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Indium-Catalyzed Hydroamination/Hydrosilylation of Terminal Alkynes and Aromatic Amines through a One-Pot, Two-Step Protocol

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We demonstrated that indium tribromide effectively functioned as a single catalyst for two successive steps in a one-pot procedure. First, the hydroamination of alkynes with anilines took place to give the Markovnikov product. Then, hydrosilylation of the imine intermediates by treatment with a hydrosilane substrate afforded the corresponding secondary amines.

Introduction

Carbon–nitrogen bond formation is important to industrial chemistry because of the various uses of the resulting secondary or tertiary amine. Central to these reactions is the catalytic hydroamination of alkynes and anilines, which shows high atom economy (100%).[1] Thus far, this molecular transformation has been consistently performed by using a number of early[2] or late transition metals,[3] main group metals,[4] and lanthanides.[5] Among them, a report by Doye et al. attracted our attention. In this case, a Ti complex functioned as a single catalyst and promoted both hydroamination and hydrosilylation reactions for the addition of terminal alkynes and anilines.[6] In a typical reductive hydroamination reaction, the second reduction (hydrogenation) step is generally achieved by using either a separate catalyst system, such as $ZnCl_2$/$NaBH_3CN$,[2a] or a strong reducing agent, such as $LiAlH_4$.[7] These procedures can create troublesome experimental procedures and require extra chemicals and solvents, and the strong reducing reagents can lead to a decrease in the chemoselectivity toward functional groups that are sensitive to reducing conditions. Therefore, the development of a one-pot method that uses a single catalyst for a reductive hydroamination reaction that occurs under mild reaction conditions would be highly worthwhile.

As an extension of these procedures, Beller et al. reported an efficient method for the reductive hydroamination of anilines and alkynes by using $Zn(OTf)_2$ (OTf = trifluoromethanesulfonate) under hydrogen.[8] Djukic and co-workers disclosed that a chromium-iridium complex successfully catalyzed the hydroamination/hydrosilylation of terminal aromatic alkynes and anilines by using the mild reducing agent Et_3SiH.[9] Several groups have reported that iridium complexes in the presence of Et_3SiH will undergo a one-pot hydroamination/hydrosilylation in an inter- or intramolecular manner.[10] Also reported was the tandem intermolecular hydroamination/transfer hydrogenation of alkynes by using a combination of a gold(I) complex and a Hantzsch ester as the reducing source.[11] Thus, we began to develop the reductive hydroamination of alkynes by using a single catalyst that contained a group 13 metal, particularly an indium compound, as the combination of indium catalysts and a hydrosilane have shown high functional-group tolerance and interesting functional-group interconversion (FGI).[12,13] Examples of employing group 13 metals include the breakthrough work of Barluenga et al. who reported the Tl-catalyzed hydroamination of alkynes and reports from the Huang and Loh or Prajapati groups who found that an indium(III) compound could catalyze the hydroamination of either alkenes or alkynes.[14] The gallium-catalyzed hydroamination of alkynes has also been reported by Li et al.[7b] Herein, we report the indium-catalyzed one-pot hydroamination/hydrosilylation of terminal alkynes and anilines in the presence of a hydrosilane. This is the first example of a one-pot reductive hydroamination by employing a main group metal, an indium(III) compound, which effectively functions as a single catalyst for successive hydroamination and hydrosilylation reactions.

Results and Discussion

Phenylacetylene and *p*-toluidine were initially treated with $InBr_3$ (10 mol-%) in toluene at 110 °C for 3 h followed by the addition of Et_3SiH (Si–H: 4 equiv.) and further heated to produce the expected secondary amine **1** in 97%

