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Research Article

An Efficient One-Pot Three-Component Synthesis of Novel Sulfanyl Tetrazoles Using Ionic Liquids

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An efficient, simple, and environmentally benign method for the synthesis of novel sulfanyl tetrazoles has been achieved by one-pot three-component reaction of phenacyl bromides/3-(2-bromoacetyl)coumarins with KSCN and NaN_3 using $[Bmim]BF_4$ ionic liquid. It could be reused and recycled for four runs without significant loss of product yield.

1. Introduction

Over the years, multicomponent reactions (MCRs) have become increasingly popular tools to ensure sufficient molecular diversity and complexity. They have gained significant popularity in recent years due to their atom-economy and straightforward reaction design due to substantial minimization of waste, labour, time, and cost [1, 2].

Tetrazoles play an important role in coordination chemistry as ligands, in medicinal chemistry as stable surrogates for carboxylic acids and in materials applications, including explosives, rocket propellants, and agriculture [3–13]. There is a particular interest for the synthesis of 5-alkyl/arylthiotetrazoles as these thiotetrazoles are having powerful activating property than the corresponding 5-akyl/aryltetrazoles used for synthesis of DNA and RNA [14, 15]. The presence of alkylthio group makes the tetrazole ring more acidic than the corresponding 5-alkyltetrazoles which improves its ability to act asan activator [16].

On the other hand, coumarins are heterocyclic organic compounds which constitute an important group of natural products having varied biological activities such as antitumor, antiinflammatory, antiviral, CNS, antioxidant, and anti-HIV activities [17–20].

Thus, in view of the diverse activity of coumarins and tetrazoles, as a part of our continuing research work on the synthesis of novel heterocyclic compounds, we thought to synthesize the compounds containing coumarin-substituted sulfanyl tetrazoles.

The most convenient method of synthesizing tetrazoles is the addition of azide ions to nitriles. Earlier reported methods for the synthesis of 5-substituted tetrazoles suffer from drawbacks such as the use of strong Lewis acids, or expensive and toxic metals, and the *in situ* generated hydrazoic acid which is highly toxic and explosive [21–24].

Several syntheses of 5-substituted tetrazoles have been reported through the [2+3] cycloaddition of nitriles using NaN_3 or $TMSN_3$ in the presence of catalysts such as $ZnCl_2$ [25], $AlCl_3$ [26], BF_3-OEt_2 [27], $Pd(PPh_3)_4$ [28], $FeCl_3$-SiO_2 [29], TBAF [30], Zn/Al hydrotalcite [31], ZnO [32], and Cu_2O [33]. Recently, LeBlanc and Jursic [34] and Demko and Sharpless [35] reported the synthesis of sulfanyl tetrazoles. Although these methods were quite useful, but having some limitations such as use of toxic solvents and use of homogeneous Lewis acid catalyst like $ZnBr_2$ which could not be recycled from the reaction mixture. All the above methods require prolonged reaction times. Therefore, we thought of developing more efficient and convenient method which is free from all the above drawbacks.

2. Results and Discussion

In recent times, ionic liquids have attracted increasing interest in the context of green synthesis. These ILs have shown great promise as an alternative to conventional solvents due to their unique properties of nonvolatility, nonflammability, thermal stability, recyclability, and controlled miscibility [36–40]. Butylimidazolium salts ILs have already been demonstrated as efficient catalysts and solvents for various organic transformations [41–44].

Our literature survey revealed that till now there were no methods reported in the literature for the synthesis of sulfanyl tetrazoles via one-pot three-component reaction using ionic liquids. As part of our ongoing research work on the developments of new routes to heterocyclic system in ionic liquids [45, 46], we, herein, wish to report a simple and efficient procedure for one-pot three-component synthesis of novel sulfanyl tetrazoles by using 3-(2-bromoacetyl)coumarins/phenacyl bromides, KSCN and NaN_3 in the presence of $[Bmim]BF_4$ ionic liquid at 100°C to afford title compounds in good yields. (Schemes 1 and 2).

