## Tetrahedron Letters 55 (2014) 6779-6783

Contents lists available at ScienceDirect

**Tetrahedron Letters** 

journal homepage: www.elsevier.com/locate/tetlet



# A convenient hydroiodination of alkynes using I<sub>2</sub>/PPh<sub>3</sub>/H<sub>2</sub>O and its application to the one-pot synthesis of trisubstituted alkenes via iodoalkenes using Pd-catalyzed cross-coupling reactions



Shin-ichi Kawaguchi, Yuhei Gonda, Haruna Masuno, Huệ Thị Vũ, Kotaro Yamaguchi, Hiroyuki Shinohara, Motohiro Sonoda, Akiya Ogawa \*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

#### ARTICLE INFO

Article history: Received 12 July 2014 Revised 3 October 2014 Accepted 7 October 2014 Available online 23 October 2014

Keywords: Hydroiodination Cross-coupling reactions Trisubstituted alkenes Phosphorus reagents One-pot synthesis

# ABSTRACT

A facile hydroiodination of alkynes using readily-available reagents such as I<sub>2</sub>, PPh<sub>3</sub>, and H<sub>2</sub>O has been developed. This is extended to the one-pot synthesis of trisubstituted alkenes from alkynes via iodoalkenes using Pd-catalyzed cross-coupling and related methods such as the Suzuki–Miyaura cross-coupling, Sonogashira cross-coupling reaction, and Mizoroki–Heck reaction.

© 2014 Elsevier Ltd. All rights reserved.

The vinyl group is one of the most versatile building blocks of organic compounds.<sup>1</sup> In particular, trisubstituted alkenes are important because of their prevalence in natural products and biologically active molecules.<sup>2</sup> There are several synthetic routes to trisubstituted alkenes. In particular, routes via vinyl halides allow access to diverse products because there are many known transition-metal-catalyzed cross-coupling reactions using vinyl halides.<sup>3</sup> Hydrohalogenation of alkynes is one of the most straightforward synthetic methods to vinyl halides. From the viewpoint of green chemistry, one-pot synthetic processe<sup>4</sup> have recently attracted increased attention because they reduce solvent usage and save time. Therefore, we studied the one-pot synthesis of substituted alkenes, including trisubstituted ones, via haloalkenes derived from alkynes (Scheme 1).

Since vinyl iodides are the most reactive of the vinyl halides,<sup>5</sup> they were often chosen as substrates for the cross-coupling reactions. Additionally, appropriate reagent choice for hydroiodination is required in order to prevent inhibition of the subsequent coupling reactions. The hydroiodination of alkynes with HI proceeds under a limited set of conditions.<sup>6</sup> Thus, several alternative methods have been reported.<sup>7</sup> Recently, we reported the hydroiodination of alkynes by the combination of iodine and phosphorus reagents such as  $(PhO)_2P(O)H/Ph_2P(O)OH$ .<sup>8</sup> These phosphorus reagents play a dual role as reductants for iodine and as hydrogen sources for the hydroiodination. On the basis of previous studies, we focused on the use of PPh<sub>3</sub> in a novel hydroiodination method because PPh<sub>3</sub> can act as a reductant for iodine<sup>9</sup> and is also widely used as a ligand in cross-coupling reactions. Herein, we report a facile hydroiodination of alkynes using PPh<sub>3</sub>/I<sub>2</sub> and its subsequent application to the one-pot synthesis of trisubstituted alkenes by cross-coupling reactions.

First, we investigated the hydroiodination of alkynes using a mixed system of PPh<sub>3</sub> and  $I_2$  in the presence of different hydrogen sources (Table 1). When diphenylphosphinic acid (Ph<sub>2</sub>P(O)OH) or monophenyl phosphate (PhOP(O)(OH)<sub>2</sub>) was used as a hydrogen source, hydroiodination of 1-octyne proceeded with quantitative



**Scheme 1.** One-pot synthesis of trisubstituted alkenes from alkynes via haloalkenes.

<sup>\*</sup> Corresponding author. Tel./fax: +81 72 254 9290. E-mail address: ogawa@chem.osakafu-u.ac.jp (A. Ogawa).

