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Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Tahir Daşkapan & Semra Çiçek (2017): High yielding electrophilic amination method for arylcopper reagents, Synthetic Communications, DOI: 10.1080/00397911.2017.1295082

To link to this article: http://dx.doi.org/10.1080/00397911.2017.1295082

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http://dx.doi.org/10.1080/00397911.2017.1295082

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High yielding electrophilic amination method for arylcopper reagents

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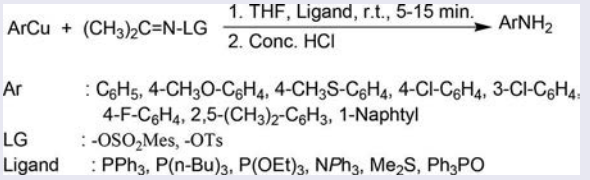
ABSTRACT

The facilitative effect of some P-, N-, S-, and O-donor ligands in the reaction of arylcoppers with acetone *O*-(mesitylenesulfonyl)oxime was examined to develop a synthesis method for functionalized primary aryl amines under mild reaction conditions. Our researches showed that electrophilic amination of monoaryl coppers with ketoximes can be facilitated using appropriate ligand to supply significant increase in the yield. Also, we have seen that this ligand-facilitated method is applicable in terms of arylcopper and ketoxime type and allows synthesis of primary aryl amines in good to high yields easily at room temperature in very short reaction time.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 22 August 2016

KEYWORDS
Amination; aryl amines; ligand; organocopper; oxime

Introduction

Arylamino group is an important building block in the synthesis of important and useful chemicals. For this reason, many studies have been made on the development of an efficient method for the preparation of aryl amines. Nucleophilic amination methods require harsh reaction conditions that limit their applicability.

Various procedures were given for the preparation of primary anilines by copper-catalyzed *N*-arylation of aryl halides with aqueous ammonia.[1–6] Although these methods allow obtaining primary aryl amines in high yields, they need high reaction temperature and/or too long reaction time for the success. In addition, some of them require special catalysts or ligands.

Helquist et al.[7] developed a copper-assisted method for the synthesis of primary anilines using NaN_3 as aminating reagent. Reactions were performed at 100 °C in the presence of 1 equiv. of CuI or Cu_2O, 1.3 equiv. of ligand and 2 equiv. of NaN_3. Generally the reactions were completed in too long reaction times.

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Knochel's group described a procedure for the preparation of primary aryl amines in high yields by oxidative coupling of aryl amidocuprates at − 78–(−50)°C in 13 h.[8]

Accordingly, developing a method allowing the synthesis of aryl amines under milder reaction conditions would be useful. Electrophilic amination is a powerful method for the synthesis of amines. Various aryl, alkyl, cycloalkyl, and heteroaryl amines have been easily prepared using suitable aminating agent and organometallic reagent.[9,10]

Organocopper compounds are the most widely used transition metal organometallic reagents in the field of organic synthesis. They are used not only in the academic laboratories but also in the industry. This popularity is due to their ability to give reactions in high chemo, regio, and stereoselectivity and to tolerate broad range of functional groups.[11–13]

In general, sp^3-hybridized nitrogen-based aminating agents were used for the amination of organocopper reagents.[9,10,14] There have been few reports on the electrophilic amination of mono-organocoppers. Genét et al.[15–18] have been developed some *N*-aryl sulfonyloxycarbamate derivatives as aminating reagents for the synthesis of sensitive primary amines without any decomposition, and they showed their activity in the electrophilic amination of aryl and heteroarylcoppers. Bhadra et al.[19] have been showed iron nanoparticle-catalyzed electrophilic amination of functionalized organocopper for the synthesis of functionalized tertiary aryl amines.