Ionic liquids (ILs) based on butylimidazolium salts were tested as solvents. In order to optimize the reaction conditions, a model reaction was performed using 4-chlorophenacyl bromide **5b**, KSCN and NaN_3 using various ionic liquids.

A mixture of 4-chlorophenacyl bromide **5b** and KSCN in ionic liquid was stirred at RT for 10 minutes. After completion of the reaction, NaN_3 was added and the reaction was continued for 12 h, there was no product formation as observed by TLC, whereas at 60°C the reaction proceeded but not to completion even after 8 h. Consequently, the reaction temperature was optimized at 100°C, which gave the sulfanyltetrazole as the sole product. The results were summarized in Table 1. As can be seen from Table 1, the best result was obtained when the reaction was carried out in $[Bmim]BF_4$ at 100°C (Table 1, entry 4). The reaction using $[Bmim]BF_4$ proceeded in higher yield and shorter reaction time than that using another ionic liquids as reaction media.

The recyclability of the ionic liquid was also investigated using the above model reaction. After completion of the reaction, the mixture was poured into water and stirred thoroughly. The solid product was isolated by filtration, and the filtrate containing ionic liquid was extracted with ethyl acetate (2 × 20 mL) to remove nonionic organic impurities. Then, the water was evaporated under reduced pressure and the recovered ionic liquid was dried at 80°C under vacuum for 2 h and reused in the next reaction. The procedure was repeated, and the results indicated that the ionic liquid could be reused for four times without evident loss in the yield of the product (Table 2). The scope and the generality of the present method were further demonstrated by the reaction of various phenacylbromides/3-(2-bromoacetyl)coumarins with KSCN and NaN_3. In all cases, up to quantitative yields in reasonable reaction times were obtained (Table 3). All the synthesized compounds were characterized by m.p, elemental analysis, IR, ^1H NMR, mass, and ^{13}C NMR data.

Table 1: Synthesis of **6b** in various ILs at 100°C.

Entry	Solvent	Time (h)[a]	Yield (%)[b]
1	[Bmim]Cl	7	74
2	[Bmim]Br	6.5	66
3	$[Bmim]PF_6$	8	48
4	$[Bmim]BF_4$	2	91

[a] Time for total completion of the reaction.
[b] Isolated yield.

Table 2: Recycling of $[Bmim]BF_4$ ionic liquid.

Entry	Cycle	Time (h)	Yield (%)[a]
1	1st run	2	91
2	2nd run	2	90
3	3rd run	2	88
4	4th run	2.5	87

[a] Isolated yield of **6b.**

3. Conclusion

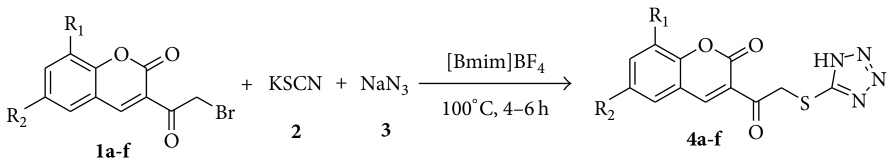
In summary, we have developed an efficient, practically convenient, and ecologically safe method for the synthesis of novel sulfanyl tetrazoles using $[Bmim]BF_4$ ionic liquid. This protocol has the advantages of simple workup, short reaction times, milder reaction conditions, good yields, and environmentally benign reusable solvent.

