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NOVEL ROUTE FOR CONSTRUCTION OF A TRIAZINE RING

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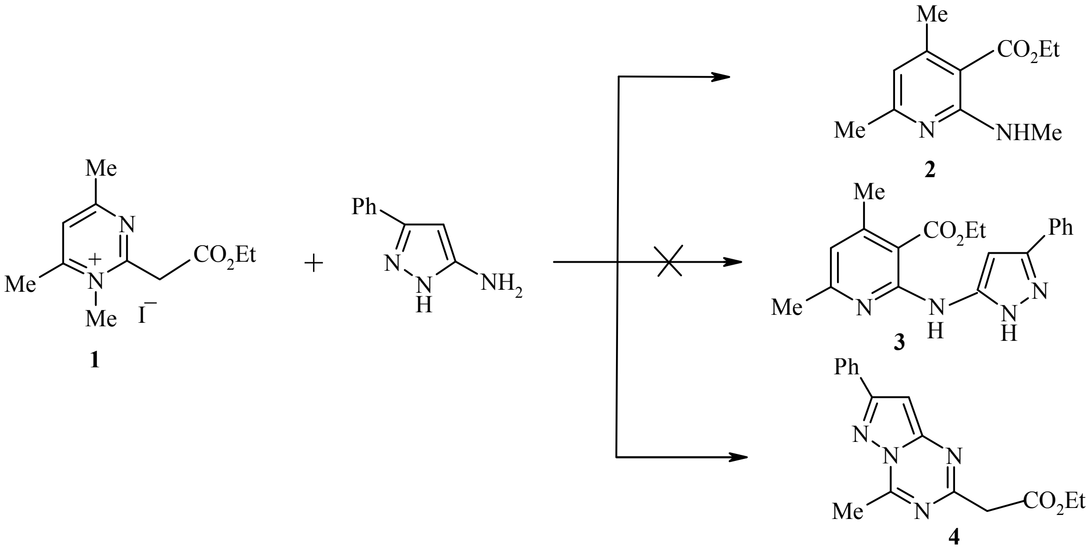
In the presence of primary aliphatic amines, pyrimidinium salts are converted to 2-alkylaminopyridine derivatives *via* a Kost-Sagitullin rearrangement and including a fragment of the amine reagent [1, 2]. A similar reaction for aromatic or heteroaromatic amines has not been studied to this time.

Our studies have shown that refluxing ethyl 1,4,6-trimethylpyrimidinium-2-acetate iodide (**1**) in alcohol with 3-amino-5-phenylpyrazole gives the product of a classical Kost-Sagitullin rearrangement, *viz.* ethyl 4,6-dimethyl-2-methylaminonicotinate (**2**). In place of the expected rearrangement product including the pyrazole fragment (compound **3**), we basically obtained a bicyclic compound which we identified as ethyl (4-methyl-7-phenylpyrazolo[1,5-*a*][1,3,5]triazin-2-yl)acetate (**4**).



Formation of compound **4** evidently follows from the fact that after primary attack of the amine reagent at position C(2) and subsequent opening at the N(1)–C(2) bond of the pyrimidine ring the reaction occurs by an unexpected route involving the endocyclic azole nitrogen atom which leads to elimination of an acetone imine

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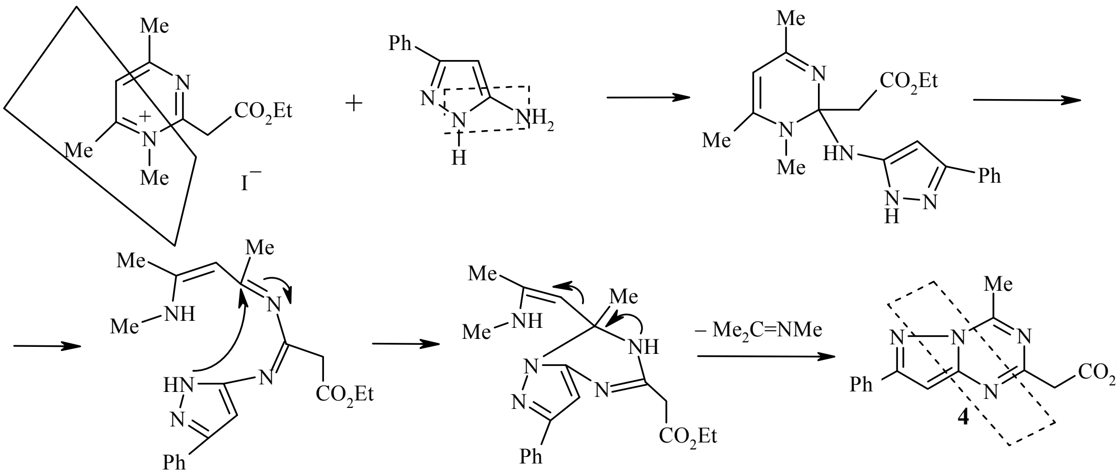
derivative and to the formation of the bicyclic compound **4**. In fact, the result of the recyclization is the substitution of the pyrimidine N(1)–C(6)–C(5) fragment by the (N–C–N) amidine fragment of the aminopyrazole.



We note that a series of recylizations have been reported in the literature which include so called "degenerative rearrangements" of pyrimidines which occur through the substitution of a three-atom pyrimidine fragment with the three-atom fragment from another reagent [3-9]. As a result, recyclization of pyrimidines to a pyridine or other, novel pyrimidine derivative occurs. However, a similar conversion of pyrimidines to triazine derivatives is reported for the first time.

^{1}H NMR spectra were taken on a Varian Mercury-300 instrument (300 MHz) using $CDCl_3$ with TMS as standard and mass spectra on an MK-1321 with direct introduction of the sample into the ion source (EI, 70 eV).

Ethyl 4-Methyl-7-phenylpyrazolo[1,5-*a*][1,3,5]triazin-2-yl Acetate (4). A solution of iodide **1** (1.35 g, 4 mmol) in absolute ethanol (16 ml) was mixed with a solution of 3-amino-5-phenylpyrazole (1.59 g, 10 mmol) in absolute alcohol (8 ml) leading to darkening of the reaction mixture and the characteristic odor of the evolved amine. Alcohol was distilled from the reaction mixture after 40 h refluxing and the residual oily mass was treated with hot hexane (it can also be extracted using a Soxhlet apparatus). After removal of the hexane the residue was chromatographed on silica gel to give the pyrazolo[1,5-*a*]triazine **4** (0.69 g, 58%); mp 90-91ºC (hexane) and R_f 0.7 (Silufol UV-254, benzene–acetone, 3:1), and the pyridine **2** (0.16 g, 19%), its constants and spectroscopic parameters agreeing with data for a known sample obtained by an alternative route [1]). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.31 (3H, t, J = 7.1, $CH_2C\underline{H}_3$); 2.45 (3H, s, 7-CH_3); 3.05 (2H, s, CH_2); 4.21 (2H, q, J = 7.1, OCH_2); 6.61 (1H, s, H-8); 7.35-7.47 and 7.90-8.05 (5H, m, C_6H_5). Mass spectrum, m/z (I_{rel}, %): 296 $[M]^+$ (100), 251 (20), 250 (44), 224 (63), 223 (21), 184 (48), 183 (40), 154 (22), 114 (55), 78 (11), 77 (37). Found, %: C 64.64; H 5.18; N 18.84. $C_{16}H_{16}N_4O_2$. Calculated, %: C 64.85; H 5.44; N 18.91.

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