Xanthan Sulfuric Acid: An Efficient Bio-Supported and Recyclable Solid Acid Catalyst for the Synthesis of 2-aminothiazole-5-carboxylates and 2-aminoselenazole-5-carboxylates

Bowroju S. Kuarm, Janganati V. Madhav and Bhargavi Rajitha*

Department of Chemistry, National Institute of Technology, Warangal, AP, India

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Abstract: An efficient method has been developed for the synthesis of 2-amino thiazole and selenazole-5-carboxylates from β-ketoesters, thiourea or seleno urea and N-bromo succinamide by using Xanthan sulfuric acid as a solid acid catalyst. The reaction work-up is very simple and the catalyst can be easily separated from the reaction mixture and reused several times in subsequent reactions.

Keywords: Bio-supported, N-bromo succinamide(NBS), recyclable, selenazoles, thiazoles, Xanthan sulfuric acid.

INTRODUCTION

The biological activity of aminothiazoles has been well documented. [1] This heterocyclic system has been employed in the preparation of different important drugs required for the treatment of inflammation, [2] hypertension, bacterial [3] and HIV infections. [4] Recently they have been employed for the treatment of pain, [5] as pibrinogen receptor antagonists with anti-thrombotic activity, [6] as inhibitors of bacterial DNA gyrase B, [7] and in the development of cyclin-dependent kinase (CDK) inhibitors. [8] The thiazole moiety in vitamin-B_1 serves as an electron sink and its coenzyme form is important for the decarboxylation of α-keto acids [9] and it is present in various natural products and herbicides. [10] Selenazole derivatives are also important in various biological applications like anti-tumor and antibacterial activities [11] and play an important role in the inhibition of lipopolysaccharide induced nitric oxide production in BV-2 cells [12]. Based on Hantzch synthesis, some newer methods such as cycloaddition of TosMIC (Tosyl methyl iso cyanide) to thione derivatives, [13] the Ugi reaction, [14] oxidation of thiazoline and thiazolidine ring systems, [15] and others, [16] have been developed. In addition to this, various aryl and olefinic moieties are introduced on to the thiazole ring system, such as palladium mediated coupling process [17] and other nucleophilic reaction of lithio thaizole to substituted thiazoles. [18] Moreover solid supported synthesis for the preparation of thiazole libraries [19] and solution phase synthesis of 2-aminothiazole combinatorial libraries [20] have been reported. To prepare these compounds, β-cyclodextrin [21] in water is also reported. Even though there are various procedures available for the synthesis of these molecules, most of the methods are time consuming, use of hazardous solvents and require strong acid catalysts, high temperature and also the tedious work up procedures. In view of these drawbacks, there is a need to develop a mild and environmentally green synthetic methodology for the high value building blocks by replacing hazards reaction conditions with simple and mild solvent free conditions using a recyclable catalyst.

In continuation of our exploration on new catalysts [22], we characterize Xanthan sulfuric acid as an efficient, bio-supported solid acid catalyst. Among different biopolymers, Xanthan is one of the most abundant natural biopolymers and has been ideally studied during the past several decades because it is a biodegradable material and a renewable resource. Its unique properties make it an attractive alternative to conventional organic or inorganic supports in catalytic applications. Recently, the approach has been shifting more towards eco-friendly and reusable catalysts. Recently, Xanthan sulfuric acid has emerged as a solid acid catalyst for acid catalyzed reactions, such as synthesis of α-aminonitriles, [23]. Xanthan sulfuric acid can be easily prepared by the reaction of inexpensive Xanthan with chlorosulfonic acid; the number of acidic (H^+) sites in the Xanthan sulfuric acid determined by acid-base titration was 0.6 meq/g.

RESULTS AND DISCUSSION

Xanthan sulfuric acid is one of the important catalysts for the selective construction of heterocyclic ring systems, especially in the synthesis of aminothiozole and selenazoles. The catalyst decreases the production of chemical waste without using some highly toxic reagents in the synthesis of these products. All the reactions were carried out at room temperature by the addition of Xanthan sulfuric acid to the mixture of β-keto ester(1), NBS(3) and either thiourea (2) or seleno urea (2); respectively (Scheme **1**). The results showed that the reactions are completed within 15-20 minutes with excellent yields (Table **1**).

We then investigated the efficiency of the Xanthan sulfuric acid compared to various sulfur analog acidic catalysts. The results are summarized in Table **2**. Xanthan sulfuric acid was found to be the most effective catalyst based on the product yield. The reaction did not proceed in the absence of catalyst (yield less than 10%).