#### Table 1

Hydroiodination of alkynes using  $\mathsf{I}_2$  and  $\mathsf{PPh}_3$  in the presence of different hydrogen sources^a

<sup>n</sup> Hex—	+ I <sub>2</sub> + PPh <sub>3</sub> +	Hydrogen	CDCl <sub>3</sub> "Hex
0.5 mmol	0.75 equiv 0.75 equiv	1.5 equiv	1a
Entry	Hydrogen source	Time (h)	Yield of <b>1a</b> <sup>b</sup> (%)
1	Ph <sub>2</sub> POH II O	24	99
2	PhOP(OH) <sub>2</sub> O	24	99
3	85% H <sub>3</sub> PO <sub>4</sub>	24	43 <sup>c</sup>
4	H <sub>2</sub> O	24	82 <sup>d</sup>
5 <sup>e</sup>	H <sub>2</sub> O	4	(80)

<sup>a</sup> Reaction conditions: I<sub>2</sub> (0.38 mmol), PPh<sub>3</sub> (0.38 mmol), hydrogen source (0.75 mmol).

<sup>b</sup> Yields are determined by <sup>1</sup>H NMR with 1,3,5-trioxane as an internal standard and the value in parentheses is the isolated yield.

 $^{\rm c}\,$  2-lodooct-2-ene (40%,  $E\!/\!Z$  mixture) and 2,2-diiodooctane (17%) are obtained as byproducts.

 $d^{-1}$  2-lodooct-2-ene (4%, *E*/*Z* mixture) and 2,2-diiodooctane (6%) are obtained as byproducts.

 $^{\rm e}$  Reaction conditions:  ${\rm I_2}$  (0.5 mmol), PPh\_3 (0.5 mmol), hydrogen source (0.5 mmol).

yield (entries 1 and 2). On the other hand, use of phosphoric acid gave a mixture of addition products including 2-iodo-1-octene (**1a**) (43%), 2-iodooct-2-ene (40%, E/Z mixture), and 2,2-diiodooctane (17%) (entry 3). Interestingly, when H<sub>2</sub>O was employed as a hydrogen source, selective hydroiodination of 1-octyne proceeded successfully to afford **1a** in 82% yield (entry 4). Moreover, a similar result was obtained by the use of equimolar amounts of the reagents (entry 5).

Next, the scope of the hydroiodination of alkynes using a mixed system of  $I_2$  and PPh<sub>3</sub> was investigated. Hydroiodination of several alkynes, including both aliphatic and aromatic alkynes, was successfully attained by the use of an  $I_2$ /PPh<sub>3</sub>/PhOP(O)(OH)<sub>2</sub> system, and the corresponding vinyl iodides were obtained in good yields (Scheme 2). In the case of the internal alkyne, 4-octyne, hydroiodination proceeded stereoselectively to give the (*Z*)-isomer.

We next examined the hydroiodination using an  $I_2/PPh_3/H_2O$  system (Table 2).<sup>10</sup> When aliphatic alkynes such as 1-octyne 1-dodecyne, 6-chloro-1-hexyne, and 3,3-dimethyl-1-butyne were employed, the hydroiodination proceeded to give the corresponding 2-iodo-1-alkenes (**1a–d**) in good yields (entries 1–4). When aromatic terminal alkynes were employed, the corresponding 1-aryl-1-iodoethenes (**1e–g**) were also obtained in good yields (entries 5–7), although in some cases prolonged reaction time was required (entries 6 and 7). In the case of an internal aliphatic alkyne, the reaction of 4-octyne provided (*Z*)-4-iodooct-4-ene (**1h**)

R	+ I <sub>2</sub> 0.75 equ	+ PPh <sub>3</sub> iiv 0.75 eo	3 + Ph quiv 0	IOP(OH) <sub>2</sub> O .75 equiv	CDCl <sub>3</sub> , rt	
		R =	<sup>n</sup> Dec	R'=	H 43 h	<b>1b</b> , 74%

CI(CH <sub>2</sub> ) <sub>4</sub>	н	37 h	<b>1c</b> , 75 (60)%
<i>n</i> Pr	<i>n</i> Pr	27 h	<b>1h</b> , 70 (64)%
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Н	19 h	<b>1f</b> , 84%
			<i></i>

\*NMR yield (isolated yield).

