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Copper-Catalyzed Preparation of *N*-Aroylated Sulfoximines from Methylarenes

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Abstract

A copper-catalyzed methodology for the preparations of *N*-aroylated sulfoximines from methylarenes was herein demonstrated. The transformation proceeded with the assistance of external oxidant *tert*-butyl hydroperoxide (TBHP), requiring for no additional solvents or ligands. The good compatibility and high efficiency of the newly-developed protocol were well-described by the 21 examples and up to 91% yields. Moreover, the protocol was proved by the control reactions to proceed through a radical pathway.

KEYWORDS: Copper catalysis, *N*-aroylated sulfoximines, TBHP, methylarenes, solvent-free

1. INTRODUCTION

Molecules with a sulfoximine moiety has gained widespread attention for being chiral precursors or ligands in asymmetric synthesis,[1] as well as for the great significance in

the pharmaceutical and agricultural applications.[2] Also, sulfoximines have been applied broadly for the construction of various heterocyclic molecules.[3] Diverse protocols such as arylation,[4] alkylation,[5] vinylation,[6] alkynylation[7] and others.[8] have been well established for the synthesis of different *N*-substituted sulfoximines. Amongst, different protocols for the acylation of sulfoximines have aroused exceptional interests for the broad applications in both biology and synthesis.[9] Usually, reactions between benzoyl chlorides, aromatic carboxylic acids and *NH*-sulfoximines were well-developed towards *N*-aroylated sulfoximines. Recently, benzaldehydes were successfully employed as the aroylation reagent for the coupling with *NH*-sulfoximines in the presence of Cu(I).[10] The coupling methodology developed by Bolm and coworkers proceeded through a dual C-H/N-H activations pathway under the oxidative conditions. Then, readily-accessible methylarenes were also successfully applied for the aroylation of *N*-chloro sulfoximines under MnO_2-mediated system by the same research group.[11] Inspired by the pioneering work, An and Sekar have disclosed different routines towards *N*-aroylated sulfoximines from methylarenes in the presence of elemental iodine[12] or a ferric-catalyst.[13] Be aware of that methylarenes were able to perform as versatile modules for the construction of carbon-heteroatom bonds[14] with the assistance of various metallic catalysts, we wish to disclosed an practical transformation towards *N*-aroylated sulfoximines in the presence of a copper catalyst and *tert*-butyl hydroperoxide (TBHP) under solvent-free conditions.

2. DISCUSSION

With *NH*-*S*-methyl-*S*-phenyl sulfoximine **1a** and toluene **2a** as the substrate for the model reaction, experiments as summarized in Table 1 were carried out for the optimal conditions of the aroylation protocol. Disappointingly, palladium catalysts such as $PdCl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(MeCN)_2Cl_2$ was totally ineffective for the transformation since no product was detected after 20 h at 80 ^oC (entries 1 - 3). Also, the combination of $AgNO_3$ and $K_2S_2O_8$ did not give a better result (entry 4). To our delight, copper catalysts expressed positive effect to the transformation, for usage of CuCl led to trace product after 20 h (entry 5). And the yields of **3aa** dramatically increased to 28% and 82% when CuBr and CuI were employed for the aroylation protocol (entries 6 and 7). But the utilizations of copper(II) catalyst such as $Cu(OTf)_2$ did not lead to the formation of any desired product (entry 8). Moreover, diverse commonly used oxidants were tested in the system for the best oxidant and TBHP performed better than others, such as di-*tert* butyl peroxide (DTBP, entry 9), H_2O_2 (enry 10), DDQ (entry 11) and oxygen (entry 12). It was noteworthy that a lower loading of CuI (5 mol%) led to a decreased yield of the desired product **3aa**, only a 65% ratio was obtained (entry 13).

With the optimal conditions in hand, the scope of the substrates was evaluated for this transformation as shown in Table 2. Different electron-rich aromatic groups decorated sulfoximines were well-tolerated under the optimal conditions. For instance, *S*-4-methylphenyl-*S*-methyl sulfoximine (**1b**), *S*-4-methoxyphenyl-*S*-methyl sulfoximine (**1c**) and *S*-2-methylphenyl-*S*-methyl sulfoximine (**1d**) reacted with toluene (**2a**) readily,

