N-Propargylation of secondary amines directly using calcium carbide as an acetylene source

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A one-pot *N*-propargylation of secondary amines has been achieved by heating the amine with formaldehyde and calcium carbide in DMSO in the presence of CuCl as a catalyst. Fifteen examples of propargylic tertiary amines, 12 of which are novel, were efficiently prepared in yields of 65–84%. The advantages of the method are broad substrate scope and a simple work-up procedure.

Keywords: N-propargylation, secondary amine, calcium carbide, acetylene source, propargylic tertiary amine

Propargylation is an efficient method to synthesise important organic intermediates and fine chemicals bearing propargyl groups. Many reagents have been utilised for the propargylation of organic compounds, such as the propargylation of aromatic compounds¹ or indoles^{2,3} with propargyl alcohol; the propargylation of polyfluoroarenes with propargyl phosphate;⁴ the propargylation of aldehydes and ketones with propargyl boronate,^{5–7} allenylboronate,⁸ potassium allenyltrifluoroborate⁹ or allenyltrichlorosilane;¹⁰ the *S*-propargylation of amines with propargyl halides;¹² the propargylation of *N*-sulfonylketimines with allenylboronate;¹³ and the propargylation of glyoxylic oxime ether with propargyl mesylate.¹⁴

The *N*-propargylation of compounds bearing nitrogen atoms is also a very important reaction. Zhu and Hu¹⁵ reported an example of *N*-propargylation of indoline using a propargylic ester. Martinaranda *et al.*^{16,17} and Rao and co-workers¹⁸ reported the *N*-propargylation of imidazoles using propargyl bromide. Curran and co-workers¹⁹ reported the *N*-propargylation of 2-pyridones using propargyl bromide. Eycken and coworkers²⁰ reported the *N*-propargylation of secondary amines with propiolic acids. However, most of the reagents for *N*-propargylation are rather expensive. Therefore, it is necessary to develop a convenient method for *N*-propargylation using cheaper reagents.

Calcium carbide, CaC_2 , is a stable and inexpensive solid that is commercially available on the ton scale, and is extensively used as a raw material to produce acetylene by hydrolysis. Several recent reports have revealed that acetylene can be generated *in situ* by using calcium carbide directly as an easyto-handle and efficient source for many types of chemical transformation (reviewed by Ananikov and co-workers²¹). Our work is a modification of a method of *N*-propargylation of secondary amines using calcium carbide as the source of the acetylene reported by Zhang and co-workers.^{22–24} In those reports, CuI was used as a catalyst, the solvent was MeCN and the main substrates were aromatic aldehydes.

In this paper, we report the convenient *N*-propargylation of a variety of secondary amines by reacting formaldehyde and calcium carbide as an acetylene source in the presence of CuCl in DMSO to synthesise propargylic tertiary amines by a onepot procedure.

Results and discussion

Initially, the reaction of tetrahydroisoquinoline (1a), calcium carbide and paraformaldehyde was selected as a model reaction to examine the feasibility of N-propargylation under various conditions, including the use of different catalysts and solvents at certain temperatures for an appropriate time (Scheme 1, Table 1). It was found that catalysts played an important role in the reaction. The reaction did not take place in the absence of a catalyst (entry 1). Copper (II) bromide and chloride as catalysts were tested, but only a trace amount of the product N-propargyl tetrahydroisoquinoline (2a) was observed (entries 2 and 3). However, cuprous halides, such as cuprous iodide, cuprous bromide and cuprous chloride, were efficient catalysts, and the reaction gave the N-propargylation product 2a in good to high yield (entries 4-6). Among them, the best yield was obtained by using cuprous chloride as a catalyst (entry 6). In addition, the selection of the solvent was also important. The reaction did not occur in EtOH, 1,4-dioxane and PhMe because of the poor solubility of calcium carbide. In contrast, DMSO, DMF and MeCN were practicable solvents, and the reaction in

 Table 1
 The effect of reaction conditions (catalyst, solvent, time, temperature) on the yield of 2a (Scheme 1)^a

Entry	Catalyst	Solvent	Time (h)	Time (h) Temperature (°C)	
1	-	DMS0	4	100	0
2	CuBr ₂	DMS0	4	100	Trace
3	CuCl	DMS0	4	100	Trace
4	Cul	DMS0	4	100	62
5	CuBr	DMS0	4	100	65
6	CuCl	DMS0	4	100	81
7	CuCl	DMF	4	100	33
8	CuCl	MeCN	4	100	Trace
9	CuCl	DMS0	12	50	32
10	CuCl	DMS0	12	80	66
11	CuCl	DMS0	12	120	73
12°	CuCl	DMSO	4	100	0

^aReaction conditions: a stirred mixture of tetrahydroisoquinoline **1a** (1 mmol), $(CH_2O)_n$ (3.0 mmol), CaC_2 (2.5 mmol), H_2O (3 mmol) and catalyst (0.1 mmol) in solvent (3 mL) was heated at a certain temperature under N_2 for an appropriate time.

