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One-pot multicomponent route to propargylamines using ferric hydrogensulfate

Hossein Eshghi*, Gholam Hossein Zohuri and Saman Damavandi

Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, IR-91775-1436, Iran

**Corresponding author at: Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, IR-91775-1436, Iran. Tel.: +98.511.8797660; fax: +98.511.8796416.*
E-mail address: heshghi@ferdowsi.um.ac.ir (H. Eshghi).

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ABSTRACT

The one-pot three-component coupling reaction of phenylacetylene, aldehyde and amine derivatives in the presence of ferric hydrogensulfate, [$(Fe(HSO_4)_3$], as an efficient heterogeneous catalyst is reported. The catalyst displayed high activity and afforded the corresponding propargylamines in good to excellent yields. This method provides the wide range of substrate applicability. Heterogeneous nature of the catalyst made it reusable for further chemical reactions.

1. Introduction

Addition reaction of carbanions to the carbonyl group of aldehydes and ketones [1-4], and addition of organometallic reagents to the C=N bonds of imines or imine derivatives are important reactions in organic synthesis [5-9]. Another useful method for carbon-carbon bond formation is usage of alkynes as a carbon nucleophile source [10,11]. The resulting alkynyl amine derivatives can undergo further transformations and are versatile synthetic tools [12-14]. However, the reactive alkynilides are usually prepared from terminal alkyne by using highly reactive organometallic reagents such as *n*-butyllithium (BuLi) [15,16], EtMgBr [17,18], or lithium diisopropylamide (LDA) [19,20] in a separate step, and many metal alkynilides are not easy to handle because the reaction must be carried out under anhydrous solvent, inert atmosphere, and low temperature conditions. Therefore, the development of a method for the direct alkynylation of imines, which doesn't need to use a stoichiometric amount of highly reactive catalyst and can be carried out under mild conditions, would be highly desirable.

Optically active propargyl amines are important synthetic intermediates for the synthesis of various nitrogen compounds such as β-lactams, oxotremorine analogues, confirmationally restricted peptides and they are components of bioactive compounds or natural products [21-23].

Recently great efforts have been devoted to develop the methodology for generating propargylamines and some direct alkynylations of carbonyl compounds with terminal alkynes have been reported [24-29]. Several transition metal salts such as gold, copper, silver, and Cu/Ru system have been employed in water as well as in ionic liquids [25-27]. Recently, solid-supported metal catalysts such as CuI/Al_2O_3, $AuCl_4$/LDH, Cu/HAP and alternative energy sources like microwave and ultrasound have been utilized in the presence of CuI to accomplish this reaction via C-H activation [26,29].

Herein, propargylamines were synthesized successfully using ferric hydrogensulfate as an efficient heterogeneous catalyst. Various amines and aldehydes were employed to generalize this study. We reported that ferric hydrogensulfate is a highly effective catalyst for the three-component coupling of aldehyde, alkyne, and amine to generate propargylamines (Figure 1).

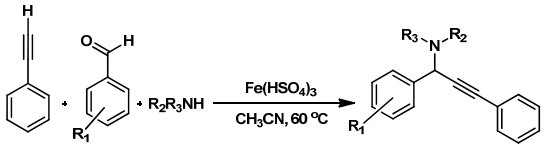

Figure 1. Ferric hydrogensulfate-catalyzed three-component synthesis of propargylamines.

2. Experimental

2.1. Chemicals and reagents

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka, and Aldrich Chemical Companies. All yields refer to isolated products. The reactions were monitored by thin-layer chromatography (TLC) carried out on silica plates. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. IR spectra were recorded on a Shimadzu-IR 470 spectrophotometer. ^{1}H NMR spectra was recorded on a Bruker-100 MHz spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. All of the products are known products and all of the isolated products gave satisfactory IR and NMR

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spectra. Ferric hydrogensulfate was prepared according to previously reported procedure [33,34].