Scheme 2. Hydroiodination of alkynes using I2, PPh3, and PhOP(O)(OH)2.

with complete stereoselectivity in excellent yield (entry 8). When unsymmetrical internal alkynes such as 1-phenyl-1-pentyne, 1methyl-4-(oct-1-yn-1-yl)benzene, and 1-methoxy-4-(oct-1-yn-1yl)benzene were used, the hydroiodination proceeded to afford Zisomer (1i-k) in good yields and the iodine atom was introduced to the aryl group substituted carbon atom selectively (entries 9-11). 1-(Oct-1-yn-1-yl)-4-(trifluoromethyl)benzene which has an electron withdrawing group on its para position gave the corresponding regioisomeric vinyl iodide (11) preferentially (entry 12). 1-Bromo-1-octyne also gave (*Z*)-1-bromo-2-iodo-1-octene (**1j**) exclusively in excellent yield (entry 13). To get further information of hydroiodination of internal alkynes, t-butylmethylacetylene and an ynone 1-phenylhept-2-yn-1-one were employed as substrates. Hydroiodination of *t*-butylmethylacetylene proceeded efficiently. but with less regioselectivity ((Z)-3-iodo-4,4-dimethylpent-2-ene:44% vield: (Z)-2-iodo-4.4-dimethylpent-2-ene: 52% vield). A bulky t-butyl group could not induce high regioselectivity of the hydroiodination. In the case of 1-phenylhept-2-yn-1-one, a stereoisomeric mixture of 3-iodo-1-phenylhept-2-en-1-one was obtained in low yield (23%, *E*/*Z* = 57/43).

Additionally, when trimethyl(*p*-tolylethynyl)silane was used as a substrate, the desilylated hydroiodination product  $(\mathbf{1f})^{8,11}$  was obtained in 98% yield (Eq. 1).



A plausible reaction pathway for the hydroiodination using  $I_2/PPh_3/H_2O$  is shown in Scheme 3 and proceeds as follows: (1) PPh<sub>3</sub> reacts with  $I_2$  to form the  $[Ph_3PI]^+[I]^-$  species<sup>12</sup> (Step a); (2) the  $[Ph_3PI]^+[I]^-$  species reacts with  $H_2O$  to generate HI and  $[Ph_3POH]^+[I]^-$  (Step b); (3) HI adds to an alkyne to afford the corresponding vinyl iodide (Step c); (4) the  $[Ph_3POH]^+[I]^-$  species may react with an alkyne to generate vinyl iodide and Ph<sub>3</sub>P=O (Step d). When the reaction is complete, the remaining  $[Ph_3POH]^+[I]^-$  species is quenched by addition of MeOH to give Ph<sub>3</sub>P=O and MeI as byproducts (Step e).

Stimulated by the fact that Ph<sub>3</sub>P=O does not inhibit the catalytic activity of transition metals and that MeI, which is formed by the quenching process, can easily be removed by evaporation, we next investigated several one-pot reactions to trisubstituted alkenes via the hydroiodination of alkynes using I<sub>2</sub>/PPh<sub>3</sub>/H<sub>2</sub>O. First, the one-pot Suzuki-Miyaura cross-coupling reaction<sup>13</sup> was investigated. To a 30 mL Schlenk flask, PPh<sub>3</sub>, I<sub>2</sub>, CHCl<sub>3</sub>, H<sub>2</sub>O, and an alkyne were added under a nitrogen atmosphere. The mixture was gently stirred for the appropriate time and MeOH was added. The solvent was removed, followed by addition of the arylboronic acid, K<sub>2</sub>CO<sub>3</sub>, dioxane/H<sub>2</sub>O, and the Pd catalyst. The mixture was heated for 20 h to afford the expected aryl alkene. The results of this one-pot synthesis of arylated alkenes from alkynes are shown in Table 3.<sup>14</sup> When 4-octyne was used as a starting alkyne, the one-pot reaction proceeded successfully to afford the corresponding trisubstituted alkenes (2a-d) regardless of which species of arylboronic acid was used (entries 1-4). In the case of unsymmetrical internal alkynes 1-phenyl-1-pentyne and 1-methyl-4-(oct-1-yn-1-yl)benzene, the corresponding (Z)-arylalkenes (**2e** and **2f**) were obtained regioselectively in good yields (entries 5 and 6). When 1-dodecyne was used as a terminal aliphatic alkyne, the desired coupling product dodec-1-en-2-ylbenzene (2g), and an E/Z mixture of the corresponding isomerization product dodec-2-en-2-ylbenzene were obtained in moderate yields (entry 7). Use of the terminal arylalkyne *p*-tolylethyne gave the corresponding coupling product in low yield (entry 8).

