Oriental Journal of Chemistry Vol. **25**(3), 743-745 (2009)

Synthesis of some new 2-substituted benzoxazol-5-carbonyl-3,5-dimethyl pyrazole and 2-substituted benzoxazol -5-carbonyl-3-methyl pyrazalones

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(Received: June 02, 2009; Accepted: July 04, 2009)

ABSTRACT

Some new 2-substituted benzoxazole-5-carbonyl-3, 5-dimethyl pyrazoles (3) and 2-substituted benzoxazol-5-carbonyl-3-methyl pyrazolones (4) were prepared from 2-substituted benzoxazol-5-carboxylic acid hydrazide (2) reaction with acetyl acetone and ethyl acetoacetate respectively. The new compounds were characterized by spectral data (IR and PMR).

Key words: 2-substituted benzoxazol-5-carbonyl-3,5-dimethyl pyrazole.

INTRODUCTION

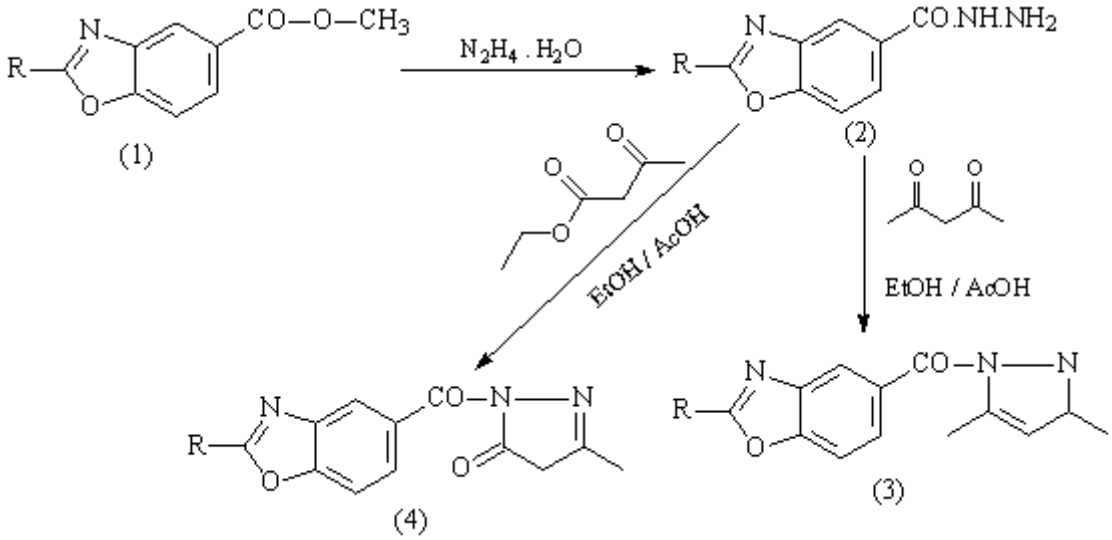
Benzoxazole possess anti-inflammatory, anticancer and antimicrobial activities. It is known that the ring system plays an important role in many biological process and many therapeutic agents containing pyrazole and pyrazolone moiety. 2-Substituted benzoxazole represent a heterocyclic system of remarkable pharmacological efficiency[1-3]. IN the past two decades a broad range of biological effects, including antiinflammatory, anticancer, antibacterial9, diuretic activities have been ascribed to their benzoxazole derivatives. In view of this and in continuation of our interest on organic transformation, we now with to report for the synthesis of 2-substitute benzoxazole 5-carbonyl-3-, 5-dimethyl pyrazoles (3) and 2-substituted benzoxazole-5-carbonyl-3-methyl pyrazolones (4).

For this purpose, 2-substituted benzoxazole-5-carboxylic acid hydrazides (2) were refluxed with acetyl acetone and ethyl acetoacetate separately in alcohol containing catalytic amount of acetic acid for 16-18 hrs. at 110°C, where the reaction took longer time and with good yields. These compounds ere purified by recrystallization and characterized by spectral data 'IR, ^{1}H NMR and Mass.

EXPERIMENTAL

All melting point were determined in open capillaries and are uncorrected. The purity of the compounds was ascertained by TLC on silica gel G plates.

The IR spectra was taken in KBr on a perkin Elmer spectrophotometer. PMR spectra were recorded on 2SCAC-5003, H, DMSO-d_6 (200m Hz) mass spectra were recorded on LC-MSD-Trap.SL.



Scheme

2-Substituted benzoxazol-5-carboxylic acid hydrazides (2)

A mixture of 2 substituted-5-carbomethoxy benzoxazole (1) (0.01 mol) and hydrazine hydrate (0.02 mol) in methanol (15 ml) was refluxed for 4 hr.. The reaction mixture was cooled and the solvent was reduced to half of its volume. The product separated was filtered, washed with small portions of cold ethanol and cold water repeatedly and dried. The product was purified by recrystallization from suitable solvents. The compounds were characterized by physical data available in literature[10].

2-Substituted benzoxazole-5-carbonyl 3,5-dimethyul pyrazoles (3) and 2-substituted benzoxazol-5-carbonyl 3-methyl pyrazolones (4)

A mixture of 2-substituted benzoxazol-5-yl carboxylic acid hydrazide (2) (0.01 mol) and acetyl acetone (0.01 mol)or Ethyl acetoacetate (0.01 mol) in alcohol (20 ml) were refluxed separately containing catalytic amount of acetic acid. The reaction mixture was poured on to crushed ice, the solid thus obtained was filtered and recrystallized from methanol to give pyrazoles and pyrazalones respectively.

Table 1 : Physical data of new 2-substituted benzoxazole-5-yl-3, 5-dimethyl pyrazoles and 2-substituted benzoxzzol-5-yl 3-methyl pyrazolone

Compound	R	Molecular	m.p °C	Yield %
3a	H	$C_{13}H_{13}O_2N_3$	138	85
3b	CH_3	$C_{14}H_{15}O_2N_3$	145	82
3c	C_2H_5	$C_{15}H_{17}O_2N_3$	149	89
4a	H	$C_{12}H_9N_3O_2$	140	85
4b	-CH_3	$C_{13}H_{12}N_3O_2$	146	76
4c	C_2H_5	$C_{14}H_{13}N_3O_2$	152	72

These compounds were characterized by physical and spectral data.

For example IR spectrum of a compound Pyrazole3a (R = H) in KBr showed absorption frequencies in (cm^{-1}) at 1685 (C = O) 1580 (C = N), 1230, 1120 (C-O-C).

^{1}H NMR: 2.25 (s, 3H, CH_3 of C_5), 2.55 (s, 3H, CH_3 at C_3), 6.0 (s, 1H, C_4H of pyrazole), 6.8 – 7.3 (m, 4H, Ar-H) including C_2H of benzoxazole.

IR spectrum in KBr of the compound pyrazolone (4a, R = H) showed absorption frequencies at 1730 (C = O), 1590 (C = N), 1220, 1115 (C-O-C) of benzoxazole.

^{1}H NMR in DMSO-d_6 (ä ppm): 2.45 (s, 3H, CH_3 of pyrazolone) 4.05 (2H, CH_2- CO pyrazolone) 6.6 - 7. 2 (m, 4H, Ar-H including C_2H of benzoxazole).

ACKNOWLEDGEMENTS

The authors are thankful to the Department of Chemistry, Kakatiya University for providing necessary facilities. We are also thankful to the Director, IICT for providing spectral data.

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