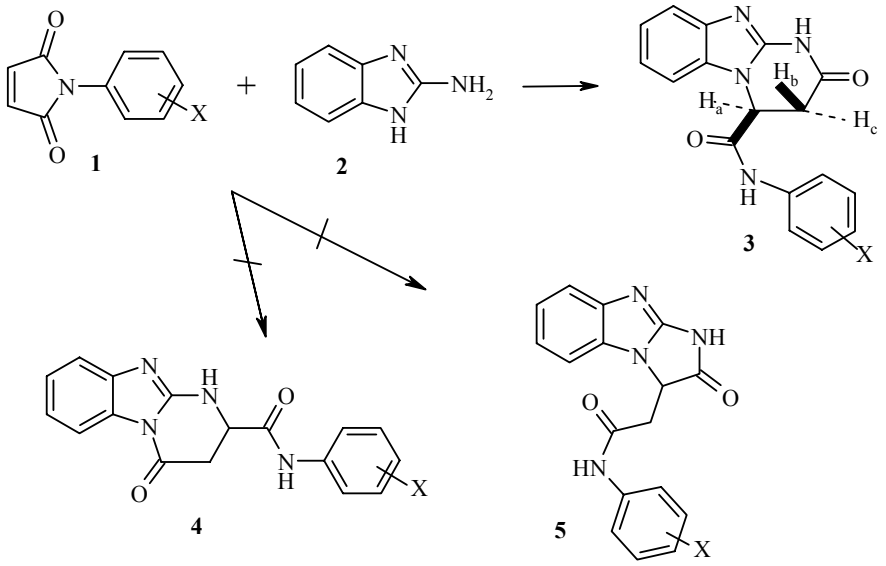
Recyclization reactions of N-arylmaleimides (**1**) have been described when they are reacted with 1,2-N,N-binucleophiles (*o*-phenylenediamine) [1] and 1,1-N,S-binucleophiles (thioamides, thiourea) [2, 3]. The reaction includes a step of addition of an amino group (in the first case) or a mercapto group (in the second case) at the activated double bond of maleimide and opening of the imide ring with transamidation relative to the free amino group of the binucleophilic substrate. In this case, depending on the direction of nucleophilic attack, isomers can form in which the methylene group occupies an *endo* or an *exo* position.

In this work, we have extended the reaction under consideration to aminoazoles: 2-aminobenzimidazole and 2-aminotriazole, which are 1,1-N,N-binucleophiles. In addition to the possibility of formation of tetrahydropyrimidine or dihydroimidazole rings as a result of recyclization, this case is complicated by the probability of formation of regioisomers, since the nucleophilic centers are not equivalent.



Detailed analysis of the ^{1}H NMR spectra let us establish that the reaction of N-(4-methoxyphenyl)maleimide **1** (X = 4-MeO) with aminobenzimidazole **2** leads exclusively to 2-oxo-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyrimidine-4-carboxy(4-methoxyanilide) (**3**), while the isomeric

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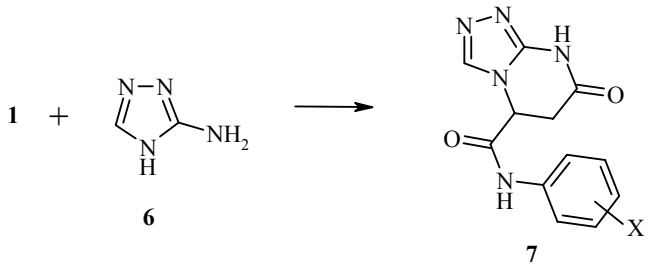
compounds **4** and **5** are not formed. This conclusion is drawn based on the assignment of the following signals: the doublet H_b with δ = 2.91 ppm, $^2J_{bc}$ = 16.7 Hz [4]; the doublet of doublets H_c with δ = 3.50 ppm, $^2J_{bc}$ = 16.7, $^3J_{ac}$ = 7.8 Hz, and the doublet H_a with δ = 5.37 ppm, $^3J_{ac}$ = 7.8 Hz ($^3J_{ab}$ = 0). In structure **4**, the proton H_a should be a doublet of doublets because of additional splitting at the proton of the adjacent NH group, which is not observed. In structure **5**, the protons H_b and H_c should be magnetically equivalent.

Analogous analysis of the ^{1}H NMR spectrum of the product of reaction between maleimide **1** and aminotriazole **6** allowed us to assign it the structure of 7-oxo-5,6,7,8-tetrahydro[1,2,4]triazolo[4,3-*a*]pyrimidine-5-carboxy-(4-fluoroanilide) (**7**).



2-Oxo-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyrimidine-4-carboxy(4-methoxyanilide) (3). Mixture of N-(4-methoxyphenyl)maleimide (2.03 g, 10 mmol) and 2-aminobenzimidazole (1.33 g, 10 mmol) in dioxane (10 ml) was boiled for 2 h. The precipitated product was filtered off, washed with acetone, and recrystallized from DMF. Yield 2.1 g (64%); mp >300°C. ^{1}H NMR spectrum (Bruker AM 300 (300 MHz), DMSO-d_6), δ, ppm (*J*, Hz): 2.91 (1H, d, $^2J_{bc}$ = 16.7, H_b); 3.50 (1H, dd, $^2J_{bc}$ = 16.7, $^3J_{ac}$ = 7.8, H_c); 3.72 (3H, s, OCH_3); 5.37 (1H, d, $^3J_{ac}$ = 7.8, H_a); 6.88 (2H, d, arom.); 7.08-7.19 (2H, m, arom.); 7.48-7.56 (4H, m, arom.); 10.50 (1H, s, NH); 11.54 (1H, s, NH). Found, %: C 64.12; H 4.88; N 16.50. $C_{18}H_{16}N_4O_3$. Calculated, %: C 64.28; H 4.79; N 16.66.

7-Oxo-5,6,7,8-tetrahydro[1,2,4]triazolo[4,3-*a*]pyrimidine-5-carboxy(4-fluoroanilide) (7). Mixture of N-(4-fluorophenyl)maleimide (1.91 g, 10 mmol) and 3-aminotriazole (0.84 g, 10 mmol) in dioxane (10 ml) was boiled for 2 h. The precipitated product was filtered off, washed with acetone, and recrystallized from DMF. Yield 1.98 g (72%); mp >300°C. ^{1}H NMR spectrum (Bruker AM 300 (300 MHz), DMSO-d_6), δ, ppm (*J*, Hz): 2.87 (1H, d, $^2J_{bc}$ = 3.3, H_b); 3.34 (1H, dd, $^2J_{bc}$ = 16.5, $^3J_{ac}$ = 7.9, H_c); 5.32 (1H, d, $^3J_{ac}$ = 7.8, H_a); 7.14-7.27 (2H, m, arom.); 7.55-7.68 (2H, m, arom.); 8.37 (1H, s, CH-triazole); 10.60 (1H, s, NH); 11.57 (1H, s, NH). Found, %: C 52.12; H 3.78; N 25.50. $C_{12}H_{10}FN_5O_2$. Calculated, %: C 52.37; H 3.66; N 25.44.

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