## Table 2

Scope of hydroiodination of alkynes using I2/PPh3/H2O

		R	$\begin{array}{rrr} PPh_3 & \texttt{+} & H_2O \\ 1 \ equiv & 1 \ equiv \end{array}$	CDCl <sub>3</sub> , rt	I a-m	
Entry	Alkyne		Time (h)	Product		Yield <sup>a</sup> (%)
1	<sup>n</sup> Hex—		4	<sup>n</sup> Hex	1a	80
2	<sup>n</sup> Dec—		24	"Dec	1b	86
3	CI	Ξ	4	Cl	1c	98
4	<sup>t</sup> Bu—		24	<sup>t</sup> Bu	1d	(95)
5	 		5			76
6 <sup>b</sup>			24		├ 1f	87
7 <sup>b</sup>	F <sub>3</sub> C	≡	48	F <sub>3</sub> C	l 1g	71
8	<sup>n</sup> Pr—— <sup>n</sup> Pr		2	<sup>n</sup> Pr	n <sub>Pr</sub> 1h	90
9	~	r	22		- <sup>n</sup> Pr I <b>1i</b>	$66^{\circ}$
10		<sup>-n</sup> Hex	3		→ → → → → → → → → → → → → → → → → → →	$80^{\mathrm{d}}$
11	MeO	── <sup>n</sup> Hex	1	MeO	→ <sup>n</sup> Hex	61 <sup>e</sup>
12	F <sub>3</sub> C	── <sup></sup> Hex	12	F <sub>3</sub> C-	I − <sup>n</sup> Hex 1I	70 <sup>f</sup>
13	<sup>n</sup> Hex——Br		28	<sup>n</sup> Hex	Br 1m	97

<sup>a</sup> Isolated yield. The value in parentheses is <sup>1</sup>H NMR yield with 1,3,5-trioxane as an internal standard.

<sup>b</sup> Reaction conditions:  $I_2$  (0.23 mmol), PPh<sub>3</sub> (0.23 mmol), H<sub>2</sub>O (0.23 mmol).

<sup>c</sup> A regioisomer (*Z*)-(2-iodopent-1-enyl)benzene (13%) was also obtained.

<sup>d</sup> A regioisomer (Z)-1-(2-iodooct-1-enyl)-4-methylbenzene (3%) and a stereoisomer (E)-1-(1-iodooct-1-enyl)-4-methylbenzene (16%) were also obtained.

<sup>e</sup> A stereoisomer (*E*)-(1-iodooct-1-enyl)-4-methoxybenzene (7%) was also obtained.

<sup>f</sup> A regioisomer (Z)-1-(1-iodooct-1-enyl)-4-(trifluoromethyl)benzene (29%) was also obtained.

