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Highly regioselective hydroiodination of terminal alkynes and silylalkynes with iodine and phosphorus reagents leading to internal iodoalkenes

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ABSTRACT

Markovnikov-type hydroiodination of terminal alkynes with iodine and $Ph_2P(O)H$ took place selectively to afford the corresponding internal iodoalkenes in good yields. Combination of $(PhO)_2P(O)H$ and $Ph_2P(O)OH$ instead of $Ph_2P(O)H$ also provided internal iodoalkenes in excellent yields. This hydroiodination is advantageous in terms of mild conditions, convenient operation, and tolerance to various functional groups. In addition, direct synthesis of internal iodoalkenes from silylalkynes was also achieved by using a mixed system of iodine and phosphorus reagents.

1. Introduction

Iodoalkenes (Fig. 1) are useful synthetic intermediates for the synthesis of various vinyl compounds by using transition-metal-catalyzed cross coupling reactions, halogen-metal exchange reactions, radical reactions, etc.[1,2] Therefore, the development of novel and highly selective synthesis of iodoalkenes is desired strongly. In this viewpoint, we are interested in addition reaction of HI to alkynes, which is one of the most straightforward methods for the synthesis of internal iodoalkenes. However, hydroiodination of alkynes with HI ordinarily does not proceed except for the reactions conducted under specific conditions.[3,4] This is because HI is generally treated in aqueous solution and can not be miscible with organic substrates in organic layer. Thus, a number of alternative methods to synthesize internal iodoalkenes from the corresponding alkynes have been reported.[5–9] However, the development of novel and highly selective synthesis of internal iodoalkenes is still desired strongly. Based on these backgrounds, we have investigated regioselective hydroiodination of alkynes mediated by phosphorus reagents. Initially we developed hydroiodination of alkynes with iodine and diphenylphosphine oxide to generate the corresponding internal iodoalkenes (Eq. 1). We also investigated an improved method of hydroiodination of alkynes using cheaper phosphorus reagents, such as diphenylphosphite and diphenylphosphinic acid, with easy operation has been developed (Eq. 2), based on the mechanistic consideration about the hydroiodination with diphenylphosphine oxide. Furthermore, when trimethylsilyl-substituted alkynes were used in this reaction, interestingly, desilylative[10,11] hydroiodination occurred and internal iodoalkenes were directly obtained (Eq. 3). Until more recently, the direct synthetic method of internal iodoalkenes from silyl-substituted alkynes has not been reported.[12] This paper deals with details about hydroiodination of alkynes and direct synthesis of silyl-substituted alkynes using iodine and phosphorus reagents Fig. 1.

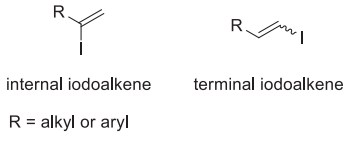
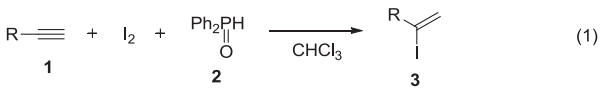
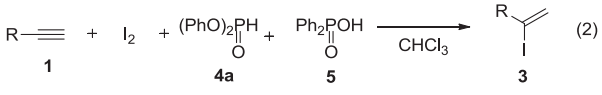


Fig. 1. Structure of internal or terminal iodoalkene.



(1)



(2)

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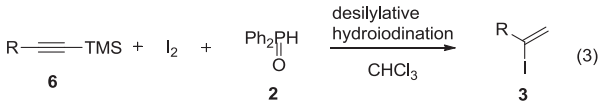
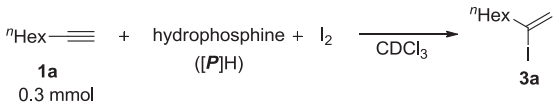


