Research Article

Copper(I)-BINOL Catalyzed Domino Synthesis of 1,4-Benzoxathiines through C_(aryl)-O Bond Formation

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1,4-benzoxathiine moieties can be synthesized by domino S_N2 ring opening of epoxide with *o*-halothiophenols followed by the copper(I)-BINOL catalyzed Ullmann-type coupling cyclization (intramolecular C_(aryl)-O bond formation) with moderate to good yields.

1. Introduction

Sulfur-containing heterocycles are found in numerous natural products and biologically active pharmaceutical products [1–4]. Particularly the compounds containing 1,4-benzoxathiine motifs have attracted considerable interest during the past few years due to their interesting biological activities [5–8]. Framework of 1,4-benzoxathiine is present in a variety of biologically active compounds such as (3-hydroxy-4-methoxyphenyl)-1,4-benzoxathiine **1**, a sweetening agent [9]; (dihydrobenzoxathiinyloxy)acetic acids **2**, potential antihypertensive agents with diuretic properties [10]; syn-2,3-bis-aryl-substituted dihydrobenzoxathiine **3**, an estrogenic agent [11]; hydroxy substituted 4-thiaflavan **4**, an antioxidant agent [12] (Figure 1). 1,4-Benzoxathiine motifs are also used as radical scavengers [13]; metal chelators [14]; and hydroperoxide quenchers [15].

Conventionally, 1,4-benzoxathiine motifs are synthesized by the treatment of 2-mercaptophenol with 1,2-dibromoethane in presence of sodiummethoxide [16]. 1,4-benzoxathiine moieties are also synthesized by multistep reaction [9, 10]. Nair et al., described the synthesis of 1,4-benzoxathiine moiety by the cycloaddition reaction of 4-isopropyl-2-thio-1,2-benzoquinone which is generated *in situ* from *N*-(2-hydroxy-5-isopropylphenyl)sulfanyl-phthalimide with the reaction of alloocimene in the presence of pyridine in dry chloroform [17].

However, these literature protocols have several limitations such as multi-step process, less availability of starting materials, harsh reaction conditions, usage of strong bases, polar and high boiling solvents such as DMF and low yields. Therefore, there is a need to develop an efficient protocol for the synthesis of 1,4-benzoxathiines. For the first time we have developed a simple, mild, and efficient copper-catalyzed domino process to prepare 1,4-benzoxathiine skeleton from readily available starting materials (Scheme 1).

As part of our continuous effort towards copper-catalyzed C_(aryl)-heteroatom bond formation and its application in important heterocycles synthesis [18–24], herein, for the first time, we report a new domino synthesis of the 1,4-benzoxathiine skeleton from easily available epoxides and *o*-halothiophenols using S_N2 epoxide ring opening followed by intramolecular Ullmann type coupling cyclization. The reaction is very effective and high yielding process using the economically cheap ligand BINOL.

2. Results and Discussion

At the outset, the domino reaction for the synthesis of (±)-*trans*-1,2,3,4,4a,10a-hexahydro phenoxathiine **7** was carried out from cyclohexeneoxide **5** with *o*-bromothiophenol **6** by a base-mediated domino S_N2 epoxide ring opening reaction followed by Ullmann coupling cyclization in the presence

FIGURE 1: Some of the 1,4-benzoxathiine motif containing biologically important molecules.

SCHEME 1

of 20 mole % of CuI and BINAM (1,1'-binaphthyl-2,2'-diamine) **L1** in acetonitrile solvent at 120°C in sealed tube. The reaction provided 12% yield of pure product **7** in 80 h (Table 1, entry 1). To increase the efficiency of the reaction we screened different oxygen- and nitrogen-based ligands **L1–L8** (Figure 2) and the results are summarized in Table 1. Among them BINOL (1-(2-hydroxynaphthalen-1-yl)naphthalen-2-ol) **L5** turned out to be the best ligand for the synthesis of 1,4-phenoxathiine **7** with 62% isolated yield (entry 5). It is important to mention that in the absence of ligand, the reaction did not offer even trace amount of coupling product **7** which indicates that ligand is mandatory for this reaction.

