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Nickel-catalyzed three-component coupling reaction of terminal alkynes, dihalomethane and amines to propargylamines

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Direct C—H and C—halogen activation is an important and practical task in C—C, C—N bond formation reactions using alkynes. Propargylic amines are synthetically versatile intermediates for the preparation of many nitrogen-containing biologically active motifs. Herein, a 15 mol% $Ni(py)_4Cl_2$/bipyridine-catalyzed three-component coupling reaction of alkynes, halomethane and amines through C—H and C—halogen activation was developed for the facile synthesis of propargylic amines. Tetramethylguanidine shows excellent basicity in acetonitrile and works under mild conditions. The reaction has very good functional group tolerance to aliphatic and aromatic alkynes. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: C—H activation; homogeneous catalysis; multi-component reactions; Nickel complex; propargylic amines

Introduction

Propargylamines have importance in pharmaceuticals as a key building block of nitrogen-containing biologically active molecules and as an intermediate for natural product synthesis.[1] The reactive alkynylides are used for C—C bond formation with alkynes as a carbon nucleophilic source. For the synthesis of alkynylides sensitive organometallic reagents like BuLi, EtMgBr or metal hydrides are used. The direct C—H and C—halogen activation for C—C bond formation is one of the most versatile and graceful tasks in organic chemistry as compared with alkynylide synthesis using conventional techniques.[2] There are four important pathways which are used for the synthesis of propargylamines: (i) by transition metal-catalyzed reactions of imines (or enamines), which can be generated from aldehydes and amines; (ii) by stoichiometric nucleophilic reactions; (iii) by a three-component coupling reaction of aldehydes, alkynes and amines (A^3 coupling), catalyzed by various transition metals;[3] and (iv) more interestingly, by the catalytic coupling of an sp C—H and sp^3 C—halogen activation by C—C, C—N bond formation with a secondary amine (AHA coupling).[4–7] Recently, Contel and co-workers reported the Au-catalyzed activation of C—H and C—halogen bonds to a new building of C—C and C—N bonds via the three-component coupling reaction of alkynes, halomethanes and amines (AHA) for propargylamine synthesis.[4] Later Cu(I),[5] nano-In_2O_3,[6] Fe(III)[7] and cobalt[8] were also proved to catalyze this kind of AHA coupling reaction. Xi and co-workers have reported the use dihalomethane as a carbon source, as well as a geminal dihalide to also act as a carbon source.[9] Unfortunately, the requirement for specially designed nano-sized catalysts and the use of precious transition metals such as Au or In are some of the drawbacks of this protocol.

Nickel compounds have many applications in catalysis as they exhibit good selectivity as well as reactivity.[10,11] Cardenas and co-workers show activity of nickel precursors, especially $Ni(py)_4Cl_2$-catalyzed reactions in organic synthesis, including its reaction mechanism.[11] Herein, we report the application of $Ni(py)_4Cl_2$ complex as a precursor for three-component coupling reaction of alkynes, haloalkanes and secondary amines (AHA), using bipyridine as a ligand with 1,1,3,3-tetramethylguanidine (TMG) as a base to synthesize propargylamines, as shown in Scheme 1.

Nickel compounds are found to be competent catalysts for the three-component coupling of secondary amines and terminal alkynes in chlorinated alkanes. We observed that the coupling involves a methylene fragment obtained from halomethane, which plays an unexpected role for dihalomethane as a CH_2 partner, by a nickel-catalyzed C—Cl bond activation. This methodology gains attention in environmental chemistry because such methodology can be used in the degradation of harmful chlorinated solvents and transition metal chemistry solves such a problem by carbon–halogen activation involved in organic reactions.[12] In literature, the activation of dichloromethane is reported by various transition metal complexes such as Pt,[13] Pd,[13] Au nanoparticles,[4] Ru,[14] Rh,[15] Cu,[5] In nanoparticles[6] and Co.[16] Development of a new highly efficient and environmentally benign catalytic system for such C—Cl and C—H bond activation is still desirable. In this context, we have developed herein an efficient protocol for the synthesis of propargylamines from alkynes, secondary amines and dihalomethane using nickel catalyst. The protocol works under milder reaction conditions with the additional advantages of easy work-up procedure and use of inexpensive base.

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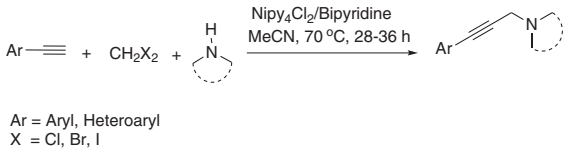
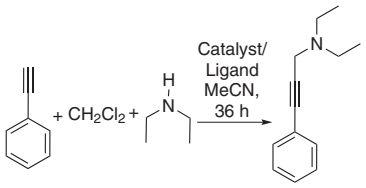


Scheme 1. Nickel-catalyzed three-component coupling of alkyne, dihaloalkane and amines (AHA).

