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COMMUNICATION

One-pot transformation of alkynes into alcohols and amines with formic acid

Jia Li,[a] Chao Wang,*[a] Dong Xue,[a] Yawen Wei,[a] and Jianliang Xiao*[a,b]

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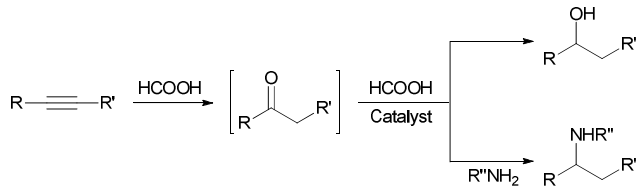
Alkynes are converted into alcohols and amines through a formic acid-participated alkyne-to-ketone transformation and transfer hydrogenation process. The reaction proceeds well under aqueous conditions, furnishing chiral alcohols directly from alkynes for the first time.

Introduction

The functionalisation of alkynes is a fundamental and important class of reaction in organic synthesis. Alkynes can be converted into carbonyl compounds or imines via hydration[1] or hydroamination[2] reactions. However, examples of direct transformation of alkynes into alcohols or amines are rare. Alkyne to alcohol transformation can be achieved by hydration/reduction processes[3] or hydroboration reactions.[4] Coupled hydration/reduction of alkynes only appeared recently.[3] By combination of hydration and transfer hydrogenation catalysts, Herzon and co-workers developed a regioselective system for alkyne to alcohol conversion.[3b] Transformation of alkynes to amines can be realized through hydration/reductive amination or hydroamination/reduction reactions.[5] Examples of reductive hydroamination of alkynes using a single catalyst for both hydroamination and reduction were reported by Che,[6] Gong,[7] Beller,[8] Djukic[9] and their co-workers. However, a hydration/reductive amination process for conversion of alkynes into amines is unknown. In this paper, we report a new process for one-pot transformation of alkynes into alcohols and amines by virtue of a formic acid-promoted alkyne-to-ketone reaction coupled with formic acid-participated transfer hydrogenation and transfer hydrogenative reductive amination (Scheme 1).

Results and Discussion

Based on our experience in aqueous transfer hydrogenation reactions,[10] we were interested to devise a system for transformation of alkynes to alcohols and amines through a hydration/transfer hydrogenation process, ideally using a single catalyst for both hydration and reduction steps and cheap hydrogen sources, e.g. formic acid or isopropanol.[11]



Scheme 1 One-pot formic acid-participated transformation of alkynes into alcohols and amines. General reaction conditions: alkynes (3 mmol), HCOOH (3 mL), amines (6 mmol), S/C = 100 - 500.

Initially, some transfer hydrogenation catalysts were screened for the hydration of *para*-methoxylphenyl acetylene in aqueous methanol. Unfortunately, common transfer hydrogenation catalysts, such as Rh-TsDPEN[12] (Ts-DPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine) or cyclometalated iridium complexes,[13] did not catalyse this step (Table S1, entries 1-2, ESI†). Although $[RuCl_2(p\text{-cymene})]_2$, $[Cp^*RhCl_2]_2$ and $[Cp^*IrCl_2]_2$ are all active for the reaction, the systems could not be extended to other alkyne substrates (Table S1, entries 3-6, ESI†).

On careful examination of the literature concerning alkyne to ketone transformation, we noticed that alkynes could be transformed into ketones with pure formic acid (Scheme 1) via a route different from hydration reactions.[14] In this reaction, alkynes react with formic acid to form ketones with the release of CO gas, which might pose toxicity issues for scaling up. Nevertheless, considering formic acid is a hydrogen source commonly used in transfer hydrogenation reactions, attention was then turned to developing a one pot system in which formic acid would react with the alkyne to give a ketone and then participate in the ketone reduction (Scheme 1). Phenylacetylene was tested in the formic acid-enabled alkyne to ketone transformation. As anticipated, acetophenone was obtained with a conversion of 93% in 0.5 h in HCOOH at 100 °C. However, addition of a transfer hydrogenation catalyst into the pure formic acid system resulted in no reduction of ketone, probably due to the strong acidic reaction conditions.