^bIsolated yield. ^cWithout water.



Scheme 1

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Table 2	Yields of	proparavlic	tertiary	amines	2a-o	(Scheme	2) ^a

Entry	Amine	Aldehyde	Product	Yield (%) ^b
1	NH	(CH ₂ 0) _n	2a	81
2	NH	CH ₃ CH ₂ CH0	2b	69
3	NH	CH ₃ CH ₂ CH ₂ CHO		71
4	NH	(CH ₂ 0) _n	Zd 2d	83
5		(CH ₂ 0) _n	2e	84
6	0 NH	(CH ₂ 0) _n	0 N 2f	78
7		(CH ₂ 0) _n	N 2g	80
8	HN	(CH ₂ 0) _n	N 2h	72
9	NH	(CH ₂ 0) _n		79
10	NH	(CH ₂ 0) _n		82
11	N H	(CH ₂ 0) _n	N 2k	77
12	N H	(CH ₂ 0) _n		73
13		(CH ₂ 0) _n	2m	71
14	→ NH	(CH ₂ 0) _n		81
15	NH	(CH ₂ 0) _n	N	65

^aReaction conditions: a stirred mixture of a secondary amine (1 mmol), an aldehyde (3.0 mmol), CaC₂ (2.5 mmol), H₂O (3 mmol) and CuCl (0.1 mmol) in DMSO (3 mL) was heated at 100 °C under N₂ for 4 h. ^bIsolated yield. these solvents gave 2a in diminishing yields (entries 6–8). The most effective solvent was DMSO, giving a yield of 81% (entry 6). Furthermore, it was found that 100 °C was an appropriate temperature for the reaction. Lower and higher temperatures did not significantly improve the yield even for prolonged reaction times (entries 9–11). In addition, the presence of 3 equiv. of water was essential, as the reaction without water gave no product (entry 12).

Using the optimised conditions, a variety of secondary amines were N-propargylated (Scheme 2) and the results are shown in Table 2. The reactions worked well for a wide range of substrates, including heterocyclic and acyclic amines, affording the desired products in good to high yield. Three-component reactions of tetrahydroisoquinoline 1a and calcium carbide with other aliphatic aldehydes such as propanal and *n*-butanal gave N-propargyltetrahydroisoquinolines 2b and 2c in high yield (entries 2 and 3). This indicated that the three-component reactions could probably be extended to longer chain aldehydes. We then carried out the N-propargylation of various secondary amines with paraformaldehyde (entries 4-15). Reactions of five heterocyclic amines gave N-propargylation products 2d-h in high yield (entries 4-8). The diamine piperazine giving a bis derivative 2g. However, the reactions of pyrrolidine and piperidine mainly gave, respectively, 1,4-di(pyrrolidin-1-yl) but-2-yne 2i (entry 9) and 1,4-di(piperidin-1-yl)but-2-yne 2j (entry 10). These results meant that the N-propargylation intermediates produced in situ were sufficiently reactive for the terminal alkynyl groups to undergo further reaction with another

equivalent of secondary amine. For the acyclic secondary amines, especially benzyl secondary amines, the corresponding reactions proceeded smoothly, and the *N*-propargylation products 2k-m were obtained in high yield (entries 11–13). However, when diisopropylamine and dibutylamine were substrates, the corresponding *N*,*N*-dialkyl-but-2-yne-1,4-diamines 2n and 2o were the major products (entries 14 and 15), which implied that the reaction did not end as *N*-propargylation products due to their small steric hindrance. Note that reactions using heterocyclic secondary amines bearing conjugate structures, such as indole, carbazole and benzotriazole, were unfruitful because of the low nucleophilicity of their NH groups. In addition, primary amines, such as aniline, benzyl amine and butyl amine, did not participate in a similar reaction either.

