Ultrasonics Sonochemistry 20 (2013) 627–632

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Short Communication

An efficient synthesis of 2-substituted benzothiazoles in the presence of $FeCl_3$/Montmorillonite K-10 under ultrasound irradiation

Guo-Feng Chen [a,*], Hui-Ming Jia [a], Li-Yan Zhang [a], Bao-Hua Chen [b], Ji-Tai Li [a]

[a] College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Chemical Biology of Hebei Province, Baoding 071002, PR China
[b] College of Pharmaceutical Sciences, Hebei University, Baoding 071002, PR China

ARTICLE INFO

Article history:
Received 28 June 2012
Received in revised form 31 August 2012
Accepted 8 September 2012
Available online 16 October 2012

Keywords:
Benzothiazoles
o-Aminothiophenol
Aromatic aldehydes
$FeCl_3$/Montmorillonite K-10
Ultrasound

ABSTRACT

2-Substituted benzothiazoles have been synthesized via one-pot reaction from aromatic aldehydes and *o*-aminothiophenol in the presence of $FeCl_3$/Montmorillonite K-10 in absolute methanol at 25–30 °C under ultrasound irradiation. The remarkable advantages are an inexpensive and easily available reagent, a simple procedure, mild conditions, short reaction times and moderate to good yields.

1. Introduction

Benzothiazole and their derivatives are often found in heterocyclic compounds, which exhibit a variety of biological activities, such as antitumor, antimicrobial and antiviral properties [1–4]. They also can be used as antioxidants, vulcanization accelerators in industry and as a dopant in light-emitting organic electroluminescent devices [5–7]. Because of the above importance, the synthesis of substituted benzothiazoles has become a focus of intense research in recent years. Several synthetic methodologies have been developed for the synthesis of 2-substituted benzothiazoles. The most synthetic approaches to the libraries are based on the condensation of *o*-aminothiophenol with substituted nitriles [8], carboxylic acids [9–12], acyl chlorides [13,14] and esters [15], or with aldehydes followed by oxidation. Subsequently, with the availability of a vast number of aldehydes, the second approach has recently become very popular. Various oxidative reagents and catalysts, such as 4-methoxy-TEMPO [4a], cetyltrimethyl ammonium bromide [16], $KAl(SO_4)_2{\cdot}12H_2O$ [17], H_2O_2/CAN [18], H_2O_2/HCl [19], NaOAc [20], poly[4-diacetoxyiodo] styrene [21], $Sc(OTf)_3$ [22], trichloroisocyanuric acid [23], I_2 [24], $HClO_4$/PANI [25], silica gel [26], PTSA [27], activated carbon-molecular oxygen [28], Ionic Liquid [29], bakers' yeast [30], SDS [31], glucose oxidase–peroxidase [32], P_2O_5 [33], Dowex 50W [34], $Fe(HSO_4)_3$ [35], etc. have all been used in the reaction. Although these methods are suitable for specific synthetic conditions, sometimes, a number of these methods suffer from one or more disadvantages such as long reaction times, expensive reagents, drastic reaction conditions, low yields, tedious work up procedures and co-occurrence of several side reactions. As a consequence, the development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic synthesis.

In the last few years, the application of ultrasound in synthetic organic chemistry has aroused more and more people's interest [36]. Sonochemistry offers a more versatile and facile pathway for a large variety of syntheses in comparison to classical methods. Thus, a large number of organic reactions can be carried out in high yield, short reaction time or mild conditions under ultrasound irradiation [37].

Recently, there has been an ongoing effort to use supported catalysts or reagents. This is mainly due to their advantages, such as non-corrosivity, high selectivity, mild reaction conditions and easy of work-up [38]. Among of them, $FeCl_3$ supported on Montmorillonite K-10 ($FeCl_3$/Montmorillonite K-10) has attracted considerable attention because of its desirable characteristics. As reported in previous papers, $FeCl_3$/Montmorillonite K-10 has been used as the catalyst in the preparation of 1,2-diaryl-1,2-ethanedione [39] to afford the desired products in higher yields. To the best of our knowledge, however, there are no reports on the synthesis of the title compound in the presence of $FeCl_3$/Montmorillonite K-10 under ultrasound irradiation. Considering the above points and in

* Corresponding author. Address: College of Chemistry and Environmental Science, Hebei University, Wusi East Road No. 180, Baoding 071002, PR China. Fax: +86 312 5079628.
E-mail address: chenguofeng@hbu.cn (G.-F. Chen).