affording the corresponding *N*-aroylated sulfoximines **3ba** – **3da** in yields ranging from 82% to 88% yields (entries 1 - 3). Similarly, halogenated aromatic groups fused sulfoximines like *S*-4-fluorophenyl-*S*-methyl sulfoximine (**1e**), *S*-4-chlorophenyl-*S*-methyl sulfoximine (**1f**) and *S*-4-bromophenyl-*S*-methyl sulfoximine (**1g**) underwent the aroylation procedure with toluene (**2a**) successfully, furnishing the desired products **3ea** – **3ga** in medium to good yields, from 79% to 84% (entries 4 - 6). Pleasingly, other functional groups substituted sulfoximines also showed good compatibility under the optimal conditions. *S*-Phenyl-*S*-ethyl sulfoximine (**1h**) and *S*-phenyl-*S*-isopropyl sulfoximine (**1i**) furnished the corresponding *N*-aroylated sulfoximines **3ha** and **3ia** under the optimal conditions, in 80% and 78% yields, separately (entries 7 and 8). Other sulfoximines such as *S*,*S*-diphenyl sulfoximine (**1j**) and *S*,*S*-dimethyl sulfoximine (**1k**) also coupled with toluene successfully, leading to the desired aroylated products **3ja** and **3ka** in 89% and 76% yields (entries 9 and 10). To our satisfactory, heteroaryl decorated sulfoximine such as *S*-(2-pyridinyl)-*S*-methyl sulfoximine (**1l**) reacted with toluene (**2a**) smoothly under the optimal conditions, offering the desired product **3la** in mediun yield (71% for entry 11).

Encouraged by the broad substrate scope of the aroylation protocol on sulfoximines, the compatibility on the methyl arenes was also evaluated as shown in Table 3. Firstly, electron-rich methylarenes were tested in the system under the optimal conditions. For example, 1,4-dimethylbenzene (**2b**) and 1-methyl-4-methoxybenzene (**2c**) afforded the

corresponding *N*-aroylated sulfoximines **3ab** and **3ac** in good yields, up to 91% (entries 1 and 2). In the same manner, *o*-xylene (**2d**) played successfully as the aroylation reagent for the corresponding product **3da** was isolated in 72% yield (entry 3). However, other benzyl C-H bond did not showed any reactivities in the system. For instance, ethylbenzene (**2l**) and isopropylbenzene (**2m**) failed to give any *N*-aroylated sulfoximines, probably because the electron-donating methyl group(s) made the C-H bonds less acidic (entries 11 and 12).

It was noteworthy that halogenated toluenes such as 4-fluorotoluene (**2e**), 4-chlorotoluene (**2f**), 4-bromotoluene (**2g**) and 4-iodotoluene (**2h**) reacted with *NH*-*S*-phenyl-*S*-methyl sulfoximine (**1a**) easily under the optimal conditions, yielding the desired sulfoximine derivatives in ratios up to 87% (entries 4 – 7). Meanwhile, the activities of the electron-deficient aromatic groups such as 4-methylbenzyl cyanide (**2i**) and 3-nitrotoluene (**2j**) were tested. They exhibited good compatibilities in the transformation and coupled with *NH*-sulfoximine **2a** smoothly, leading to the desired products in acceptable yields, up to 79% (entries 8 and 9). To our satisfaction, polyaromatic group was also well-tolerated in the copper catalysis and the reaction between 2-methylnaphthalene (**2k**) and *NH*-sulfoximine **1a** took place smoothly, resulting in *N*-aroylated sulfoximine **3ak** in 80% yield (entry 10).

To probe the mechanism of the aroylation protocol, control experiments were carried out for clarification as shown in Scheme 1. Despite that the addition of the radical scavenger like 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) did not afford the formation of the TEMPO-benzoyl adduct, a dramatic decrease in the generation of **3aa** was observed for only trace product was detected after 20 h (Sheme 1, **A**). The results indicated that copper-catalyzed aroylation reaction probably proceeded through a radical pathway. Meanwhile, to have a better understanding on the role that the catalyst played in the system, the activities of different copper catalysts, such as CuCl and CuBr, were also tested when KI was used as the iodine source. Within our expectations, almost the same yields were obtained, providing 78% and 80% yields, respectively (Scheme 1, **B**). Based on the literal investigations, the reaction might proceeded through two different key intermediates. Thus, the reactions of benzaldehyde or benzyl iodide with *NH*-sulfoximine (**1a**) were carried out separately, offering completely different results. The desired product **3aa** was obtained in 52% yield with benzaldehyde used as the acyl reagent, but no product was detected when **1a** reacted with benzyl iodide (Scheme 1, **D**). The results indicated the mechanism likely took place *via* the acyl radical particles.