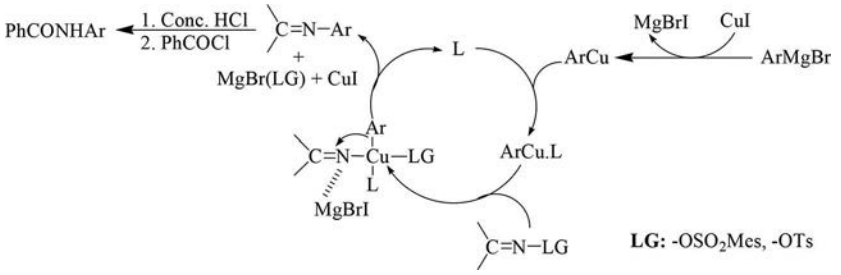
As far as we know, there have been only two studies about amination of mono-organocoppers with ketoximes. One of them showed the use of phenylcopper to furnish aniline in low yield.[20] The other study[21,22] described the preparation of alkylamines by electrophilic amination of corresponding alkylcoppers with 4,4′-bis(trifluoromethyl) benzophenone *O*-methylsulfonyloxime at low temperatures and in the presence of a coordinating solvent in low to high yields. But synthesis of aryl amines could not be achieved by this method.

So, the development of a new method for the electrophilic amination of arylcoppers would be a complementary study in terms of the literature. Previously we described some electrophilic amination methods for organozinc,[23–25] organomagnesium,[26] and organocadmium[27] reagents. In this paper, an alternative method for the preparation of aryl amines including electrophilic amination of functionalized arylcoppers under mild reaction conditions is described.

Results and discussion

At the first stage of this work we focused on the development of an easily applicable synthesis method for functionalized primary aryl amines using corresponding arylcopper reagents. We used acetone *O*-(2,4,6-trimethylphenylsulfonyl)oxime (**1**), that we are familiar with from our previous studies,[23–27] as aminating agent. It can be prepared easily and stored for a long time without any decomposition. We used the corresponding functionalized arylmagnesiums prepared in tetrahydrofuran (THF) for the preparation of arylcoppers, because magnesium was thought to increase the electrophilic character of the aminating reagent by coordinating with its nitrogen atom.

Aryl amines as the final products were removed from the reaction mixture as their benzamide derivatives and identified from their melting points,[28–30] Fourier transform infrared (FT-IR) and ^{1}H NMR analysis.[30–34]



Scheme 1. Ligand-facilitated electrophilic amination of arylcoppers with ketoximes.

d-Orbitals of arylcopper compounds are low lying and their energies are not sufficient to give nucleophilic substitution in high yield.[35] In our work, ArCu reacts with ketoxime by nucleophilic displacement between Ar^- and $–OSO_2Mes$ or –OTs (Scheme 1). As is seen in Table 1, phenylcopper reacted with **1** at room temperature under ligand-free conductions to give aniline in low yield (Entries 1, 2).

Previously we have observed that copper-catalyzed electrophilic amination of organozinc reagents[25–27] occurred under milder reaction conditions and resulted in higher yields, by the use of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU). DMPU is a dipolar aprotic solvent and coordinates to metal ions to increase the nucleophilicity of

Table 1. Optimization of reaction conditions.

$$PhCu^{a} + \underset{\mathbf{1}}{(CH_3)_2C{=}NOSO_2Mes} \xrightarrow[2.\ Conc.\ HCl]{1.\ THF,\ ligand,\ r.t.,\ 5\text{-}30\ min.} PhNH_2{}^{b}$$

Entry	Ligand (%)	Time (min)	$PhNH_2$ (%)
1	—	5	50
2	—	30	41
3	—	30	30[c]
4	PPh_3, 25	30	70
5	PPh_3, 25	5	85
6	PPh_3, 15	5	70
7	P(*n*-Bu)$_3$, 20	15	82
8	P(*n*-Bu)$_3$, 20	5	72
9	P(*n*-Bu)$_3$, 10	15	84
10	P(*n*-Bu)$_3$, 5	15	70
11	P(OEt)$_3$, 25	30	58
12	P(OEt)$_3$, 25	15	71
13	P(OEt)$_3$, 15	15	71
14	P(OEt)$_3$, 10	15	63
15	Ph_3PO, 5	15	63
16	Ph_3PO, 5	5	65
17	NPh_3, 20	15	65
18	NPh_3, 5	15	66
19	Me_2S, 20	15	51
20	Me_2S, 10	15	72
21	Me_2S, 10	5	44

DMPU, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone.
[a]PhCu/**1** = 2.
[b]Yield of amine was isolated as its benzamide derivative.
[c]DMPU/PhCu = 0.2.

their counter ions. For this reason, we added catalytic amount of DMPU to the reaction mixture. But it led to negative effect on the amination reaction of phenylcopper with **1**, and as seen in Table 1 it caused a further drop in the yield of aniline (Entry 3). After these results, we decided to add a ligand in a catalytic amount to the reaction mixture. Because in this way, coordination of the added ligand to Cu-I will make its d-orbitals sufficiently high for a successful amination reaction.