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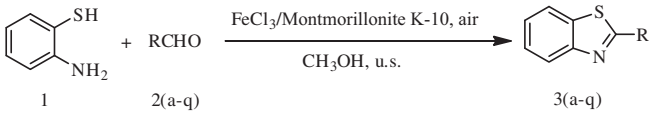
http://dx.doi.org/10.1016/j.ultsonch.2012.09.010



Scheme 1. Synthesis of 2-substituted benzothiazoles.

continuation of our work on ultrasound-promoted organic reactions [40], herein, we report a new and simple synthesis of 2-substituted benzothiazoles promoted by $FeCl_3$/Montmorillonite K-10 via condensation of *o*-aminothiophenol and aldehydes under ultrasound irradiation (Scheme 1).

2. Experimental

2.1. Apparatus, materials and measurements

All chemicals were obtained from commercial suppliers and were used without further purification. Melting points were uncorrected and determined using an X-4 apparatus. IR spectra were obtained using a NICOLET 380 FT-IR spectrometer instrument. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a Bruker AVANCE III 600 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as internal standard at room temperature. Mass spectrometric data were determined on Agilent Technologies 6310 Lon Trap LC/MS. Sonication was performed using a Shanghai Branson BUG 40–06 ultrasonic cleaner (with a frequency of 40 kHz and a nominal power 250 W).

2.2. Preparation of $FeCl_3$/Montmorillonite K-10

$FeCl_3$/Montmorillonite K-10 (10% w/w) was prepared by following process. Hydrated ferric chloride ($FeCl_3{\cdot}6H_2O$) 8 g was mixed with methanol (72 mL) and Montmorillonite K-10 (43.2 g). The mixture was stirred at room temperature for 1 h and methanol was removed under reduced pressure. The resulting yellow-green powder was dried at 120 °C for 4 h. The content of $FeCl_3$ was determined to be about 10%.

2.3. General procedure for synthesis of 2-substituted benzothiazoles

Aromatic aldehydes (**2**, 1.0 mmol), *o*-aminothiophenol (**1**, 1.0 mmol), $FeCl_3$/Montmorillonite K-10 (160 mg, 0.1 mmol, based on $FeCl_3$) and absolute methanol (5 mL) were added into a 25 mL conical flask. The reaction flask was placed in the ultrasonic cleaner bath, where the surface of reactants was slightly lower than the water level and irradiated at 25–30 °C for the period of time (sonication was continued until aromatic aldehydes disappeared as indicated by TLC) as indicated in Tables 1–4. After completion of the reaction, the reaction mixture was dissolved in ethyl acetate and $FeCl_3$/Montmorillonite K-10 was filtered off. The filtrate was concentrated and purified by silica-gel column chromatography (200–300 mesh) using petroleum ether or the mixture of petroleum ether and ethyl acetate as eluent to give a light yellow crystalline solid. All of the products described herein were previously reported in the literatures [16–35]. The authenticity of the products was established by spectroscopic data and by comparing their melting points with literature values.

2.3.1. Compound 3a

2-Phenylbenzothiazole: light yellow crystals, IR (KBr, cm^{-1}): 3062, 1589, 1510, 1477, 1456, 1433, 1283, 1252, 1224, 1158, 962, 765; ^{1}H NMR: δ_H 8.11–8.14 (m, 3H, ArH), 7.93 (d, J = 8.0 Hz, 1H, ArH), 7.51–7.54 (m, 4H, ArH), 7.42 (t, J = 8.0 Hz, 1H, ArH); ^{13}C NMR: δ_C 168.1, 154.2, 135.1, 133.6, 131.0, 129.0, 127.6, 126.3, 125.2, 123.3, 121.6; m/z (ESI): 212 $[M+H]^+$.

Table 1
The effect of solvent and temperature on the synthesis of 2-phenylbenzothiazole (**3a**).[a]

Entry	Solvent	T/°C	Time/h	Isolated yield [%]
1	C_2H_5OH	25–30	1	83.8
2	$CH_3COOC_2H_5$	25–30	1	81.0
3	CH_2Cl_2	25–30	1	84.3
4	DMF	25–30	1	76.8
5	CH_3CN	25–30	1	79.2
6	THF	25–30	1	77.9
7	$CHCl_3$	25–30	1	83.5
8	1,4-Dioxane	25–30	1	14.9
9	CH_3OH	25–30	1	85.0
10	CH_3OH	30–35	1	85.0
11	CH_3OH	35–40	1	83.2
12[b]	CH_3OH	25–30	1	72.5

[a] *o*-Aminothiophenol (1.0 mmol) and benzaldehyde (1.0 mmol), $FeCl_3$/Montmorillonite K-10 was 0.1 mmol (based on $FeCl_3$), the reactions were carried out in the presence of air.
[b] Operated in nitrogen atmosphere.