2.2. General procedure for preparation of propargylamines

Amines (1.1 equiv.), aldehydes (1.0 equiv.), phenyl acetylene (1.0 equiv), and ferric hydrogensulfate (0.1 equiv.) were successively added to CH_3CN (10 mL). The progress of reaction was monitored by TLC. After the reaction was completed, chloroform (5 mL) was added and the slurry was stirred, and then filtered using a sintered-glass funnel. The residue was washed to ensure removal of the product from the surface of the catalyst. The combined organic phases were dried over Na_2SO_4 and concentrated to give the almost pure corresponding propargylamine. The final product was purified by short column chromatography (eluent; hexane: ethyl acetate (4:1)). All of the products are known compounds and have been reported already.

N-(1,3-Diphenyl-2-propynyl)morpholine (entry 1): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.00-7.60 (m, 10H), 4.70 (s, 1H), 3.50-3.60 (m, 4H), 2.75-2.90 (m, 4H).

N-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]morpholine (entry 2): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.10-7.60 (m, 9H), 4.90 (s, 1H), 3.60-3.70 (m, 4H), 2.35-2.45 (m, 4H).

N-[1-(4-Methylphenyl)-3-phenyl-2-propynyl]morpholine (entry 3): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.00-7.30 (m, 9H), 4.95 (s, 1H), 3.40-3.55 (m, 4H), 2.25-2.45 (m, 4H), 2.30 (s, 3H).

N-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]morpholine (entry 4): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.10-7.40 (m, 9H), 4.75 (s, 1H), 3.95 (s, 3H), 3.40-3.60 (m, 4H), 2.40-2.55 (m, 4H).

N-[1-(Furfuryl)-3-phenyl-2-propynyl]morpholine (entry 5): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 6.70-7.15 (m, 8H), 4.65 (s, 1H), 3.55-370 (m, 4H), 2.25-2.35 (m, 4H).

N-[1-(3-Phenylprop-2-ynyl)]morpholine (entry 6): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.00-7.30 (m, 5H), 3.45–3.60 (m, 4H), 3.25 (s, 2H), 2.65–2.75 (m, 4H).

N-(1,3-Diphenyl-2-propynyl)pyrolidine (entry 7): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 6.80-7.60 (m, 10H), 4.90 (s, 1H), 2.95-3.30 (m, 4H), 0.90 (t, 4H, *J*=8 Hz).

N-(1-(4-Chlorophenyl)-3-phenyl-2-propynyl)pyrolidine (entry 8): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.10-7.60 (m, 9H), 4.80 (s, 1H), 2.65 (t, 4H, *J*=8 Hz), 1.10 (t, 4H, *J*=8 Hz).

N-[1-(4-Methylphenyl)-3-phenyl-2-propynyl]pyrolidine (entry 9): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.00-7.50 (m, 9H), 4.95 (s, 1H), 2.35-2.60 (m, 4H), 2.55 (s, 3H), 1.20 (t, 4H, *J*=8 Hz).

N-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]pyrolidine (entry 10): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 6.90-7.60 (m, 9H), 5.05 (s, 1H), 3.25 (s, 3H), 2.85–3.05 (m, 4H), 0.90-1.10 (m, 4H).

N-[1-(Furfuryl)-3-phenyl-2-propynyl]pyrolidine (entry 11): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 6.95-7.25 (m, 8H), 4.80 (s, 1H), 2.50-2.65 (m, 4H), 1.25 (t, 4H, *J*=8 Hz).

N-(1,3-Diphenyl-2-propynyl)piperidine (entry 12): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.00-7.55 (m, 10H), 4.90 (s, 1H), 2.60-2.80 (m, 4H), 1.75 (m, 6H).

N-[1-(4-Methylphenyl)-3-phenyl-2-propynyl]piperidine (entry 13): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.15-7.70 (m, 9H), 4.80 (s, 1H), 2.45-2.55 (m, 4H), 2.20 (s, 3H), 1.40-1.68 (m, 6H).