2. Results and discussions

Initially, the reactions of 1-octyne (**1a**) with I_2 in the co-presence of several hydrophosphines ([***P***]H) were examined under several conditions (Table 1). When diphenylphosphine was employed, Markovnikov-type hydroiodination of **1a** successfully took place regioselectively to give 2-iodo-1-octene (**3a**) in moderate yield (entry 1). Use of diphenylphosphine oxide (**2**) significantly improved the yield of hydroiodination product **3a** (entry 2). When $Ph_2P(O)H/I_2$ with the ratio of 1/1 was used, a certain amount of 1,2-diiodo-1-octene was obtained as a byproduct. Therefore, the ratio of $Ph_2P(O)H/I_2$ was changed. In the case of the 2/1 ratio of $Ph_2P(O)H/I_2$, hydroiodination of 1-octyne took place selectively and efficiently (entry 3). On the other hand, when phosphorous acids, such as $(EtO)_2P(O)H$ (**4b**) and $(PhO)_2P(O)H$ (**4a**) were used, the yields of **3a** were low and complex mixture were obtained (entries 4, 5). Conducting the reaction at higher temperature resulted in decrease in the yield of **3a** (entry 6). Without hydrophosphine, the hydroiodination did not occur at all (entry 7).

Table 1
Hydroiodination of 1-octyne with iodine using several hydrophosphines



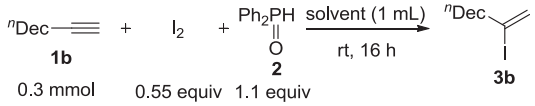
Entry	[***P***]H	Alkyne/[***P***]H/I_2	Time	Temp	Yield of **3a**[a]
1	Ph_2PH	3/1/1	16 h	Rt	47%[b]
2	$Ph_2P(O)H$ **2**	3/1/1	24 h	Rt	74%[b]
3	$Ph_2P(O)H$ **2**	1/1.5/0.75	16 h	Rt	88%[c]
4	$(EtO)_2P(O)H$ **4b**	1/1.5/0.75	16 h	Rt	4%[c]
5	$(PhO)_2P(O)H$ **4a**	1/1.5/0.75	24 h	Rt	13%[c]
6	$Ph_2P(O)H$ **2**	1/1.5/0.75	16 h	60 °C	50%[c]
7	None	3/0/1	36 h	Rt	0%

[a] Determined by ^1H NMR.
[b] Based on phosphorus compound.
[c] Based on alkyne.

Next, hydroiodination of 1-dodecyne with $Ph_2P(O)H/I_2$ in several solvents was investigated (Table 2). In halogenated solvents, the hydroiodination took place efficiently (entries 1, 2). When EtOH or THF[13] was used, iodination of the solvent occurred in preference to the hydroiodination of 1-dodecyne (entries 3, 4). On the other hand, the hydroiodination in toluene proceeded successfully (entry 6). These results seem to be influenced partly by the solubility of I_2 for each solvent.

To get some information about the mechanism for this hydroiodination, several reactions were examined. The hydroiodination of alkynylphosphine oxide (**1c**) afforded 1-(diphenylphosphinyl)-2-iodo-1-octene (**3c**), regioselectively (Eq. 4). When the reaction of (*E*)-1-(diphenylphosphinyl)-2-iodo-1-octene ((***E***)-**3c**) with diphenylphosphine oxide was conducted, any product

Table 2
Hydroiodination of 1-dodecyne in several solvent



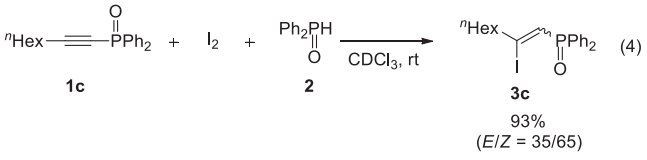
Entry	Solvent	Yield of **3b**[a]
1	$CHCl_3$	67%
2	CH_2Cl_2	62%
3	EtOH	4%
4	THF	0%
5	MeCN	33%
6	toluene	61%
7	benzene	49%

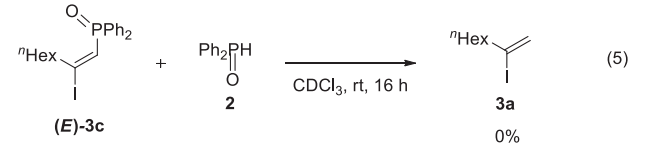
[a] Determined by ^1H NMR.