Based on the reported precedents and the results of the control experiments, the mechanism of the demonstrated transformation was proposed as shown in Figure 1. Firstly, iodide radical particle, which was generated under the oxidative conditions, reacted with methylarenes **1**, offering the acyl intermediate **A**. Meanwhile, Cu(II)

coordinated with **2** for a metal-substrate complex **B**. Then the two intermediates **A** and **B** coupled, leading to another key intermediate **C**, which generated the desired aroylated sulfoximines **3** with a release of a Cu(II) particle.

3. CONCLUSIONS

In summary, we have disclosed a novel and efficient synthetic method towards *N*-aroylated sulfoximines under the copper catalysis. The system exhibited good functional groups tolerance and broad substrate scope. Moreover, control reactions were conducted to clarify the transformation proceed through a radial pathway *via* a key acyl intermediate. The methodology offers a practical and facile synthetic tool towards the useful compounds.

4. EXPERIMENTAL

4.1 Typical Synthetic Procedure Of *N*-Benzoyl-*S*-Methyl-*S*-Phenyl Sulfoximine 3

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with the *NH*-sulfoximine **2** (0.5 mmol), CuI (9.5 mg, 5 mol%) in dry methyl arene **1** (3.5 mL), then TBHP (258 mg, 2.0 mmol, 70% in water) was added dropwise, and the reaction mixture was allowed to stir at 80 °C for 20 h. After cooling to room temperature, the mixture was filtered through a short celite pad and washed with chloroform (15 mL × 3). The filtrate was concentrated, and the oily crude product was purified by column

chromatography using silica gel (200 – 300 mesh) as stationary phase and a mixture of *n*-hexane and ethyl acetate as eluent to give the *N*-aroylated sulfoximines **3**.

4.2 Spectra Data Of *N*-Aroyl Sulfoximines 3

***N*-Benzoyl-*S*-Methyl-*S*-Phenyl Sulfoximine (3aa)**

White solid, m.p.: 103 – 105 ^{o}C. Yield: 82%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 7.3 Hz, 2H), 8.05 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 3.45 (s, 3H) (ppm). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 174.3, 139.0, 135.6, 133.9, 132.3, 129.8, 129.5, 128.1, 127.2, 44.4 (ppm). **MS** (EI): *m*/*z* = 77.1 (53), 94.1 (56), 104.1 (48), 105.1 (38), 125.1 (16), 141.1 (9), 156.1 (100), 157.1 (8), 182.1 (88), 244.1 (15). **IR** (in KBr): ν = 3020, 2925, 1628, 1577, 1447, 1314, 1281, 1219, 1172, 1136, 1092, 1068, 978, 838, 716 (cm^{-1}). **HRMS** (ESI) (m/z) [$C_{14}H_{13}NO_2S+H^+$]: Calcd. 260.0740, Found 260.0748. The data was in accordance with Ref 12 and 13.

SUPPORTING INFORMATION

Full experimental details, ^{1}H and ^{13}C NMR spectra are accessible *via* the "Supplementary Content" section of this article's webpage.

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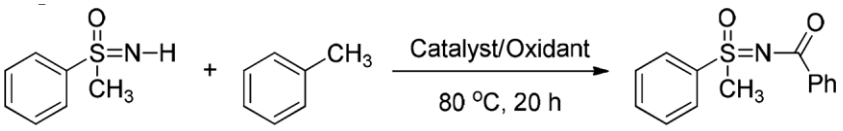
Table 1. Optimization of reaction conditions[a]

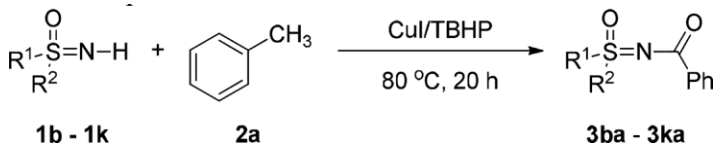


1a **2a** **3aa**

Entry	Catalyst	Oxidant	Yiled (%)[b]
1	$PdCl_2$	TBHP	n.d.[c]
2	$Pd(PPh_3)_2Cl_2$	TBHP	n.d.
3	$Pd(MeCN)_2Cl_2$	TBHP	n.d.
4	$AgNO_3$	$K_2S_2O_8$	n.d.
5	CuCl	TBHP	trace
6	CuBr	TBHP	28
7	CuI	TBHP	82
8	$Cu(OTf)_2$	TBHP	n.d.
9	CuI	DTBP	72
10	CuI	H_2O_2	n.d.
11	CuI	DDQ	n.d.
12	CuI	O_2[d]	n.d.
13[e]	CuI	TBHP	65

Notes: [a] conditions: **1a** (0.3 mmol), **2a** (2.0 mL), catalyst (10 mol%), oxidant (2.0 eqvuialents) at 80 ^{o}C for 20 h. [b] Isolated yields. [c] stands for not detected. [d] O_2 baloon (1 atm) was used. [e] 5 mol% of the catalyst was used.