As is seen in Table 1, addition of PPh_3 to reaction mixture supplied a dramatic increase in the yield of aniline (Entries 4–6). These results have paved the way for a new synthesis method for functional group containing aryl amines. For this purpose, we planned to investigate the facilitative effects of various P-, N-, S-, and O-donor ligands on electrophilic amination of arylcoppers. Our works started with determination of optimal reaction conditions using reaction of PhCu with **1** as model reaction (Table 1).

We used three types of P-donor ligands; PPh_3, $P(n\text{-}Bu)_3$, and $P(OEt)_3$. PPh_3 gave the best result in 5 min when it was used in 25% mol amount (Table 1, entry 5). 10 mol% of $P(n\text{-}Bu)_3$ was enough for high yield of aniline, but the reaction completed in 15 min (Entry 9). $P(OEt)_3$ showed the lowest facilitative reactivity.

As is seen in Scheme 1, the added donor ligand coordinetes with Cu-I atom and increases electron density on it. By this interaction, ArCu becomes more susceptible to react with electrophilic nitrogen atom of ketoxime. Oxidative addition of ArCu to ketoxime gives a Cu-III complex. Then this complex decomposes to give aryl imine intermediate, which forms target product following acidic hydrolysis.

$P(n\text{-}Bu)_3$ is a soft ligand and strong donor. Therefore, its coordination with Cu-I atom to facilitate amination reaction is more preferred than that of other two P-donor ligands. Second, it is a bulky ligand, with three *n*-Bu- groups in α -position relative to copper atom and this facilitates decomposition of Cu-III complex to form aryl amine. Hence, as is seen in Table 1, it increased the yield of aniline from 50 to 82% (Entries 1 and 7). PPh_3 is less donor than $P(n\text{-}Bu)_3$ because of -I effect of phenyl groups. So, it is less effective in facilitation of interaction of ArCu with ketoxime. But it is a bulkier ligand and therefore it can show more facilitative effect on the formation of aryl amine from Cu-III complex. As a result, PPh_3 allows yield of amine to be as high as $P(n\text{-}Bu)_3$ provides. Three etoxy groups make $P(OEt)_3$ the weakest P-donor ligand. In addition it is not a bulky ligand. These characteristics make it the least effective P-donor ligand in the electrophilic reaction of arylcopper reagents with ketoximes.

Coordination of Ph_3PO to the copper atom occurs through its oxygen atom. However, this coordination is not as preferable as coordination with PPh_3 or $P(n\text{-}Bu)_3$ for Cu-I, a soft Lewis acid. In addition, Ph_3PO, as a hard ligand, increases stability of Cu-III complex but does not create steric hindrance around Cu-III, since three phenyl groups are not in α-position relative copper atom (Ph–P–O–Cu). This is not facilitative for decomposition of Cu-III complex to N-aryl imine. For these reasons, Ph_3PO did not show significant activity in the amination reaction (Table 1, entries 15, 16).

NPh_3 is a hard base and the results showed that it is not so effective in the improvement of aryl amine yield (Table 1, entries 17, 18). Being bulky ligand, it did not provide a significant benefit in this regard. As in the case of Ph_3PO, also in the electrophilic amination reaction involving NPh_3, oxidative addition of arylcopper to ketoxime following coordination to Cu-I atom appears to be dominant.

Due to its soft Lewis-base and hard donor feature, Me_2S was expected to facilitate the electrophilic amination of arylcoppers and to greatly increase amine yield. But as is seen in Table 1, it is not effective as much as P(*n*-Bu)$_3$ or PPh_3. We attributed this to the fact that Me_2S is a small ligand. Thus, it can approach to copper atom more closely and form a stable complex. Formation of such a complex is easier but its decomposition to give desired product is more difficult. Consequently, it showed a moderate activity in the amination of arylcoppers.