A plausible mechanism is proposed for the *N*-propargylation of secondary amines using calcium carbide as an acetylene source (Scheme 3). Calcium carbide first reacts with water to give ethynylcalcium hydroxide **A** as an intermediate, which can further react with cuprous chloride to afford cuprous acetylide intermediate **B**. Nucleophilic intermediate **B** attacks the iminium ion **C** generated *in situ* from secondary amine **1** and paraformaldehyde to give the corresponding propargylamine intermediate **D** which can be readily converted into the corresponding final product propargyl tertiary amines **2a–h** and **2k–m** in the presence of water. In some cases, propargyl tertiary amines could further combine with cuprous chloride to form intermediate **E**. **E** further reacts with iminium ion **C** to give but-2-yne-1,4-diamines **2i**, **2j**, **2n** and **2o**.



Scheme 3

In conclusion, we have successfully developed a highly effective three-component reaction of a secondary amine, an aldehyde and calcium carbide to synthesise propargyl tertiary amines in a one-pot reaction. This cost-efficient procedure can be easily employed for the preparation of important propargylamine building blocks using standard laboratory equipment. Moreover, these reactions confirm the potential of using calcium carbide as an acetylene replacement in organic synthesis. This easy-tohandle protocol will help contribute to the effort to use calcium carbide as a sustainable and cost-efficient carbon source in modern organic synthesis.

Experimental

All starting materials were commercially available and used as received. Calcium carbide was purchased from Aldrich (purity: 80%). Unless otherwise noted, the solvents and reagents were reagent grade and used without any further purification. Column chromatographic separations were carried out on a flash chromatographic system using silica gel and petroleum ether (60–90 °C)/ethyl acetate as the eluent. For thin layer chromatography (TLC), silica gel plates precoated with GF-254 were used. ¹H NMR and ¹³C NMR spectra were recorded on a Mercury-600 BB or 400 BB instrument using CDCl₃ as the solvent and Me₄Si as the internal standard. Elemental analyses were performed on a Vario El Elemental Analysis instrument.

Preparation of propargyl tertiary amines (2a-o); general procedure

A mixture of secondary amine (1.0 mmol), calcium carbide (0.20 g, 2.5 mmol), aldehyde (3 mmol), cuprous chloride (0.01 g, 0.1 mmol) and water (0.05 mL, 3 mmol) in DMSO (3 mL) was stirred at 100 °C under N₂ for 4 h. The reaction was monitored by TLC. After reaction completion, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3 × 10 mL) and washed with saturated brine (3 × 10 mL). The resulting organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography using petroleum ether and ethyl acetate (v/v 10:1) as the eluent.

2-(*Prop-2-yn-1-yl*)-*1*,2,3,4-tetrahydroisoquinoline (**2a**): Brown liquid; ¹H NMR (600 MHz, CDCl₃): δ 7.16–7.11 (m, 3H), 7.05–7.02 (m, 1H), 3.77 (s, 2H), 3.51 (d, J = 2.4 Hz, 2H), 2.95 (t, J = 6.0 Hz, 2H), 2.84 (t, J = 6.0 Hz, 2H), 2.28 (t, J = 2.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 134.5, 133.7, 128.6, 126.6, 126.1, 125.6, 78.7, 73.3, 54.29, 49.7, 46.7, 29.2. Anal. calcd for C₁₂H₁₃N: C, 84.17; H, 7.65; N, 8.18; found: C, 84.11; H, 7.68; N, 8.21%.

2-(*Pent-1-yn-3-yl*)-*1*,2,3,4-tetrahydroisoquinoline (**2b**): Brown liquid; ¹H NMR (600 MHz, CDCl₃): δ 7.16–7.12 (m, 3H), 7.08–7.05 (m, 1H), 3.87 (d, J = 14.6 Hz, 1H), 3.73 (d, J = 14.6 Hz, 1H), 3.48–3.45 (m, 1H), 2.96–2.93 (m, 3H), 2.75–2.71 (m, 1H), 2.32 (d, J = 2.1 Hz, 1H), 1.84–1.79 (m, 2H), 1.09 (t, J = 7.4 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 135.1, 134.4, 128.6, 126.7, 126.0, 125.6, 81.3, 73.4, 58.9, 51.8, 47.2, 29.6, 26.7, 11.2. Anal. calcd for C₁₄H₁₇N: C, 84.37; H, 8.60; N, 7.03; found: C, 84.42; H, 8.58; N, 7.00%.