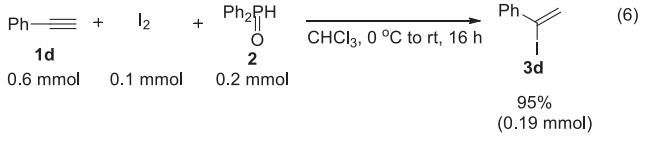
with loss of phosphinyl group was not obtained at all (the starting materials are recovered quantitatively) (Eq. 5). This result indicates that the present hydroiodination does not proceed via the formation of 1-phosphinyl-2-iodoalkene species as an intermediate.

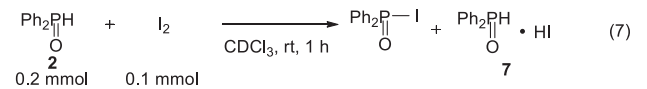
On the other hand, when excess amounts of an alkyne were used for the present reaction, the corresponding internal iodoalkene was obtained in 95% yield (the yield is based on iodine atom) (Eq. 6). Interestingly, both two atoms of iodine molecule were used as hydroiodination reagent. This fact is an important clue to know the reaction pathway.

When 2 equiv of diphenylphosphine oxide (**2**) were allowed to react with iodine (0.1 mmol), ^{31}P NMR measurement indicated that **2** (δ 21.6 ppm, in $CDCl_3$) completely converted to the different two phosphorus compounds (δ 36.6 and 40.8 ppm, in $CDCl_3$). We assume these two peaks are assigned to $Ph_2P(O)I$[13,14] and $Ph_2P(O)H\cdot HI$ (**7**),[15] respectively (Eq. 7).

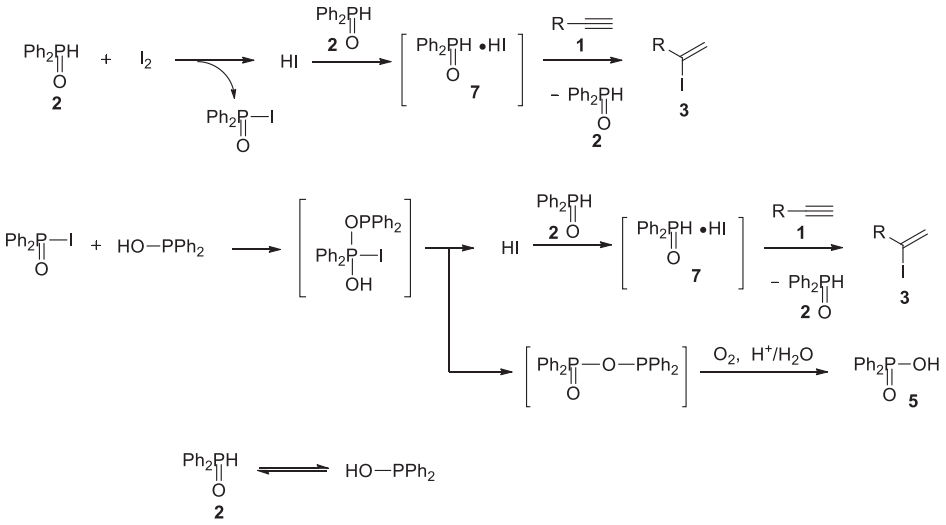








Based on the results of these experiments, a possible reaction pathway for the present hydroiodination is proposed, as shown in Scheme 1. First, $Ph_2P(O)H$ (**2**) reacts with I_2 to generate $Ph_2P(O)I$ and HI. HI immediately forms a complex with **2**,[15] to generate the complex (**7**). The complex **7** acts as an active species for the Markovnikov-type hydroiodination of alkynes to give the iodoalkenes (**3**).[16] On the other hand, **2** has the tautomeric form of trivalent phosphinous acid (Ph_2POH).[17] Ph_2POH reacts with $Ph_2P(O)I$

