



Photoinduced metal-free diboration of alkynes in the presence of organophosphine catalysts



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ARTICLE INFO

Article history:

Received 6 March 2016

Received in revised form 6 June 2016

Accepted 13 June 2016

Available online 23 June 2016

Keywords:

Diboration

Organophosphine catalyst

Anti-addition

Metal-free

Photoinduced radical addition

ABSTRACT

In sharp contrast to the transition metal-catalyzed diboration of alkynes with diboron species such as B_2pin_2 , which affords vicinal *cis*-diborated alkenes, the organophosphine-catalyzed addition of B_2pin_2 to alkynes proceeds under metal-free conditions upon photoirradiation to give the corresponding vicinal *trans*-diborated alkenes with good stereoselectivity. For example, the photoinduced diboration of 1-octyne with B_2pin_2 in the presence of tris(*o*-methylphenyl)phosphine afforded 1,2-diborated octene with excellent *trans* selectivity (*trans/cis*=95/5). The influence of various organophosphines on the diboration is described in detail. The diboration does not occur in the dark or in the absence of an organophosphine catalyst. Moreover, ESR (electron spin resonance) measurements of the reaction mixture revealed a radical species around $g=2.003$, supporting a radical pathway for the organophosphine-catalyzed diboration. In addition, the photoinduced *cis* to *trans* isomerization of vicinal *cis*-diborated alkenes in the presence/absence of organophosphines is discussed.

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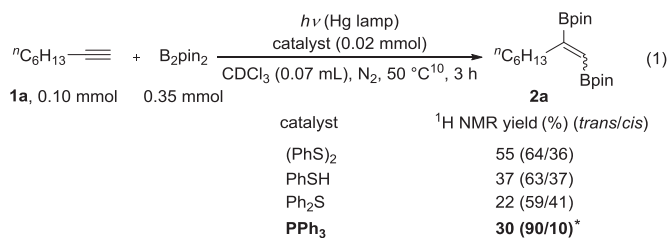
1. Introduction

Organoboron compounds have been widely used as a class of coupling partners in synthetic organic chemistry.¹ Therefore, a number of approaches towards organoboron compounds have been described to date. In particular, the addition of diboron compounds to carbon–carbon unsaturated compounds such as alkynes is one of the most useful and eco-friendly methods for the synthesis of organoboron compounds; transition metal catalysts comprised of Pt, Pd, Ni, Rh, and Ir are frequently used for this purpose.² The transition metal-catalyzed diboration of alkynes with diboron species such as B_2pin_2 generally affords the corresponding vicinal *cis*-diborated alkenes stereoselectively, which are important key intermediates for the synthesis of various *cis*-alkenes via cross coupling reactions. As well as *cis*-alkenes, the corresponding *trans*-alkenes are also very important in organic synthesis. However, examples of synthetic methods for vicinal *trans*-diborated alkenes from alkynes are rare. Furthermore, to avoid the high cost of rare metals and impurities associated with heavy metals, metal-free approaches towards organoboron

compounds are now attracting considerable attention.³ The use of boryl radicals may facilitate the development of metal-free approaches. However, the applications of boryl radicals are less explored because of their instability. To overcome this issue, boryl radicals stabilized by coordination with Lewis bases such as NHCs,⁴ pyridine derivatives,⁵ phosphines,⁶ and *N*-heterocycles⁷ have been studied recently.

Previously, our research groups reported the introduction of heteroatom-containing functionalities, involving group 15 (P) and group 16 (S, Se, Te) elements, to carbon–carbon unsaturated bonds of alkenes, alkynes, allenes, and conjugate dienes through the generation of heteroatom-centered radicals under photoirradiation.⁸ This success prompted us to examine the photoinduced addition of group 13 elements such as diboron species to carbon–carbon unsaturated bonds through the generation of boron-centered radicals under photoirradiation. Recently, we used a series of heteroatom-containing compounds as organocatalysts in combination with diboron compounds to induce metal-free diboration and found that B_2pin_2 successfully added to terminal alkynes in the presence of a catalytic amount of organosulfides under light to produce the corresponding *vic*-diborylated alkenes in good yields (Eq. 1).⁹

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Additionally, we found that not only organosulfide catalysts but also organophosphine catalysts promoted the metal-free diboration (Eq. 1). More surprisingly, the *trans/cis* ratio of the product was extremely high when PPh₃ was used, as compared to when organosulfide catalysts were utilized. Herein, we report the organophosphine-catalyzed *trans*-selective diboration of alkynes under photoirradiation.