*Address correspondence to this author at the Department of Chemistry, National Institute of Technology, Warangal, AP, India; Tel: 0870-2459445; Fax: 0091-0870-2459547; E-mail: rajithabhargavi@ymail.com

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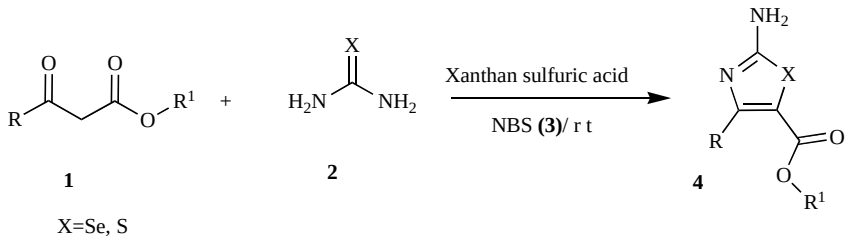
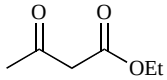
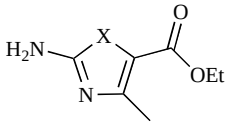
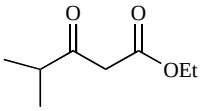
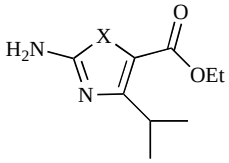
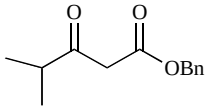
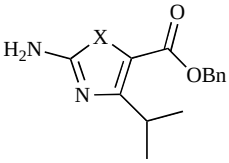
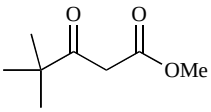
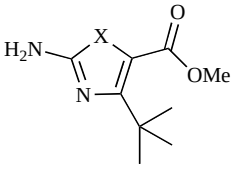
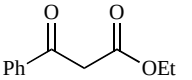
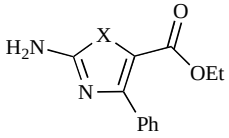


Scheme 1.

Table 1. Preparation of Aminothiazoles and Selenazoles by Employing Xanthan Sulfuric Acid

Entry	β-keto ester	product[a]	X	time (min)	yield (%)[b]
1			S	15	97
2			Se	15	96
3			S	18	95
4			Se	15	97
5			S	20	95
6			Se	15	95
7			S	15	92
8			Se	18	94
9			S	18	96
10			Se	15	97

[a]All the products were conformed by ^{1}H NMR, IR, and mass spectral data, and compared with those of authentic samples.
[b]Isolated yields after purification.

Table 2. Effect of Catalysts on Yield[a]

Entry	Catalyst	Quantity	yield (%) [b]
1	Xanthan sulfuric acid	0.08g	97
2	Silica sulfuric acid	0.08g	92
3	Methane sulfonic acid	0.1mmol	84
4	Sulfuric acid in acetic acid	0.1mmol	59
5	No catalyst	None	10

Reaction conditions:
[a]Mixture of EAA(1 mmol), NBS (1.2 mmol), thiourea (1.2 m mol) were stirred at room temperature.
[b]isolated yield.

Table 3. Influence of the Catalytic Amounts of Xanthan Sulfuric Acid[a]

Entry	Catalyst (grams)	Time (min)	Yield (%)[b]
1	None	60	Trace
2	0.01	15	29
3	0.03	15	55
4	0.05	15	78
5	0.08	30	97
6	0.08	15	97

Reaction conditions:
[a]Mixture of EAA(1 mmol), NBS (1.2 mmol), thiourea (1.2 m mol) and Xanthan sulfuric acid were stirred at room temperature.
[b]isolated yield.

We examined the amount of catalyst in this reaction. The best results were obtained using 0.08g of catalyst (97%). Using lower amounts of catalyst resulted in lower yields, in the absence of catalyst the yield of the product was found to be very low (Table **3**).

EXPERIMENTAL

All the melting points were uncorrected. The progress of the reaction was monitored by (TLC). IR spectra (KBr) were recorded on Shimadzu FTIR model 8010 spectrometer and the ^{1}H NMR spectra on Varian Gemini 200 MHz or Bruker-300 spectrometer using TMS as internal standard. The C, H, and N analysis of the compounds was done on a Carlo Erba model EA1108. Mass spectra were recorded on a JEOL JMS D-300 Spectrometer. All solvents and reagents were purchased from Aldrich and Fluka firms.

General Procedure

Mixture β-ketoester (1 mmol), NBS (1.2 mmol), thiourea or selenourea (1.2 m mol) and Xanthan sulfuric acid (0.08 g) was stirred at r.t for the appropriate time, as shown in Table **1**. Completion of the reaction was indicated by TLC monitoring. After completion of the reaction, EtOAc was added, and the Xanthan sulfuric acid was filtered off. The filtrate was concentrated to dryness, and the crude solid product was further purified by column chromatography (EtOAc:hexane, 2:8). The recovered catalyst can be reused at least three additional times in subsequent reactions without significant loss in product yield (Table **4**).