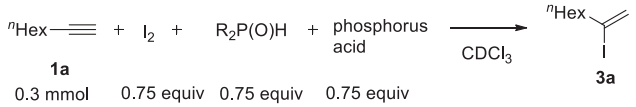


Scheme 1. A plausible pathway for hydroiodination with I_2 and $Ph_2P(O)H$.

to generate HI, which gives iodoalkenes **3** similarly as mentioned above. The resulting phosphine residue finally changes diphenylphosphinic acid (**5**) upon treatment with oxygen and proton source.

This reaction pathway indicates that $Ph_2P(O)H$ (**2**) plays two roles as reducing agent for iodine and as hydrogen source by the tautomeric form of trivalent phosphinous acid (Ph_2POH). We considered that each role of **2** could be respectively replaced with other compounds, which are cheaper and easier handling. First, a half amount of **2** was replaced with $Ph_2P(O)OH$ (**5**) as a cheaper hydrogen source. As the result, the desired hydroiodination took place as well (Table 3, entry 1). Since **5** was obtained as a byproduct after the reaction, this condition can reduce the amount of **2**. Next, the use of phosphorous acid as a reducing agent for iodine was examined. When $(EtO)_2P(O)H$ (**4b**) as phosphorous acid and **5** were used instead of **2**, the yield of 2-iodo-1-octene (**3a**) was low (entry 2). However, use of a combination of $(PhO)_2P(O)H$ (**4a**) and **5** dramatically improved the yield of the desired iodoalkene **3a** (entry 3). Prolonged reaction time led to increase in the yield of **3a** (entry 4). Elevated temperatures made it possible to reduce reaction time (entries 5, 6). But further higher temperatures caused the formation of some byproducts[18] in about 5–10% yields. In the absence of phosphorous acid, the hydroiodination did not proceed at all (entry 7). In this case, only bisiodination of 1-octyne exclusively occurred. Use of H_3PO_4 instead of **5** gave **3a** in moderate yield (entry 8).

Table 3
Hydroiodination of 1-octyne with iodine by combinations of phosphorus reagents



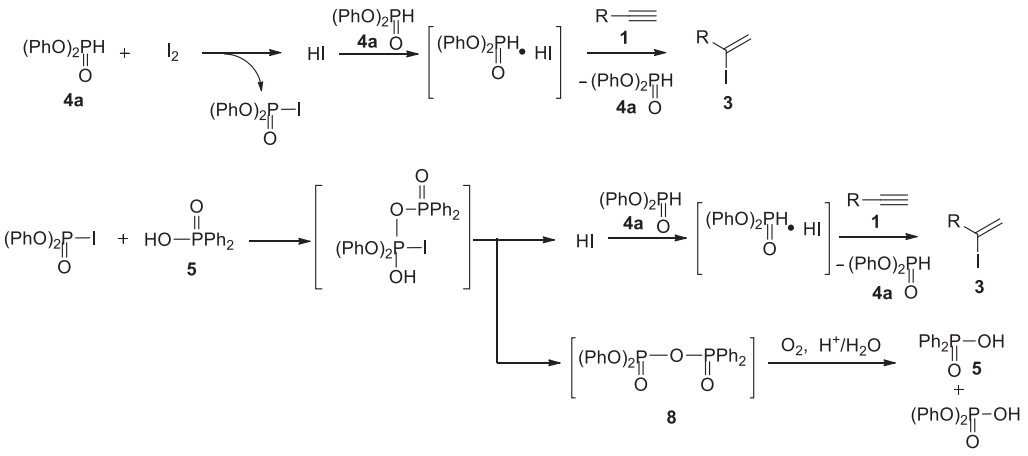
Entry	$R_2P(O)H$	Phosphorus acid	Temp (°C)	Time	Yield of **3a**[a]
1	$Ph_2P(O)H$ **2**	$Ph_2P(O)OH$ **5**	Rt	24 h	88%
2	$(EtO)_2P(O)H$ **4b**	$Ph_2P(O)OH$ **5**	Rt	24 h	24%
3	$(PhO)_2P(O)H$ **4a**	$Ph_2P(O)OH$ **5**	Rt	24 h	61%
4	$(PhO)_2P(O)H$ **4a**	$Ph_2P(O)OH$ **5**	Rt	48 h	82%
5	$(PhO)_2P(O)H$ **4a**	$Ph_2P(O)OH$ **5**	30	36 h	84%
6	$(PhO)_2P(O)H$ **4a**	$Ph_2P(O)OH$ **5**	40	18 h	78%
7[b]	—	$Ph_2P(O)OH$ **5**	Rt	24 h	0%
8	$(PhO)_2P(O)H$ **4a**	H_3PO_4	Rt	24 h	53%