2.3.2. Compound 3b

2-(4-Chlorophenyl)benzothiazole: white crystals, IR (KBr, cm^{-1}): 3054, 1589, 1508, 1474, 1434, 1399, 1315, 1287, 1251, 1090, 1012, 965, 828, 756; ^{1}H NMR: δ_H 8.09 (d, J = 8.1 Hz, 1H, ArH), 8.05 (d, J = 8.5 Hz, 2H, ArH), 7.92 (d, J = 8.0 Hz, 1H, ArH), 7.51–7.54 (m, 1H, ArH), 7.49 (d, 1H, J = 8.6 Hz, ArH), 7.41–7.44 (m, 1H, ArH); ^{13}C NMR: δ_C 166.6, 154.1, 137.1, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7; m/z (ESI): 246 $[M+H]^+$.

2.3.3. Compound 3c

2-(4-Methylphenyl)benzothiazole: white crystals, IR (KBr, cm^{-1}): 3058, 3023, 1608, 1484, 1457, 1434, 1312, 1286, 1253, 1227, 1122, 959, 834, 817, 761; ^{1}H NMR: δ_H 8.10 (d, J = 7.9 Hz, 1H, ArH), 8.02 (d, J = 8.2 Hz, 2H, ArH), 7.91 (d, J = 8.0 Hz, 1H, ArH), 7.50–7.53 (m, 1H, ArH), 7.38–7.41 (m, 1H, ArH), 7.32 (d, J = 7.9 Hz, 2H, ArH), 2.45 (s, 3H, CH_3); ^{13}C NMR: δ_C 168.3, 154.2, 141.5, 134.9, 131.0, 129.7, 127.5, 125.0, 126.3, 123.1, 121.6, 21.5; m/z (ESI): 226 $[M+H]^+$.

2.3.4. Compound 3d

2-(4-Hydroxyphenyl)benzothiazole: brown crystals, IR (KBr, cm^{-1}): 3063, 2995, 1605, 1540, 1523, 1482, 1465, 1430, 1380, 1317, 1284, 1249, 1224, 1167, 1108, 1073, 977, 827, 798, 755; ^{1}H NMR (DMSO-d_6): δ_H 10.25 (s, 1H, OH), 8.07 (d, J = 7.9 Hz, 1H, ArH), 7.98 (d, J = 8.1 Hz, 1H, ArH), 7.94 (d, J = 8.5 Hz, 2H, ArH), 7.49–7.51 (m, 1H, ArH), 7.39–7.41 (m, 1H, ArH), 6.94–6.96 (m, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ_C 167.9, 161.0, 160.8, 154.2, 134.6, 129.5, 126.9, 125.4, 124.6, 122.8, 122.6, 116.6, 116.5; m/z (ESI): 228 $[M+H]^+$.

2.3.5. Compound 3e

2-(4-Methoxyphenyl)benzothiazole: light yellow crystals, IR (KBr, cm^{-1}): 3064, 2995, 2937, 2835, 1605, 1591, 1555, 1522, 1484, 1466, 1455, 1434, 1412, 1310, 1303, 1286, 1257, 1225, 1182, 1171, 1074, 1027, 968, 832, 791; ^{1}H NMR: δ_H 8.06–8.07 (m, 3H, ArH), 7.90 (d, J = 8.0 Hz, 1H, ArH), 7.48–7.51 (m, 1H, ArH), 7.37–7.39 (m, 1H, ArH), 7.02–7.03 (m, 2H, ArH), 3.91 (s, 3H, OCH_3); ^{13}C NMR: δ_C 167.9, 161.9, 154.2, 134.9, 129.1, 126.5, 126.2, 124.80, 122.8, 121.5, 114.4, 55.5; m/z (ESI): 242 $[M+H]^+$.

2.3.6. Compound 3f

2-(4-*N*,*N*-Dimethylphenyl)benzothiazole: light yellow crystals, IR (KBr, cm^{-1}): 3052, 2895, 2806, 1609, 1576, 1540, 1507, 1485,

Table 2
The synthesis of 2-substituted benzothiazoles derivatives in the presence of $FeCl_3$/Montmorillonite K-10 under ultrasound.

