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FORMATION OF Δ^2-PYRAZOLINE DERIVATIVES IN THE REACTION OF 1,5-DIAMINOTETRAZOLE WITH CHALCONES

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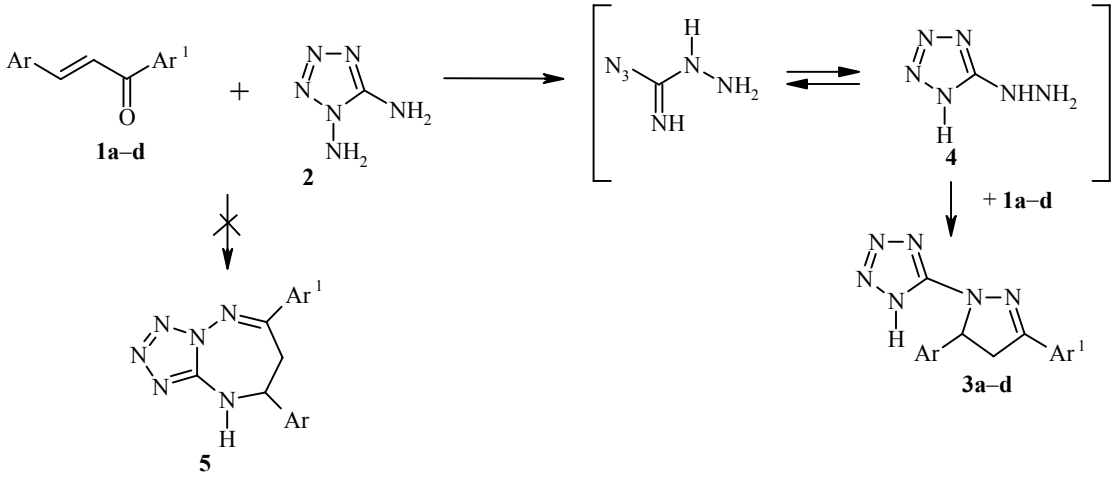
Keywords: 5-hydrazinotetrazole, 1,5-diaminotetrazole, 2,4-diaryl-1-(5-tetrazolyl)-Δ^2-pyrazolines, Dimroth rearrangement, chalcones.

The reaction of a series of 1,2-diaminoazoles with chalcones and their α,β-dibromo derivatives involves the endocyclic reaction site of the diaminoazole and one of the amino groups, leading to azoloazine systems [1-3].

However, a different reaction direction was found for the condensation of chalcones **1a-d** with 1,5-diaminotetrazole **2**. Heating the starting reagents in DMF at reflux for 3 h led to pyrazolines **3a-d**.

The structures of **3a-d** were established by IR and ^{1}H NMR spectroscopy. In addition, an X-ray diffraction structural analysis was carried out for **3b**, indicating the formation of 5-(*p*-methoxyphenyl)-3-phenyl-1-(5-tetrazolyl)-4,5-dihydro-2-pyrazoline. We propose that diamine **2** undergoes a Dimroth rearrangement, converting to 5-hydrazinotetrazole (**4**). Then, **4**, similar to aromatic hydrazines, reacts with chalcones to give pyrazolines **3a-d**. In previous work [4], we assigned dihydrodiazepin structure **5** to **3a** and **3b**. We should note that the physical indices as well as the IR and ^{1}H NMR spectral data of **3a** and **3b** obtained in the present work and reported previously almost coincide with the exception that in our previous work [4], we failed to detect the broad singlet at 15.6-15.7 ppm assigned to the tetrazole ring NH proton.



1, **5 a** Ar = Ar^1 = Ph, **b** Ar = Ph, Ar^1 = *p*-MeC$_6$H$_4$, **c** Ar = *p*-MeOC$_6$H$_4$, Ar^1 = Ph, **d** Ar = *p*-MeC$_6$H$_4$, Ar^1 = Br

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Pyrazoline 3c was obtained in 68% yield; mp 201°C (ethanol). IR spectrum (KBr tablet), ν, cm^{-1}: 1620, 3426. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.22 (1H, dd, CH_2, J_{AB} = -17.8); 3.72 (3H, s, OCH_3); 4.02 (1H, dd, CH_2, J_{AX} = 11.5); 5.56 (1H, dd, J_{BX} = 7.5); 6.85-7.80 (9H, m, arom CH); 15.60 (1H, br. s, NH).

Pyrazoline 3d was obtained in 39% yield; mp 223°C (ethanol). IR spectrum (KBr tablet), ν, cm^{-1}: 1628, 3431. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.45 (3H, s, CH_3); 3.33 (1H, dd, CH_2, J_{AB} = -17.6); 4.06 (1H, dd, CH_2, J_{AX} = 11.5); 5.52 (CH, dd, J_{BX} = 7.6); 7.15-7.65 (8H, m, arom CH); 15.72 (1H, br. s, NH).

Pyrazoline 3a was obtained in 60% yield (55% [4]); mp 228°C (ethanol) (227°C [4]). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 15.69 (1H, br. s, NH).

Pyrazoline 3b was obtained in 56% yield (58% [4]), mp 225°C (ethanol) (225°C [4]). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 15.62 (1H, br. s, NH).

The elemental analysis data for nitrogen for **3c** and **3d** correspond to the calculated values.

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