Results and Discussion

A series of experiments were performed to optimize the reaction conditions for AHA coupling of phenyl acetylene, dichloromethane and diethyl amine to propargylamines. Initially we checked the effect of various nickel precursors such as $NiCl_2$, $Ni(acac)_2$, $Ni(oAc)_2$, $Ni(tppe)_2Cl_2$, $Ni(py)_4Cl_2$ in the presence of bipyridine ligand, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base and acetonitrile as a solvent at 80°C (Table 1, entries 1–5). Among all the screened catalysts precursors, $Ni(py)_4Cl_2$ was found to be the most effective, providing an excellent yield of desired propargylamine in 36 h (Table 1, entry 5). We have studied the effect of various nitrogen-containing bidentate ligands, such as bipyridine, phenanthroline, bathophenanthroline, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*′-dimethylethylenediamine (DMEDA-1) and *N*,*N*-dimethylethylenediamine (DMEDA-2) (Table 1, entries 6–11). Among the screened ligands, bipyridine gives 72% yield of propargylamine and results can be explained by a bite angle effect (Table 1, entry 5). We also performed the reaction using ligand-free conditions, but it gave only 15% yield of *N*,*N*-diethyl-3-phenylprop-2-yn-1-amine, indicating the necessity of ligand for formation of *in situ* transition metal complex which can activate C—H, C—Cl bonds for catalyzing the AHA coupling reaction (Table 1, entry 11).

Table 1. Catalyst screening for AHA reaction[a]



Entry	Catalyst	Ligand	Yield (%)[b]
1	$NiCl_2$	Bipyridine	37
2	$Ni(acac)_2$	Bipyridine	35
3	$Ni(oAc)_2$	Bipyridine	36
4	$Ni(tppe)_2Cl_2$	Bipyridine	47
5	$Ni(py)_4Cl_2$	Bipyridine	72
6	$Ni(py)_4Cl_2$	Phenanthroline	60
7	$Ni(py)_4Cl_2$	Bathophenanthroline	64
8	$Ni(py)_4Cl_2$	TMEDA	58
9	$Ni(py)_4Cl_2$	DMEDA-1	40
10	$Ni(py)_4Cl_2$	DMEDA-2	48
11	$Ni(py)_4Cl_2$	—	15

[a]Reaction conditions: phenylacetylene (1 mmol), diethylamine (2 mmol), dichloromethane (2 mmol), catalyst (20 mol%), ligand (50 mol%), DBU (2 mmol), MeCN, 3ml; temperature, 80°C); time, 36 h.

[b]GC yields.

Noting the importance of base in the reaction, we have screened various organic as well as inorganic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), tetramethylguanidine (TMG), triethylamine (TEA) and 1,4-diazabicyclo[2.2.2]octane (DABCO), K_2CO_3, K_3PO_4. We observed that base-free conditions cannot catalyze the reaction (Table 2, entries 1–6). The base TMG gives an excellent yield of propargylamine because it has a very high pK_a as compared to others, is very strongly basic and non-nucleophilic in nature as well as having very good solubility[17]; therefore it was used for further studies. Furthermore, we have also studied the effect of catalyst loading and it was found that the yield of propargylamine decreases up to 80%, with catalyst concentration decreasing from 15 to 10 mole %; hence 15 mol% catalyst loading was used for further studies (Table 2, entries 7 and 8). The formation of organometallic complex depends upon the metal-to-ligand ratio and we found that a 1:1 ratio was sufficient to catalyze the reaction efficiently (Table 2, entries 9 and 10). We have also checked various polar as well as non-polar solvents, and acetonitrile gave better yields (Table 2, entries 11–13). In the presence of dichloromethane as a solvent the reaction yields were lower, as the required temperature of reaction could not be attained (Table 2, entry 13). Temperature is a crucial factor for this reaction. If we conducted the reaction above 80°C, we observed some small quantities of dimerization product of phenyl acetylene. At 70°C, we obtained an excellent yield of the desired product and at this temperature dimerization was suppressed (Table 2, entries 14–16). A substrate ratio of 1:2:3 (alkyne:dichlorometane:amine) gave the highest yield of propargylamine, and the optimum time required for catalyzing the reaction was 28 h (Table 2, entries 17–21).