Next, a one-pot synthesis of alkynylalkenes from alkynes, via iodoalkenes, using the Sonogashira cross-coupling reaction<sup>15</sup> was examined (Table 4). When an aliphatic internal alkyne was used under typical conditions for the Sonogashira reaction, the corresponding alkynylalkenes (3a-d) were obtained in good yields (entries 1-4). Unsymmetrical internal alkynes 1-methyl-4-(oct-1vn-1-vl)benzene and 1-(oct-1-vn-1-vl)-4-(trifluoromethyl)benzene also afforded the corresponding alkynylalkenes (3e and 3f) in moderate yields, respectively (entries 5 and 6). In the case of the terminal alkyne 1-dodecyne, the cross-coupling reaction also proceeded to give (3-methylenetridec-1-yn-1-yl)benzene (3g) as well as an (E/Z)-mixture of (3-methyltridec-3-en-1-yn-1-yl)benzene in good yield (entry 7). When terminal alkynes 3,3-dimethylbut-1-yne and *p*-tolylethyne, which do not contain a propargylic hydrogen, were employed, the corresponding coupling products (3h and 3i) were obtained exclusively in moderate yields (entries 8 and 9).





$$HI + R \longrightarrow R \longrightarrow (c)$$

$$[Ph_3POH]^+[I]^- \xrightarrow{R \longrightarrow} R \xrightarrow{R} + Ph_3P=O \quad (d)$$



Scheme 3. Suggested reaction pathway for hydroiodination of alkynes using  $I_2/\ \mathrm{PPh}_3/\mathrm{H}_2\mathrm{O}.$ 

1) PPh<sub>3</sub> 1 equiv

#### Table 3

One-pot synthesis of arylalkenes from alkynes via iodoalkenes using the Suzuki-Miyaura cross-coupling

			$\begin{array}{c} 1 \text{ equiv} \\ \text{PO}  1 \text{ equiv} \\ \text{HCl}_3, \text{ rt} \\ \text{eOH 1 mL} \\ \text{aporation} \end{array} \xrightarrow{\begin{array}{c} 3 \\ \text{PO} \\ $	$\frac{1}{1+r} = \frac{R^1}{Ar} + \frac{R^2}{2a-h}$	
Entry	$R^1$	$R^2$	Time for hydroiodination (h)	Ar	Yield of <b>2</b> <sup>a</sup> (%)
1	<sup>n</sup> Pr	<sup>n</sup> Pr	2	Ph	<b>2a</b> , 70
2	<sup>n</sup> Pr	<sup>n</sup> Pr	2	4-Me-C <sub>6</sub> H <sub>4</sub> -	<b>2b</b> , 68
3	<sup>n</sup> Pr	<sup>n</sup> Pr	2	4-F-C <sub>6</sub> H <sub>4</sub> -	<b>2c</b> , 76
4	"Pr	"Pr	2	4-HCO-C <sub>6</sub> H <sub>4</sub> -	<b>2d</b> , 77
5	Ph	"Pr	22	4-Me-C <sub>6</sub> H <sub>4</sub> -	<b>2e</b> , 63 <sup>b</sup>
6	4-MeO-C <sub>6</sub> H <sub>4</sub> -	"Hex	1	Ph	<b>2f</b> , 61
7	<sup>n</sup> Dec	Н	24	Ph	<b>2g</b> , 11 <sup>c</sup>
8 <sup>d</sup>	4-Me-C <sub>6</sub> H <sub>4</sub> -	Н	24	Ph	<b>2h</b> , 36

<sup>a</sup> Isolated yield.

<sup>b</sup> A mixture of (*Z*)-1-methyl-4-(1-phenylpent-1-en-1-yl) benzene (**2e**) (63%) and (*Z*)-1-methyl-4-(1-phenylpent-1-en-2-yl)benzene (13%) was obtained.

<sup>c</sup> A mixture of dodec-1-en-2-ylbenzene (**2f**) (11%) and dodec-2-en-2-ylbenzene was obtained (38%, *E*/*Z* mixture).

<sup>d</sup> Reaction conditions: I<sub>2</sub> (0.75 mmol), PPh<sub>3</sub> (0.75 mmol), H<sub>2</sub>O (0.75 mmol).