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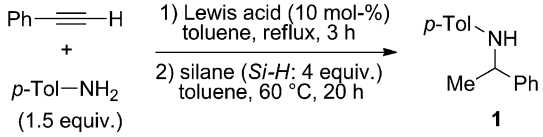
yield (see Table 1, Entry 1). This reaction showed a high degree of selectivity for the Markovnikov product. During the series of reactions, it is noteworthy that the indium compound showed high catalytic activity for the two steps, that is, the hydroamination and then the subsequent hydrosilylation. Of the screened hydrosilanes, 1,1,3,3-tetramethyldisiloxane (TMDS), polymethylhydrosiloxane (PMHS), phenylsilane ($PhSiH_3$), and methyldiphenylsilane (Ph_2MeSiH), none had the same effect with regard to the reductive hydroamination (see Table 1, Entries 2–5). In contrast, dimethyl(phenyl)silane ($PhMe_2SiH$) was an outstanding reducing agent (see Table 1, Entry 6). When the amount of the indium compound or the hydrosilane was decreased to 5 mol-% or 3 equiv. (Si–H), respectively, the product was afforded in low yield (see Table 1, Entries 7 and 8). Although 1 equiv. of the hydrosilane is sufficient stoichiometrically for the reduction of the imine, there is no clear reason for the remarkable decrease in yield. Conducting the hydroamination with $InCl_3$, $In(OTf)_3$, and In_2O_3 led to a reduced product yield, but in the case of InI_3, the reaction proceeded in nearly quantitative yield (see Table 1, Entries 9–12). Consequently, the system that employed $In(OTf)_3$, as reported by Prajapati et al., could not be applied to this sequence.[14b] Other group 13 metal compounds, such as $AlCl_3$ and $GaCl_3$, did not show high catalytic activity (see Table 1, Entries 13 and 14). To compare the results in which $Zn(OTf)_2$ promoted the reductive hydroamination of alkynes with anilines under hydrogen,[8] a similar reaction was carried out with $Zn(OTf)_2$ and $PhMe_2SiH$. This reducing system, however, required high temperature (>110 °C) to complete the hydroamination step (see Table 1, Entries 15 and 16).

With optimal conditions, the scope of the reductive hydroamination was examined by using phenylacetylene and a variety of anilines (see Table 2). In most cases, with anilines that had either an electron-donating or weakly electron-withdrawing group, the reductive hydroamination process proceeded cleanly to produce the corresponding secondary aromatic amines **2**–**10** in good to excellent yields. In addition, the location of the substituent on the benzene ring had almost no effect on the yield of the hydroamination product. The trifluoromethyl, cyano, and nitro groups, which are generally sensitive to conventional reducing conditions, were exceptions and had a high tolerance to the $InBr_3/PhMe_2SiH$ reducing system. Unlike the $In(OTf)_3/Et_3SiH$ system in *N*,*N*-dimethylformamide (DMF),[13h] our system in toluene would not reduce the nitro group on a benzene ring. These strong electron-withdrawing substituents required a longer reaction time to consume the alkyne in the first addition step, which may have led to the decreased total yield. Compared with using other metal catalysts such as $GaCl_3$[7b] or $Zn(OTf)_2$,[4d] the employment of $InBr_3$ was successfully applied to the reductive hydroamination of an aromatic secondary amine. For example, when the reaction was carried out with *N*-methylaniline, *N*,*N*-diphenylamine, and *N*-methylbenzylamine, the corresponding

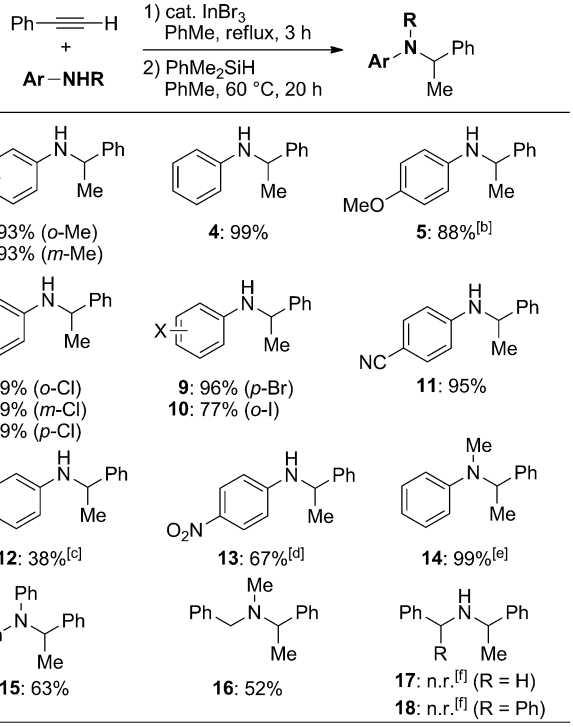
Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Hydrosilane	Yield [%][b]
1	$InBr_3$	Et_3SiH	97
2	$InBr_3$	TMDS	64
3	$InBr_3$	PMHS	26
4	$InBr_3$	$PhSiH_3$	76
5	$InBr_3$	Ph_2MeSiH	n.d.[c]
6	$InBr_3$	$PhMe_2SiH$	98[d]
7[e]	$InBr_3$	$PhMe_2SiH$	20
8[f]	$InBr_3$	$PhMe_2SiH$	42
9	$InCl_3$	$PhMe_2SiH$	6
10	$In(OTf)_3$	$PhMe_2SiH$	56
11	In_2O_3	$PhMe_2SiH$	10
12	InI_3	$PhMe_2SiH$	98
13	$AlCl_3$	$PhMe_2SiH$	n.d.[c]
14	$GaCl_3$	$PhMe_2SiH$	25
15	$Zn(OTf)_2$	$PhMe_2SiH$	30
16[g]	$Zn(OTf)_2$	$PhMe_2SiH$	90