Table 4. The Effect of Reusability of Xanthan Sulfuric Acid[a]

Run	Cycle	Yield [b](%)
1	0	97
2	1	95
3	2	92
4	3	85

Reaction conditions:
[a]Mixture of EAA(1 mmol), NBS (1.2 mmol), thiourea (1.2 m mol) and Xanthan sulfuric acid (0.08 g) were stirred at room temperature.
[b]Yields refer to the pure isolated recovered catalyst.

Analytical Data

Ethyl 2-amino-4-methylthiazole-5-carboxylate (Table 1, entry-1)

White solid.

Mp 174-176 ^{o}C. IR (KBr): 3372, 3300, 1675, 1651, 1517, 1279, 1095 cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.35(t, *J* =7.9Hz. 3H), 2.05 (brs, 2H), 2.49(S, 3H), 4.25 (q, *J* =7.9Hz, 2H). ^{13}CNMR ($CDCl_3$) δ=10.8, 14.1, 60.9, 115.8, 156.6, 166.6, 169.2; ESI-MS; m/z = 187 (100) $[M+1]^+$. Anal. Calcd for $C_7H_{10}N_2O_2S$: C, 45.15; H, 5.41; N, 15.04; S, 17.22. Found: C, 45.21; H, 5.25; N, 14.89; S, 17.09.

Ethyl 2-amino-4-methylselenazole-5-carboxylate (Table 1, entry-2)

White solid.

Mp 163-165 ^{o}C. IR (KBr): 3375, 3064, 2929, 2757, 1665, 1124, 1086 cm^{-1}.^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.35(t, *J* =7.03Hz, 3H), 2.05 (s, 3H), 4.22 (q, *J* = 7.03 Hz, 2H), 7.73 (brs, 2H); ^{13}CNMR ($CDCl_3$) δ=14.2, 23.9, 61.4, 113.0, 153.2, 164.8, 169.0; ESI-MS; m/z = 235 (100) $[M+1]^+$. Anal. Calcd for $C_7H_{10}N_2O_2Se$: C, 36.06; H, 4.32; N, 12.02. Found: C, 35.90; H, 4.21; N, 12.16.

Ethyl 2-amino-4-isopropylthiazole-5-carboxylate (Table 1, entry-3)

White solid.

Mp 179-181 ^{o}C. IR (KBr): 3386, 3304, 1659, 1511, 1305, 1081 cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): δ = 1.15(d, *J* = 6.49Hz. 6H), 1.35(t, *J* = 6.49 Hz, 3H), 3.85 (sept, *J* = 6.49 Hz, 1H), 4.25 (q, *J* = 6.49 Hz, 2H), 5.60 (brs, 2H); ^{13}CNMR ($CDCl_3$) δ=14.0, 23.1, 23.2, 32.1, 60.7, 114.6, 151.2, 166.5, 169.5; ESI-MS; m/z =215 (100) $[M+1]^+$. Anal. Calcd for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.59; N, 13.07; S, 14.96. Found: C, 50.32; H, 6.48; N, 13.19; S, 15.12.

Ethyl 2-amino-4-isopropylselenazole-5-carboxylate (Table 1, entry-4)

White solid.

Mp 192-194 ^{o}C. IR (KBr): 3396, 3295, 3105, 2963, 1637, 1502, cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.15 (t, *J* =7.89 Hz, 6H), 1.30 (t, *J* = 7.06 Hz, 3H) 3.85 (sept, *J* = 7.89 Hz, 1H), 4.15(q, *J* = 7.06 Hz, 2H), 7.30 (br s, 2H); ^{13}CNMR

($CDCl_3$) δ=14.5, 19.5, 19.7, 37.2, 61.8, 112.9, 155.8, 164.2, 168.9; ESI-MS; m/z =263 (100) $[M+1]^+$. Anal. Calcd for $C_9H_{14}N_2O_2Se$: C, 41.39; H, 5.40; N, 10.73. Found: C, 41.25; H, 5.25; N, 10.93.

Benzyl 2-amino-4-isopropylthiazole-5-carboxylate (Table 1, entry-5)

White solid.

Mp 166-168 °C. IR (KBr): 3380, 3316, 3161, 2957, 1692, 1645, 1518, 1470, 1306, 1264, 1193, 1087 cm^{-1}.^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.17(d, *J* = 7.53Hz. 6H), 3.85 (sept, *J* = 7.53 Hz, 1H), 5.21 (s, 2H), 5.51 (br s, 2H), 7.25-7.40 (m, 5H); ^{13}CNMR ($CDCl_3$) δ=23.1, 23.2, 32.4, 68.4, 115.7, 127.2, 127.3, 127.7, 129.0, 129.1, 141.5, 150.4, 166.4, 169.3; ESI-MS; m/z = 277 (100) $[M+1]^+$. Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14; S, 11.60. Found: C, 60.73; H, 5.98; N, 10.29; S, 11.48.