## Table 4

One-pot synthesis of alkynylalkenes from alkynes via iodoalkenes using the Sonogashira cross-coupling



Entry	$R^1$	$R^2$	Time for hydroiodination (h)	R <sup>3</sup>	Yield of <b>3</b> <sup>a</sup> (%)
1	<sup>n</sup> Pr	<sup>n</sup> Pr	2	Ph	<b>3a</b> , 66
2	<sup>n</sup> Pr	<sup>n</sup> Pr	2	4-MeO-C <sub>6</sub> H <sub>4</sub> -	<b>3b</b> , 65
3	<sup>n</sup> Pr	<sup>n</sup> Pr	2	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	<b>3c</b> , 77
4 <sup>b</sup>	<sup>n</sup> Pr	<sup>n</sup> Pr	2	<sup>n</sup> Hex	<b>3d</b> , 55
5	4-Me-C <sub>6</sub> H <sub>4</sub> -	<sup>n</sup> Hex	3	Ph	<b>3e</b> , 51 <sup>c</sup>
6	"Hex	$4-CF_{3}-C_{6}H_{4}-$	12	Ph	<b>3f</b> , 65 <sup>d</sup>
7 <sup>e</sup>	<sup>n</sup> Dec	Н	24	Ph	<b>3g</b> , 50 <sup>f</sup>
8 <sup>b,g</sup>	<sup>t</sup> Bu	Н	24	$4^{-n}C_8H_{17}-C_6H_4-$	<b>3h</b> , 44
9 <sup>b,h</sup>	4-Me-C <sub>6</sub> H <sub>4</sub> -	Н	24	Ph	<b>3i</b> , (49)

<sup>a</sup> Isolated yield. The value in parentheses is <sup>1</sup>H NMR yield with 1,3,5-trioxane as an internal standard.

<sup>b</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol %), rt, 48 h.

<sup>c</sup> A mixture of (*Z*)-1-(et-phenylethynyl)oct-1-en-1-yl)-4-(trifluoromethyl)benzene (**3e**) (51%) and (*E*)-1-methyl-4-(1-phenyldec-3-en-1-yn-3-yl)benzene (7%) was obtained. <sup>d</sup> A mixture of (*Z*)-1-(2-(phenylethynyl)oct-1-en-1-yl)-4-(trifluoromethyl)benzene (**3f**) (65%) and (*Z*)-1-(1-phenyldec-3-en-1-yn-3-yl)-4-trifluoromethyl)benzene (20%)

was obtained.

<sup>e</sup> Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol %), rt, 24 h.

<sup>f</sup> A mixture of (3-methylenetridec-1-yn-1-yl)benzene (**3g**) (50%) and (3-methyltridec-3-en-1-yn-1-yl)benzene (13%, *E/Z* mixture) was obtained.

<sup>g</sup> Without evaporation after the hydroiodination.

<sup>h</sup> Reaction conditions: I<sub>2</sub> (0.75 mmol), PPh<sub>3</sub> (0.75 mmol), H<sub>2</sub>O (0.75 mmol).

## Table 5

One-pot synthesis of dienes from alkynes via iodoalkenes using the Mizoroki-Heck reaction

p1 — p2	1) PPh <sub>3</sub> 1 equiv l <sub>2</sub> 1 equiv H <sub>2</sub> O 1 equiv CHCl <sub>3</sub> , rt	3) R <sup>3</sup> 1.2 equiv Pd(PPh <sub>3</sub> ) <sub>4</sub> 5 mol% NEt <sub>3</sub> 2 equiv	R <sup>1</sup> R <sup>2</sup>
n — R 1 mmol	2) MeOH 1 mL evaporation	CH <sub>3</sub> CN, 70 °C, 20 h	R <sup>3</sup> 4a-d

Entry	$R^1$	$R^2$	Time for hydroiodination (h)	R <sup>3</sup>	Yield of <b>4</b> <sup>a</sup> (%)	E/Z ratio <sup>b</sup>
1	<sup>n</sup> Pr	<sup>n</sup> Pr	2	Ph	<b>4a</b> , 46	18/82
2	<sup>n</sup> Pr	<sup>n</sup> Pr	2	COOMe	<b>4b</b> , 83	27/73
3	4-Me-C <sub>6</sub> H <sub>4</sub> -	<sup>n</sup> Hex	3	COOMe	<b>4c</b> , 82	33/67
4	4-MeO-C <sub>6</sub> H <sub>4</sub> -	<sup>n</sup> Hex	1	COOMe	<b>4d</b> , 74	41/59

Isolated yield.