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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterisation data. See DOI: 10.1039/b000000x

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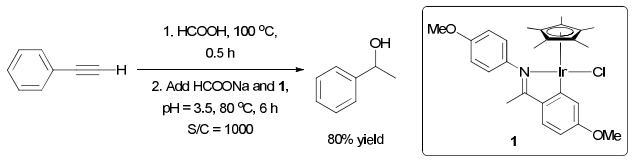
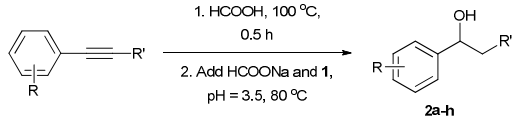
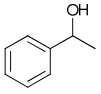
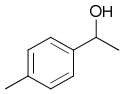
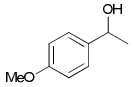
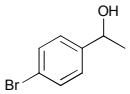
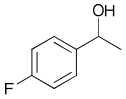
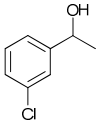
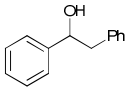
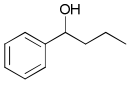
Ketones and aldehydes can be reduced by aqueous transfer hydrogenation using formic acid as hydrogen source. A recent example was developed by our group, using the cyclometalated iridium catalysts with aqueous HCOOH/HCOONa. However, the reaction took place only at a suitable pH.[10f] For example, acetophenone was reduced to 1-phenylethanol at pH 3.5 with catalyst **1**. Inspired by this study, phenylacetylene was stirred in pure formic acid for 0.5 h at 100 °C, and then saturated HCOONa was added to adjust the pH to 3.5. After addition of 0.1 mol% of **1**, the mixture was stirred at 80 °C for a further 6 h. To our delight, 1-phenylethanol was isolated with 80% yield (Scheme 2).



Scheme 2 One pot transformation of phenylacetylene to 1-phenylethanol. Reaction conditions: Phenylacetylene (3 mmol), HCOOH (3 mL), HCOONa (5.6 mL, 15.5 mol/L), **1** (0.003 mmol).

Table 1 One pot transformation of alkynes into achiral alcohols[a]



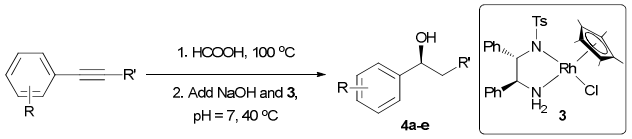
Entry	Product	Time (h)[b]	Yield (%)[c]
1[d]		0.5/6	80
2		3/6	85
3		5/6	52
4[e,f]		5/6	86
5		5/6	81
6[e]		5/6	87
7[e]		5/6	79
8[e,f]		2/14	85

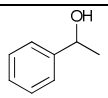
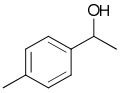
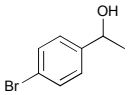
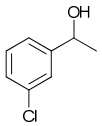
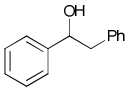
[a] Conditions: Alkyne (3 mmol), HCOOH (3 mL), S/C = 500. [b] Numbers before and after the slash represent time for the first and second step, respectively. [c] Isolated yield. [d] S/C = 1000. [e] TsOH·H_2O (20 mol %) was added. [f] S/C = 200.

The substrate scope of the systems was then examined with different alkynes. A substrate to catalyst ratio (S/C) of 500 was generally used for the second step. Various aromatic terminal alkynes could be converted into alcohols with moderate to good yields (Table 1, entries 1-6). The 1-*para*-methoxylphenyl alcohol was obtained with low yield, probably due to the difficulty of reduction of the corresponding ketone under the conditions employed (Table 1, entry 3).[10f] Generally, substrates with electron donating substituents displayed higher activities for the first step. 20 mol% of *p*-toluenesulfonic acid monohydrate was added to accelerate the first step for substrates with 4-Br and 3-Cl substituents, and a S/C of 200 was used for the 4-Br substituted substrate (Table 1, entry 4). Internal alkynes are viable substrates, albeit also requiring the addition of *p*-toluenesulfonic acid monohydrate or a higher catalyst loading, probably due to their steric hindrance (Table 1, entries 7-8). Aliphatic alkynes were also examined under these conditions. However, no alcohol product was obtained. For example, although 1-octyne could be converted into 2-octanone with 84% yield in 5 h in pure HCOOH, no alcohol product was observed after performing the second step.