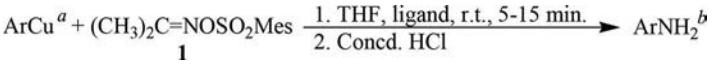
Our investigations on finding optimal reaction conditions showed that the molar ratio of arylcopper to ketoxime must be 2:1. The use of less than 2 mmol of arylcopper led to the decrease in the yield of amine.

In the second part of this study, the ligand-facilitated electrophilic amination method that we developed in the first stage was examined whether it is applicable for the synthesis of functional group bearing aryl amines. For this reason, aminations of various functionalized arylcopper reagents with **1** were performed under optimized reaction conditions. As is seen in Table 2, all reactions were conducted successfully and functionalized aryl amines were synthesized in good to high yields.

We observed that this electrophilic amination method was unsuccessful in the amination of alkyl cycloalkyl and benzylcopper reagents with **1**.

Acetone oxime *O*-tosylate (**2**) reacted with arylcopper reagents successfully to form corresponding functionalized aryl amines in good to high yields (Table 3). These results show that our ligand-facilitated electrophilic amination method is applicable from the point of ketoxime type.

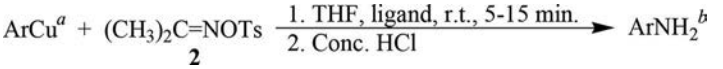
Table 2. Scope and limitations of ligand-facilitated electrophilic amination of ArCu with **1**.



Entry	Ar	Ligand (%)	Time (min)	$ArNH_2$ (%)
1	4-$CH_3OC_6H_4$	PPh_3, 25	5	73
2	4-$CH_3SC_6H_4$	PPh_3, 25	5	74
3	4-ClC_6H_4	PPh_3, 25	5	72
4	3-ClC_6H_4	PPh_3, 25	5	73
5	4-FC_6H_4	PPh_3, 25	5	76
6	1-Naphtyl	PPh_3, 25	5	71
7	2,5-$(CH_3)_2C_6H_3$	PPh_3, 25	5	87
8	4-CH_3S–C_6H_4	P(*n*-Bu)$_3$, 10	15	81
9	4-Cl–C_6H_4	P(*n*-Bu)$_3$, 10	15	61
10	3-Cl–C_6H_4	P(*n*-Bu)$_3$, 10	15	64
11	4-F–C_6H_4	P(*n*-Bu)$_3$, 10	15	73
12	2,5-$(CH_3)_2$–C_6H_4	P(*n*-Bu)$_3$, 10	15	78
13	4-CH_3S–C_6H_4	NPh_3, 5	15	74
14	4-CH_3O–C_6H_4	NPh_3, 5	15	65
15	3-Cl–C_6H_4	NPh_3, 5	15	67
16	2,5-$(CH_3)_2$–C_6H_4	P(OEt)$_3$, 15	15	69
17	4-CH_3O–C_6H_4	P(OEt)$_3$, 15	15	60
18	3-Cl–C_6H_4	P(OEt)$_3$, 15	15	72
19	2,5-$(CH_3)_2$–C_6H_4	Ph_3PO, 5	5	66
20	4-CH_3S–C_6H_4	Ph_3PO, 5	5	55
21	3-Cl–C_6H_4	Me_2S, 10	15	56
22	(4-CH_3S–C_6H_4)	Me_2S, 10	15	61
23	4-F–C_6H_4	Me_2S, 10	15	55

[a]ArCu:**1** = 2:1.
[b]Yield of amine was isolated as its benzamide derivative.

Table 3. Scope and limitations of ligand-facilitated electrophilic amination of ArCu with **2**.



Entry	Ar	Ligand (%)	Time (min)	$ArNH_2$ (%)
1	3-Cl–C_6H_4	PPh_3, 25	5	67
2	2,5-$(CH_3)_2$–C_6H_4	PPh_3, 25	5	75
3	1-Naphtyl	PPh_3, 25	5	74
4	4-CH_3O–C_6H_4	P(*n*-Bu)$_3$, 10	15	75
5	4-Cl–C_6H_4	P(*n*-Bu)$_3$, 10	15	58
6	4-F–C_6H_4	P(*n*-Bu)$_3$, 10	15	68
7	2,5-$(CH_3)_2$–C_6H_4	NPh_3, 5	15	69
8	3-Cl–C_6H_4	NPh_3, 5	15	68
9	2,5-$(CH_3)_2$–C_6H_4	$P(OEt)_3$, 15	15	70
10	3-Cl–C_6H_4	$P(OEt)_3$, 15	15	68
11	2,5-$(CH_3)_2$–C_6H_4	Ph_3PO, 5	5	64
12	C_6H_5	Me_2S, 10	15	66
13	3-Cl–C_6H_4	Me_2S, 10	15	55
14	4-F–C_6H_4	Me_2S, 10	15	57

[a]ArCu/**2** = 2.
[b]Yield of amine was isolated as its benzamide derivative.