With these optimized reaction conditions, the scope of the developed protocol was extended for the synthesis of various propargylamine derivatives. As illustrated in Table 3, the reaction proceeds efficiently with various alkynes and secondary amine derivatives to provide a wide range of substituted propargylamines in good to excellent yields. The prominent feature of the present protocol was that this system had very good functional group tolerance for aliphatic and heterocyclic substituted alkynes, secondary amine derivatives as well as dihalomethanes like dichloromethane, dibromomethane and diiodomethane (Tables 3 and 4).

Aromatic acetylene derivatives such as phenylacetylene, 4-methyl phenylacetylene, 4-methoxyphenylacetylene, 4-hydroxyphenylacetylene and 4-aminophenylacetylene underwent coupling with dichloromethane and diethylamine smoothly to afford the respective propargylamines in good to excellent yields of 82–92% (Table 3, entries 1–5). It is worth mentioning that the heteroaromatic acetylene derivatives also gave acceptable yields of 70–72%, but required more time to complete the reaction (Table 3, entries 6 and 7). Aliphatic acetylenes such as cyclohexyl acetylene work very well and gave 86% yield of corresponding propargylamines (Table 3, entry 8). In the three-component AHA coupling reaction various functional groups such as 4-CF_3 and 4-dimethylamino on the aromatic core of phenylacetylene also gave good yields of propargylamines (Table 3, entries 9 and 10). We also checked the reaction of methyl oct-7-ynoate with dichloromethane and diethylamine but the reaction could not proceed due to low nucleophilicity of alkyne as well as the carbonyl group present in the molecule (Table 3, entry 11).

Reactions with secondary amines such as morpholine, piperidine, pyrrolidine, diisopropylamine, dipropylamine, dibutylamine

Table 2. Optimization of reaction parameters for AHA reaction[a]

Entry	Catalyst loading (mol%)	Substrate ratio (AHA)	Base	Solvent	Temperature (°C)	Yield (%)[b]
Base screening						
1	20	1:2:2	TMG	MeCN	80	86
2	20	1:2:2	TEA	MeCN	80	62
3	20	1:2:2	DABCO	MeCN	80	68
4	20	1:2:2	K_2CO_3	MeCN	80	80
5	20	1:2:2	K_3PO_4	MeCN	80	78
6	20	1:2:2	—	MeCN	80	n.r.
Loading of catalyst						
7	10	1:2:2	TMG	MeCN	80	74
8	15	1:2:2	TMG	MeCN	80	86
Metal:ligand ratio						
9[c]	15	1:2:2	TMG	MeCN	80	86
10[d]	15	1:2:2	TMG	MeCN	80	86
Solvent screening						
11	15	1:2:2	TMG	Toluene	80	n.r.
12	15	1:2:2	TMG	Dioxane	80	n.r.
13	15	1:2:2	TMG	DCM	80	50
Temperature study						
14	15	1:2:2	TMG	MeCN	r.t.	n.r.
15	15	1:2:2	TMG	MeCN	60	80
16	15	1:2:2	TMG	MeCN	70	88
Substrate ratio (*alkyne*:*halomethane*:*amine*)						
17	15	1:1:1	TMG	MeCN	70	60
18	15	1:1.2:1.2	TMG	MeCN	70	72
19	15	1:2:3	TMG	MeCN	70	95
Time study						
20[e]	15	1:2:3	TMG	MeCN	70	95
21[f]	15	1:2:3	TMG	MeCN	70	83

[a]Reaction conditions: phenylacetylene (1 mmol), diethylamine (2 mmol), dichloromethane (2 mmol), $Ni(py)_4Cl_2$ (20 mol%), bipyridine (50 mol%), DBU (2 mmol), MeCN (3ml), time (36 h); n r., no reaction; r.t., room temperature.

[b]GC yields.

[c]Metal:ligand ratio (1:2).

[d]Metal:ligand ratio (1:1).

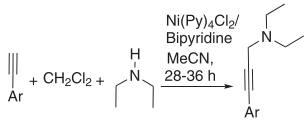
[e]Time (28 h).

[f]Time (22 h).

and *N*-methylpiperazine were efficiently catalyzed and gave corresponding propargylamine derivatives with excellent yields in the range of 50–90% (Table 4, entries 1–7). Among these, dibutylamine required more time to complete due to steric hindrance and lower nucleophilicity. Furthermore, we checked the activity of sterically hindered secondary amines for entitled reaction and works smoothly to give targeted propargylamines with appreciable yields (Table 4, entries 8 and 9). Aromatic amines like *N*-methylaniline cannot gives the respective propargylamine because reactivity of aromatic amines are lower as compare to secondary amines(Table 4, entry 10). We also performed the reaction of 4-methylphenylacetylene and pyrrolidine with dichloromethane, which gave a very good yield of the corresponding product (Table 4, entry 11). Various C_1 sources such as dibromomethane and diiodomethane also showed excellent activity under the present reaction conditions (Table 4, entries 12 and 13).

