Organic & Biomolecular Chemistry



View Article Online

PAPER



Cite this: Org. Biomol. Chem., 2019, 17, 181

Received 22nd November 2018, Accepted 3rd December 2018 DOI: 10.1039/c8ob02912a

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Introduction

Alkynes are essential structural motifs and ubiquitous intermediates in synthetic transformations for building fine chemicals, pharmaceuticals and polymeric photo-/electronic materials.¹ The past several decades have witnessed tremendous development of alkyne synthesis in organic chemistry. The general approaches *via* the $C(sp^3)$ –C(sp) bond formation rely on the addition reaction with organometallic reagents,² and transition-metal-catalyzed coupling reactions using Pd,³ Cu,⁴ Co,⁵ Ni,⁶ Ag⁷ and Fe⁸ complexes (Scheme 1, reaction (a)). However, the tedious reaction conditions and the use of relatively expensive metals led chemists to explore alternative protocols under mild conditions in an environmentally benign manner.⁹

The visible-light-induced catalysis is becoming a fascinating methodology in modern organic synthesis,¹⁰ including those for $C(sp^3)$ –C(sp) coupling reactions (Scheme 1, reaction (b)). For example, in 2014, Chen *et al.* reported a visible-light-induced deboronative alkynylation reaction with $[Ru(bpy)_3]$ (PF₆)₂/BI–OH.¹¹ This reaction worked with alkyl trifluoroborates or boronic acids to generate substituted alkynes. In 2015, Hashmi *et al.* reported a gold-catalyzed radical $C(sp^3)$ –H alkynylation of tertiary aliphatic amines using readily available 1-iodoalkynes as a radical alkynylation reagent in the presence of $[Au_2(\mu$ -dppm)₂]²⁺ under photocatalysis conditions.¹² The reaction shows excellent regioselectivity and good functional-group compatibility. However, these reactions require expensive transition metals/ligands and limitations of the substrate

Visible light promoted coupling of alkynyl bromides and Hantzsch esters for the synthesis of internal alkynes†

A metal-free visible light promoted $C(sp^3)-C(sp)$ coupling reaction of alkynyl bromides and Hantzsch esters was developed, giving internal alkynes with primary, secondary, tertiary alkyl or other functional groups in good to high yields.

scope. In 2015, Li *et al.* reported a pioneering metal-free coupling of an alkyne and alkyl iodide under ultraviolet irradiation (Scheme 1, reaction (c)).¹³

Recently, Hantzsch esters $(HEs)^{14}$ have been extensively used in transfer-hydrogenation reactions and transfer-alkylation reactions, especially in photoredox reactions.¹⁵ In 2011, Nishibayashi and coworkers reported the first visible-lightinduced reaction of HEs *via* alkyl radicals.¹⁶ After that, the reactions of HEs have been successfully used for the $C(sp^3)-C(sp^3)^{17}$ and $C(sp^3)-C(sp^2)^{18}$ bond formation. Very



Scheme 1 Synthesis of internal alkynes via C(sp³)–C(sp) coupling.

Metal-free

None oxidant

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 $[\]dagger\, Electronic$ supplementary information (ESI) available. See DOI: 10.1039/ c8ob02912a

recently, Cheng and co-workers reported the alkynylation of HEs with benziodoxole-activated alkynes under oxidative conditions (Scheme 1, reaction (d)).¹⁹ In this paper, we report a visible-light-induced radical C(sp³)–C(sp) coupling of alkynyl bromides and Hantzsch esters for the synthesis of internal alkynes (Scheme 1, reaction (e)). Our work provides a photocatalytic approach from readily available alkynyl bromides without any additional oxidant, which leads to good tolerance of functional groups.

