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ECOFRIENDLY SOLVENT FREE MICROWAVE INDUCED KNOEVENAGEL CONDENSATION OF 2-BENZO [1, 3] DIOXOL-5-YL-[3, 4^1] BITHIAZOLYL-5-ONE WITH SUBSTITUTED AROMATIC ALDEHYDES

P. JALAPATHI* and M. DEVENDER

Department of Chemistry, PG College of Saifabad, Osmania University, HYDERABAD (A.P.) INDIA

ABSTRACT

A rapid, cleaner, cost effective and ecofriendly synthesis of substituted 2-benzo [1,3] dioxol -5-yl-[3,4^1] bithiazolyl-5-one in solvent free conditions using solid support under microwave irradiation is achieved. The structures of all synthesized compounds have been determined by FTIR and ^{1}H NMR spectral methods.

Key words: Aromatic aldehydes, Knoevenagel conditions, Microwave irradiation.

INTRODUCTION

In recent years, the use of solid support as well as microwaves[1,2] has been well established as a pollution free technique, which is currently under investigation by synthetic organic chemists[3,4]. Microwave induced Organic Reaction Enhancement (MORE) chemistry[5-7] allows reaction to occur on a preparative scale in open vessels under solvent free conditions, which avoids the risk of high pressures and explosions[8,9]. Heterocyclic molecules with thiozole systems have been reported in the literature to show biological activity[10,14]. The thiazolidine nucleus is well known for its diverse biological functions. Earlier, We have reported Knovenagal condensation[15] reactions between barbityric acid and substituted carbocyclic and heterocyclic aldehydes under noncatalytic, solvent free condensation by microwave irradiation conditions- with excellent yields in very short reaction times. We have also reported same type of reactions between 2-benzo [1, 3] dioxol-5-y1 [3, 4^1] bithiazolyl-5-one and α, β - unsaturated aromatic/heterocyclic/ carbocyclic aldehyde without use of solvent and catalyst conditions under MWI conditions[16]. To the best of our knowledge, this is the first time that this procedure has been used for promotion of

*Author for correspondence

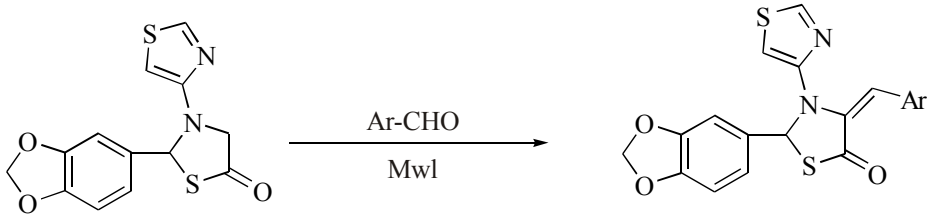
Knoevenagel condensation between above molecules. The advantages of this method are (i) no catalyst (ii) no solvent (iii) very simple experimental procedure (iv) applicable to both; electron releasing and electron–withdrawing aromatic aldehydes and (v) excellent yields and very short reaction times. This method may find important applications in organic synthesis.

EXPERIMENTAL

The reactions were monitored by TLC performed on precoted aluminum sheet. Melting points were taken in open capillaries and are uncorrected. FTIR spectra were recorded on a Perkin – Elmer spectrum BX series FTIR spectrophotometer. NMR spectra were obtained using Varion Gemini (200 MHz) spectrometer, TMS was used a internal standard and $CDCl_3$, DMSO-d_6 as the solvents. All the aromatic aldehydes (Analar Grade) are commercially available and were used without further purification. The Schiff's bases of pipernal and 4-aminothiazole were prepared by condensation procedure and used in the reaction after purification and fully characterization.

The Schiff's base is allowed to react with mercaptoacetic acid in the presence of ethanol with pinch of $ZnCl_2$ to get 2-benzo [1,3] dioxol-5-yl-[3,4^1] bithiazolyl-5-one **(1a)** and it is used for condensation reaction with substituted aromatic aldehydes under catalyst and solvent free condition using microwave oven. The reactions are usually completed within 30 to 60 seconds. The product was separated by washing with water followed by ether. After drying, the resulted yields are 80-90%. The reaction is carried out with different aldehydes and the results are summarized in Table 1.