2-(*Hex-1-yn-3-yl*)-*1*,2,3,4-tetrahydroisoquinoline (**2c**): Brown liquid; ¹H NMR (600 MHz, CDCl₃): δ 7.13–7.11 (m, 3H), 7.06–7.04 (m, 1H), 3.86 (d, *J* = 14.6 Hz, 1H), 3.71 (d, *J* = 14.6 Hz, 1H), 3.56–3.54 (m, 1H), 2.99–2.86 (m, 3H), 2.73–2.69 (m, 1H), 2.31–2.28 (m, 1H), 1.81–1.71 (m, 2H), 1.62–1.46 (m, 2H), 0.98 (t, *J* = 7.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 135.1, 134.3, 128.6, 126.7, 125.9, 125.5, 81.4, 73.3, 56.8, 51.8, 47.2, 35.5, 29.6, 19.8, 13.8. Anal. calcd for C₁₅H₁₉N: C, 84.46; H, 8.98; N, 6.57; found: C, 84.41; H, 9.01; N, 6.59%.

2-(*Prop-2-yn-1-yl*)*isoindoline* (**2d**): Brown liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.19 (s, 4H), 4.06 (s, 4H), 3.62 (d, J = 2.4 Hz, 2H), 2.29 (t, J = 2.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 139.8, 126.8, 122.3, 79.1, 73.9, 57.1, 42.7. Anal. calcd for C₁₁H₁₁N: C, 84.04; H, 7.05; N, 8.91; found: C, 84.08; H, 7.04; N, 8.88%.

1-(Prop-2-yn-1-yl)-1,2,3,4-tetrahydroquinoline (**2e**): Yellow liquid; ¹H NMR (600 MHz, CDCl₃): δ 7.09 (t, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 4.02 (d, *J* = 2.3 Hz, 2H), 3.31–3.27 (m, 2H), 2.77 (t, *J* = 6.5 Hz, 2H), 2.14 (t, $J = 2.3 \text{ Hz}, 1\text{H}), 2.03-1.99 \text{ (m, 2H)}; {}^{13}\text{C NMR} (150 \text{ MHz}, \text{CDCl}_3); \delta$ 144.6, 129.1, 126.9, 124.0, 117.5, 112.0, 79.7, 71.5, 49.2, 40.7, 27.7, 22.4. Anal. calcd for C₁₂H₁₃N: C, 84.17; H, 7.65; N, 8.18; found: C, 84.24; H, 7.62; N, 8.14%.

4-(*Prop-2-yn-1-yl*)*morpholine* (**2f**): Bright yellow liquid (lit.²⁵ colourless oil; lit.²⁶ colourless solid); ¹H NMR (600 MHz, CDCl₃): δ 3.71–3.63 (m, 4H), 3.23 (d, *J* = 2.3 Hz, 2H), 2.50 (bs, 4H), 2.23 (t, *J* = 2.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 78.3, 73.4, 66.7, 52.1, 47.1. Anal. calcd for C₃H₁₁NO: C, 67.17; H, 8.86; N, 11.19; found: C, 67.08; H, 8.89; N, 11.23%.

l,4-*Di*(*prop*-2-*yn*-*I*-*yl*)*piperazine* (**2g**): Colourless liquid; ¹H NMR (600 MHz, CDCl₃): δ 3.30 (d, J = 2.4 Hz, 4H), 2.64 (bs, 8H), 2.24 (t, J = 2.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 78.6, 73.3, 51.6, 46.7. Anal. calcd for C₁₀H₁₄N₂: C, 74.03; H, 8.70; N, 17.27; found: C, 73.98; H, 8.68; N, 17.34%.

1-Benzhydryl-4-(prop-2-yn-1-yl)piperazine (**2h**): White solid; m.p. 97–99 °C (petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ 7.44–7.38 (m, 4H), 7.28–7.22 (m, 4H), 7.18–7.13 (m, 2H), 4.22 (s, 1H), 3.29 (d, *J* = 2.4 Hz, 2H), 2.59 (m, 5H), 2.45 (bs, 3H), 2.24 (t, *J* = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 142.8, 128.5, 128.0, 127.0, 79.0, 76.2, 73.2, 52.1, 51.8, 46.8. Anal. calcd for C₂₀H₂₂N₂: C, 82.72; H, 7.64; N, 9.65; found: C, 82.77; H, 7.62; N, 9.61%.

1,4-Di(pyrrolidin-1-yl)but-2-yne (**2i**): Yellow liquid; ¹H NMR (600 MHz, CDCl₃): δ 3.41 (s, 4H), 2.60 (t, *J* = 6.0 Hz, 8H), 1.78 (m, 8H); ¹³C NMR (150 MHz, CDCl₃): δ 79.8, 52.5, 43.2, 23.8. Anal. calcd for C₁₂H₂₀N₂: C, 74.95; H, 10.48; N, 14.57; found: C, 74.96; H, 10.44; N, 14.60%.