Entry	R	Product	Time [h]	Isolated yield [%]	m.p., [°C] (lit)
1	C_6H_5	**3a**	1.0	85.0	112–114(112–114) [17]
2	C_6H_5	**3a**	1.0	67.5[a]	
3	C_6H_5	**3a**	1.0	58.7[b]	
4	C_6H_5	**3a**	1.0	32.8[c]	
5	4-ClC_6H_4	**3b**	0.7	86.0	114–116(114–115) [17]
6	4-$CH_3C_6H_4$	**3c**	1.0	85.7	80–84(83) [17]
7	4-OHC_6H_4	**3d**	1.2	95.3	230–234(231) [31]
8	4-$CH_3OC_6H_4$	**3e**	1.4	81.4	123–124(121) [31]
9	4-$(Me)_2NC_6H_4$	**3f**	1.4	72.0	180–182(173) [31]
10	2-ClC_6H_4	**3g**	4.9	75.4	80–82(80–82) [20]
11	2-$CH_3OC_6H_4$	**3h**	1.7	77.8	110–112(120–122) [16]
12	2-HOC_6H_4	**3i**	3.9	73.8	132–134(129–131) [24]
13	3-ClC_6H_4	**3j**	1.3	82.6	98–100(94–95) [25]
14	3-$NO_2C_6H_4$	**3k**	5.0	33.4	200–204(183–185) [16]
15	3,4-$Cl_2C_6H_3$	**3l**	2.4	83.1	123–124(118–120) [4c]
16	2,4-$Cl_2C_6H_3$	**3m**	1.5	51.4	150–152(144–145) [4b]
17	4-HO-3-$MeOC_6H_3$	**3n**	1.4	89.2	180–182(162–164) [34]
18	2-HO-3-$MeOC_6H_3$	**3o**	1.7	51.1	175–177(162–163) [35]
19	3,4-$OCH_2OC_6H_3$	**3p**	2.9	73.3	129–130(125–127) [16]
20	2-Furyl	**3q**	5.0	72.3	110–113(106) [31]
21	2-$NO_2C_6H_4$		3.8[d]	–	–
22	2,4-$(NO_2)_2C_6H_3$		5.0[d]	–	–
23	$CH_3CH_2CH_2$		4.8[d]	–	–
24	$CH_3(CH_2)_5$		4.8[d]	–	–

[a] In the presence of $FeCl_3$.
[b] In the presence of Montmorillonite K-10.
[c] Without $FeCl_3$/Montmorillonite K-10.
[d] No reaction.

Table 3
Contrast experiments of 3(a–d) in the presence of $FeCl_3$/Montmorillonite K-10 with ultrasound or without ultrasound.

Entry	R	Product	Time [h]	Isolated yield (%)	
				A	B
1	C_6H_5	**3a**	1.0	85.0	82.6
2	4-ClC_6H_4	**3b**	0.7	86.0	58.8
3	4-$CH_3C_6H_4$	**3c**	1.0	85.7	70.3
4	4-OHC_6H_4	**3d**	1.2	95.3	68.9

Condition: A, ultrasound; B, stirring alone without ultrasound.

Table 4
Synthesis of 2-phenylbenzothiazole (3a) with recovered $FeCl_3$/Montmorillonite K-10.

Number of cycles	Fresh	Recycle I	Recycle II	Recycle III
Isolated yield (%)	85.0	78.6	73.4	69.0

1456, 1431, 1369, 1314, 1287, 1255, 1227, 1188, 1062, 963, 843, 800, 752; ^{1}H NMR: δ_H 8.02 (d, 1H, J = 8.0 Hz, ArH), 7.98–8.00 (m, 2H, ArH), 7.86 (d, 1H, J = 8.4 Hz, ArH), 7.45–7.48 (m, 1H, ArH), 7.32–7.34 (m, 1H, ArH), 6.75–6.78 (m, 2H), 3.07 (s, 6H, CH_3); ^{13}C NMR: δ_C 168.8, 154.4, 152.2, 134.6, 128.9, 126.0, 124.2, 122.3, 121.4, 111.7, 40.2; m/z (ESI): 255 $[M+H]^+$.