N-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]piperidine (entry 14): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.00-7.65 (m, 9H), 4.85 (s, 1H), 3.81 (s, 3H), 2.50-2.70 (m, 4H), 1.45-1.65 (m, 6H).

N-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]piperidine (entry 15): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.20-7.62 (m, 9H), 4.80 (s, 3H), 2.45-2.65 (m, 4H), 1.50-1.75 (m, 6H).

N-[1-(Furfuryl)-3-phenyl-2-propynyl]piperidine (entry 16): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.35-7.61 (m, 8H), 4.76 (s, 3H), 2.60-2.75 (m, 4H), 1.45-1.75 (m, 6H).

N-[1-(3-Phenylprop-2-ynyl)]piperidine (entry 17): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.20-7.55 (m, 5H), 3.50 (s, 2H), 2.40-2.55 (m, 4H), 1.35-1.50 (m, 6H).

N-Cyclohexyl-3-phenylprop-2-ynylamine (entry 18): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.25-7.65 (m, 5H), 4.55 (s, 1H), 3.75 (s, 2H), 2.45 (m, 1H), 1.80-1.95 (m, 4H), 1.45-1.60 (m, 6H).

1-(1-Cyclopentyl-3-phenylprop-2-ynyl)piperidine (entry 20): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.25-7.55 (m, 5H), 3.75 (d, 1H, *J*=5 Hz), 2.50 (m, 4H), 1.8-1.95 (m, 5H), 1.4-1.65 (m, 5H), 0.9-1.15 (m, 5H).

1-(1-Cyclohexyl-3-phenylprop-2-ynyl)pyrrolidine (entry 22): ^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.00-7.40 (m, 5H), 3.85 (d, 1H, *J*=8 Hz), 2.50 (t, 4H, *J*=8 Hz), 1.05-1.80 (m, 15H).

3. Results and discussion

Using morpholine as the amine, phenyl acetylene as the alkyne and benzaldehyde as the aldehyde component in a stoichiometric ratio of 1.1:1:1 and 0.1 equiv. ferric hydrogensulfate (based on the alkyne component), we designed a reaction as a model in order to find the optimum reaction solvent and the results are shown in Table 1.

Table 1. Influence of solvent on Fe-catalyzed reaction of benzaldehyde, morpholine and phenylacetylene and reusability study.

Entry	Solvent	Yield (%)[a,b]
1	Tetrahydrofuran	35
2	Toluene	52
3	Ethanol	60
4	Dichloromethane	75
5	Methanol	80
6	Acetonitrile	90
7[c]	Acetonitrile	90
8[d]	Acetonitrile	88
9[e]	Acetonitrile	87
10[f]	Acetonitrile	84

[a] Reaction conditions: 1.0 equiv. of benzaldehyde, 1.0 equiv. of morpholine, 1.1 equiv of phenylacetylene, 10 mol% ferric hydrogenesulfate and reflux condition; [b] Isolated yields; [c-f] Reusability of the recovered catalyst in new runs.

Among the various solvent investigated, CH_3CN was found to be the best choice (Table 1, entry 6), while toluene and ethanol afforded lower yields (Table 1, Entries 2 and 3). Moderate yields were obtained when the reactions were carried out in CH_3OH and CH_2Cl_2 (Table 1, Entries 4 and 5). Poor results were observed when the reactions were carried out in THF (Table 1, Entry 1). This may be due to the high polarity associated with CH_3CN, which may result in the stabilization of the alkenyl-Fe intermediate.

In the present work reusability of the catalyst was studied in the reaction of benzaldehyde, morpholine, and phenylacetylene in the presence of the catalyst in acetonitrile as a solvent. After completion of each run, the catalyst was recovered and used for further reactions. As it can be seen in Table 1, the catalyst could be reused without significant loss of its catalytic activity until at least 4 times.