<sup>b</sup> The ratio was determined by <sup>1</sup>H NMR.

Finally, we investigated the one-pot strategy for application to the Mizoroki–Heck reaction.<sup>16</sup> Table 5 shows the one-pot synthesis of substituted alkenes via iodoalkenes from alkynes using the Mizoroki-Heck reaction. When 4-octyne, as an internal alkyne, and styrene or methyl acrylate as olefin were employed under typical conditions of the Mizoroki-Heck reaction, the corresponding dienes (4a and 4b) were successfully obtained via the one-pot reaction (entries 1 and 2). Unsymmetrical internal alkynes 1methyl-4-(oct-1-yn-1-yl)benzene and 1-methoxy-4-(oct-1-yn-1yl)benzene also gave the corresponding dienes (**4c** and **4d**) in good vields.

In conclusion, we have developed a hydroiodination of alkynes using readily available I<sub>2</sub>, PPh<sub>3</sub>, and H<sub>2</sub>O. Moreover, a one-pot synthesis of substituted alkenes from alkynes via iodoalkenes, using Pd-catalyzed cross-coupling reactions such as the Suzuki-Miyaura reaction. Sonogashira reaction, and Mizoroki-Heck reaction, has been developed. This process can contribute to decreasing environmental load by reducing solvent use.

# Acknowledgment

This work was financially supported by JSPS KAKENHI Grant Number 25410051.

# Supplementary data

Supplementary data (detailed experimental procedures and compound characterization data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.tetlet.2014.10.039.

### **References and notes**

- 1. (a) Comprehensive Organic Functional Group Transformations; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, UK, 1995; Vol. 1, (b) Comprehensive Organic Synthesis: Selectivity, Strategy and Efficiency in Modern Organic Chemistry; Heathcock, C., Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1992; Vol. 2,
- (a) Jeffrey, C. S.; Leonard, M. D.; Glassmire, A. E.; Dodson, C. D.; Richards, L. A.; Kato, M. J.; Dyer, L. A. J. Nat. Prod. 2014, 77, 148-153; (b) Costa, R.; Negrão, R.; Valente, I.; Castela, Â.; Duarte, D.; Guardão, L.; Magalhães, P. J.; Rodrigues, J. T.; Guimarães, J. T.; Gomes, P.; Soares, R. J. Nat. Prod. 2013, 76, 2047-2053; (c) Weber, A.; Dehn, R.; Schläger, N.; Dieter, B.; Kirschning, A. Org. Lett. 2014, 16, 568-571
- Metal-catalyzed Cross-coupling Reactions; Diederich, F., Stang, P. J., Eds., 1st ed.; Wiley-VCH: Weinheim, Germany, 1998.