2.3.7. Compound 3g

2-(2-Chlorophenyl)benzothiazole: white crystals, IR (KBr, cm^{-1}): 3055, 1590, 1564, 1492, 1456, 1431, 1317, 1299, 1271, 1250, 1061, 1016, 966, 757, 748; ^{1}H NMR: δ_H 8.23–8.26 (m, 1H, ArH), 8.17 (d, J = 8.1 Hz, 1H, ArH), 7.98 (d, J = 8.0 Hz, 1H, ArH), 7.55–7.58 (m, 2H, ArH), 7.43–7.48 (m, 3H, ArH); ^{13}C NMR: δ_C 164.2, 152.5, 136.1, 132.8, 132.3, 131.8, 131.2, 130.8, 127.1, 126.3, 125.5, 123.5, 121.4; m/z (ESI): 246 $[M+H]^+$.

2.3.8. Compound 3h

2-(2-Methoxyphenyl)benzothiazole: light yellow crystals, IR (KBr, cm^{-1}): 3035, 3015, 2965, 2936, 2831, 1617, 1598, 1581, 1558, 1540, 1521, 1499, 1460, 1429, 1309, 1284, 1248, 1216, 1174, 1160, 1115, 1017, 962, 945, 757, 728; ^{1}H NMR: δ_H 8.58 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.6 Hz, ArH), 8.14 (d, J = 8.2 Hz, 1H, ArH), 7.96 (d, J = 7.9 Hz, 1H, ArH), 7.47–7.54 (m, 2H, ArH), 7.40 (t, J = 7.3 Hz, 1H, ArH), 7.17 (t, J = 7.4 Hz, 1H, ArH), 7.08 (d, J = 8.3 Hz, 1H, ArH), 4.07 (s, 3H, CH_3); ^{13}C NMR: δ_C 163.1, 157.3, 152.2, 136.2, 131.8, 129.6, 125.9, 124.6, 122.8, 122.4, 121.2, 111.7, 55.7; m/z (ESI): 242 $[M+H]^+$.

2.3.9. Compound 3i

2-(2-Hydroxyphenyl)benzothiazole: white crystals, IR (KBr, cm^{-1}): 3057, 2923, 1621, 1589, 1543, 1522, 1483, 1457, 1437, 1419, 1315, 1272, 1251, 1219, 1165, 1150, 1033, 973, 871, 860, 757, 742; ^{1}H NMR: δ_H 12.55 (s, 1H, OH), 8.00 (d, 1H, J = 8.0 Hz ArH), 7.91 (d, 1H, J = 7.9 Hz ArH), 7.71 (dd, 1H, J_1 = 7.9 Hz, J_2 = 1.1 Hz, ArH), 7.51–7.54 (m, 1H, ArH), 7.40–7.44 (m, 2H, ArH), 7.14 (dd, 1H, J_1 = 8.3 Hz, J_2 = 0.8 Hz, ArH), 6.97–6.99 (m, 1H, ArH); ^{13}C NMR: δ_C 169.4, 158.0, 151.9, 132.7, 132.6, 128.4, 126.7, 125.5, 122.2, 121.5, 119.5, 117.9, 116.8; m/z (ESI): 228 $[M+H]^+$.

2.3.10. Compound 3j

2-(3-Chlorophenyl)benzothiazole: white crystals, IR (KBr, cm^{-1}): 3053, 1622, 1588, 1569, 1541, 1501, 1473, 1458, 1434, 1423, 1294, 1268, 1245, 1232, 1161, 1076, 943, 886, 861, 783, 759, 732; ^{1}H NMR: δ_H 8.14 (t, 1H, J = 1.8 Hz ArH), 8.11 (d, 1H, J = 8.2 Hz, ArH), 7.96–7.97 (m, 1H, ArH), 7.93 (d, 1H, J = 8.4 Hz, ArH), 7.52–7.55 (m, 1H ArH), 7.47–7.49 (m, 1H, ArH), 7.42–7.45 (m, 2H, ArH); ^{13}C NMR: δ_C 166.3, 154.0, 135.3, 135.2, 135.1, 130.9, 130.2, 127.4, 126.5, 125.7, 125.6, 123.5, 121.7; m/z (ESI): 246 $[M+H]^+$.

