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Research Article

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Ionic liquid mediated a facile and convenient synthesis of new selanyl tetrazoles *via* one-pot three-component reaction

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ABSTRACT

A new, simple and convenient procedure for the synthesis of novel selanyl tetrazoles has been developed by one-pot three-component reaction of phenacyl bromides/3-(2-bromoacetyl)coumarins with KSeCN and NaN_3 using [Bmim]BF_4 ionic liquid. The protocol proves to be efficient and environmentally benign in terms of good yields, low reaction times, simple work-up, ease of recovery, and reusability of reaction medium (ionic liquid).

Keywords [Bmim]BF_4, Potassium selenocyanate, Phenacyl bromides, 3-(2-bromoacetyl)coumarins, Tetrazole

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INTRODUCTION

One of the main challenges in medicinal chemistry is the design and synthesis of biologically active molecules. Multi-component reactions (MCRs) have emerged as a powerful tools in the synthesis of diverse and complex compounds as well as small and drug like heterocycles,[1] because of their productivity, simple procedures, convergence, facile execution, and atom economy.[2]

Selenium is an element which resembles sulfur in terms of its chemical properties. Humans and animals need selenium for various biological functions which involve some organoselenium compounds. Adult human beings have to take up 15 μg/kg of selenium daily [3]. Deficiency of selenium in human's body may cause cancer, subfertility, and heart diseases [4,5]. It is also known that many selenium-containing organic compounds are known as effective insecticides, microbicides, prooxidants, antibacterial and antifungal agents [6].

Coumarin constitutes one of the major classes of naturally occurring compounds. Recently, coumarins have drawn much attention due to its diverse pharmacological activities. Many coumarins and their derivatives underwent extensive investigations aimed to assess their potential beneficial effects on human health [7,8]. Coumarin has been reported to serve as antibacterial [9], antioxidant [10], antiinflammatory [11,12], anticoagulant [12], antitumour and antidepressant agents [13]. The different substituents in the coumarin nucleus strongly influence the biological activity of the resulting derivatives.

Tetrazole derivates are well known as compounds with a high level of biological activity [14]. Tetrazoles have received much attention and have been used in variety of synthetic and medicinal chemistry applications as well as in material science including propellants and explosives [15]. They are also regarded as biologically equivalent to carboxylic acid group [16]. It was also noticed that toxic properties of a drug can decrease through the introduction of a tetrazole ring into the molecule [17]. Thus, synthesis of this heterocyclic nucleus is of much current importance. In this context, we planned to synthesize coumarin linked selanyl tetrazoles.

The most convenient method of synthesizing tetrazoles is the addition of azide ions to nitriles. 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. However, most of these protocols have some disadvantages, such as the use of strong Lewis

acids, expensive reagents, toxic metals, low yield, harsh reaction conditions and the *in situ* generated hydrazoic acid which is highly toxic and explosive [18-20]. In addition, all of the known methods use organic solvents, in particular, dipolar aprotic solvents, such as DMF. Thus, the development of a convenient and safe process for the preparation of new tetrazole derivatives is an interesting problem for investigation.

The use of room temperature ionic liquids (ILs) as solvents for chemical reactions offers several advantages from the environmental perspective [21,22]. In this context, in recent times, room temperature ionic liquids (RTILs), especially those based on the 1,3- dialkylimidazolium salts, have shown great promise as an attractive alternative to conventional solvents. They possess the unique advantages of high thermal stability, negligible vapour pressure, immiscibility with a number of organic solvents, and recyclability [23].

Therefore, as part of our program aimed for the synthesis of new heterocycles in ionic liquids [24], we herein report an efficient one-pot three-component reaction for the synthesis of selanyl tetrazoles using ionic liquid. To the best of our knowledge, this protocol has not been reported yet in the literature.

EXPERIMENTAL SECTION

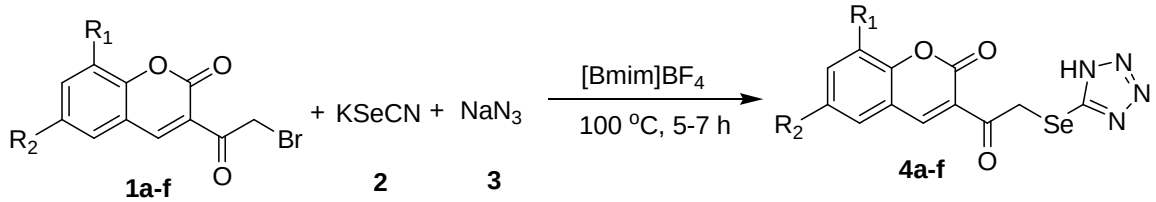
Melting points were recorded in open capillary and were uncorrected. Column chromatography was performed using silica–gel (100–200 mesh size) purchased from Thomas Baker and TLC was carried out using aluminium sheets pre-coated with silica gel 60F254 purchased from Merck. IR spectra (KBr) were recorded on a Bruker WM-4(X) spectrometer (577 model). ^{1}H 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.

