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Synthesis of Phenylhydrazone of 5-Acetyl-3-(Methylsulfanyl)-1,2,4-Triazine and 3-Methyl-5-(Methylsulfanyl)-1-Phenyl-1*H*-Pyrazolo[4,3-*e*][1,2,4]Triazine from Pivotal Intermediate

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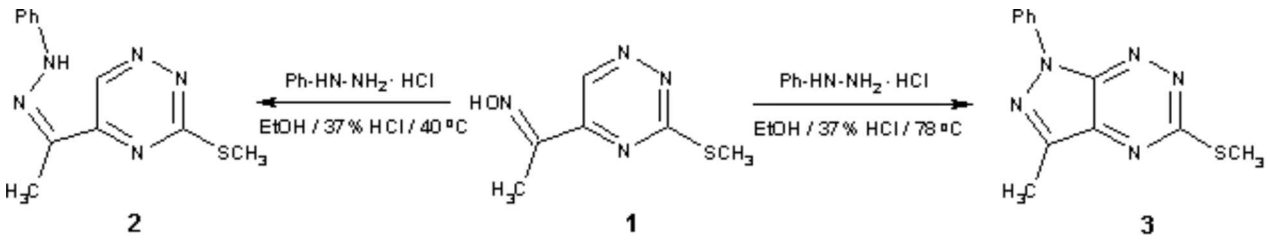
As part of ongoing research programme on bicyclic heterocycles [1-4] we have elaborated a new approach to 1*H*-pyrazolo[4,3-*e*][1,2,4]triazine derivative **3** and its synthetic precursor **2** by reaction of oxime 5-acetyl-3-(methylsulfanyl)-1,2,4-triazine (**1**) with phenylhydrazine hydrochloride under different reaction conditions.



Phenylhydrazone of 5-acetyl-3-(methylsulfanyl)-1,2,4-triazine 2

To a solution of the oxime **1** (184 mg, 1 mmol) and phenylhydrazine hydrochloride (288 mg, 2 mmol) in ethanol (10 ml) 37% HCl (0.3 ml) was added. The mixture was heated at 40 ^{o}C for 9 hours and then the solvent was evaporated *in vacuo*. The solid was collected by filtration, washed with water and recrystallized from ethanol/water mixture (1:1) to give **2** in 27% yield.

Melting point: 224 ^{o}C.

^{1}H-NMR ($CDCl_3$): δ= 2.30 (s, 3H); 2.69 (s, 3H); 6.99-7.08 (m, 1H); 7.23-7.28 (m, 2H); 7.32-7.41 (m, 2H); 8.05 (s, 1H, NH); 9.63 (s, 1H).

IR (KBr, cm^{-1}): 3240 (NH); 2980, 1600, 700.

EI-MS (70eV, *m/z*): 259 (7) [M^{+}]; 147 (45); 129 (100); 112 (54); 70 (90).

Elemental Analysis: Calculated for $C_{12}H_{13}N_5S$: C 55.60%; H 5.02%; N 27.03%. Found: C 55.53%; H 5.09%; N 26.99%.

3-Methyl –5-(methylsulfanyl)-1-phenyl-1*H*-pyrazolo[4,3-*e*][1,2,4]triazine 3

To a solution of the oxime **1** (184 mg, 1 mmol) and phenylhydrazine hydrochloride (216 mg, 1.5 mmol) in ethanol (10 ml) was added 37% HCl (0.3 ml). The mixture was heated at reflux for 5 hours and then the

solvent was evaporated *in vacuo*. The solid was collected by filtration, washed with water and recrystallized from ethanol/water mixture (1:1) to give **3** in 18% yield.

Melting point: 105 ^{o}C.

^{1}H-NMR (200 MHz, $CDCl_3$): δ= 2.73 (s, 3H); 2.77 (s, 3H); 7.29-7.40 (m, 1H); 7.50-7.61 (m, 2H); 8.31-8.38 (m, 2H).

IR (KBr, cm^{-1}): 2920, 1590, 1500, 1390, 760.

EI-MS (70eV, *m*/*z*): 257 (43) [M^+]; 232 (3); 216 (22); 93 (41); 77 (100).

Elemental Analysis: Calculated for $C_{12}H_{11}N_5S$: C 56.03%; H 4.28%; N 27.23%. Found: C 55.67%; H 4.13%; N 27.05%.

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