2. Results and discussion

First, we optimized the reaction conditions of the metal-free diboration of 1-octyne **1a** with B₂pin₂ in the presence of PPh₃ as an organocatalyst (Table 1).

Table 1
Photoinduced diboration of 1-octyne with B₂pin₂ in the presence of PPh₃

$${}^n\text{C}_6\text{H}_{13}\text{—C}\equiv\text{C} + \text{B}_2\text{pin}_2 + \text{PPh}_3 \xrightarrow[\text{C}_6\text{D}_6 (0.25 \text{ mL}), 40^\circ\text{C}^{10}]{h\nu (\text{Xe lamp})} {}^n\text{C}_6\text{H}_{13}\text{—C}(\text{Bpin})=\text{C}(\text{Bpin})$$

1a, 0.3 mmol

Entry	B ₂ pin ₂ (equiv.)	PPh ₃ (equiv.)	Time (h)	Yield (%) ^a	
				2a (<i>trans/cis</i>)	1a
1	3.5	0.4	12	42 (90/10)	23
2 ^b	3.5	0.4	12	45 (85/15)	31
3 ^c	3.5	0.8	12	Trace	73
4	3.5	0.2	3	16 (95/5)	73
5	3.5	0.2	6	27 (94/6)	60
6	3.5	0.2	12	45 (89/11)	36
7	3.5	0.2	24	47 (88/12)	27
8	3.5	0.8	12	36 (91/9)	50
9	7.0	0.2	12	35 (91/9)	47

^a Yields refer to ¹H NMR yields.

^b Hg lamp (through Pyrex) was used.

^c CDCl₃ was used as a solvent with W lamp (through Pyrex).

In a previously reported study regarding (PhS)₂-catalyzed diboration of alkynes, the representative reaction conditions were as follows: alkyne (0.1 mmol), B₂pin₂ (3.5 equiv), and (PhS)₂ (0.2 equiv) in CDCl₃.⁹ Under similar conditions, the influence of different light sources on the diboration was investigated. Although a higher yield of diboration product **2a** was obtained when a high pressure mercury lamp was utilized at an ambient temperature (50 °C),¹⁰ the *trans/cis* ratio was better when a xenon lamp at 40 °C was used (Entries 1, 2). However, irradiation with a tungsten lamp through Pyrex did not afford **2a** (Entry 3). These results clearly indicated that irradiation with near-UV light (*hν*=300–400 nm) was important for the diboration. Prolonging the reaction time increased the yield of product **2a**, but the *trans/cis* ratios gradually decreased with increasing reaction times (Entries 4–7). The use of 0.8 equivalents of PPh₃ or 7.0 equivalents of B₂pin₂ resulted in decreased yields of **2a** (Entries 8, 9). The starting materials were not completely consumed in any of the reactions.

Next, we examined the PPh₃-catalyzed diboration of 1-octyne **1a** with B₂pin₂ in various solvents; the results are shown in Table 2. The PPh₃-catalyzed diboration proceeded in various solvents such as toluene, benzene, THF, chloroform, acetone, DMSO,

acetonitrile, and methanol to give diborated product **2a** in similar yields with the preferential formation of the *trans*-isomer (Table 2). These results clearly contrasted to those of the previously reported (PhS)₂-catalyzed diboration. In the (PhS)₂-catalyzed diboration, lower yields of the *vic*-diborated products were observed in methanol, DMSO, and acetonitrile, probably due to the formation of a complex between B₂pin₂ and the solvent.⁹ When PPh₃ was used as the organocatalyst, the higher coordination ability of PPh₃ to boron as compared to that of (PhS)₂ inhibited the solvent coordination and facilitated the diboration in various solvents. Furthermore, because the solvent did not exhibit considerable influence on the PPh₃-catalyzed diboration under light, the generation of ionic intermediates as key species might be ruled out.