2.3.11. Compound 3k

2-(3-Nitrophenyl)benzothiazole: light yellow crystals, IR (KBr, cm^{-1}): 3085, 1623, 1593, 1579, 1570, 1558, 1530, 1472, 1458,

1432, 1363, 1345, 1311, 1288, 1244, 1128, 1101, 987, 888, 843, 810, 761; ^{1}H NMR: δ_H 8.93 (s, 1H, ArH), 8.42 (d, J = 7.7 Hz, 1H, ArH), 8.34 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.3 Hz, ArH), 8.13 (d, J = 8.2 Hz, 1H, ArH), 7.96 (d, J = 8.0 Hz, 1H, ArH), 7.70 (t, J = 7.9 Hz, 1H, ArH), 7.56 (t, J = 7.5 Hz, 1H, ArH), 7.47 (t, J = 7.6 Hz, 1H, ArH); ^{13}C NMR: δ_C 164.9, 153.9, 148.8, 135.3, 135.2, 133.0, 130.1, 126.8, 126.0, 125.1, 123.7, 122.3, 121.8; m/z (ESI): 257 $[M+H]^+$.

2.3.12. Compound 3l

2-(3,4-Dichlorophenyl)benzothiazole: white crystals, IR (KBr, cm^{-1}): 3061, 1587, 1473, 1464, 1456, 1419, 1388, 1374, 1310, 1279, 1257, 1245, 1230, 1136, 1027, 985, 824, 786, 757, 725; ^{1}H NMR: δ_H 8.23 (d, J = 2.1 Hz, 1H, ArH), 8.09 (d, J = 8.2 Hz, 1H, ArH), 7.93 (d, J = 7.9 Hz, 1H, ArH), 7.90 (dd, 1H, J_1 = 8.3 Hz, J_2 = 2.0 Hz, ArH), 7.57 (d, J = 8.3 Hz, 1H, ArH), 7.52–7.55 (m, 1H, ArH), 7.43–7.45 (m, 1H, ArH); ^{13}C NMR: δ_C 165.0, 154.0, 135.1, 133.5, 131.0, 129.0, 126.7, 126.5, 125.7, 123.5, 121.7; m/z (ESI): 280 $[M+H]^+$.

2.3.13. Compound 3m

2-(2,4-Dichlorophenyl)benzothiazole: white crystals, IR (KBr, cm^{-1}): 3067, 1624, 1583, 1549, 1508, 1481, 1457, 1449, 1377, 1316, 1258, 1220, 1162, 1106, 1078, 1060, 964, 859, 826, 794, 754, 725; ^{1}H NMR: δ_H 8.26 (d, J = 8.5 Hz, 1H, ArH), 8.15 (d, J = 8.2 Hz, 1H, ArH), 7.97 (d, J = 8.0 Hz, 1H, ArH), 7.55–7.58 (m, 2H, ArH), 7.45–7.48 (m, 1H, ArH), 7.42 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.0 Hz, ArH); ^{13}C NMR: δ_C 163.0, 152.4, 136.6, 136.1, 133.3, 132.5, 130.8, 130.6, 127.6, 126.5, 125.7, 123.5, 121.4; m/z (ESI): 280 $[M+H]^+$.

2.3.14. Compound 3n

2-(3-Methoxy-4-hydroxyphenyl)benzothiazole: brown crystals, IR (KBr, cm^{-1}): 3099, 3004, 2934, 1616, 1604, 1584, 1559, 1529, 1478, 1462, 1427, 1387, 1364, 1315, 1279, 1256, 1194, 1124, 1033, 1011, 894, 872, 776, 756, 727; ^{1}H NMR: δ_H 9.85 (s, 1H, OH), 8.06 (d, J = 8.2 Hz, 1H, ArH), 7.89 (d, J = 7.9 Hz, 1H, ArH), 7.75 (d, J = 1.8 Hz, 1H, ArH), 7.56 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.9 Hz, ArH), 7.48–7.51 (m, 1H, ArH), 7.37–7.39 (m, 1H, ArH), 7.03 (d, J = 8.2 Hz, 1H, ArH), 4.00 (s, 3H, CH_3); ^{13}C NMR: δ_C 168.2, 154.0, 148.6, 147.0, 134.8, 126.3, 126.2, 124.9, 122.7, 122.0, 121.5, 114.8, 109.3, 56.2; m/z (ESI): 258 $[M+H]^+$.