4. Experimental

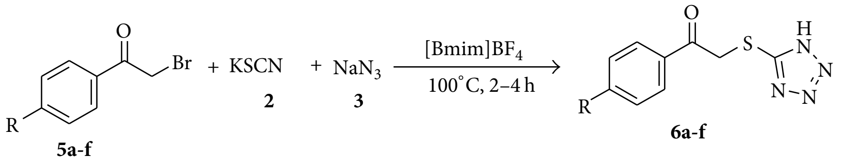
4.1. General. Melting points were recorded in open capillary and were uncorrected. Column chromatography was performed using silicagel (100–200 mesh size) purchased from Thomas Baker and TLC was carried out using aluminium sheets precoated with silica gel 60F254 purchased from Merck. IR spectra (KBr) were recorded on a Bruker WM-4(X) spectrometer (577 model). ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Bruker AC-300 spectrometer in $CDCl_3$ and DMSO-d_6 with TMS as an internal standard. Mass spectra (ESI) were recorded on JEOL SX-102 spectrometer. CHN analysis was done by Carlo Erba EA 1108 automatic elemental analyzer. The chemicals and solvents used were of commercial grade and were used without further purification unless, otherwise, stated.

4.2. Typical Procedure. A mixture of phenacylbromide **5a–f** (1 mmol) or 3-(2-bromoacetyl)coumarin **1a–f** (1 mmol) and KSCN (1.2 mmol) in $[Bmim]BF_4$ (3 mL) was stirred at RT for 10 min (in case of 3-(2-bromoacetyl)coumarins; 45 min), after completion of the reaction (single spot on TLC), NaN_3 (1.2 mmol) was added portion wise to the reaction mixture and then it was stirred at 100°C for appropriate time. After completion of the reaction (monitored by TLC), it was cooled to RT and poured into ice cold water, the solid separated was filtered, washed with water, dried, and purified by column chromatography using silicagel (ethylacetate/n-hexane: 2/8) to afford title compounds **4a–f** and **6a–f** in good yields.

3-(2-(1H-Tetrazol-5-ylsulfanyl)-acetyl)-chromen-2-one **(4a)**. m.p. 154–156°C; IR (KBr, cm^{-1}) 3347, 3073, 1729, 1680,



Scheme 1



Scheme 2

1551; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96 (s, 2H, $-CH_2$), 7.34–7.36 (m, 2H, ArH), 7.95 (d, 2H, ArH), 8.80 (s, 1H, C_4 of coumarin); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.89, 123.21, 125.22, 128.32, 129.65, 130.36, 135.15, 145.16, 148.84, 155.18, 158.94, 185.66; MS *m/z*: 289 $(M+1)^+$; Anal. Calcd for $C_{12}H_8N_4O_3S$; C, 50.00; H, 2.80; N, 19.43. Found: C, 50.12; H, 2.71; N, 19.37%.

6-Chloro-3-(2-(1H-tetrazol-5-ylsulfanyl)-acetyl)-chromen-2-one **(4b)**. m.p. 161–163°C; IR (KBr, cm^{-1}) 3342, 3075, 1719, 1676, 1554; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.94 (s, 2H, $-CH_2$), 7.44–7.46 (m, 2H, ArH), 7.96 (s, 1H, ArH), 8.82 (s, 1H, C_4 of coumarin); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.64, 125.34, 128.41, 129.65, 130.36, 131.52, 135.11, 145.05, 147.89, 154.52, 158.58, 184.37; MS *m/z*: 323 $(M+1)^+$; Anal. Calcd for $C_{12}H_7ClN_4O_3S$: C, 44.66; H, 2.19; N, 17.36. Found: C, 44.52; H, 2.26; N, 17.40%.

6,8-Dichloro-3-(2-(1H-tetrazol-5-ylsulfanyl)-acetyl)-chromen-2-one **(4c)**. m.p. 173–175°C; IR (KBr, cm^{-1}) 3347, 3071, 1711, 1672, 1557; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.94 (s, 2H, $-CH_2$), 7.58 (s, 1H, ArH), 7.84 (s, 1H, ArH), 8.80 (s, 1H, C_4 of coumarin); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.66, 124.16, 127.93, 129.42, 131.35, 134.32, 136.17, 142.86, 146.91, 154.56, 158.77 184.37; MS *m/z*: 358 $(M+1)^+$; Anal. Calcd for $C_{12}H_6Cl_2N_4O_3S$: C, 40.35; H, 1.69; N, 19.85. Found: C, 40.46; H, 1.61; N, 19.80%.