Typical procedure

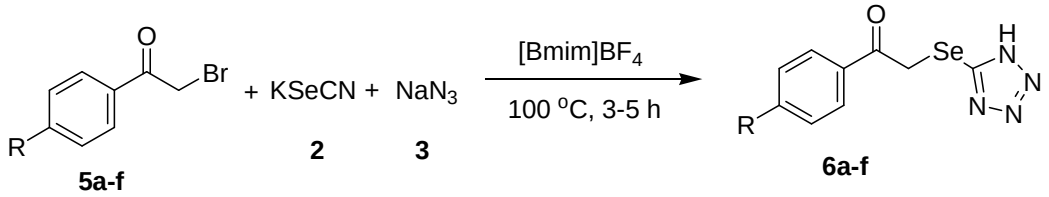
To a mixture of phenacylbromide **1** (1 mmol) or 3-(2-bromoacetyl)coumarin **5** (1 mmol) in [Bmim]BF_4 (3 mL), KSeCN (1.2 mmol) was added and the reaction mixture was stirred at room temperature for 45 min, after completion of the reaction (single spot on TLC), NaN_3 (1.2 mmol) was added portion wise to the reaction mixture and then it was stirred at 100 ^{o}C for appropriate time. After completion of the reaction (monitored by TLC), it was cooled to RT and poured into ice cold water and carefully acidified (pH <5) with conc. HCl, 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.

RESULTS AND DISCUSSION

Preliminary experiments were carried out in order to determine the best reaction conditions. The reaction of 4-chloro phenacyl bromide **5b**, KSeCN and NaN_3 was chosen as a model reaction and experiment was carried out in various ILs. The results reported in Table 1 revealed that [Bmim]BF_4 was better suited to afford the tetrazole in good yields at 100 ^{o}C in 4 h (Table 1, entry 4).



Scheme 1



Scheme 2

After optimizing the reaction conditions, we next examined the generality of this condition using various phenacyl bromides. The results are summarized in Table 2. Phenacyl bromides carrying different functional groups were subjected to the reactions and in all cases the desired product was obtained in good yields. It was observed that

under similar conditions, a wide range of phenacyl bromides containing electron-withdrawing as well as electron-donating groups underwent condensation in short reaction times with good isolated yields. The optimized condition is also worked well with heterocyclic systems such as 3-(2-bromoacetyl)coumarins to generate the corresponding products **4a-f** with good yields (Table 2).

During the work-up controlling the pH is very important because the compounds obtained (usually organoselenium) decompose and form a precipitate of elemental red selenium at a pH <5. The precipitation of selenium causes both low yield and presence of some impurities.

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 acidified (pH <5) with conc. HCl and stirred thoroughly. The solid product was isolated by filtration, and the filtrate containing ionic liquid was extracted with ethyl acetate (2x20 mL) to remove non-ionic organic impurities. Then the water was evaporated under reduced pressure and the recovered ionic liquid was dried at 80 ^{o}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 significant loss in the yields of products (Table 3). All the synthesized compounds were characterized by m.p, elemental analysis, IR, ^{1}H NMR, mass and ^{13}C NMR data.

Table 1. Synthesis of selanyl tetrazoles using various ILs at 100 ^{o}C

S.No	Solvent	Time (h)[a]	Yield (%)
1	[Bmim]PF_6	11	40
2	[Bmim]Br	8	62
3	[Bmim]Cl	6	76
4	[Bmim]BF_4	4	90

[a]Time for total completion of the reaction

Table 2. Synthesis of selanyl 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	5	87
2	-	H	Cl	4b	6	85
3	-	Cl	Cl	4c	6.5	79
4	-	H	Br	4d	6.5	84
5	-	Br	Br	4e	7	75
6	-	OMe	H	4f	6	82
7	H	-	-	6a	3	89
8	4-Cl	-	-	6b	4	90
9	4-Br	-	-	6c	4	85
10	4-Me	-	-	6d	3.5	87
11	4-OMe	-	-	6e	4.5	84
12	4-NO_2	-	-	6f	5	80

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

Table 3. Recycling of [Bmim]BF_4 ionic liquid

Entry	Cycle	Time (h)	Yield (%)[a]
1	1st run	4	90
2	2nd run	4	90
3	3rd run	4.5	88
4	4th run	4.5	86

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

Characterization data

3-(2-(1*H*-Tetrazol-5-ylselanyl)-acetyl)-chromen-2-one (4a):