Based on the literature results,[4-7,11] the reaction mechanism was proposed as shown in Scheme 2. The classical mechanism of AHA coupling of alkyne starts with oxidative addition of the haloalkane to an Ni(0) complex to give an alkyl–Ni(II) derivative in the initiation process. Propagation steps of the radical chain reaction involve activation of the terminal alkyne in presence of base by Ni(I) species to give Ni(III) derivatives. Ni-catalyzed cross-coupling reactions have been developed recently,[18] and mechanistic evidence has been obtained both experimentally as well as computationally.[19] Radical Ni(I) derivatives as the actual catalysts activate the terminal alkyne by oxidative addition in the presence of base and an Ni(I)–Ni(III) catalytic cycle takes place.[11] Ni(I) complexes may be formed from Ni(II) precursors with alkyne or alkyl halide in the presence of nitrogen terdentate ligands by comproportionation of Ni(II) intermediates with Ni(0) species formed by reductive elimination of dialkyl–Ni(II) complexes.[20] Alkyl–Ni(I) complexes containing terdentate ligands such as terpyridine (terpy) or pyridine bis(oxazoline) (pybox) derivatives show the unpaired electron delocalized on the p orbitals of the ligand, and exhibit square-planar geometry. For these reasons they may be described as Ni(II) complexes with two formally anionic ligands. In accordance with these models, we considered other mechanistic alternatives that involved Ni(I)–Ni(III) catalytic cycles (Scheme 2). In the first cycle (A) transmetalation takes place

Table 3. The scope of Nickel catalyzed AHA coupling of diethyl amine, dichloromethane with various alkynes[a]

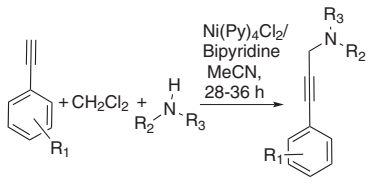


Entry	Ar	Product	Time (h)	Yield (%)[b]
1	Ph	a	28	92
2	*p*-CH_3—Ph—	b	28	90
3	*p*-OCH_3—Ph—	c	28	90
4	*p*-OH—Ph—	d	28	85
5	*p*-NH_2—Ph—	e	28	82
6	2-Pyridyl-	f	36	70
7	3-Pyridyl-	G	36	72
8	C_6H_{11}—	h	28	86
9	*p*-CF_3—Ph—	i	28	78
10	*p*-$(CH_3)_2N$—Ph—	j	28	72
11	$CH_3OCO(CH_2)_5$—	k	36	n.r.

[a]Reaction conditions: alkyne (1 mmol), dichloromethane (2 mmol), diethyl amine (3 mmol), $Ni(py)_4Cl_2$ (15 mol%), ligand (15 mol%), TMG (2 mmol), MeCN (3ml); n.r., no reaction.

[b]Isolated yields.

Table 4. The scope of nickel-catalyzed AHA coupling of coupling partner with various amines and dihalomethanes[a]



Entry	R_2, R_3	Product	Time (h)	Yield (%)[b]
1	$O(CH_2—CH_2)_2$—	l	28	90
2	—$(CH_2)_5$—	m	28	90
3	—$(CH_2)_4$—	n	28	86
4	R_2, $R_3 = CH(CH_3)_2$—	o	28	50
5	R_2, $R_3 = CH_3(CH_2)_2$—	p	28	76
6	R_2, $R_3 = CH_3(CH_2)_3$—	q	32	74
7	$CH_3N(CH_2)_2$—	r	28	78
8	—CH_2—Ph—$(CH_2)_2$—	s	28	70
9	$PhCH_2CH(CH_2)_2$—	t	28	66
10	R_2 = Ph, $R_3 = CH_3$	u	36	n.r.
11 [c]	—$(CH_2)_5$—	v	28	86
12 [d]	R_2, R_3 = —CH_2CH_3	w	28	90
13[e]	R_2, R_3 = —CH_2CH_3	x	28	90