1,4-Di(piperidin-1-yl)but-2-yne (**2j**): Yellow liquid; ¹H NMR (600 MHz, CDCl₃): δ 3.29 (s, 4H), 2.52–2.48 (m, 8H), 1.67–1.57 (m, 8H), 1.42–1.41 (m, 4H); ¹³C NMR (150 MHz, CDCl₃): δ 80.0, 53.3, 47.9, 25.8, 23.9. Anal. calcd for C₁₄H₂₄N₂: C,76.31; H, 10.98; N, 12.71; found: C, 76.41; H, 10.93; N, 12.66%.

N-*Benzyl*-N-*methylprop*-2-*yn*-1-*amine* (**2k**): Colourless liquid (lit.²⁶ colourless liquid); ¹H NMR (400 MHz, CDCl₃): δ 7.39–7.28 (m, 5H), 3.58 (s, 2H), 3.31 (d, *J* = 2.4 Hz, 2H), 2.35 (s, 3H), 2.28 (t, *J* = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 138.3, 129.2, 128.3, 127.3, 78.6, 73.4, 60.0, 44.9, 41.8. Anal. calcd for C₁₁H₁₃N: C, 82.97; H, 8.23; N, 8.80; found: C, 82.90; H, 8.26; N, 8.84%.

N-Benzyl-N-ethylprop-2-yn-1-amine (21): Colourless liquid; ¹H NMR (400 MHz, CDCl₃): δ 7.28–7.15 (m, 5H), 3.54 (s, 2H), 3.25 (d, *J* = 2.4 Hz, 2H), 2.52 (q, *J* = 7.2 Hz, 2H), 2.13 (t, *J* = 2.4 Hz, 1H), 1.03 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.8, 129.2, 128.3, 127.1, 78.6, 73.1, 57.6, 47.4, 40.9, 12.9. Anal. calcd for C₁₂H₁₅N: C, 83.19; H, 8.73; N, 8.08; found: C, 83.24; H, 8.70; N, 8.06%.

N,N-*Dibenzylprop-2-yn-1-amine* (**2m**): Yellow liquid (lit.²⁶ colourless solid; lit.²⁷ yellow crystals, m.p. 42 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 7.2 Hz, 4H), 7.34–7.30 (m, 4H), 7.26–7.22 (m, 2H), 3.69 (s, 4H), 3.26 (d, *J* = 2.3 Hz, 2H), 2.28 (t, *J* = 2.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 138.8, 129.0, 128.3, 127.2, 78.5, 73.4, 57.4, 41.2. Anal. calcd for C₁₇H₁₇N: C, 86.77; H, 7.28; N, 5.95; found: C, 86.73; H, 7.30; N, 5.97%.

N^{*I*},N^{*I*},N⁴,N⁴-*Tetraisopropylbut-2-yne-1,4-diamine* (**2n**): Yellow liquid; ¹H NMR (600 MHz, CDCl₃): δ 3.40 (s, 4H), 3.19–3.15 (m, 4H), 1.08 (d, J = 6.6 Hz, 24H); ¹³C NMR (150 MHz, CDCl₃): δ 81.9, 48.2, 34.3, 20.6. Anal. calcd for C₁₆H₃₂N₂: C, 76.13; H, 12.78; N, 11.10; found: C, 76.22; H, 12.73; N, 11.05%.

N^{*i*},N^{*i*},N⁴,N⁴-*Tetrabutylbut*-2-*yne*-1,4-*diamine* (**20**): Colourless liquid; ¹H NMR (600 MHz, CDCl₃): δ 3.40 (s, 4H), 2.43 (t, *J* = 7.2 Hz, 8H), 1.44–1.38 (m, 8H), 1.34–1.26 (m, 8H), 0.90 (t, *J* = 7.8 Hz, 12H); ¹³C NMR (150 MHz, CDCl₃): δ 79.3, 53.6, 41.9, 29.7, 20.7, 14.0; Anal. calcd for C₁₉H₃₈N₂: C, 77.48; H, 13.01; N, 9.51; found: C, 77.56; H, 12.96; N, 9.48%.

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Electronic Supplementary Information

ESI for ¹H NMR and ¹³C NMR of products **2a–o** is available through:

stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

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