The reaction was optimized further with different copper salts, solvents, bases, and different ratios of Cu salt-**L5** and results are summarized in Table 2. Although several Cu salts catalyzed the reaction, CuI turned out to be the best Cu salt of choice in view of yield (entry 1 versus entries 2–7). Acetonitrile is the best choice of solvent among the solvents examined (entry 1 versus entries 8–11); Cs_2CO_3 is the best

choice of the base (entry 1 versus entries 12, 13). It was also found that decreasing CuI-**L5** catalyst loading from 20 mol% each of CuI and **L5** to 10 mol% each of CuI and **L5** reduced the yield drastically (entry 14) and other Cu : **L5** ratios also reduced the yields of the cyclized product **7** (entry 15). In the absence of CuI or **L5** or both, the reaction did not afford even trace amount of coupling product (entries 16–18). It is important to mention that both Cu salt and ligand are mandatory for coupling reaction. In the absence of base, the reaction did not proceed (entry 19). On lowering the temperature from 120°C to 82°C we did not observe any coupling product.

Using the above-mentioned optimized reaction conditions we initiated our investigation into the scope of the CuI-**L5** complex catalyzed domino $\text{S}_\text{N}2$ epoxide opening and Ullmann coupling cyclization for the synthesis of 1,4-benzoxathiine skeleton from various epoxides and *o*-halo thiophenols and the results are summarized in Tables 3 and 4. Both *o*-bromo and *o*-iodo thiophenols reacted with various

FIGURE 2: Ligands screened for the Cu-catalyzed domino reaction.

epoxides and provided corresponding products with more or less the same yields. In all the cases the products were observed along with respective ring opening product.

The possible mechanism for the formation of the 1,4-benzoxathiine moiety by domino S_N2 epoxide opening followed by Ullmann coupling cyclization is shown in Figure 3. First *o*-bromothiophenol 5 is deprotonated by base to give thiophenolate ion 15 which then opens epoxide in S_N2 fashion to give opened product 16. The coordination of oxygen of 16 with CuI to give complex 17 followed by oxidative addition gives compound 18. Which then undergoes reductive elimination to give the product ($\pm$)-*trans*-1,2,3,4,4a,10a-hexahydro phenoxathiine 7, then the copper catalyst is regenerated which enters into the catalytic cycle.

In conclusion, for the first time we have demonstrated a novel and efficient protocol for the synthesis of very important 1,4-benzoxathiine motifs by a domino S_N2 epoxide opening reaction followed by Ullmann coupling cyclization using easily available CuI-BINOL complex as catalyst. A variety of 1,4-benzoxathiine motifs have been synthesized from corresponding epoxides and *o*-halo thiophenols in moderate to good yields under relatively mild conditions.

3. Experimental Section

All reactions were carried out in sealed tubes under nitrogen atmosphere. All reagents are commercially available and used without further purification. 2-bromothiophenol, epoxides, CuI, and Cs_2CO_3 were purchased from Sigma-Aldrich Company. 2-iodothiophenol was prepared by literature procedure [25]. Ligands **L2**, **L3**, and **L6** were prepared using literature procedure [26–31]. Acetonitrile was dried over calcium hydride, freshly distilled, and used for reactions. Reaction temperatures were controlled by Varivolt temperature modulator, thin-layer chromatography (TLC) was performed

TABLE 1: Ligand screening for Cu-catalyzed domino reaction for the synthesis of 1,4-benzoxathiine moiety^a.

Entry	Ligand	Time (h)	Yield (%) ^b
1	L1	80	12
2	L2	80	14
3	L3	80	11
4	L4	95	39
5	L5	80	62
6	L6	95	13
7	L7	72	19
8	L8	95	14
9	L9	80	16

^a Reactions were carried out in pressure tube; ^b isolated yield.

using Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm) and visualized by UV fluorescence quenching. Silica gel (particle size 100–200 mesh) purchased from SRL India was used for chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz instrument. ¹H NMR spectra were reported relative to Me₄Si (δ 0.0 ppm) or residual CHCl₃ (δ 7.26 ppm). ¹³C NMR were reported relative to CDCl₃ (δ 77.16 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and are reported in frequency of absorption (cm⁻¹). High-resolution mass spectra (HRMS) were recorded on Q-ToF Micro mass spectrometer. GC-MS were recorded on JEOL GC/MATE II mass spectrometer.