Results and discussion

Initially, the reaction of 1-bromo-2-phenylacetylene (1a) with 4-cyclohexyl Hantzsch ester (2a) was investigated under photocatalysis (Table 1). We were encouraged to find that the desired cyclohexyl alkyne (3aa) was obtained in 19% yield when the reaction was carried out with 2 mol% of 4CzIPN (2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile) as the photocatalyst in dichloromethane at room temperature for 12 h under the irradiation of blue LEDs (entry 1). The yield was increased to 66% when the reaction time was prolonged to 36 h (entry 2). The addition of a silver salt showed no apparent improvement (entry 3). Screening of solvents and bases revealed that 1,2-dichloroethane is the best choice (entries

Table 1 Optimization of the alkynylation reaction^a

Ph 1a X 1a' X 1a'' X	X + = Br = CI = Ts		2Et PC (2 base (solvent (0.5 degas, bl	mol%) 3 eq.) M), rt, 36 h lue LEDs Ph	3aa
Entry	1	PC	Base	Solvent	Yield ^b (%)
1 ^{<i>c</i>}	1a	4CzIPN	K_3PO_4	CH_2Cl_2	19
2	1a	4CzIPN	K_3PO_4	CH_2Cl_2	66
3^d	1a	4CzIPN	K_3PO_4	CH_2Cl_2	67
4	1a	4CzIPN	K_3PO_4	DMF	Trace
5	1a	4CzIPN	K_3PO_4	DMSO	45
6	1a	4CzIPN	K_3PO_4	MeCN	55
7	1a	4CzIPN	K_3PO_4	Acetone	57
8	1a	4CzIPN	K_3PO_4	DCE	70
9	1a	4CzIPN	Cs_2CO_3	DCE	60
10	1a	4CzIPN	NaOAc	DCE	51
11	1a	4CzIPN	t-BuOK	DCE	NR
12	1a	4CzIPN	DBU	DCE	22
13	1a	<i>fac</i> -Ir(ppy) ₃	K_3PO_4	DCE	71
14	1a	Ru(ppy) ₃ Cl ₂	K_3PO_4	DCE	76
15	1a	Mes-Acr-Me	K_3PO_4	DCE	3
16^e	1a	4CzIPN	K_3PO_4	DCE	$83(75)^{f}$
17^e	1a'	4CzIPN	K_3PO_4	DCE	$(45)^{f}$
18^e	1a″	4CzIPN	K_3PO_4	DCE	$(21)^{f}$

^{*a*} Unless otherwise specified, **1a** (0.2 mmol), **2a** (0.3 mmol), photocatalyst (2 mol%), base (0.6 mmol), solvent (4 mL, [0.5 M]), rt. ^{*b*} Yields determined by ¹H NMR (400 MHz) spectroscopy with CH₂Br₂ as the internal standard. ^{*c*} The reaction was terminated after 12 h. ^{*d*} AgNO₃ (0.2 mmol) was added as an additive. ^{*e*} **2a** (0.4 mmol) was used. ^{*f*} Isolated yields in parentheses. DCE = 1,2-dichloroethane, 4CzIPN = 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile, ppy = 2-phenylpyridine, Mes-Acr-Me = 10-methyl-9-mesitylacridinium.

4–8), and K_3PO_4 performed best compared to other inorganic and organic bases (entries 8–12). Evaluation of photocatalysts showed that Ir- and Ru-based photocatalysts only afforded the product with a slightly increased yield (entries 13 and 14), while the organic photocatalyst of 10-methyl-9-mesitylacridinium gave only a trace amount of product (entry 15). Considering the environmental benignity of organic photocatalysts compared to transitional metals, the metal-free photocatalyst 4CzIPN was chosen for the reaction. A higher yield was achieved when the loading of Hantzsch ester 2a was increased to two equivalents (entry 16). It is worth noting that the reaction using alkynyl chloride (1a') or sulfone (1a'') instead of bromide (1a) resulted in some loss of yield (entries 17 & 18).