Table 2. Substrate scope of *NH*-sulfoximines[a]

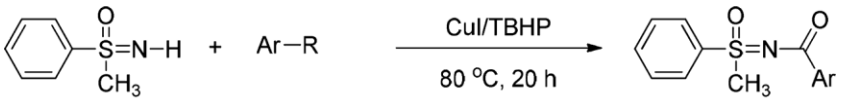


1b - 1k **2a** **3ba - 3ka**

Entry	**1**	R^1	R^2	**3**	Yield (%)[b]
1	**1b**	4-$CH_3C_6H_4$	CH_3	**3ba**	85
2	**1c**	4-$CH_3OC_6H_4$	CH_3	**3ca**	88
3	**1d**	2-$CH_3C_6H_4$	CH_3	**3da**	82
4	**1e**	4-FC_6H_4	CH_3	**3ea**	82
5	**1f**	4-ClC_6H_4	CH_3	**3fa**	79
6	**1g**	4-BrC_6H_4	CH_3	**3ga**	84
7	**1h**	Ph	Et	**3ha**	80
8	**1i**	Ph	*i*-Pr	**3ia**	78
9	**1j**	Ph	Ph	**3ja**	89
10	**1k**	Me	Me	**3ka**	76
11	**1l**	2-Pyridinyl	Me	**3la**	72

Notes: [a] Conditions: **1** (0.5 mmol), **2a** (2.0 mL), CuI (10 mol%), TBHP (75% in water, 2.0 eq.). [b] Isolated yields.

Table 3. Substrate scope of methylarenes[a]



1a **2a - 2k** **3aa - 3ak**

Entry	**2**	Ar (R)	**3**	Yield (%)[b]
1	**2b**	4-$CH_3C_6H_4$ (CH_3)	**3ab**	89
2	**2c**	4-$CH_3OC_6H_4$ (CH_3)	**3ac**	91
3	**2d**	2- $CH_3C_6H_4$ (CH_3)	**3ad**	72
4	**2e**	4-FC_6H_4 (CH_3)	**3ae**	87
5	**2f**	4-ClC_6H_4 (CH_3)	**3af**	80
6	**2g**	4-BrC_6H_4 (CH_3)	**3ag**	85
7	**2h**	4-IC_6H_4 (CH_3)	**3ah**	79
8	**2i**	4-CNC_6H_4 (CH_3)	**3ai**	79
9	**2j**	3-$NO_2C_6H_4$ (CH_3)	**3aj**	72
10	**2k**	2-Naphthyl (CH_3)	**3ak**	80
11	**2l**	C_6H_5 (CH_2CH_3)	**3al**	n.d.[c]
12	**2m**	C_6H_5 [$CH(CH_3)_2$]	**3am**	n.d.[c]

Notes: [a] Conditions: **1a** (0.5 mmol), **2** (2.0 mL), CuI (10 mol%), TBHP (75% in water, 2.0 eq.). [b] Isolated yields. [c] n.d. for not detected.

Scheme 1. Control experiments

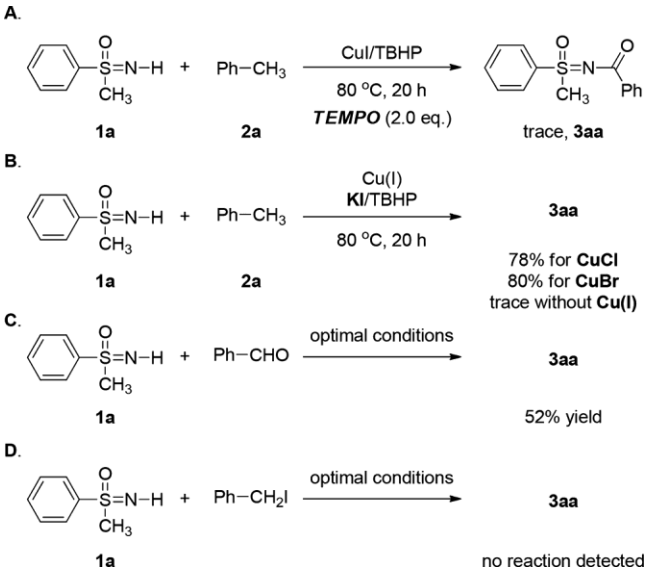


Figure 1. Proposed mechanism