2.3.15. Compound 3o

2-(2-Hydroxy-4-methoxyphenyl)benzothiazole: brown crystals, IR (KBr, cm^{-1}): 3055, 2937, 2837, 1583, 1540, 1470, 1460, 1438, 1293, 1279, 1247, 1177, 1117, 1084, 1003, 936, 777, 756, 725; ^{1}H NMR: δ_H 9.85 (s, 1H, OH), 8.06 (d, J = 8.1 Hz, 1H, ArH), 7.89 (d, J = 7.9 Hz, 1H, ArH), 7.75 (d, J = 1.4 Hz, 1H, ArH), 7.56 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.7 Hz, ArH), 7.49 (t, J = 7.6 Hz, 1H, ArH), 7.38 (t, J = 7.6 Hz, 1H, ArH), 7.03 (d, J = 8.2 Hz, 1H, ArH), 3.99 (s, 3H, CH_3); ^{13}C NMR: δ_C 168.2, 154.0, 148.6, 147.0, 134.8, 126.3, 126.2, 124.9, 122.7, 122.0, 121.5, 114.8, 109.3, 56.2; m/z (ESI): 258 $[M+H]^+$.

2.3.16. Compound 3p

2-(3′,4′-Methylenedioxyphenyl)benzothiazole: light yellow crystals, IR (KBr, cm^{-1}): 3058, 2987, 2908, 1602, 1497, 1473, 1440, 1350, 1254, 1132, 1108, 1071, 1031, 988, 940, 881, 834, 804, 756, 727; ^{1}H NMR: δ_H 8.05 (d, J = 8.1 Hz, 1H, ArH), 7.88 (d, J = 7.9 Hz, 1H, ArH), 7.61–7.64 (m, 2H, ArH), 7.48–7.51 (m, 1H, ArH), 7.37–7.40 (m, 1H, ArH), 6.92 (d, J = 8.0 Hz, 1H, ArH), 6.07 (s, 2H, CH_2); ^{13}C NMR: δ_C 167.6, 154.0, 150.1, 148.4, 134.8, 128.0, 126.3, 125.0, 122.9, 122.5, 121.5, 108.7, 107.5, 101.7; m/z (ESI): 256 $[M+H]^+$.

2.3.17. Compound 3q

2-(2-Furanyl)benzothiazole: brown crystals, IR (KBr, cm^{-1}): 3143, 3121, 3048, 1598, 1541, 1522, 1502, 1473, 1455, 1433, 1420, 1385, 1313, 1253, 1244, 1218, 1155, 1012, 897, 882, 769, 761, 747; ^{1}H NMR: δ_H 8.08 (d, J = 8.2 Hz, 1H, ArH), 7.90 (d, J = 7.9 Hz, 1H, ArH), 7.62 (s, 1H, FuranH), 7.51 (t, J = 7.3 Hz, 1H, ArH), 7.40 (t, J = 7.3 Hz, 1H, ArH), 7.22 (d, J = 2.8 Hz, 1H, FuranH), 6.61 (d, J = 1.5 Hz, 1H, FuranH); ^{13}C NMR: δ_C 157.6, 153.7, 148.8, 144.7, 134.3, 126.5, 125.2, 123.1, 121.6, 112.5, 111.5; m/z (ESI): 202 $[M+H]^+$.

3. Results and discussion

In the initial experiment, we investigated various conditions in the model reaction of *o*-aminothiophenol (**1**) with benzaldehyde (**2a**) in the presence of $FeCl_3$/Montmorillonite K-10 under ultrasound irradiation and the results were summarized in Table 1. The effect of various solvents (such as EtOH, $CH_3COOC_2H_5$, CH_2Cl_2, DMF, CH_3CN, THF, $CHCl_3$, 1,4-dioxane and MeOH) on the model reaction was conducted in the presence of $FeCl_3$/Montmorillonite K-10. The results indicated that the solvents had a significant effect on the product yield. The use of 1,4-dioxane as solvent gave poor yields (Table 1, Entry 8). Solvents like DMF, CH_3CN and THF gave moderate yields (Table 1, Entries 4, 5 and 6). The best conversion was observed when the reaction was performed in CH_3OH (Table 1, Entry 9). Based on these results, CH_3OH was then selected as the solvent for further investigations.

The effect of reaction temperature on the model reaction in the presence of $FeCl_3$/Montmorillonite K-10 under ultrasound irradiation was also observed. As shown in Table 1, when the temperature was 25–30, 30–35 and 35–40 °C, the yield of **3a** was 85.0% (Entry 9), 85.0% (Entry 10) and 83.2% (Entry 11) respectively. Consequently, the reaction temperature had little effect on the reaction. In addition, the reaction was slow and gave unsatisfactory yield (72.5%) of 2-phenylbenzothiazole (**3a**) under nitrogen atmosphere (Table 1, Entry 12), it showed that aerial oxygen played an oxidant role in this reaction.