With the optimized reaction conditions in hand, we then investigated the substrate scope. A variety of arylethynyl bromides worked well for the reaction (Table 2). Both electrondonating groups (1b-1f) and electron-withdrawing groups (1g-1m) were tolerated at the ortho-, meta- or para-position, giving the internal alkynes 3aa-3ma in good to high yields (entries 1-13). All arylethynyl bromides with 4-phenyl or α -naphthyl and heteroarylethynylbromide derived from indole or thiophene worked as well (3na-3qa) (entries 14-17). Notably, the ester and ketone were also tolerable for the reaction to give the corresponding product (3ra) and estronederived alkyne (3sa) in good yields (entries 18 &19). The reaction of a series of 4-alkyl Hantzsch esters is shown in Table 3. It was found that benzyl, acyclic and cyclic secondary alkyl could be easily coupled with the alkynyl bromides to give the products (3db-3ld) in good to high yields (entries 1-4). More importantly, the tertiary alkyl, which is difficult to introduce by the classical nucleophilic substitution reaction, worked best due to the relative stability of their radicals (3ae-3qe) (entries 5–11). It should be noted that Meyer nitrile $2e^{20}$ was used instead of Hantzsch esters due to the difficulty in their synthesis. Furthermore, the reaction of the piperidine-derived Hantzsch ester went smoothly to give product 3df in 65% yield (entry 12).

The scale-up reaction using 1.05 g (5 mmol) of alkynyl bromide **1e** gave product **3ea** in 78% yield (Scheme 2).

The photocatalytic alkynyl–alkyl coupling reaction is believed to proceed *via* a radical intermediate.²¹ Control experiments revealed that the reaction was completely suppressed with no desired product detected when TEMPO (2,2,6,6-tetramethyl-1-oxylpiperdine) was added as the radical-trapping reagent (Scheme 3).

The plausible mechanism for the reaction is shown in Fig. 1. The readily available photocatalyst 4CzIPN is irradiated under blue LEDs to the photoexcited state (4CzIPN*), which features a high redox potential $(E_{1/2}^{(PC^{*}/PC^{*-})} = +1.43 vs. SCE)^{22}$ (PC = 4CzIPN) to promote the photooxidative reaction. The substituted Hantzsch esters $(E_{1/2}^{red} = +1.08 \text{ V } vs. \text{ SCE})^{17a}$ were cleaved by the oxidation of photoexcited 4CzIPN* to generate the alkyl radical I and radical anion II. The addition of alkyl radical I to arylethynyl-bromide affords the bromoalkenyl radical IIII,²³ which is collapsed to give alkylalkyne 3 and a bromine radical.²⁴ The

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Table 2 Scope of alkynyl bromides Table 3 Scope of 4-alkyl Hantzsch esters 4CzIPN (2 mol%) K₃PO₄ (3 eq.) 4CzIPN (2 mol%) K₃PO₄ (3 eq.) DCE (0.5 M), rt, 36h degas, blue LEDs CO₂Et EtO₂C N 1 2b-2f DCE (0.5 M), rt, 36h degas, blue LEDs A 3db-3df 'n Δ, 1a-1s 2a 3aa-3sa Yield (%) 1 2 3 Entry Yield (%) 1d Ph Entry 1 3 1 92 EtO₂0 CO₂Et В 3db X٠ 2b x٠ **1a** (X = H) 3aa 75 1 EtO₂ O₂Ef 2 1b(X = 2 - Me)3ba 87 3 1c(X = 3-Me)3ca 77 4 1d(X = 4-Me)3da 84 2 1d 2c 3dc 89 5 1e (X = 4-MeO) 3ea 85 3 1k 2c3kc 72 6 1f(X = 4-t-Bu)3fa 64 4 **1l** 91 7 **1**g (X = 2-F) 76 3ga 8 1h(X = 3-F)3ĥa 55 EtO₂C CO₂Et 9 1i (X = 4-F 3ia 69 Br 1j(X = 2-Cl)103ja 81 3ld $\mathbf{1}\mathbf{k}$ (X = 4-Cl) 3ka 11 74 2d 1l(X = 4-Br)93 12 3la $1\dot{m}(X = 4 - CF_3)$ 13 70 3ma Br 1479 5 1a 2e 3ae(X = H)91 3ee(X = MeO)89 6 **1e** 2e 1n 7 **1l** 2e 3le(X = Br)91 3na 2e 63 8 1m $3me(X = CF_3)$ 15 53 B 9 1n 2e3ne(X = Ph)89 10 1r 2e $3re(X = CO_2Me)$ 99 11 1q 2e 5110 **3**0a 16 62 3qe 12 1d 65 CO₂Ef EtO₂C 1p 3df 3pa 17 45 2f 1q 3qa 18 66 4CzIPN (2 mol%) K₃PO₄ (3 eq.) EtO₂C CO₂Et DCE (0.5 M), rt, 36h degas, blue LEDs MeO MeO 1r 3ea, 0.84 g, 78%, 1e, 1.05 g, 5 mmol 2a. 10 mmol 3ra 19 56 Scheme 2 Gram-scale experiment. в TEMPO (2 eq.) **1**s 4CzIPN (2 mol%) K₃PO₄ (3 eq.) 3sa EtO₂C CO₂Et DCE (0.5 M), rt, 36h degas, blue LEDs