M.p. 145–147 ^{o}C; IR (KBr, cm^{-1}) ν = 3316, 3048, 1712, 1664, 1555; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.64 (s, 2H, –CH_2), 7.44-7.54 (m, 2H, ArH), 7.81 (d, 1H, ArH), 8.02 (s, 1H, ArH), 8.90 (s, 1H, C_4 of coumarin); ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.88, 116.28, 118.06, 122.08, 125.27, 131.15, 135.32, 149.13, 153.76, 154.70, 158.76, 190.44; MS *m/z* = 336 $[M+1]^+$; Anal. Calcd. for $C_{12}H_8N_4O_3Se$: C, 43.00; H, 2.41; N, 16.72. Found: C, 43.12; H, 2.47; N, 16.67.

6-Chloro-3-(2-(1*H*-tetrazol-5-ylselanyl)-acetyl)-chromen-2-one (4b):

M.p. 172–174 ^{o}C; IR (KBr, cm^{-1}) ν = 3322, 3067, 1717, 1672, 1554; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.72 (s, 2H, –CH_2), 7.44-7.50 (m, 2H, ArH), 7.86 (s, 1H, ArH), 8.88 (s, 1H, C_4 of coumarin); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 47.90, 122.18, 125.61, 128.53, 129.47, 131.41, 132.61, 135.05, 147.89, 150.12, 158.43, 190.37; MS *m/z* = 370 $[M+1]^+$; Anal. Calcd. for $C_{12}H_7ClN_4O_3Se$: C, 38.99; H, 1.91; N, 15.16. Found: C, 38.93; H, 1.96; N, 15.20.

6,8-Dichloro-3-(2-(1*H*-tetrazol-5-ylselanyl)-acetyl)-chromen-2-one (4c):
M.p. 182–184 ^{o}C; IR (KBr, cm^{-1}) ν = 3329, 3061, 1711, 1674, 1553; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.74 (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 ($CDCl_3$, 75 MHz): δ 47.92, 125.16, 127.13, 129.34, 131.52, 134.67, 136.27, 141.74, 146.81, 149.56, 157.94, 190.42; MS *m/z* = 405 $[M+1]^+$; Anal. Calcd. for $C_{12}H_6Cl_2N_4O_3Se$: C, 35.67; H, 1.50; N, 13.87. Found C, 35.61; H, 1.57; N, 13.82.

6-Bromo-3-(2-(1*H*-tetrazol-5-ylselanyl)-acetyl)-chromen-2-one (4d):
M.p. 153–155 ^{o}C; IR (KBr, cm^{-1}) ν = 3334, 3063, 1727, 1670, 1561; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.86 (s, 2H, –CH_2), 7.46-7.50 (m, 2H, ArH), 7.95 (s, 1H, ArH), 8.84 (s, 1H, C_4 of coumarin); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 47.91, 122.29, 125.94, 129.91, 131.78, 132.66, 136.51, 142.83, 149.23, 154.52, 158.84, 190.43; MS *m/z* = 415 $[M+1]^+$; Anal. Calcd. for $C_{12}H_7BrN_4O_3Se$: C, 34.81; H, 1.70; N, 13.53. Found: C, 34.90; H, 1.76; N, 13.58.

6,8-Dibromo-3-(2-(1*H*-tetrazol-5-ylselanyl)-acetyl)-chromen-2-one (4e):
M.p. 201–202 ^{o}C; IR (KBr, cm^{-1}) ν = 3327, 3073, 1714, 1673, 1557; ^{1}H NMR ($CDCl_3$, 300 MHz): 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 ($CDCl_3$, 75 MHz): δ 47.93, 123.26, 128.71, 129.83, 131.47, 133.21, 136.62, 142.58, 148.73, 154.65, 158.93, 190.47; MS *m/z* = 493 $[M+1]^+$; Anal. Calcd. for $C_{12}H_6Br_2N_4O_3Se$: C, 29.24; H, 1.23; N, 11.37. Found: C, 29.31; H, 1.28; N, 11.43.

8-Methoxy-3-(2-(1*H*-tetrazol-5-ylsulfanyl)-acetyl)-chromen-2-one (4f):
M.p. 160–162 ^{o}C; IR (KBr, cm^{-1}) ν = 3336, 3078, 1721, 1681, 1562; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.82 (s, 3H, –OCH_3), 4.93 (s, 2H, –CH_2), 7.32-7.38 (m, 3H, ArH), 8.92 (s, 1H, C_4 of coumarin); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 42.96, 55.67, 115.72, 121.07, 123.12, 129.43, 130.14, 134.03, 137.18, 154.27, 158.63, 161.12, 190.56; MS *m/z* = 366 $[M+1]^+$; Anal. Calcd. for $C_{13}H_{10}N_4O_4Se$: C, 42.75; H, 2.76; N, 15.34. Found: C, 42.82; H, 2.71; N, 15.30.