To test the generality of this reaction, a series of aromatic aldehydes with both electron-donating and electron-withdrawing substituents were reacted with *o*-aminothiophenol under the optimized reaction conditions, and the corresponding 2-substituted benzothiazoles (**3a**–**q**) were obtained under ultrasound irradiation or silent conditions. The results are summarized in Tables 2 and 3.

As shown in Tables 2 and 3, a series of aromatic aldehydes were successfully employed to prepare the corresponding benzothiazole derivatives in excellent yields. In general, the yields of benzothiazole derivatives are similar or higher than those described in literatures. The outstanding character of the present procedure is to save the reaction time and improve the yield.

According to the method catalyzed by 4-methoxy-TEMPO in presence of oxygen [4a], the time and yield of **3a** were 9 h and 80% respectively heating at 120 °C in xylene for the condensation of *o*-aminothiophenol and benzaldehyde. The present procedure gave 85% yield within 1 h (Table 2, Entry 1) at 25–30 °C. In the reaction catalyzed by Dowex 50 W in water under aerial oxygen [34], **3d** was obtained in 92% yield at 70 °C for 10 h, whereas the present procedure afforded **3d** in 95.3% yield within 1.2 h at 25–30 °C (Table 2, Entry 7).

In the present procedure, furfuraldehyde (**2q**) also afforded the desired products in moderate yields (72.3%) within 5.0 h (Table 2, Entry 20). 2-Nitrobenzaldehyde and 2,4-dinitrobenzaldehyde (Table 2, Entries 21 and 22) were failed. Aliphatic aldehyde was less reactive than arylaldehyde, no product was obtained when

aliphatic aldehyde was used (Entries 23 and 24). It seems that this protocol has its limitations.

We also did the same scale reaction in the presence of $FeCl_3$ alone. The yield of **3a** was 67.5% after 1.0 h under ultrasound (Table 2, Entry 2). A relatively low reactivity (58.7%) for the synthesis of **3a** was found when only using the Montmorillonite K-10 after 1.0 h under ultrasound (Table 2, Entry 3), however, the reactivity was increased drastically after introduction of $FeCl_3$ (Table 2, Entry 1).

We also did the experiment for the reaction of *o*-aminothiophenol (**1**) and benzaldehyde (**2a**) in the absence of $FeCl_3$/Montmorillonite K-10 under ultrasound, and the yield of **3a** was only 32.8% within 1.0 h. It seems that $FeCl_3$/Montmorillonite K-10 plays an important role in the reaction (Table 2, Entry 4).

In order to verify the effect of ultrasound irradiation, we also did the contrast experiments under stirring without ultrasound irradiation. As shown in Table 3, compound **3a**, **3b**, **3c** and **3d** were obtained in 82.6%, 58.8%, 70.3% and 68.9% yields within 1.0, 0.7, 1.0 and 1.2 h respectively. Whereas under ultrasound irradiation, **3a**, **3b**, **3c** and **3d** were obtained in 85.0%, 86.0%, 85.7% and 95.3% yields respectively. It's clear that ultrasound can accelerate the condesation of *o*-aminothiophenol with aromatic aldehydes and improve the result. The phenomenon of cavitation produced by ultrasound may be responsible for competitive advantages of present procedure [36].

The recycling performance of the $FeCl_3$/Montmorillonite K-10 in the model reaction was also inverstigated. After completion of the reaction, the isolated $FeCl_3$/Montmorillonite K-10 was washed with ethyl acetate and reactivated at 120 °C for 4 h, and can be reused three times, the yield of **3a** decreased from 85.0 to 69.0% (Table 4). This may due to the leaching of the active component (i.e. iron), which can be seen from the color change of the solvent when washed with ethyl acetate in the post-processing [41]. Further work is necessary to strongly bind the $FeCl_3$ on Montmorillonite K-10.

4. Conclusion

In summary, we have found an efficient and practical procedure for the preparation of 2-substituted benzothiazoles in the presence of $FeCl_3$/Montmorillonite K-10 under ultrasound irradiation. This methodology offers the competitive advantages of mild reaction conditions, short reaction times, high yields and an inexpensive and easily available reagent.

Acknowledgements

The project was supported by Natural Science Foundation of Hebei Province (B2011201072), the Science Project of the Hebei Education Department (ZD200910) and Foundation of Hebei University (2009-163).

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