Scheme 3 Radical-trapping reaction.

2a

1e

Published on 04 December 2018. Downloaded on 1/20/2019 10:48:35 PM.

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MeO

3ea, 0%,



Fig. 1 Plausible reaction mechanism.

reduction of the bromine radical by radical anion species II $(E_{1/2}^{(\text{PC}^-/\text{PC})} = -1.21 \nu s. \text{SCE})^{25}$ regenerates the photocatalyst and furnishes the catalytic cycle.

Conclusions

In summary, the photocatalytic synthesis of internal alkynes $via C(sp^3)$ –C(sp) bond coupling of bromoalkynes and Hantzsch esters was developed. All the primary, secondary and tertiary alkyl radicals generated from the Hantzsch ester derivatives worked well for the reaction. The reaction features good tolerance of many functional groups, including esters and ketones, under metal-free conditions.

Experimental

Unless otherwise indicated, all reactions were carried out with N₂ protection with magnetic stirring. Anhydrous CH₂Cl₂ was distilled from CaH₂. Column chromatography was performed on silica gel (200–300 mesh). All ¹H NMR (300 or 400 or 500 MHz) and ¹³C NMR (75 or 101 or 126 MHz) spectra were recorded on a Bruker-DMX 300 or 400 or 500 spectrometer in CDCl₃, with CH₂Br₂ as an internal standard and reported in parts per million (ppm, δ). ¹H NMR spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). Infrared spectra were recorded on a Nicolet 6700 spectrophotometer and reported in wavenumbers (cm⁻¹).

Visible light promoted coupling of alkynyl bromides and Hantzsch esters

General procedure. To a solution of alkynyl bromides 1 (0.2 mmol) in a 10 mL reaction tube were added Hanzsch ester 2 (0.4 mmol, 2.0 equiv.), 4CzIPN (3.15 mg, 0.004 mmol, 2 mol%) and K_3PO_4 (127 mg, 0.6 mmol, 3.0 equiv.) under a nitrogen atmosphere at room temperature. The tube was sealed

and 4 mL of DCE were injected. Then the solvent was degassed 3 times. The reaction mixture was stirred for 36 h at room temperature and irradiated by 24 W blue LEDs. After the completion of the reaction, the mixture was diluted with H_2O and extracted with DCM 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to give the desired coupling product **3**.

Radical-trapping experiment

To a solution of alkynyl bromides **1e** (42 mg, 0.2 mmol) in a 10 mL reaction tube were added Hanzsch ester **2a** (134 mg, 0.4 mmol, 2.0 equiv.), 4CzIPN (3.15 mg, 0.004 mmol, 2 mol%), TEMPO (2,2,6,6-tetramethyl-1-oxylpiperidine, 62.5 mg, 0.4 mmol, 2.0 equiv.) and K_3PO_4 (127 mg, 0.6 mmol, 3.0 equiv.) under a nitrogen atmosphere at room temperature. The tube was sealed and 4 mL of DCE was injected. Then the solvent was degassed 3 times. The reaction mixture was stirred for 36 h at room temperature and irradiated by 24 W blue LEDs. No desired product was observed by TLC.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Financial support from the National Natural Science Foundation of China (no.: 21425207, 21521002, 21672216) is gratefully acknowledged.

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