Benzyl 2-amino-4-isopropylselenazole-5-carboxylate (Table 1, entry-6)

White solid.

Mp 176-178 °C. IR (KBr): 3385, 3285, 3135, 2962, 2926, 2860, 1664, 1633, 1501, cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.17(d, *J* = 7.64Hz. 6H), 3.90 (sept, *J* =7.64, 1H), 5.20 (s, 2H), 5.65 (brs, 2H).7.25-7.40 (m, 5H); ^{13}CNMR ($CDCl_3$) δ= 19.1, 19.3, 37.2, 68.6, 114.9, 127.3, 127.5, 127.8, 129.1, 129.3, 141.8, 153.4, 165.8, 169.0; ESI-MS; m/z = 325 (100) $[M+1]^+$. Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 52.02; H, 4.99; N, 8.67. Found: C, 52.24; H, 5.12; N, 8.79.

Methyl 2-amino-4-4-tert-butylthiazole-5-carboxylate (Table 1, entry-7)

White solid.

Mp 161-163 °C. IR (KBr): 3442, 3285, 1691, 1504, 1256, 1085 cm^{-1}.^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.40(s, 9H), 3.75(s, 3H), 5.50(br s, 2H); ^{13}CNMR ($CDCl_3$) δ=31.3, 31.4, 31.6, 31.9, 59.5, 115.9, 151.4, 166.5, 169.5; ESI-MS; m/z = 215 (100) $[M+1]^+$. Anal. Calcd for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.59; N, 13.07; S, 14.96. Found: C, 50.26; H, 6.37; N, 13.19; S, 15.16.

Methyl 2-amino-4-tert-butylselenazole-5-carboxylate (Table 1, entry-8)

White solid.

Mp 146-148 °C. IR (KBr): 3403, 3308, 3156, 2956, 1687, 1642, 1468 cm^{-1}.^{1}HNMR ($CDCl_3$, 300 MHz): δ = 1.40(s, 9H), 3.70(s, 3H), 7.30 (brs, 2H); ^{13}CNMR ($CDCl_3$) δ=28.4, 28.5, 28.6, 44.9, 62.0, 114.9, 152.4, 165.9, 169.5; ESI-MS; m/z = 263 (100) $[M+1]^+$. Anal. Calcd for $C_9H_{14}N_2O_2Se$: C, 41.39; H, 5.40; N, 10.73. Found: C, 41.54; H, 5.65; N, 10.59.

Ethyl 2-amino-4-phenylthiazole-5-carboxylate (Table 1, entry-9)

White solid.

Mp 170-172 °C. IR (KBr): 3394, 3280, 1658, 1515, 1302, 1169, 1087 cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.25 (t, *J* = 7.32 Hz, 3H), 4.18 (q, *J* = 7.32 Hz, 2H), 5.59 (brs, 2H), 7.30-7.40(m, 3H), 7.60-7.70(m, 2H); ^{13}CNMR ($CDCl_3$) δ=14.1, 61.4, 115.4, 127.4, 127.5, 128.7, 129.4, 129.5, 133.2, 153.9, 166.4, 169.7; ESI-MS; *m/z* = 249 (100) $[M+1]^+$. Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87; N, 11.28; S, 12.91. Found: C, 58.17; H, 5.07; N, 11.45; S, 12.75.

Ethyl 2-amino-4-phenyl selenazole-5-carboxylate (Table 1, entry-10)

White solid.

Mp 178-180 °C. IR (KBr): 3404, 3274, 1648, 1513, 1292, 1071 cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): δ= 1.15(t, *J* = 7.41 Hz. 3H), 2.95 (br s, 2H), 4.05 (q, *J* = 7.41 Hz, 2H), 7.20-7.30(m, 2H), 7.50-7.60 (m, 3H); ^{13}CNMR ($CDCl_3$) δ=14.3, 61.9, 115.0, 126.4, 126.5, 128.0, 128.5, 128.6, 136.7, 152.8, 165.4, 169.0; ESI-MS; m/z = 297 (100) $[M+1]^+$. Anal. Calcd for $C_{12}H_{12}N_2O_2Se$: C, 48.82; H, 4.10; N, 9.49. Found: C, 48.95; H, 4.27; N, 9.32.

CONCLUSIONS

In conclusion, we have developed an efficient method for the synthesis of 2-amino thiazole and selenazole-5-carboxylates in good yields with high purity under Solvent free conditions. The notable factors of this reaction are an extremely simple experimental procedure, mild reaction conditions, environmentally friendly synthesis with no product wastes or toxic solvents, and a reusable catalyst.

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