1-Phenyl-2-(1*H*-tetrazol-5-ylselanyl)-ethanone (6a):
M.p. 156–158 ^{o}C; IR (KBr, cm^{-1}) ν = 3323, 3076, 1672, 1578; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 4.94 (s, 2H, –CH_2), 7.68-7.92 (m, 5H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 49.06, 127.94, 130.76, 133.54, 139.62, 154.63, 190.12; MS *m/z* = 268 $[M+1]^+$; Anal. Calcd. for $C_9H_8N_4OSe$: C, 40.46; H, 3.02; N, 20.97. Found: C, 40.41; H, 3.11; N, 20.92.

1-(4-Chlorophenyl)-2-(1*H*-tetrazol-5-ylselanyl)-ethanone (6b):
M.p. 173–175 ^{o}C; IR (KBr, cm^{-1}) ν = 3338, 3071, 1676, 1586; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 5.02 (s, 2H, –CH_2), 7.70 (d, 2H, ArH), 8.10 (d, 2H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 48.25, 128.83, 130.22, 133.81, 138.72, 154.86, 190.82; MS *m/z* = 302 $[M+1]^+$; Anal. Calcd. for $C_9H_7ClN_4OSe$: C, 35.84; H, 2.34; N, 18.58. Found: C, 35.89; H, 2.38; N, 18.47.

1-(4-Bromophenyl)-2-(1*H*-tetrazol-5-ylselanyl)-ethanone (6c):
M.p. 191–193 ^{o}C; IR (KBr, cm^{-1}) ν = 3327, 3077, 1678, 1592; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 5.06 (s, 2H, –CH_2), 7.74 (d, 2H, ArH), 8.08 (d, 2H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 48.16, 126.18, 130.87, 132.04, 135.51, 155.18, 190.93; MS *m/z*: 347 $[M+ 1]^+$; Anal. Calcd. for $C_9H_7BrN_4OSe$: C, 31.24; H, 2.04; N, 16.19. Found: C, 31.30; H, 2.11; N, 16.23.

1-(4-Methylphenyl)-2-(1*H*-tetrazol-5-ylselanyl)-ethanone (6d):
M.p. 181–183 ^{o}C; IR (KBr, cm^{-1}) ν = 3348, 3073, 1670, 1581; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.40 (s, 3H, CH_3) 4.88 (s, 2H, –CH_2), 7.60-7.82 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 25.32, 48.02, 126.74, 130.07, 134.13, 142.68, 154.12, 190.67; MS *m/z*: 282 $[M+1]^+$; Anal. Calcd. for $C_{10}H_{10}N_4OSe$: C, 42.72; H, 3.58; N, 19.93. Found: C, 42.65; H, 3.52; N, 19.98.

1-(4-Methoxyphenyl)-2-(1*H*-tetrazol-5-ylselanyl)-ethanone (6e):
M.p. 201–203 ^{o}C; IR (KBr, cm^{-1}) ν = 3343, 3091, 1671, 1578; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.72 (s, 3H, OCH_3), 4.94 (s, 2H, –CH_2), 7.65 (d, 2H, ArH), 7.84 (d, 2H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 48.16, 55.87, 120.32, 129.13, 131.24, 155.02, 162.67, 190.78; MS *m/z* = 298 $[M+1]^+$; Anal. Calcd. for $C_{10}H_{10}N_4O_2Se$: C, 40.42; H, 3.39; N, 18.85. Found: C, 40.49; H, 3.31; N, 18.90.

1-(4-Nitrophenyl)-2-(1*H*-tetrazol-5-ylselanyl)-ethanone (6f):
M.p.152–154 ^{o}C; IR (KBr, cm^{-1}) ν = 3341, 3094, 1680, 1574; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 5.08 (s, 2H, –CH_2), 7.82-8.02 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 48.04, 127.23, 129.34, 141.17, 150.28, 155.08, 190.81; MS *m/z* = 313 $[M+1]^+$; Anal. Calcd. for $C_9H_7N_5O_3Se$: C, 34.63; H, 2.26; N, 22.44. Found: C, 34.76; H, 2.32; N, 22.36.

CONCLUSION

In conclusion, we have described an efficient and convenient method for the preparation of selanyl tetrazoles using [Bmim]BF_4 ionic liquid. The present green synthesis shows attractive characteristics, such as one-pot conditions, short reaction times, easy work-up, and recyclability of ionic liquid and reduced waste production without using any additive agent.

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