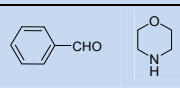
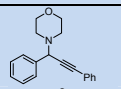
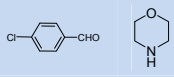
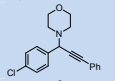
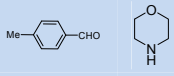
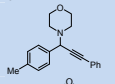
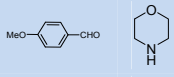
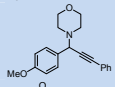
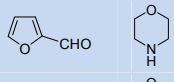
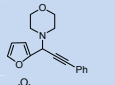
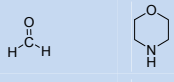
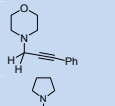
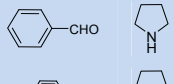
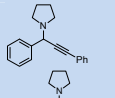
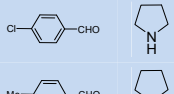
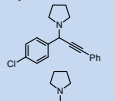
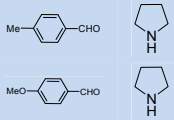
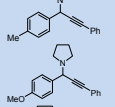
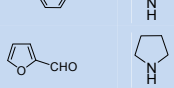
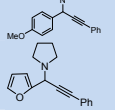
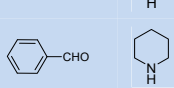
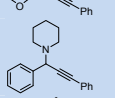
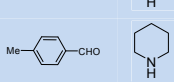
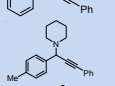
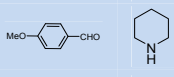
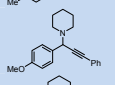
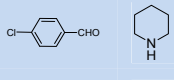
Subsequently, to extend the study of this three-component coupling reaction, we used different derivatives of aldehydes and amines in reaction with phenylacetylene. Actually, phenylacetylene was used as a model substrate, and various amines and aldehydes were examined (Table 2, Entries 1-18).

The results indicated that heterocyclic secondary aliphatic amines gave excellent yields of products at the reaction conditions, while the selected primary aliphatic amine, cyclohexylamine, generated the corresponding secondary propargylamines in moderate yield (Table 2, Entry 18).

Among the various amines used, piperidine showed the highest reactivity in terms of yields and reaction times. It can be inferred that electronically nature of substitutions affected the reaction to some extent. The aldehydes containing an electron-withdrawing group afforded better yields (Table 2, Entries 2,8,15) than those with an electron-donating group (Table 2, Entries 4, 10 and 14). Heteroaromatic aldehyde, furfuraldehyde, reacted to obtain the corresponding

propargylamines in good to excellent yields (Table 2, entries 5,11,16).

Table 2. Results of propargylamine compounds preparation using ferric hydrogensulfate.

Entry	Aldehyde	Amine	Product[b]	Yield (%)[c]	Time (h)
1				87	6
2				88	5
3				88	9
4				71	8.5
5				83	4.5
6				90	4
7				78	5
8				90	6.5
9				90	8
10				73	9
11				85	6
12				94	4
13				90	5.5
14				84	7
15				94	7
16				90	4
17				95	4
18				55	7
19				82	7
20				92	5
21				85	5
22				94	5

[a] Reaction conditions: 1.1:1:1 equiv. of amine, phenlacetylene and aldehyde, 1.0 equiv. $Fe(HSO_4)_3$ and reflux condition. [b] The products were identified by ^1H NMR and IR spectra. [c] Isolated yields.

The scope was extended by using a variety of structurally diverse aliphatic aldehydes (Table 2, Entries 19-22). The results reveal that ferric hydrogensulfate can promote the condensation of aliphatic aldehydes, amines, and phenylacetylene and the corresponding propargylamines were obtained in high yields.

On the basis of several literature publications [30-32], it is believed that the coupling reaction mechanism proceeds by terminal alkyne C-H bond activation by ferric hydrogensulfate catalyst (Figure 2). The Fe-alkenyl (acetylide) intermediate would attack on iminium ion, which is prepared in situ from the aldehyde and secondary amine, to obtain the corresponding propargylamine and regenerated the catalyst for further reactions.