Conclusion

Our studies revealed that it is possible to conduct the electrophilic amination of monoaryl coppers with ketoximes successfully in the presence of a suitable ligand. By this method, functionalized aryl amines were synthesized in high yields at room temperature and in too short reaction times. Since arylcoppers have high functional group tolerance, we think this method will be useful for direct insertion of a $–NH_2$ group to an organic molecule.

This method is an easily applicable method; ligands used as facilitator are simple, stable, and commercial compounds which do not require special preparation methods.

Experimental

General procedures

All reactions involving organocopper reagents were performed in flame-dried glassware with standard syringe/cannula techniques[36] under an atmosphere of dry, oxygen-free argon. Melting points were determined on a Gallencamp capillary melting point. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR (or Shimadzu-brand FT-IR) spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at room temperature on a Varian-Mercury 400 MHz (FT)-NMR spectrometer. All chemical shifts were given in ppm downfield from tetramethylsilane.

Tetrahydrofuran was freshly distilled from solution of sodium/benzophenone under dry argon. DMPU was distilled under reduced pressure prior to use and kept over molecular sieves (4 Å 4–8 mesh) and under argon atmosphere. Cu-I iodide was purified prior to use and stored at dry argon atmosphere.[37]

Magnesium turnings for Grignard reactions (Fischer) were used without any purification. Aryl bromides (Sigma-Aldrich) were in high purities and used without any further purification.

Arylmagnesium bromides were prepared in THF by conventional standard methods and their concentrations were determined by the method of Watson and Eastham.[38]

Acetone *O*-(mesitylenesulfonyl)oxime[39] (**1**) and acetone oxime *O*-tosylate[40,41] (**2**) were prepared as described in the literature and stored for months without any decomposition. Ligands were commercially available in high purity and used without further purification.

The final product, aryl amine was isolated as its *N*-benzoyl derivative that was identified by its melting point,[28–30] FT-IR, and ^{1}H NMR spectrums.[30–34]

Ligand-facilitated amination reaction of arylcopper reagents with ketoxime

A suspension of CuI (0.762 g, 4 mmol) in anhydrous THF (6 mL) was cooled to − 5 °C under argon atmosphere and phenylmagnesium bromide (4 mmol) in THF was added dropwise by a syringe. The reaction mixture was stirred for an additional 15 min, the cooling bath was removed and the resulting suspension was allowed to warm to room temperature for 10–15 min. To this mixture, ligand (5–25 mol%), and a solution of acetone *O*-(mesitylenesulfonyl)oxime, **1** (2 mmol) in dry THF (3 mL) were added. The reaction mixture was stirred at room temperature for 5–30 min and then worked up by addition of concentrated HCl and with stirring at room temperature overnight. The aqueous phase was washed with diethyl ether (2 × 60 mL), made basic with concentrated NaOH, and the free aniline was extracted with diethyl ether (3 × 60 mL). The solvent was evaporated and the crude product was converted to its *N*-benzoyl derivative by reaction with benzoyl chloride in the presence of NaOH. The product was recrystallized from ethanol:water (4:1) mixture. Mp: 160–162 °C (lit.[30] 160 °C); FT-IR (υ_{max}/cm^{-1}): 3342, 3051, 1653 (amide, –CO), 1597, 1524, 1453, 1319, 1255, 748, 714, 688, 642. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H 7.96 (s, 1H), 7.88–7.85 (m, 2H), 7.67–7.64 (m, 2H), 7.56–7.52 (m, 1H), 7.48–7.44 (m, 2H), 7.39–7.34 (m, 2H), 7.17–7.13 (m, 1H).

Funding

Financial support from Ankara University Research Found (Grant No. 09B4240005) is greatly acknowledged by the authors.

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