[a] Alkyne (0.30 mmol), *p*-methylaniline (0.45 mmol), catalyst (0.030 mmol), hydrosilane (1.2 mmol), and toluene (0.60 mL). [b] NMR yield. [c] n.d. = not determined. [d] Isolated yield. [e] $InBr_3$ (5 mol-%) was employed. [f] $PhMe_2SiH$ (3 equiv.). [g] Temperature of 110 °C in the second step.

Table 2. Reductive hydroamination of phenylacetylene with amines.[a]

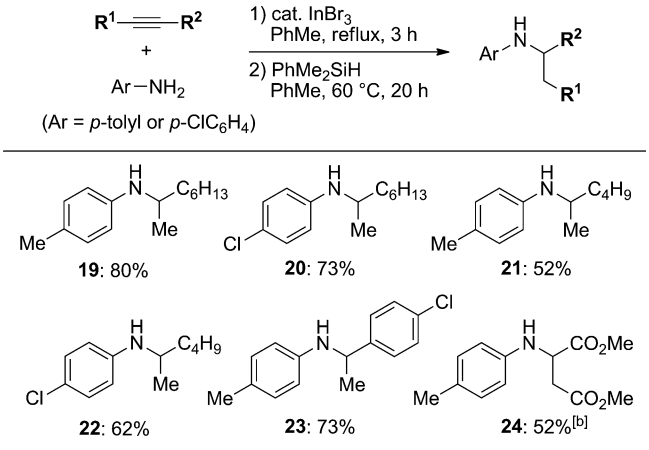


[a] Alkyne (0.30 mmol), amine (0.45 mmol), $InBr_3$ (0.030 mmol), hydrosilane (Si–H: 1.2 mmol), toluene (0.60 mL), 3 h for the first step, 20 h for the second step. [b] InI_3 was employed as the catalyst. [c] 6 h for the first step. [d] 24 h for the first step. [e] 30 h for the second step. [f] n.r. = no reaction.

tertiary amines **14**–**16**, respectively, were obtained in relatively good yields. Unfortunately, the reductive hydroamination with a primary aliphatic amine did not produce the expected secondary amine.

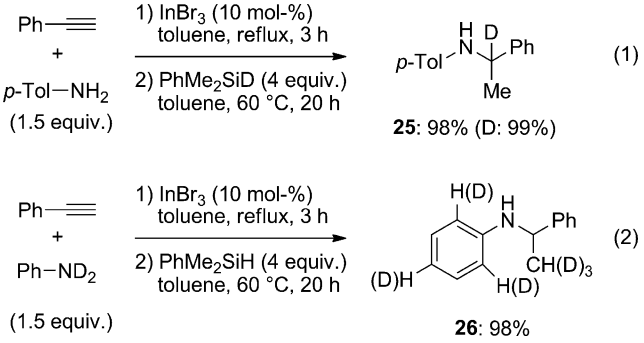
Then, the reductive hydroamination of other alkynes, besides phenylacetylene, with either 4-methylaniline or 4-chloroaniline was conducted under the optimal conditions (see Table 3). The employment of a terminal alkyne with an aliphatic substituent, such as 1-octyne and 1-hexyne, produced the corresponding secondary amines **19**–**22** in relatively good yields. When the reaction was carried out with a chloro-substituted phenylacetylene derivative, the corresponding amine **23** was obtained in good yield. Dimethyl acetylenedicarboxylate (DMAD) was then used in this reductive hydroamination reaction to lead to aspartic acid derivative **24** in a practical yield. Unlike our previous system that involved $InBr_3$/Et_3SiH in chloroform, this reducing system, which consisted of an indium(III) compound/$PhMe_2SiH$ in toluene, would not reduce an ester moiety. When the reductive hydroamination method was applied to an alkyne with a monoester moiety, such as ethyl propiolate or ethyl phenylpropiolate, the first hydroamination step did not occur, and the starting amine and alkyne were recovered. Therefore, this reducing system does not have an effect on monoester groups. Unfortunately, this method could not be applied to a terminal alkyne with bulky substituents such as 3,3-dimethyl-1-butyne and internal alkynes such as 5-decyne and diphenylacetylene. On the basis of these results, it seems that the hydroamination step was influenced by the steric factors of the alkyne.