6-Bromo-3-(2-(1H-tetrazol-5-ylsulfanyl)-acetyl)-chromen-2-one **(4d***)*. m.p. 146–148°C; IR (KBr, cm^{-1}) 3344, 3073, 1729, 1680, 1562; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96 (s, 2H, $-CH_2$), 7.44–7.46 (m, 2H, ArH), 7.95 (s, 1H, ArH), 8.84 (s, 1H, C_4 of coumarin); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.78, 120.19, 127.91, 129.89, 130.78, 132.44, 136.31, 146.75, 149.03, 154.62, 158.71 184.43; MS *m/z*: 368 $(M+1)^+$; Anal. Calcd for $C_{12}H_7BrN_4O_3S$: C, 39.25; H, 1.92; N, 15.26. Found C, 39.18; H, 1.98; N, 15.20%.

6,8-Dibromo-3-(2-(1H-tetrazol-5-ylsulfanyl)-acetyl)-chromen-2-one **(4e)**. m.p. 167–169°C; IR (KBr, cm^{-1}) 3341, 3078, 1714, 1677, 1557; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.92 (s, 2H, $-CH_2$), 7.62 (s, 1H, ArH), 7.85 (s, 1H, ArH), 8.80 (s, 1H, C_4 of coumarin); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.70, 123.26, 128.71, 129.83, 131.47, 133.21, 136.31, 143.47, 147.82, 154.48, 158.63 184.32; MS *m/z*: 447 $(M+1)^+$; Anal. Calcd for $C_{12}H_6Br_2N_4O_3S$: C, 32.31; H, 1.36; N, 12.56. Found: C, 32.44; H, 1.28; N, 12.50%.

8-Methoxy-3-(2-(1H-tetrazol-5-ylsulfanyl)-acetyl)-chromen-2-one **(4f)**. m.p. 131–133°C; IR (KBr, cm^{-1}) ν = 3346, 3080, 1724, 1684, 1566; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H, $-OCH_3$), 4.90 (s, 2H, $-CH_2$), 7.22–7.30 (m, 3H, ArH), 8.82 (s, 1H, C_4 of coumarin); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.94, 55.71, 115.93, 121.17, 123.21, 129.65, 130.24, 134.11, 137.16, 154.38, 157.84, 160.21, 185.66; MS *m/z*: 319 $(M+1)^+$; Anal. Calcd. for $C_{13}H_{10}N_4O_4S$: C, 49.05; H, 3.17; N, 17.60. Found: C, 49.12; H, 3.24; N, 17.52%.

1-Phenyl-2-(1H-tetrazol-5-ylsulfanyl)-ethanone **(6a)**. m.p. 143–145°C; IR (KBr, cm^{-1}) 3423, 3076, 1672, 1588; ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.90 (s, 2H, $-CH_2$), 7.66–7.95 (m, 5H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 49.23, 128.82, 131.43, 133.97, 139.82, 151.73, 192.12; MS *m/z* = 221 $[M+1]^+$; Anal. Calcd. for $C_9H_8N_4OS$: C, 49.08; H, 3.66; N, 25.44. Found: C, 49.21; H, 3.51; N, 25.39%.

1-(4-Chlorophenyl)-2-(1H-tetrazol-5-ylsulfanyl)-ethanone **(6b)**. m.p. 166–168°C; IR (KBr, cm^{-1}) ν = 3417, 3070, 1678, 1593; ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.04 (s, 2H, $-CH_2$), 7.71 (d, 2H, ArH), 8.10 (d, 2H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 48.05, 128.95, 130.32, 133.84, 138.76, 151.58, 191.94; MS *m/z* = 255 $[M+1]^+$; Anal. Calcd. for $C_9H_7ClN_4OS$: C, 42.44; H, 2.77; N, 22.00. Found: C, 42.53; H, 2.89; N, 21.87%.