Scheme



(1a) **(2a-2l)** **(3a-3l)**

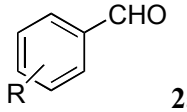
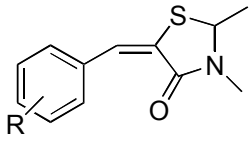
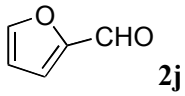
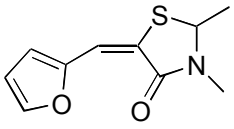
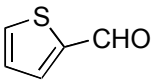
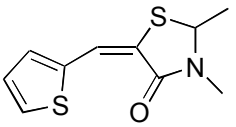
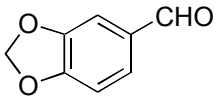
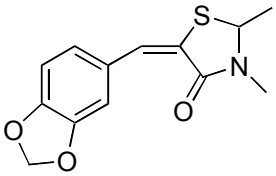
General procedure for the synthesis of disubstituted [3, 4^1] bithiazolyl-5-ones

A mixture of methanol (one drop), 2-benzo (1, 3) dioxol-5-yl [3, 4^1] bithiazolyl-5-one **(1)** (0.01mole) and aromatic carbocyclic / heterocyclic aldehyde (0.01mole) was taken in a glass test tube (length 15 cm, diameter 2.5 cm) and kept at a center of the bath, which contains alumina. The alumina bath is a (250 mL) glass beaker with 9.5 cm height. Then

alumina bath was kept inside the microwave oven and mixture was irradiated at 160 W microwave power. After cooling, the product was stirred in cold water (3 x 20 mL) and the solid was filtered, washed with cold water (3 x 20 mL) and ether (3 x 10 mL). After drying, the crude product was recrystalized from ethyl acetate / hexane.

RESULTS AND DISCUSSION

Table 1: Microwave promoted synthesis of disubstituted {3, 4[1]} bithiazolyl-5-ones

Entry	Aldehyde	Time (sec)	Product	Yield (%)	m.p (^{o}C)
1	 **2a**	30	 **3a**	90	280-282
2	4-Me **2b**	30	4-Me **3b**	91	285-287
3	4-OH **2c**	30	4-OH **3c**	92	290-292
4	2-OH **2d**	35	2-OH **3d**	90	240-243
5	4-Cl **2e**	35	4-Cl **3e**	85	270-273
6	3-Cl **2f**	35	3-Cl **3f**	88	250-252
7.	4-N(Me)$_2$ **2g**	30	4-N-N(Me)2 **3g**	90	260-263
8.	4-NO$_2$ **2h**	30	4-NO$_2$ **3h**	82	265-268
9	3-NO$_2$ **2i**	60	3-NO$_2$ **3i**	80	230-232
10	 **2j**	30	 **3j**	90	260-262
11	 **2k**	30	 **3k**	92	265-266
12	 **2l**	30	 **3l**	93	266-267

2-(Benzo [d [1, 3] dioxol-5-yl)-4-benzylidene-3-(thiazol-4-yl) thiazolidin-5-one (3a)

Yield: 90%; IR (KBr): 1690, 1670, 1650 and 1702 cm^{-1}

^1H NMR: δ 1H 8.75 (s, -CH=C; 5H 7.2 to 7.3 (m); (1H+ 1H) 7.76(s), 7.70(s) of thiazole moity; 1H 3.12 (s) oxothiazoloine moiety; 2H 5.9(s), - O-CH_2-O- pipernal moity.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(4-methylbenzylidene) -3-(thiazol-4-yl) thiazolidin-5-one (3b)

Yield: 91%; IR (KBr): 1275, 1699, 1720 and 1689 cm^{-1}

^1H NMR: δ 1H 8.7(s) –CH=C-; 2H 7.8(d), aldehyde moity; 1H + 1H 7.75(s), 7.70(s) of thiazole moiety; 3H 7.0(s) 7.77 (d) of pipernal moiety; 2H 5.85(s) –O-CH_2-O; 3H 2.9(s), -CH_3.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(4-hydroxybenzylidene)-3-(thiazol-4-yl) thiazolidin -5-one (3c)

Yield: 92%; IR (KBr): 3620, 1230, 1690, 1700 and 1710 cm^{-1}

^1H NMR: δ 1H 8.70(s) –CH=C-; 4H 7.5(m), aromatic; 1H + 1H 7.75(s), 7.7(s) thiazole moiety; 1H 3.11(s), oxothiozoline; 3H 7.0(s) - 7.78(d); 2H 5.8(s)-O-CH_2.O.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(2-hydroxybenzylidene)-3-(thiazol-4-yl) thiazolidin -5-one (3d)

Yield: 90%; IR (KBr): 3600, 1260, 1750 and 1685 cm^{-1}

^1H NMR: δ 1H 8.70(s) – CH=C-; 4H 7.5(m) aromatic, 1H + 1H 7.75(s), 7.7(s); 1H 3.11(s) oxothiozoline moity. 3H 7.1(s), 7.77(s), pipernal moiety; 2H 5.80(s), O-CH_2.O.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(2-chlorobenzylidene)-3-(thiazol-4-yl) thiazolidin-5-one (3e)