TABLE 2: Cu salt, solvent, base screening for domino synthesis of 1,4-benzoxathiine moiety^a.

Entry	Cu salt	Solvent	Base	Cu : L5 (mol %)	Yield (%) ^b
1	CuI	CH ₃ CN	Cs ₂ CO ₃	20 : 20	62
2	CuBr	CH ₃ CN	Cs ₂ CO ₃	20 : 20	41
3	CuCl	CH ₃ CN	Cs ₂ CO ₃	20 : 20	39
4	CuCl ₂	CH ₃ CN	Cs ₂ CO ₃	20 : 20	47
5	Cu(OAc) ₂	CH ₃ CN	Cs ₂ CO ₃	20 : 20	35
6	Cu(OTf) ₂	CH ₃ CN	Cs ₂ CO ₃	20 : 20	37
7	Cu ₂ O	CH ₃ CN	Cs ₂ CO ₃	20 : 20	08
8	CuI	DMF	Cs ₂ CO ₃	20 : 20	15
9	CuI	DMSO	Cs ₂ CO ₃	20 : 20	—
10	CuI	Dioxane	Cs ₂ CO ₃	20 : 20	07
11	CuI	Toluene	Cs ₂ CO ₃	20 : 20	12
12	CuI	CH ₃ CN	K ₂ CO ₃	20 : 20	44
13	CuI	CH ₃ CN	K ₃ PO ₄	20 : 20	45
14	CuI	CH ₃ CN	Cs ₂ CO ₃	10 : 10	35
15	CuI	CH ₃ CN	Cs ₂ CO ₃	20 : 10	31
16	—	CH ₃ CN	Cs ₂ CO ₃	— : 20	—
17	CuI	CH ₃ CN	Cs ₂ CO ₃	20 : —	—
18	—	CH ₃ CN	Cs ₂ CO ₃	— : —	—
19	CuI	CH ₃ CN	—	20 : 20	—

^aReactions were carried out in pressure tube; ^bisolated yield.TABLE 3: Scope of the domino reaction with various epoxides and *o*-bromothiophenol for the synthesis of 1,4-benzoxathiine moieties^a.

Entry	Epoxide	1,4-Benzoxathiines	Time (h)	Yield (%) ^b
1			80	62
2			78	40
3			78	32
4			87	21

^aReactions were carried out in pressure tube; ^bisolated yield.

TABLE 4: Scope of the domino reaction with various epoxides and *o*-iodothiophenol for the synthesis of 1,4-benzoxathiine moieties^a.

Entry	Epoxide	1,4-benzoxathiines	Time (h)	Yield (%) ^b
1			72	60
2			75	43
3			78	27
4			84	24

^a Reactions were carried out in pressure tube; ^b isolated yield.

3.1. Typical Experimental Procedure. 2-bromothiophenol (94.5 mg, 0.50 mmol), cyclohexene oxide (49.1 mg, 0.5 mmol), BINOL **L5** (28.6 mg, 0.1 mmol), CuI (19.2 mg, 0.1 mmol), and Cs₂CO₃ (325.8 mg, 1.0 mmol) were taken in a sealed tube and equipped with screw cap. The sealed tube was evacuated and backfilled with nitrogen. Acetonitrile (2 mL) was added to the reaction mixture at room temperature and the mixture was heated at 120°C. After 80 h (progress of the reaction was followed by TLC), the mixture was allowed to cool to room temperature and the solvent was removed by rotary evaporation. The crude residue was directly purified by column chromatography on silica gel (ethyl acetate/hexanes as eluents) to afford 63.8 mg (62%) of (±)-*trans*-1,2,3,4,4a,10a-hexahydrophenoxathiine (**7**) as a white solid. The *trans* geometry was confirmed by NOE experiment.

