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A convenient one pot synthesis of some novel benzothiazole and its derivatives

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Abstract

The one pot synthesis of 3-amino-4-imino-8-methoxy- (2H) Pyrazolo [3',4';4,5] pyrimido[2,1-*b*] benzothiazole and its 2-substituted derivatives is convenient over tradinational rout of synthesis of this organic compound. The novel compound are prepare by condensation of 3-cyno-4-imino-2-methylthio-8-methoxy-4H-pyrimido [2,1-*b*] benzothiazole with 80% Hydrazine hydrate and other reagent. The structure of the compound was verified by ^{1}H NMR and other spectroscopic techniques.

Keywords: Benzothiazole, Hetrocyles, One pot synthesis, Pyrazoles.

Introduction

The 5-oxo-5H Pyrido[2',3';4,5] pyrimido [2,1-*b*] benzothiazole have been synthesized from oxidation of 3-aryl-4-oxo-2-thioxo-1,2,3,4-tetrahydro pyrido[2,3-*b*] pyrimidine with concentrate H_2SO_4 by Javier Grain [1]. In addition to Uros and Urleb [2-6], a preparative method of new tetra cyclic system 12(H)-pyrido [3',2';4,5] pyrimido [2,1-*b*] benzothiazole-12-one from condensation of ethyl-3-isothiocynato pyridine-2-carboxylate with 2-aminothiophenol in good yield. Javier Grain [7] et al reported the synthesis of 1H,4H-4-oxo-1-phenyl pyrazolo[3',4',4,5] pyrimido[2,1-b] benzothiazole from pyrazolo[3,4-*d*] pyrimidine in the presence of NBS/sulphuric acid and NCS/sulphuric acid, product was obtained in good yield. The synthesis of 3-amino-4-oxo-2H pyrazolo[3',4';4,5] pyrimido [2,1-*b*] benzothiazole and its 2 and 3 substituted derivatives starting from 3-cyno-2-methylthio-4-oxo-4H pyrimido[2,1-*b*] benzothiazole has been recently reported by our research group and other [8-15]. In the present

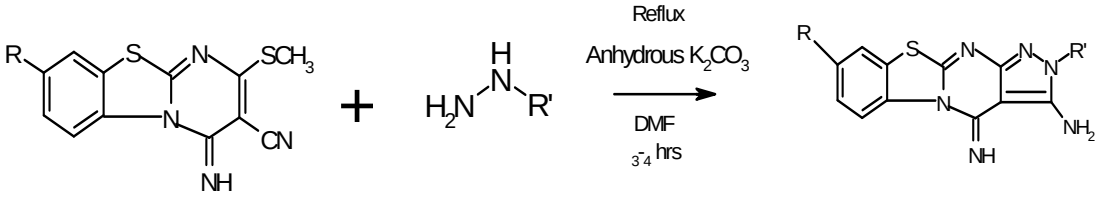
work, we report one pot synthesis of 3-amino-4-imino-8-methoxy (2H) Pyrazolo [3',4';4,5] pyrimido [2,1-*b*] bezothiazole and its 2-substituted derivatives.

Material and Methods

The chemical used in this work where reagent grade including hydrazine hydride (Aldrich 99.99%), N,N-Dimethylfarmamide (Merck, 99.99%), pyridine (Merck, 99.90%), ethanol (Merck, 99 %), potassium carbonate (Merck, 99.00%), and distilled water were used.

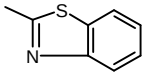
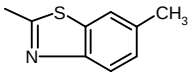
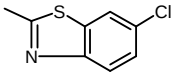
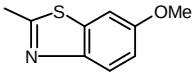
A mixture of 3-cyno-4-imino-2-methylthio-8-methoxy-4H-pyrimido [2,1-*b*] benzothiazole(1 mmol) and 80% Hydrazine hydrate **3a**, 2-hydrazinobenzothiazole **3b,** 6-methyl-2-hydrazinobenzothiazole **3c**, 6-chloro-2-hydrazinobenzothaizole **3d,** 6-methoxy-2-hydrazinobenzothaizole **3e** (2 mmol) were reflux in the presence of N,N-Dimethylfarmamide (5 ml) and catalytic amount of Potassium Carbonate for 4 hrs. After cooling the solid that appeared were collected by filtration and recrystallised from mixture solvent of DMF and ethyl alcohol to afford crystalline solid of **3a-e**.