Figure 2. Synthetic route to prepare propargylamines.

In order to show the merit of this study, we compared the obtained results with the results reported recently. For this purpose, the reactions of phenylacetylene, piperidine and some aldehydes were chosen as model reactions and comparison was carried out on the basis of reaction conditions, reaction time, and percentage yields obtained (Table 3). It is worth mentioning that this method is faster and simpler than some of the existing methods. The efficiency, advantages and generality of the ferric hydrogensulfate can be elucidated by comparison of the results obtained in this study with those reported already.

4. Conclusion

In conclusion, we have reported an efficient synthesis of propargylamines through three-component coupling of aldehydes, amines and phenylacetylene via C-H activation by ferric hydrogensulfate as a suitable heterogeneous catalyst. Recyclability of the catalyst without significant loss of catalytic activity, easy procedure and work-up, broad substrate applicability, high yields attained in almost short reaction times can be mentioned as advantages of this method. Finally, this approach could make a valuable contribution to the existing processes in the field of propargylamine synthesis.

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Table 3. Comparison of propargylamine formation by $Fe(HSO_4)_3$ with literature reported methods.

Entry	Substrate	Catalyst	Reaction conditions	Time (h)/Yield (%) [Lit.]
1	Benzaldehyde	SiO_2-NH-Cu, 2 mol%	Solventless, r.t.	24/79 [24]
		Cu Zeolites, 20 mg	CH_3CN, 60 °C	25/35 [25]
		CuCl, 10 mol%	Dioxane/ionic liquid/US irradiation	0.1/97 [26]
		Zn dust, 15 mol %	CH_3CN, reflux	9/90 [35]
		Au nanoparticles, 10 mol%	CH_3CN, 75–80 °C	5/94 [36]
		Gold(III) salen, 0.05 mol%	H_2O, N_2, 40 °C	24/94 [37]
		AgI, 3 mol%	100 °C, water	14/70 [38]
		CuI, 10 mol%	100 °C, Ionic liquid	5/78 [39]
		Nanocrystalline CuO	Toluene, 90 °C	6/82 [41]
		12-tungstophosphoric acid 30 mg	CH_3CN, reflux	5/92 [42]
		$NiCl_2$ 5 mol%	Toluene, 111°C	8/95 [43]
		$Fe(HSO_4)_3$, 10 mol%	CH_3CN, reflux	4/94 [a]
2	4-Chlorobenzaldehyde	SiO_2-NH-Cu, 2 mol%	Solventless, r.t.	24/93 [24]
		CuCl, 10 mol%	Dioxane/ionic liquid/US irradiation	0.1/99 [26]
		Zn dust, 15 mol %	CH_3CN, reflux	8/95 [35]
		$InBr_3$, 10 mol%	Toluene, 80 °C	7/70 [40]
		Nanocrystalline Cu	Toluene, 90 °C	6/85 [41]
		12-tungstophosphoric acid 30 mg	CH_3CN, reflux	4/98 [42]
		$NiCl_2$	Toluene, 111 °C	9/87 [43]
		$Fe(HSO_4)_3$, 10 mol%	CH_3CN, reflux	7/94 [a]
3	Formaldehyde	SiO_2-NH-Cu 2 mol%	Solventless, r.t	24/95 [24]
		$NiCl_2$ 5mol%	Toluene, 111 °C	8/81 [43]
		$Fe(HSO_4)_3$, 10 mol%	CH_3CN, reflux	4/95 [a]
4	Cyclohexylaldehyde	SiO_2-NH-Cu 2 mol%	Solventless, r.t.	24/89 [24]
		Zn dust, 15 mol %	CH_3CN, reflux	12/75 [35]
		Nanocrystalline Cu	Toluene, 90 °C	5/84 [41]
		12-tungstophosphoric acid 30 mg	CH_3CN, reflux	3/95 [42]
		$Fe(HSO_4)_3$, 10 mol%	CH_3CN, reflux	5/85 [a]

[a] Present study.

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