Yield : 85%; IR (KBr) : 1255, 1705, 1749, 1690 cm^{-1}

^1H NMR: δ 8.72 (s) – CH=C-; 4H 7.6-7.7(m) aromatic aldehyde; 1H + 1H 7.70(s), 7.75(s) (thiazole moity); 1H 3.14(s) (oxothiozoline moity); 3H, 7.75-779(s); 2H 5.8(s) – O-CH_2.O-.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(4-chlorobenzylidene)-3-(thiazol-4-yl) thiazolidin-5-one (3f)

Yield: 92%; IR (KBr): 1205, 1690, 1720 and 1680 cm^{-1}

^1H NMR: δ 1H. 8.72(s), -HC=C-; 4H 7.6-7.7(m), aromatic aldehyde; 1H + 1H 7. 71(s), 7.73(s); 1H(s), 3.15(s) oxothiozoline moity; 3H 7.2 – 7.62(s), 2H 5.79(s) O-CH_2.O pipernal moity.

2(Benzo [d] [1, 3] dioxol-5-yl)-4-(4-(dimethylamino)benzylidene)-3-(thiazol-4-yl) thiazolidin-5-one (3g)

Yield: 90%; IR (KBr): 1200, 1678, 1710 and 1680 cm^{-1}

^1H NMR: δ 1H, 8.18(s) –CH=C-; 4H 7.6-7.8(m), aldehyde moiety; 6H 3.12(s), N $(CH_3)_2$; 1H + 1H 7.7(s) & 7.73(s) thiazole moity; 1H 3.14(s) oxothiozoline moity, 3H 7.2(s), 7.6(s); 2H 5.77, O-CH_2O- pipernal moiety.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(4-nitrobenzylidene)-3-(thiazol-4-yl) thiazolidin-5-one (3h)

Yield: 82%; IR (KBr): 1205, 1670, 1700 and 1679 cm^{-1}

^1H NMR: δ 1H 8.42(s) -CH=C-; 4H 8.6(d) aromatic aldehyde moiety; 1H + 1H 7.7(s) & 7.6(s) thiazole moiety; 1H 3.0(s) oxothiozoline moiety, 3H 7.0 - 7.19 (m); 2H 5.67(s) O-CH_2O pipernal moiety.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(3-nitrobenzylidene)-3-(thiazol-4-yl) thiazolidin-5-one (3i)

Yield: 80%; IR (KBr): 1208, 1673, 1709 and 1680 cm^{-1}

^1H NMR: δ 1H 8.46(s) – CH=C-; 4H 7.7(m), aromatic aldehyde moiety; 1H + 1H 7.3(s) & 7.35(s), thiazole moiety; 1H 3.15(s), oxothiozoline moiety; 3H 7.69(s) – 7.75(s); 2H 5.7(s), O-CH_2O pipernal moiety.

2-(Benzo [d] [1, 3] dioxol-5-yl)-4-(furan-2-ylmethylene)-3-(thiazol-4-yl) thiazolidin-5-one (3j)

Yield: 90%; IR (KBr): 1206, 1669, 1689 and 1702 cm^{-1}

^{1}H NMR: δ 1H 8.16(s) -CH=C-; 3H 6.75 – 7.78(m) thiazole moiety; 1H & 1H 7.28(s) & 7.4(s), thiazole moiety; 1H 3.2(s) oxothiozoline moiety 3H 7.68(s), 7.72(s) and 2H 5.7(s) O-CH_2.O- pipernal moiety.

2-(Benzo [d] [1, 3] dioxol-5-yl)-3-(thiazol-4-yl)-4-(thiophen-2-ylmethylene) thiazolidin-5-one (3k)

Yield: 92%; IR (KBr): 1209, 1670, 1679 and 1709 cm^{-1}

^{1}H NMR: δ 1H 8.49) (s), -CH=C-; 3H 6.69-7.72(m); 1H 3.1(s), oxothiozoline moiety; 3H 7.6(s) 7.8(d) and 2H, 5.8(s) O-CH_2O- pipernal moiety.

2-(benzo [d] [1, 3] dioxol-5-yl)-4-(benzo [d] [1, 3] dioxol-5-ylmethylene)-3-(thiazol-4-yl) thiazolidin-5-one (3l)

Yield: 93%; IR (KBr): 1200, 1676, 1688 and 1720 cm^{-1}

^{1}H NMR: δ 1H 8.0(s) –HC=C-; 1H + 1H 7.10(s) & 7.42(s) thiozole moiety; 1H 3.0(s) oxothiozoline moiety; 2x3 H, 7.6(s) 7.61(s); and 2H 5.8(s) O-CH_2.O- pipernal moiety.

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