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SYNTHESIS OF NOVEL HETEROCYCLIC SYSTEM 9-METHYL-8-PHENYL-1,4-DIHYDRO-5H-PYRAZOLO-[5',1':2,3]PYRIMIDO[4,5-*e*][1,2,4]TRIAZEPIN-5-ONE

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Keywords: 7-imino-2-methyl-3-phenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimdine-6-carbohydrazide, 9-methyl-8-phenyl-1,4-dihydro-5H-pyrazolo[5',1':2,3]pyrimido[4,5-*e*][1,2,4]triazepin-5-one, ethyl 7-imino-2-methyl-3-phenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-6-carboxylate.

The reaction of ethyl 7-imino-2-methyl-3-phenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-6-carboxylate (**1**) [1] with hydrazine hydrate in *n*-butanol medium gave 7-imino-2-methyl-3-phenyl-4,7-dihydropyrazolo-[1,5-*a*]pyrimidine-6-carbohydrazide (**2**).

Treatment of compound **2** with triethyl orthoformate gives compound **4** which can possibly exist in the tautomeric forms **A-D**. Formation of the expected pyrimidine ring containing compound **3** did not occur. This was evidence by the absence of a signal for the two protons of an exocyclic amino group along with the observation of two broadened singlets for NH group protons at 8.35 and 9.10 ppm which corresponds to structure **4**. Moreover, compound **4** does not take part in a reaction with benzaldehyde and isothiocyanates which points to the absence of a primary amino group in the structure discussed. The absence of a signal for a hydroxyl group proton in the low field region points to the existence of compound **4** in a keto form. The position and intensity of the signals for the remaining protons in the ^{1}H NMR spectrum confirm the formation of the pyrazolopyrimidotriazepino system but, for a precise definition of the predominant tautomeric form of compound **4**, we have used a ^{1}H NMR 2D NOESY experiment.

Hence the absence of a cross peak for an *o*-proton of the phenyl substituent with one of the NH proton signals points to the occurrence of the pyrimidine ring in an aromatic form and so excludes the structural variant **4A**. The absence of a cross peak for the proton on position C-6 with other protons confirms the proposal that compound **4** exists in a keto form. The absence of a mutual splitting of the NH protons excludes its possible existence in form **4C**. In addition, the {^{1}H-^{1}H} NOESY spectrum has a cross peak corresponding to the interaction of the NH proton at 8.35 ppm with water and this points to the existence of exchange processes in the system studied so explaining the absence of an interaction of the protons with the C-2 and N-1 atoms.