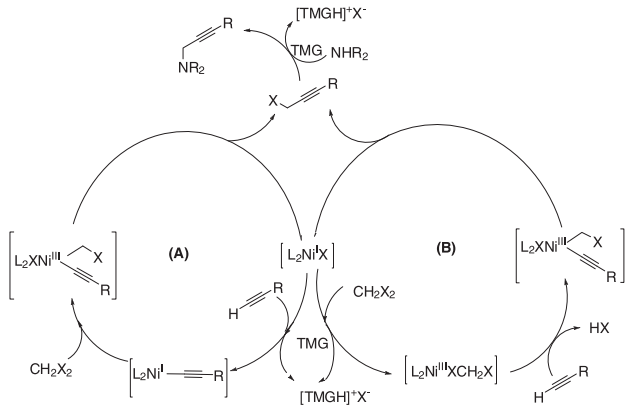
[a]Reaction conditions: phenylacetylene (1 mmol), dihalomethane (2 mmol), amine (3 mmol), $Ni(py)_4Cl_2$ (15 mol%), ligand (15 mol%), TMG (2 mmol), MeCN (3ml); n.r., no reaction.

[b]Isolated yields.

[c]4-Methylphenylacetylene.

[d]CH_2Br_2 used.

[e]CH_2I_2 used.



Scheme 2. Plausible reaction mechanism of nickel-catalyzed three-component coupling of alkyne, dihaloalkane and amines (AHA).

on Ni(I) before oxidative addition of the alkyne in the presence of TMG as a base. In the second cycle (B) the active catalyst oxidatively adds the haloalkane, and the resulting Ni(III) complex reacts with the terminal alkyne. The resulting Ni(III) complex on reductive elimination gives an alkynyl halide which, after reaction with secondary amine in the presence of strong base TMG, furnishes a propargylamine product.

Conclusion

We have established a novel, efficient, three-component coupling reaction of alkynes, haloalkanes and amines through C—H and C—halogen activation for facile synthesis of propargylic amines under milder conditions using $Ni(py)_4Cl_2$/bipyridine catalyst. It was observed that CH_2Cl_2 can be activated by nickel catalyst and provide CH_2 as a very good partner for the C_1 source in multi-component reactions. This methodology is environmentally benign because such a methodology used in the degradation of harmful chlorinated solvents to useful propargylamines and $Ni(py)_4Cl_2$ with bipyridine ligand and TMG as a base solves the problem of carbon–halogen activation. The reaction has very good functional group tolerance to aliphatic and aromatic alkynes, generating the corresponding propargylic amines in high yields. This multi-component reaction represents the first-time use of a novel nickel catalyst for C—H and C—Cl bond activation.

Experimental

Materials and Instruments

All chemicals were purchased from Sigma-Aldrich, SD Fine Chemicals, Lancaster (Alfa-Aesar) and other commercial suppliers. Progress of the reaction was monitored by gas chromatography (GC) on a PerkinElmer Clarus 400 gas chromatograph equipped with flame ionization detector with capillary column (30 m × 0.25 mm × 0.25 mm) using an external standard method and thin-layer chromatography with Merck silica gel 60 F254 plates. The product was visualized with a 254 nm UV lamp. All yields reported in Tables 1 and 2 are GC yields, and yields in Tables 3 and 4 are isolated yields. All compounds were reported and confirmed by comparison with authentic samples using GC and GC-MS techniques. The GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness 0.25 μm) (column flow

2 ml min^{-1}, 80–240°C at 10°C min^{-1} rise). ^1H and ^{13}C NMR (δ, ppm) spectra were recorded on a Varian Mercury 400 NMR spectrometer at operating frequencies of 400 and 100 MHz, respectively, in $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) as the internal standard. *J* (coupling constant) values are reported in hertz. Proton splitting patterns are described as s (singlet), d (doublet), t (triplet) and m (multiplet). All products are known in the literature.

General Procedure for Nickel-Catalyzed Three-Component Reaction of Alkynes, Dichloromethane and Amines

In a typical experiment, a mixture of phenylacetylene (1.0 mmol, 102 mg), dichloromethane (2.0 mmol, 169.9 mg), diethylamine (3.0 mmol, 219.4 mg), TMG (2.0 mmol, 230 mg), $Ni(py)_4Cl_2$ catalyst (66.98 mg, 15 mol%) and bipyridine ligand (23.4 mg, 15 mol%) was charged in the spin bar containing a sealed tube (10 ml) with 3.0 ml CH_3CN at 70°C for 28 h. After completion of the reaction, the mixture was diluted with H_2O (10 ml) and the aqueous layers were extracted with diethyl ether (20×5 ml), dried over anhydrous Na_2SO_4 and concentrated to give the crude product. The residue obtained was purified by column chromatography (silica gel, 60:20 mesh; hexane–ethyl acetate, 20:1) to afford the desired pure propargylic amines. The organic solution was analyzed by GC and confirmed by GC-MS and NMR. Purity of the compounds was determined by GC-MS analysis.

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