Table 2
Photoinduced diboration of 1-octyne with B₂pin₂ in various solvents

$${}^n\text{C}_6\text{H}_{13}\text{—C}\equiv\text{C} + \text{B}_2\text{pin}_2 + \text{PPh}_3 \xrightarrow[\text{solvent}, 50^\circ\text{C}, 12 \text{ h}]{h\nu (\text{Hg lamp})} {}^n\text{C}_6\text{H}_{13}\text{—C}(\text{Bpin})=\text{C}(\text{Bpin})$$

1a, 0.10 mmol 3.5 equiv. 0.80 equiv.

Entry	Solvent ^a (mL)	Yield (%) (<i>trans/cis</i>) ^b
1	C ₆ H ₅ CH ₃ (0.075 mL)	43 (86/14)
2	C ₆ H ₆ (0.075 mL)	45 (85/15)
3	THF (0.075 mL)	51 (85/15)
4	CHCl ₃ (0.075 mL)	52 (80/20)
5	(CH ₃) ₂ CO (0.075 mL)	44 (82/18)
6	DMSO (0.10 mL)	53 (75/25)
7	CH ₃ CN (0.075 mL)	48 (80/20)
8	CH ₃ OH (0.075 mL)	55 (71/29)

^a Deuterated solvents were used.

^b Yields refer to ¹H NMR yields.

A variety of phosphorous-containing compounds were investigated as catalysts in the metal-free diboration; the results are shown in Table 3. When tris(2-methylphenyl)phosphine **3b** and tris[2-(1-methylethyl)phenyl]phosphine **3c**, which are relatively bulky phosphines, were used, higher *trans/cis* ratios of **2a** were observed (Entries 2, 3). The use of bulkier tris(2,6-dimethylphenyl)phosphine **3d** did not result in the formation of **2a** (Entry 4). Other *p*-substituted triaryl phosphines **3e**, **3f**, and **3g** could also promote the reaction regardless of the electronic nature of the *p*-substituents (Entries 5–7), whereas electron-deficient ligand, tris(3,4,5-trifluorophenyl)phosphine **3h**, did not give **2a** (Entry 8). Trialkylphosphines **3i** and **3j** did not promote the diboration at all (Entries 9, 10). However, diarylmonoalkyl phosphine **3k** could induce the diboration (Entry 11). Penta-valent phosphine oxide **3l** was ineffective (Entry 12).

The scope and limitation of the reaction were investigated; the results are shown in Table 4. The diboration was conducted under two different sets of reaction conditions, i.e., Conditions **A** and **B**. Under condition **A**, a Xe lamp and 20 mol % of PPh₃ were used in C₆D₆, whereas, under condition **B**, a Hg lamp and 80 mol % of PPh₃ were employed in CDCl₃. The reaction scale under condition **A** was three-fold larger than that under condition **B**. In general, the *trans/cis* ratios of diborated products **2** under condition **A** were greater than those under condition **B**.¹¹ In contrast, the product yields under condition **B** were greater than those under condition **A**. Aliphatic acetylenes (**1a**–**1j**) successfully underwent the metal-free diboration (Entries 1–10). Ester, chloro, cyano, hydroxyl, and ether groups were tolerated (Entries 6–10). In contrast to aliphatic alkynes, the diboration of aromatic alkyne such as phenylacetylene (**1k**) did not proceed at all (Entry 11), even though vinyl radicals bearing aryl groups on the carbon radical center are more stable than those bearing alkyl groups (the former radicals form π -radicals,¹² whereas the latter radicals generate σ -radicals).¹³ In the case of phenylacetylene, polymerization proceeded rather than the desired diboration.

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