1-(4-Bromophenyl)-2-(1H-tetrazol-5-ylsulfanyl)-ethanone **(6c)**. m.p. 178–180°C; IR (KBr, cm^{-1}) 3420, 3079, 1678, 1598; ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.08 (s, 2H, $-CH_2$), 7.75 (d, 2H, ArH), 8.12 (d, 2H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 48.04, 126.92, 130.48, 131.54, 136.32, 151.68,

Table 3: Synthesis of sulfanyl tetrazoles **4a–f** and **6a–f** in [Bmim]BF_4 ionic liquid.

Entry	R	R_1	R_2	Product	Time (h)[a]	Yield (%)[b]
1	—	H	H	**4a**	4	88
2	—	H	Cl	**4b**	4.5	85
3	—	Cl	Cl	**4c**	4.5	78
4	—	H	Br	**4d**	5	82
5	—	Br	Br	**4e**	5.5	75
6	—	OMe	H	**4f**	6	81
7	H	—	—	**6a**	3	90
8	4-Cl	—	—	**6b**	2	91
9	4-Br	—	—	**6c**	3	88
10	4-Me	—	—	**6d**	3.5	83
11	4-OMe	—	—	**6e**	4	86
12	4-NO_2	—	—	**6f**	2.5	80

[a] Time for total completion of the reaction.

[b] Isolated yield.

191.93; MS *m/z*: 300 $(M+1)^+$; Anal. Calcd for $C_9H_7BrN_4OS$: C, 36.13; H, 2.36; N, 18.73. Found: C, 36.22; H, 2.27; N, 18.63%.

1-(4-Methylphenyl)-2-(1H-tetrazol-5-ylsulfanyl)-ethanone **(6d)**. m.p. 161–163°C; IR (KBr, cm^{-1}) 3388, 3073, 1670, 1571; ^1H NMR (300 MHz, DMSO-d_6) δ 2.42 (s, 3H, CH_3) 4.84 (s, 2H, $-CH_2$), 7.62–7.84 (m, 4H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 25.30, 47.82, 126.94, 130.27, 134.78, 142.84, 151.18, 191.87; MS *m/z*: 235 $(M+1)^+$; Anal. Calcd for $C_{10}H_{10}N_4OS$: C, 51.27; H, 4.30; N, 23.91. Found: C, 51.36; H, 4.22; N, 23.98%.

1-(4-Methoxyphenyl)-2-(1H-tetrazol-5-ylsulfanyl)-ethanone **(6e)**. m.p. 150–152°C; IR (KBr, cm^{-1}) 3443, 3091, 1671, 1578; ^1H NMR (300 MHz, DMSO-d_6) δ 3.75 (s, 3H, OCH_3), 4.96 (s, 2H, $-CH_2$), 7.67 (d, 2H, ArH), 7.82 (d, 2H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 48.16, 55.91, 120.26, 129.47, 131.52, 151.02, 162.73, 191.70; MS *m/z*: 251 $(M+1)^+$; Anal. Calcd for $C_{10}H_{10}N_4O_2S$: C, 47.99; H, 4.03; N, 22.39. Found: C, 47.86; H, 3.96; N, 22.32%.

1-(4-Nitrophenyl)-2-(1H-tetrazol-5-ylsulfanyl)-ethanone **(6f)**. m.p. 176–178°C; IR (KBr, cm^{-1}) 3341, 3094, 1680, 1574; ^1H NMR (300 MHz, DMSO-d_6) δ 5.10 (s, 2H, $-CH_2$), 7.80–8.02 (m, 4H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 48.07, 127.14, 129.67, 141.36, 150.12, 152.03, 191.78; MS *m/z*: 266 $(M+1)^+$; Anal. Calcd for $C_9H_7N_5O_3S$: C, 40.75; H, 2.66; N, 26.40. Found: C, 40.86; H, 2.62; N, 26.31%.

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