Chiral alcohols can be obtained, if the formic acid-participated alkyne to ketone transformation is coupled with asymmetric transfer hydrogenation. The Rh-(*S,S*)-TsDPEN complex **3** is known to catalyse aqueous asymmetric transfer hydrogenation[10c] and was chosen to test the feasibility of this hypothesis. The solution pH was tuned to 7 with a NaOH solution after the first step and **3** was subsequently introduced.[10c] The transfer hydrogenation was carried out at 40 °C at a typical S/C of 200.

Table 2 One pot transformation of alkynes into chiral alcohols[a]



Entry	Product	Time (h)[b]	Yield (%)[c]	ee (%)[d]
1		0.5/3	87	>99
2		3/6	72	98
3[e,f]		5/6	86	99
4[e]		5/12	86	95
5[e,f]		5/12	84	96

[a] Conditions: Alkyne (3 mmol), HCOOH (3 mL), S/C = 200. [b] Numbers before and after the slash represent time for the first and second step, respectively. [c] Isolated yield. [d] Determined by Chiral HPLC. [e] TsOH·H_2O (20 mol %) was added. [f] S/C = 100.

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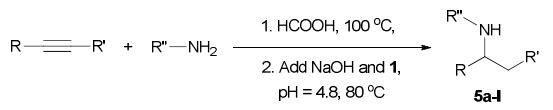
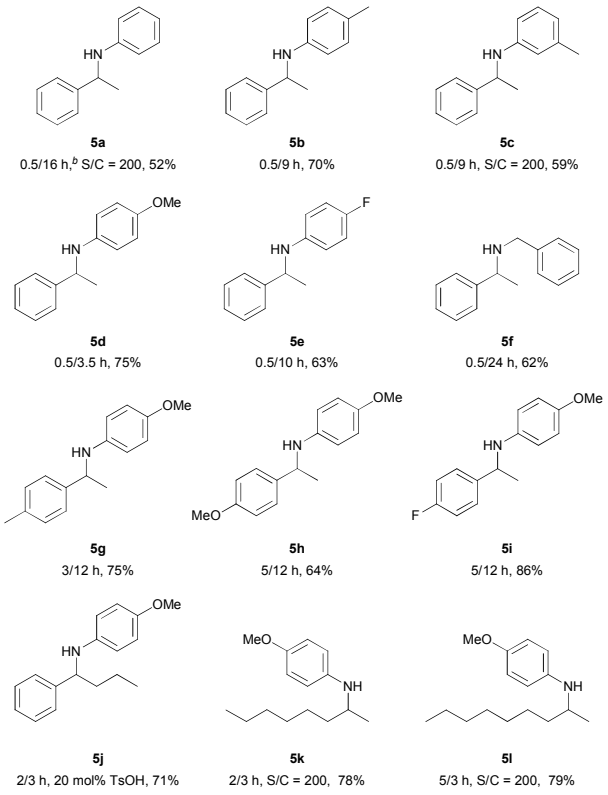
Table 3 One pot transformation of alkynes into amines[a]





[a] Conditions: Alkyne (3 mmol), HCOOH (3 mL), amine (6 mmol), **1** (0.006 mmol), S/C = 500, isolated yield. [b] Numbers before and after the slash represent time for the first and second step, respectively (the same for the other examples).

Chiral alcohols were indeed obtained with good yields and enantioselectivities (Table 2). Terminal aromatic alkynes could be converted to the corresponding alcohols with ees up to 99% (Table 2, entries 1-4). An internal alkyne also reacted to afford the chiral alcohol **4e** in 84% yield and 96% ee in a total time of 17 h (Table 2, entry 5).

One pot alkyne to ketone and transfer hydrogenative reductive amination reaction was then examined in order to produce amines from alkynes, employing an aqueous reductive amination system recently developed by our group.[10e] For this process, the pH was adjusted to 4.8 for the reductive amination step.[10e] Upon finishing the first step, a NaOH solution was added to adjust the pH to the desired level, followed by the addition of catalyst **1** and amine source. As can be seen from Table 3, primary aromatic amines reacted with phenylacetylene to afford the corresponding secondary amines with moderate to good yields (**5a-e**). An example of aliphatic amines also worked (**5f**). Again, aromatic terminal alkynes with different substituents worked well with yields up to 86% (**5g-i**). Aromatic internal alkyne was less reactive in the first step, requiring the addition of 20 mol% of *p*-toluenesulfonic acid monohydrate (**5j**). Unlike in the alkyne-to alcohol transformation, aliphatic alkynes are suitable substrates for alkyne-to-amine reaction. Good yields were obtained for the two aliphatic alkynes tested (**5k-l**).