- 4. Ishikawa, H.: Honma, M.: Hayashi, Y. Angew, Chem., Int. Ed. 2011, 50, 2824-2827
- 5. The Mizoroki-Heck Reaction; Oestreich, M., Ed.; John Wiley & Sons Ltd: West Sussex, UK, 2009.
- 6 Kropp, P. J.; Crawford, S. D. J. Org. Chem. 1994, 59, 3102-3112.
- (a) Pross, A.; Sternhell, S. Aust. J. Chem. 1970, 23, 989-1003; (b) Hara, S.; Dojo, 7. H.; Takinami, S.; Suzuki, A. Tetrahedron Lett. 1983, 24, 731-734; (c) Brown, H. C.; Somayaji, V.; Narasimhan, S. J. Org. Chem. 1984, 49, 4822-4827; (d) Reddy, Ch. K.; Periasamy, M. Tetrahedron Lett. 1990, 31, 1919-1920; (e) Kamiya, N.; Chikami, Y.; Ishii, Y. Synlett 1990, 675-676; (f) Gao, Y.; Harada, K.; Hata, T.; Urabe, H.; Sato, F. J. Org. Chem. 1995, 60, 290-291; (g) Campos, P. J.; García, B.; Rodríguez, M. A. Tetrahedron Lett. 2002, 43, 6111-6112; (h) Shimizu, M.; Toyoda, T.; Baba, T. Synlett 2005, 2516–2518; (i) Bartoli, G.; Cipolletti, R.; Di Antonio, G.; Giovannini, R.; Lanari, S.; Marcolini, M.; Marcantoni, E. Org. Biomol. Chem. 2010, 8, 3509-3517; (j) Kawaguchi, S-i.; Ogawa, A. Org. Lett. 2010, 12, 1893-1895; (k) Ez-Zoubir, M.; Brown, J. A.; Ratovelomanana-Vidal, V.; Michelet, V. J. Organomet. Chem. 2011, 696, 433-441.
- 8 Kawaguchi, S-i.; Masuno, H.; Sonoda, M.; Nomoto, A.; Ogawa, A. Tetrahedron 2012, 68, 9818-9825.
- du Mont, W.-W.; Ruthe, F. Coord. Chem. Rev. 1999, 189, 101-133.
- The general procedure for the synthesis of iodoalkenes using  $I_2$ , PPh<sub>3</sub>, and  $H_2O$ : 10 under a nitrogen atmosphere, PPh3 (78.6 mg, 0.3 mmol), I2 (76.1 mg, 0.3 mmol), and H<sub>2</sub>O (5.40 mg, 0.3 mmol) were placed in a Schlenk tube, followed by addition of CDCl3 (0.6 mL) at room temperature. The alkyne (0.3 mmol) was then added to the reaction mixture and the mixture was slowly stirred for the appropriate time (see Table 2) at room temperature, followed by quenching with MeOH (0.3 mL). The solvent and MeI were then removed under reduced pressure. The crude product was purified by preparative TLC (silica gel).
- Sato, A. H.; Mihara, S.; Iwasawa, T. Tetrahedron Lett. 2012, 53, 3585-3589. 11.
- 12. (a) Barnes, N. A.; Godfrey, S. M.; Khan, R. Z.; Pierce, A.; Pritchard, R. G. Polyhedron 2012, 35, 31-46; (b) Deplano, P.; Godfrey, S. M.; Lsaia, F.; McAuliffe, C. A.; Mercurp, M. L.; Trogu, E. F. Chem. Ber. 1997, 130, 299-305; (c) Ruthe, F.; Jones, P. G.; du Mont, W.-W.; Deplano, P.; Mercuri, M. L. Z. Anorg. Allg. Chem. **2000**, 626, 1105–1111.
- Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457-2483.
- The general procedure for the one-pot synthesis of arylated alkenes using the Suzuki-Miyaura cross coupling reaction: under a nitrogen atmosphere, PPh3 (262.2 mg, 1.0 mmol), I<sub>2</sub> (253.8 mg, 1.0 mmol), and H<sub>2</sub>O (180 mg, 1.0 mmol) were placed in a 30 mL Schlenk flask, followed by addition of CHCl<sub>3</sub> (2 mL) at room temperature. The alkyne (1.0 mmol) was then added to the reaction mixture and the mixture was slowly stirred for the appropriate time (see Table 3) at room temperature, followed by quenching with MeOH (1 mL). The solvent and MeI were then removed under reduced pressure. Dioxane (2 mL), arylboronic acid (1.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (57.7 mg, 0.05 mmol) and  $K_2CO_3$  (414.6 mg, 3.0 mmol) dissolved in H<sub>2</sub>O (1 mL) were added to the same Schlenk flask. The mixture was stirred at 70 °C for 20 h, followed by addition of water (30 mL) and the resulting mixture was extracted with diethyl ether  $(3 \times 30 \text{ mL})$ . The combined organics were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography.
- 15
- (a) Mizoroki, T.; Mori, K.; Ozaki, A. Bull. Chem. Soc. Jpn. **1975**, *16*, 4467–4470. 16. R. F.; Nolley, J. P. J. Org. Chem. 1972, 37, 2320-2322.