Table 3. Reductive hydroamination of alkynes with anilines.[a]



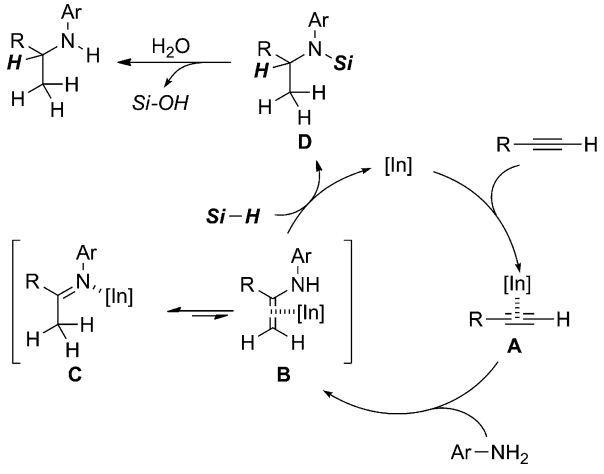
[a] Alkyne (0.30 mmol), amine (0.45 mmol), $InBr_3$ (0.030 mmol), hydrosilane (Si–H, 1.2 mmol), toluene (0.60 mL), 3 h for the first step, 20 h for the second step. [b] InI_3 was employed as the catalyst.

The hydroamination of phenylacetylene with *p*-toluidine was then conducted with $PhMe_2SiD$ under the optimal conditions, and amine **25**, which showed a high H/D exchange ratio at the benzyl position, was obtained in a good yield [see Scheme 1, Equation (1)]. When the reaction was carried out with $PhND_2$, the secondary amine **26**, which incorporated deuterium atoms into the methyl moiety, was obtained after a common workup [see Scheme 1, Equation (2)]. The ^1H and ^2D NMR spectroscopic data of product **26** showed the incorporation of deuterium atoms into the benzene ring as a result of the starting aniline (incorporation ratio of deuterium $D_{ortho}/D_{para}/CD_3$: 2:3:10).[15]



Scheme 1. Deuterium-labeling experiments with $PhMe_2SiD$ and $PhND_2$.

On the basis of these deuterium-labeling experiments, we suggest a plausible reaction path for the reductive hydroamination (see Scheme 2). First, the alkyne coordinates with the indium compound to form activated alkyne **A**, which facilitates a subsequent nucleophilic attack of the aniline[16] to give enamine intermediate **B**. Intermediate **B** can rapidly transform into its more stable tautomer, imine intermediate **C**. Then, intermediate **C**, which is activated by the indium compound, is smoothly hydrosilylated to produce the reduced product **D**. Finally, product **D** is hydrolyzed by a common workup procedure to produce the corresponding amine derivative. During the reductive hydroamination series, it has been inferred that the indium compound mainly promotes the initial hydroamination step,[17] and excess amounts (0.5 equiv.) of the amine do not result in an undesired side reaction.[18]



Scheme 2. Plausible reaction path for hydroamination and hydrosilylation.

Conclusions

We have demonstrated that indium tribromide effectively catalyzes the reductive hydroamination of terminal alkynes and aromatic amines to produce the corresponding secondary and tertiary amines in good yields. Also, compared with a sequential reaction protocol, this one-pot reductive hydroamination method avoids troublesome experimental procedures and the isolation an intermediate. As a result, there is a reduced need for extra chemicals and solvents.

Experimental Section

General Methods: The ^{1}H NMR spectroscopic data were recorded at 500 or 300 MHz by using tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectroscopic data were measured at 125 or 75 MHz by using the resonances of the residual solvent as the internal standard. High-resolution mass spectra (FAB or ESI) were measured by using *p*-nitrobenzyl alcohol (for FAB) as a matrix. Thin-layer chromatography was conducted on silica gel 60 F_{254}. Column chromatography was performed with silica gel 60 F_{254}. Manipulations were carried out under nitrogen, unless otherwise noted. Toluene was distilled from CaH_2 and then kept dry over molecular sieves (3 Å). The indium compounds, hydrosilanes, alkynes, and anilines were commercially available. The indium compounds and hydrosilanes were used without further purification. The anilines and alkynes were purified by using a common purification procedure.