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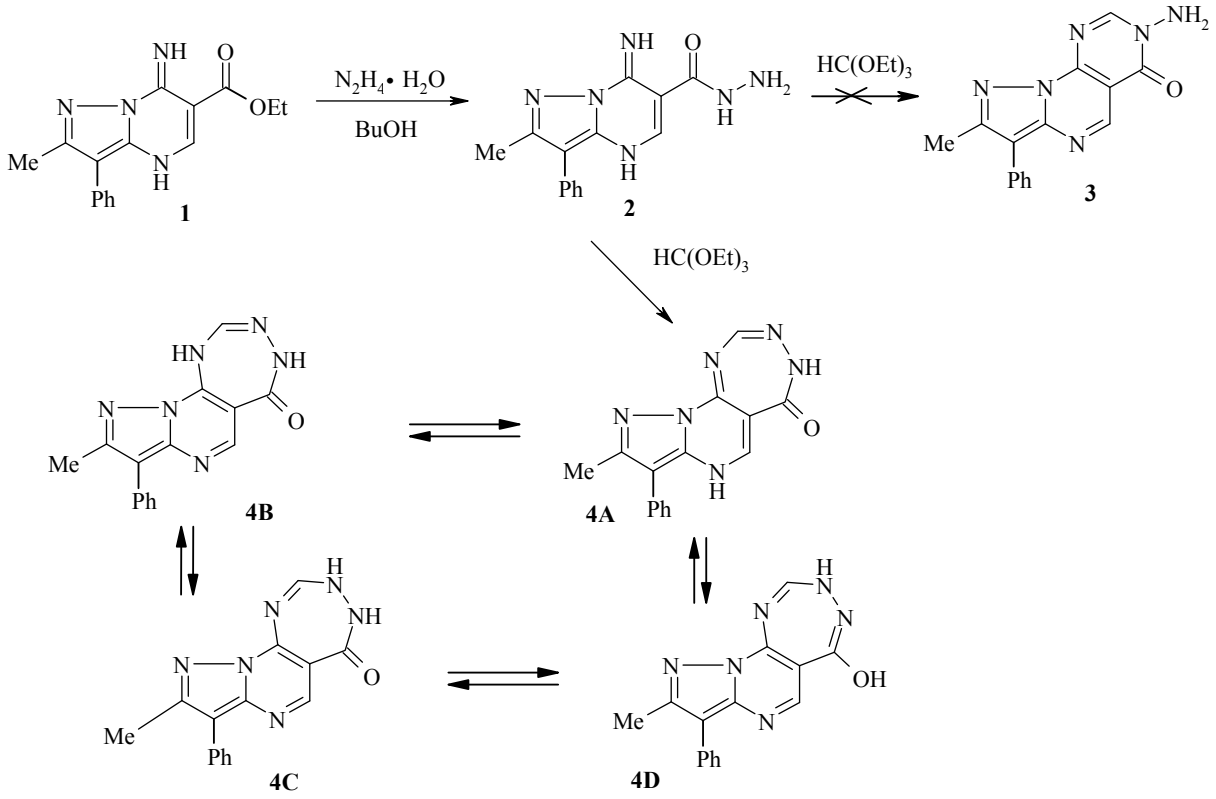
Hence the reaction of 7-imino-2-methyl-3-phenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-6-carbohydrazide **2** with triethyl orthoformate gives the novel heterocyclic system 9-methyl-8-phenyl-1,4-dihydro-5H-pyrazolo[5',1':2,3]pyrimido[4,5-*e*][1,2,4]triazepin-5-one (**4B**).



^{1}H NMR and {^{1}H-^{1}H} NOESY spectra were recorded on a Bruker DRX-500 (500 MHz) instrument using DMSO-d_6.

7-Imino-2-methyl-3-phenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimidine-6-carbohydrazide (2). A mixture of ester **1** (1 g, 3.4 mmol) and hydrazine hydrate (0.67 g, 13.5 mmol) was refluxed in *n*-butanol (5 ml) for 3 h. The precipitated white crystals were filtered off, washed with 2-propanol, and recrystallized from a mixture of toluene and DMF. Yield 0.6 g (63%). ^{1}H NMR spectrum, δ, ppm: 2.56 (3H, s, CH_3); 4.33 (2H, br. s, NH_2); 7.20-7.75 (5H, m, Ph); 8.42 (1H, s, imino-NH); 8.55 (1H, s, pyrimid. NH); 8.61 (1H, s, H-5); 9.73 (1H, s, NH). Found, %: C 59.50; H 5.02; N 29.65. $C_{14}H_{14}N_6O$. Calculated, %: C 59.56; H 5.00; N 29.77.

9-Methyl-8-phenyl-1,4-dihydro-5H-pyrazolo[5',1':2,3]pyrimido[4,5-*e*][1,2,4]triazepin-5-one (4B) was prepared by refluxing hydrazide **2** (2.82 g, 0.01 mol) in triethyl orthoformate with addition of a catalytic amount of acetic acid. It was recrystallized from acetic acid. Yield 2.2 g (75%). ^{1}H NMR spectrum, δ, ppm: 2.60 (3H, s, CH_3); 7.30-7.75 (5H, m, Ph); 8.35 (1H, br. s, NH); 8.65 (1H, s, H-6); 9.10 (1H, br. s, NH); 9.33 (1H, s, H-2). Found, %: C 61.65; H 4.13; N 28.75. $C_{15}H_{12}N_6O$. Calculated, %: C 61.64; H 4.14; N 28.75.

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