Conclusions

In conclusion, one pot transformation of alkynes into alcohols and amines has been achieved by formic acid-enabled alkyne-to-ketone conversion coupled with pH-regulated aqueous transfer hydrogenation using formic acid as hydrogen source. Chiral alcohols were derived from alkynes for the first time. The study also provides the first example of transforming alkynes into amines through an alkyne-to-ketone/reductive amination process, which could inspire new thoughts on alkyne-to-amine transformations. The idea of "switch on" a reaction by tuning solution pH may find applications in devising new one-pot aqueous-phase reactions.

Experimental section

Typical procedure for transforming alkynes to achiral alcohols

A tube was charged with a magnetic stir bar and phenylacetylene (3 mmol). HCOOH (3 mL, 99%) was introduced into the tube with a syringe. The resulting mixture was bubbled with argon for 15 min. The tube was then sealed and the mixture was stirred at 100 °C for 0.5 h. Upon cooling to room temperature, the tube was opened and 5.6 mL of aqueous HCOONa solution (15.5 mol/L) was added to adjust the solution pH to 3.5. After addition of catalyst **1** (0.003 mmol), the resulting mixture was stirred at 80 °C for 6 h. After cooling to room temperature, the reaction mixture was transferred to a beaker containing 30 mL of MeOH and the resulting mixture was basified with KOH (pH = 9~10) and stirred for 30 min to hydrolyse any formyl ester product. MeOH was then removed from the mixture under vacuum and the aqueous solution was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removing ethyl acetate under vacuum, the residue was purified by flash chromatography [petroleum ether (m.p = 60~90 °C): ethyl acetate = 8:1] to afford 1-phenylethanol in 80% yield.

Typical procedure for transforming alkynes to chiral alcohols

A tube was charged with a magnetic stir bar and phenylacetylene (3 mmol). HCOOH (3 mL , 99%) was introduced into the tube with syringe. The resulting mixture was bubbled with argon for 15 min. The tube was then sealed and the mixture was stirred at 100 °C for 0.5 h. Upon cooling to room temperature, the tube was opened and aqueous NaOH solution (17 mol/L) was added to adjust the solution pH to 7. After addition of catalyst **3** (0.015 mmol), the resulting mixture was stirred at 40 °C for 3 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removing ethyl acetate under vacuum, the residue was purified by flash chromatography [petroleum ether (m.p = 60~90 °C): ethyl acetate = 8:1] to afford 1-phenylethanol in 87% yield. The enantiomeric excess of product was determined by chiral HPLC analysis: Chiralcel OD-

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H (hexane/*i*PrOH = 97/3, flow rate: 0.5 mL/min), t_R (major) = 25.67 min, t_S (minor) = 35.55 min, 87% ee.

Typical procedure for transforming alkynes to amines

A tube was charged with a magnetic stir bar and phenylacetylene (3 mmol). HCOOH (3 mL, 99%) was introduced into the tube with syringe. The resulting mixture was bubbled with argon for 15 min. The tube was then sealed and the mixture was stirred at 100 °C for 0.5 h. Upon cooling to room temperature, the tube was opened and 4.7 mL of aqueous NaOH solution (17 mol/L) was added to adjust the solution pH to 4.8. After addition of catalyst **1** (0.006 mmol) and *p*-anisidine (6 mmol), the resulting mixture was stirred at 80 °C for 3.5 h. After cooling to room temperature, aqueous HCl solution (3 mol/L) was added to adjust solution pH to 2-3 and the mixture was stirred at room temperature for 10 min to hydrolyse any imines. The resulting mixture was then basified with NaOH solution (6 mol/L) to pH around 9-10 and extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removing ethyl acetate under vacuum, the residue was purified by flash chromatography [petroleum ether (m.p = 60~90 °C): ethyl acetate = 40:1] to afford 4-methoxy-*N*-(1-phenylethyl)aniline in 75% yield.

Acknowledgements

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Graphic Abstract:

Alcohols and amines are directly produced from alkynes through a one-pot formic acid-participated alkyne-to-ketone transformation and transfer hydrogenation process.