(±)-1,2,3,4,4a,10a-Hexahydrophenoxathiine (**7**) (see Figure 4). White solid; mp 64–65°C; R_f 0.43 (hexanes); FTIR (neat) 744, 1231, 1283, 2862, 2936, 3064 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.35–1.49 (m, 4H), 1.67–1.90 (m, 2H), 1.95–2.07 (m, 1H), 2.13–2.25 (m, 1H), 2.97–3.08 (m, 1H), 3.65–3.76 (m, 1H), 6.73–6.80 (m, 2H), 6.87–6.97 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 24.7 (C₄), 25.4 (C₃), 31.1 (C₂), 32.4 (C₅), 41.9 (C₁), 78.2 (C₆), 118.1 (C₈), 119.1 (C₁₂), 121.5 (C₁₀), 125.4 (C₉), 126.9 (C₁₁), 151.7 (C₇); HRMS [M + H⁺] Calcd for C₁₂H₁₅OS: 207.0844; found: 207.0848.

(±)-2,3,3a,9a-Tetrahydro-1H-benzo[*b*]cyclopenta[*e*][1,4]oxathiine (**9**) (see Figure 5). White solid; mp 62°C; R_f 0.37

(hexanes); FTIR (neat) 742, 1217, 1278, 2878, 2962, 3061 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.54–2.05 (m, 4H), 2.18–2.43 (m, 2H), 3.04–3.21 (m, 1H), 3.95–4.11 (m, 1H), 6.83–6.94 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 19.2 (C₃), 28.0 (C₂), 28.9 (C₄), 41.0 (C₁), 81.9 (C₅), 118.3 (C₁₁), 118.8 (C₇), 121.7 (C₉), 125.7 (C₈), 128.0 (C₁₀), 152.5 (C₆); GC-MS EI+: *m/z* = 192.

(±)-5a,6,7,8,9,10,11,11a-Octahydrobenzo[*b*]cycloocta[*e*][1,4]oxathiine (**11**) (see Figure 6). White solid; mp 57°C; R_f 0.42 (hexanes); FTIR (neat) 746, 1233, 1295, 2859, 2920, 3050 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.42–2.34 (m, 12H), 3.39–3.46 (m, 1H), 4.03–4.11 (m, 1H), 6.80–6.87 (m, 2H), 6.94–7.00 (m, 1H), 7.02–7.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 23.9 (C₆), 25.6 (C₃), 25.9 (C₄), 26.4 (C₅), 29.0 (C₂), 31.9 (C₇), 42.5 (C₁), 80.5 (C₈), 118.1 (C₁₀), 120.2 (C₁₄), 121.3 (C₁₂), 125.3 (C₁₁), 126.7 (C₁₃), 152.4 (C₉); HRMS [M + H⁺] Calcd for C₁₄H₁₉OS: 235.1157; found: 235.1160.

(±)-2-Phenyl-2,3-dihydrobenzo[*b*][1,4]oxathiine (**13**) (see [9], Figure 7). Semisolid; R_f 0.32 (hexanes); FTIR (neat) 695, 744, 1233, 2924, 3058 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.02 (dd, *J* = 13.2 Hz, 1.6 Hz, 1H), 3.17 (dd, *J* = 13.2 Hz, 9.6 Hz, 1H), 5.12 (dd, *J* = 9.6 Hz, 2 Hz, 1H), 6.79–6.89 (m, 2H), 6.93–6.99 (m, 1H), 7.05 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.27–7.38 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 32.1 (C₁), 76.7 (C₂), 117.4 (C₁₂), 118.9 (C₈), 121.8 (C₁₀), 125.8

FIGURE 3: Possible mechanism for the domino synthesis of 1,4-benzoxathiine moiety.

FIGURE 4

FIGURE 6

FIGURE 5

FIGURE 7

(C₉), 126.2 (C_{4,4'}), 127.4 (C₁₁), 128.6 (C₆), 128.9 (C_{5,5'}), 140.4 (C₃), 152.5 (C₇); GC-MS EI⁺: m/z = 230.

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