Scheme –I

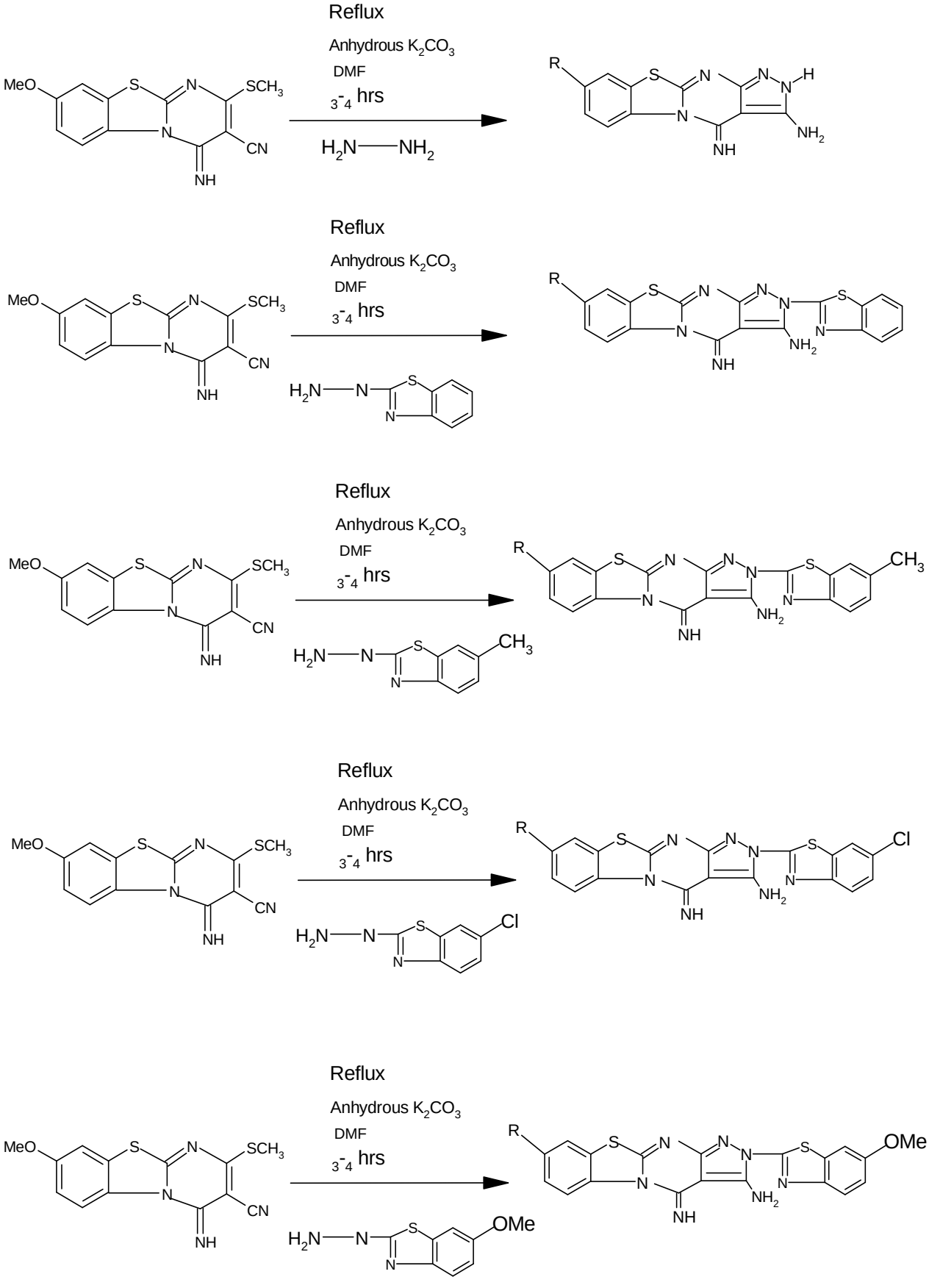


(3a-e)