[a] Determined by ^1H NMR. The yields are based on alkyne **1a**.
[b] Diphenylphosphinic acid (1.5 equiv) was employed.

A plausible pathway for the hydroiodination by a combination of I_2, $(PhO)_2P(O)H$ (**4a**), and $Ph_2P(O)OH$ (**5**) is proposed in Scheme 2. Initially, **4a** reacts with I_2 to generate HI and $(PhO)_2P(O)I$. The formation of $(PhO)_2P(O)I$ was observed by ^{31}P NMR measurement at −49 ppm in $CDCl_3$.[19] Phosphorus reagent **4a** promotes the addition of HI to alkyne[20] and Markovnikov-type iodoalkene **3** is formed. On the other hand, $(PhO)_2P(O)I$ reacts with **5** to generate HI as well as the case of $Ph_2P(O)H$ (**2**), and HI affords iodoalkenes **3**. The resulting phosphorus compounds finally converted to phosphinic acid and diphenyl phosphate via species **8**.

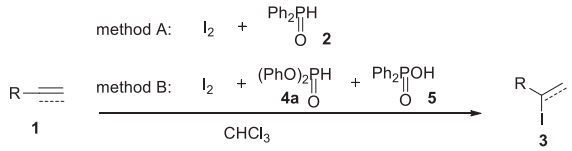
Table 4 represents the results of the hydroiodination of several aliphatic alkynes and an alkene by a combination of iodine and diphenylphosphine oxide (method A) or iodine, diphenylphosphite, and diphenylphosphinic acid (method B). A gram-scale hydroiodination of 1-octyne using method B successfully took place to provide 1.75 g of iodoalkene **3a** (entry 1). The hydroiodination of aliphatic terminal alkynes, such as 1-dodecyne (**1b**), 5-chloro-1-pentyne (**1e**), and aliphatic alkene, such as 1-octene (**1f**) also proceeded to give the corresponding Markovnikov-type adducts in good yields with excellent regioselectivity, respectively, using each method (entries 2–7). Internal alkyne, such as 4-octyne (**1g**) was quantitatively converted to the corresponding iodoalkene with conspicuous selectivity[21] by using each method (entries 8, 9).

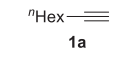
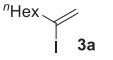
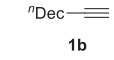
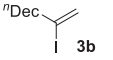
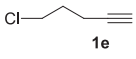
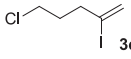
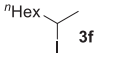
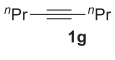
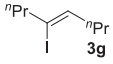
Table 5 shows the results of the hydroiodination of several terminal aromatic alkynes. In the case of aromatic alkynes, Markovnikov-type adducts were also obtained in good yields (entries 1–11). The hydroiodination of aromatic alkynes having alkyl group at the *para* position proceeded more quickly, compared with the case of phenylacetylene (entries 3, 5). In the case of aromatic alkynes with electron-withdrawing group, prolonged reaction time was required (entries 10, 11). When alkynone (**1n**) was used, (*Z*)-3-iodo-2-alkene-1-one (**3n**) was obtained stereoselectively (Eq. 8).