General Procedure for the Indium-Catalyzed Reductive Hydroamination: In a glove box, $InBr_3$ (10.6 mg, 0.0300 mmol) was weighed directly into a glass vial with a screw cap. The vial was sealed with a PTFE-sealed (PTFE = polytetrafluoroethylene) screw cap under N_2 and then removed from the glove box. Into the vial were successively added distilled toluene (0.6 mL), the alkyne (0.30 mmol), and the aniline (0.45 mmol). The solution was stirred at 110 °C for 3 h. Then, $PhMe_2SiH$ (163.5 mg, 1.200 mmol) was added by syringe, and the resultant mixture was further heated at 60 °C for the appropriate reaction time (see Tables 1 and 2 as well as Scheme 1). The reaction was quenched with aqueous Na_2CO_3 (1 mL), and the aqueous layer was extracted with AcOEt (3× 5 mL). The combined organic phases were dried with Na_2CO_3, filtered, and then concentrated under reduced pressure. The crude product was purified by silica gel chromatography (hexane/AcOEt, 9:1) to give the corresponding amine derivative.

***N*-Benzyl-*N*-(α-phenylethyl)-*p*-toluidine (16):** Orange oil (47 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.56 (d, J = 7.0 Hz, 3 H), 2.20 (s, 3 H), 4.36 (d, J = 17.5 Hz, 1 H), 4.45 (d, J = 17.5 Hz, 1 H), 5.20 (q, J = 7.0 Hz, 1 H), 6.67 (d, J = 8.0 Hz, 2 H), 6.95 (d, J = 8.0 Hz, 2 H), 7.17–7.32 (m, 10 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.9, 18.6, 48.8, 55.7, 113.0, 124.6, 124.7, 124.8, 125.1, 125.3, 126.6, 126.8, 127.9, 138.6, 141.4, 145.3 ppm. MS (FAB): *m*/*z* = 301 $[M]^+$. HRMS (FAB): calcd. for $C_{22}H_{23}N$ 301.1830; found 301.1833.

***p*-Chloro-*N*-(2-hexyl)aniline (22):** Yellow oil (39 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.9 Hz, 3 H), 1.15 (d, J = 6.0 Hz, 3 H), 1.29–1.54 (m, 6 H), 3.40 (sept, J = 6.0 Hz, 1 H), 3.43 (br. s, 1 H), 6.48 (d, J = 8.7 Hz, 2 H), 7.09 (d, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 20.6, 22.7, 28.3, 36.7, 48.6, 114.0, 121.1, 129.0, 146.2 ppm. MS (FAB): *m*/*z* = 212 [M + H]. HRMS (FAB): calcd. for $C_{12}H_{19}ClN$ 212.1206; found 212.1199.

***N*-([α-D]α-Phenylethyl)-*p*-toluidine (25):** Yellow solid (63 mg, 99% yield); m.p. 68–69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 3 H), 2.18 (s, 3 H), 3.88 (br. s, 1 H), 6.42 (d, J = 7.5 Hz, 2 H), 6.89 (d, J = 7.5 Hz, 2 H), 7.20 (t, J = 7.0 Hz, 1 H), 7.28 (t, J = 7.0 Hz, 2 H), 7.35 (d, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6, 23.2, 51.5 (t, J = 21.0 Hz), 111.7, 124.1, 124.6, 125.1, 126.9, 127.9, 143.3, 143.6 ppm. HRMS (FAB): calcd. for $C_{15}H_{16}DN$ 212.1424; found 212.1447.

[D_2]*N*-(α-Phenylethyl)aniline (26): Yellow liquid (59 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (m, 1.8 H), 4.00 (br. s, 1 H), 4.46 (m, 1 H), 6.49 (d, J = 7.5 Hz, 1.6 H), 6.63 (t, J = 7.5 Hz, 0.8 H), 7.08 (m, 2 H), 7.20 (t, J = 7.5 Hz, 1 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.35 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.9 (q, J = 19.1 Hz), 51.6 (q, J = 7.6 Hz), 115.6, 115.5, 124.1, 125.1, 126.9, 127.4 (m), 143.5, 145.6 (m) ppm. HRMS (EI): calcd. for $C_{14}H_{13}D_2N$ 199.1330; found 199.1322.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures and characterization data of the products that were obtained by this method as well as copies of the ^{1}H and ^{13}C NMR spectra of the all products.

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[18] In those table entries with moderate yields, no byproduct formation, such as a dimer or polymer of an alkyne or the hydrolyzed product of an imine intermediate, was observed. In most cases, the unreacted starting amine was recovered.

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