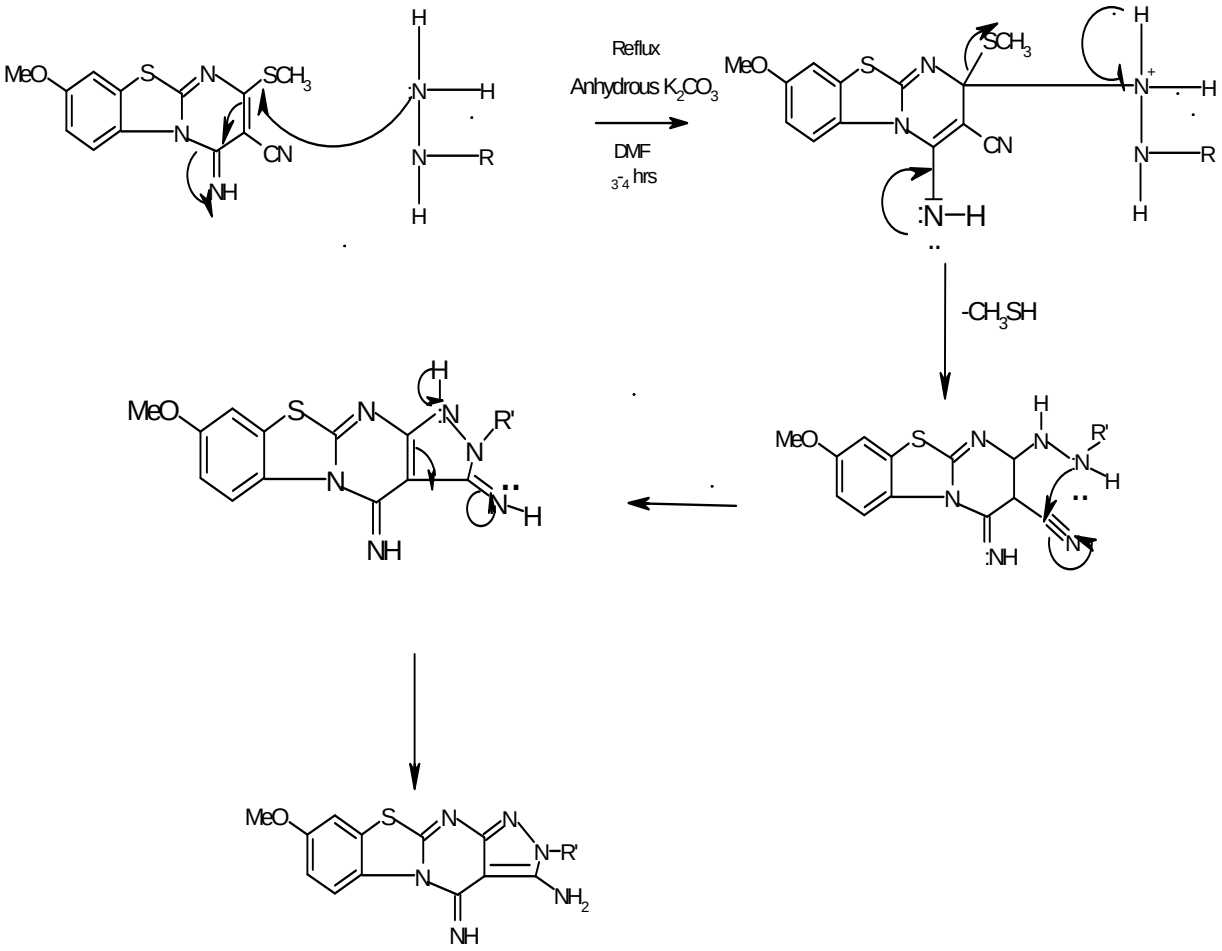
Table – 1

R	R'	
-OCH_3	H_2N-NH_2	3 a
-OCH_3		3 b
-OCH_3		3 c
-OCH_3		3 d
-OCH_3		3 e

Scheme-II


Reflux
Anhydrous K_2CO_3
DMF
3-4 hrs
MeO
SCH3
CN
NH
H2N—NH2
R
NH2
H2N—N
S
N
CH3
Cl
OMe

Tentative mechanism for the formation of compound (3a-e)

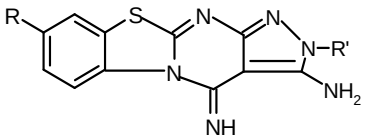


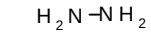
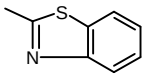
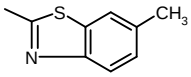
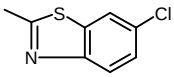
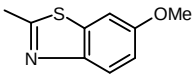
The melting points were determined in open capillary tube, and were found to be uncorrected. ^{1}H NMR spectra were measured on Gemini 200 MHz spectrometer with TMS as an internal slandered. ^{13}C NMR spectrums were measured on Brucker DPX-400 at 100 MHz with TMS as an internal standard. IR spectrums were recorded in Nujol / KBr palates on Bomen MB 104 FT IR spectrometer. Elemental analyses were performed using a Heraus C, H, N, O rapid analyzer. All reactions were carried out under ambient atmosphere and monitored by Thinlayer Chromatography carried out on 0.2 mm Silica Gel-G-plate using iodine vapor for detection. Mass spectrums were recorded on FT VG-7070 μH Mass spectrophotometer using the EI technique at 70 ev.