Scheme 2. A proposed pathway for hydroiodination by a combination of I_2, **4a**, and **5**.

Table 4
Scope of a hydroiodination of aliphatic alkynes and an alkene[a]



Entry	Alkyne (alkene)	Method	Temp (°C)	Time	Product	Yield[b]
1[c]	 **1a**	B	30	36 h	 **3a**	75%
2	 **1b**	A	Rt	16 h	 **3b**	73%[d]
3		B	30	36 h		65%
4	 **1e**	A	Rt	16 h	 **3e**	59%
5		B	30	16 h		99%
6	 **1f**	A	Rt	16 h	 **3f**	91%[d]
7		B	30	16 h		98%
8	 **1g**	A	30	5 h	 **3g**	99%
9		B	30	16 h		99%

[a] Reaction conditions (A): alkyne (alkene) (0.20 mmol), I_2 (0.15 mmol), $Ph_2P(O)I$ (0.30 mmol), $CHCl_3$ (0.6 mL). Reaction conditions (B): alkyne (alkene) (0.50 mmol), I_2 (0.38 mmol), $(PhO)_2P(O)H$ (0.38 mmol), $Ph_2P(O)OH$ (0.38 mmol), $CHCl_3$ (0.6 mL).
[b] Isolated yield.
[c] The reaction was conducted using 10 mmol of 1-octyne.
[d] Determined by ^1H NMR.

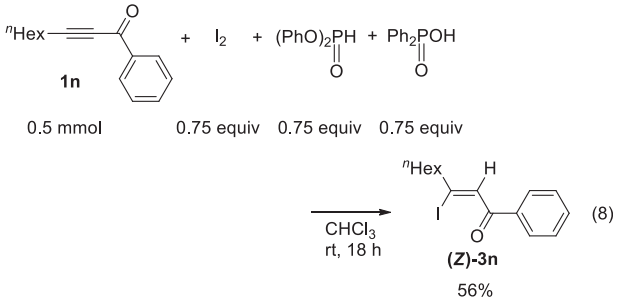
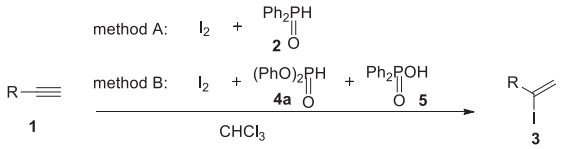
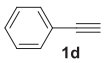
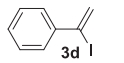
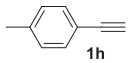
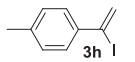
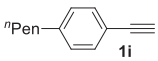
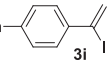
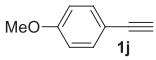
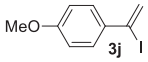
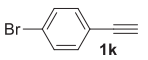
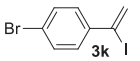
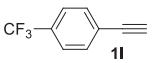
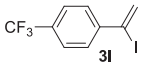
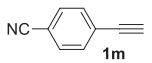
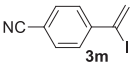


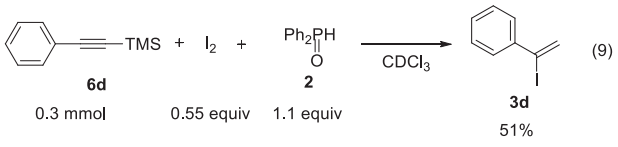
Table 5
Scope of a hydroiodination of aromatic alkynes[a]