Result and Discussion

When 3-cyno-4-imino-2-methylthio-8-methoxy-4H-pyrimido [2,1-*b*] benzothiazole were reflux independently with 80% Hydrazine hydrate **(3a)**, 2-hydrazinobenzothiazole **(3b)**, 6-methyl-2-hydrazinobenzothiazole **(3c)**, 6-chloro-2-hydrazinobenzothaizole **(3d)**, 6-methoxy-2-hydrazinobenzothaizole **(3e)**, in the presence of N, N-Dimethylfarmamide and catalytic amount of Potassium Carbonate to obtained 2-substituted derivative of 3-amino-8-methoxy-4-imino-2-(2'-benzthiazolyl) **(5a-e)** respectively.

Table-2 : Characterization benzothiazole



Comp.	R	R'	Formula M_r	W_i(calc.) / W_i (found) % C	 H	 N	M.p. (^{0}C)
1	-OCH_3		$C_{12}H_{10}N_6OS$	50.34 50.31	3.49 3.46	29.37 29.33	267.1
2	-OCH_3		$C_{19}H_{13}N_7OS_2$	54.41 54.38	3.10 3.05	23.38 23.25	165.7
3	-OCH_3		$C_{20}H_{15}N_7OS_2$	55.42 55.40	3.46 3.43	22.63 22.60	110.3
4	-OCH_3		$C_{19}H_{12}N_7S_2OCl$	50.33 50.30	2.64 2.61	21.63 21.59	145.2
5	-OCH_3		$C_{20}H_{15}N_7O_2S_2$	53.45 53.41	3.34 3.31	21.82 21.80	160.1

Spectroscopic Characterization

1) 3-amino-4-imino-8-methoxy (2H)-pyrazolo[3',4';4,5] pyrimido[2,1-b] benzothiazole [3a]
(KBr/cm^{-1}) 3317-3250 cm^{-1}(bs), 3168-2914, 1635, 1571, 1456, 1282, 1047; δ_H(200 MHz, DMSO-D6) δ3.7 (s, 3H), δ3.4 (bs, 2H), δ6.9-7.7 (m, 3H), δ7.9 (s, 1H), δ8.3 (s, 1H), m/z (EI, 70ev) 286 (M^+), 258, 229, 176, 138.

2)3-amino-4-imino-8-methoxy-2-(2'-benzothiazolyl)pyrazolo[3',4';4,5]pyrimido[2,1-b] benzothiazole [3b]
(KBr/cm^{-1}) 3481-3363, 3240, 2948, 1629, 1562, 1462, 1278, 1180 cm^{-1}; δ_H (200 MHz, DMSO-D6) δ3.3 (s, 3H), δ3.5 (s, 2H), δ6.7-7.6 (m, 7H), δ8.1 (s, 1H); m/z (EI, 70ev) 419(M^+).

3)3-amino-4-imino-8-methoxy-2-(6'-methyl-2'-benzothiazolyl)pyrazolo[3',4';4,5]pyrimido[2,1-b] benzothiazole [3c]
(KBr/cm^{-1}) 3342-3309 (bs), 3140, 2943, 1649, 1521, 1461, 1292, 1112; δ_H (200 MHz, DMSO-D6) δ3.0(s, 3H), δ3.6(s, 2H), δ7.0-7.9 (m, 3H), δ8.1(s, 1H); m/z (EI, 70ev) 433 (M^+, 100%).

4)3-amino-4-imino-8-methoxy-2-(6'-chloro-2'-benzothiazolyl)pyrazolo[3',4';4,5] pyrimido[2,1-b] benzothiazole [3d]

(KBr/cm^{-1}) 3370-3255(bs), 3190, 2929, 1609, 1516, 1432, 1278, 1184; δ_H(200 MHz, DMSO-D6) δ2.3(s, 3H), δ2.5(s, 3H), δ3.5 (s, 2H), δ6.9-7.7 (m, 3H); δ8.2(s, 1H).

5)3-amino-4-imino-8-methoxy-2(6'-methoxy-2'-benzothiazolyl)pyrazolo[3',4';4,5]pyrimido[2,1-b] benzothiazole [3e]
(KBr/cm^{-1}) 3390-3267, 3182, 2960, 1625, 1543, 1440, 1274, 1125; δ_H(200 MHz, DMSO-D6) δ2.4(s, 3H), δ3.4(bs, 2H), δ3.9 (s,3H), δ6.9-7.8 (m, 6H); δ8.4 (s, 1H).

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