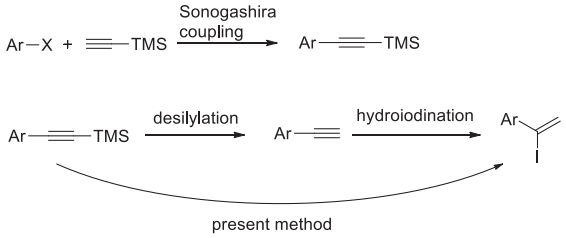
Entry	Alkyne	Method	Temp (°C)	Time	Product	Yield[b]
1	 **1d**	A	0–rt	16 h	 **3d**	95%
2		B	30	16 h		83%
3	 **1h**	B	rt	5 h	 **3h**	89%
4	 **1i**	A	0–rt	16 h	 **3i**	77%
5		B	rt	5 h		81%
6	 **1j**	A	0–rt	16 h	 **3j**	81%
7	 **1k**	A	0–rt	16 h	 **3k**	67%
8		B	30	16 h		85%
9[c]	 **1l**	A	0–rt	16 h	 **3l**	81%
10		B	30	36 h		71%
11	 **1m**	B	rt	120 h	 **3m**	67%

[a] Reaction condition (A): alkyne (0.60 mmol), I_2 (0.10 mmol), $Ph_2P(O)H$ (0.20 mmol), $CHCl_3$ (0.6 mL). Reaction condition (B): alkyne (0.50 mmol), I_2 (0.38 mmol), $(PhO)_2P(O)H$ (0.38 mmol), $Ph_2P(O)OH$ (0.38 mmol), $CHCl_3$ (0.6 mL).
[b] Isolated yield.
[c] Alkyne (0.20 mmol), I_2 (0.15 mmol), $Ph_2P(O)H$ (0.30 mmol) were used.

Next, when trimethylsilyl (TMS)-substituted phenylacetylene (**6d**) was employed in the presence of I_2 and $Ph_2P(O)H$ (**2**), α-iodostyrene (**3d**) was directly obtained via desilylation (Eq. 9).

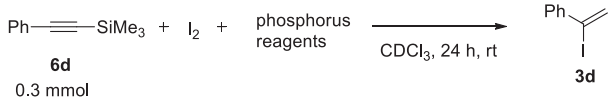


One of the synthetic strategy of α-iodostyrene derivative is generally proposed as following: (1) Sonogashira coupling of aryl halide with (trimethylsilyl)acetylene to generate trimethylsilyl-substituted arylacetylene;[22] (2) desilylation of (trimethylsilyl)arylacetylene to generate arylacetylene;[10,11] (3) hydroiodination of arylacetylene to generate α-iodostyrene derivative.[5] The present hydroiodination method has the advantage that it can reduce desilylation step (Scheme 3). Thus, we investigated the present synthetic method of internal iodoalkenes mediated by phosphorus reagents in detail. One-step desilylation and hydroiodination of (trimethylsilyl)ethynylbenzene (**6d**) was conducted by the combination of iodine and phosphorus reagents (Table 6). When $Ph_2P(O)H$ (**2**), the combination of **2** and $(PhO)_2P(O)H$ (**4a**), the combination of **2** and $Ph_2P(O)OH$ (**5**), or the combination of **4a** and **5** was used as phosphorus reagents, desilylative hydroiodination took place and α-iodostyrene (**3d**) was obtained in one-step in each case (entries 1–4). Ethynylbenezene was not observed at all in every case. Use of 0.75 equiv of I_2 was more suitable for the desired reaction (entry 5).



Scheme 3.

Table 6
Desilylative hydroiodination of (trimethylsilyl) ethynylbenzene using I_2 and several phosphorus reagents[a]

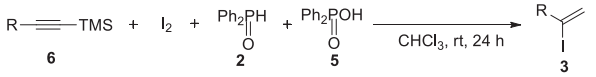


Entry	Phosphorus reagents	I_2	Yield of **3d**[a]
1[b]	$Ph_2P(O)H$ (**2**)	0.55 equiv	51%
2[c]	$Ph_2P(O)H$ (**2**) + $(PhO)_2P(O)H$ (**4a**)	0.55 equiv	51%
3[c]	$Ph_2P(O)H$ (**2**) + $Ph_2P(O)OH$ (**5**)	0.55 equiv	65%
4[c]	$(PhO)_2P(O)H$ (**4a**) + $Ph_2P(O)OH$ (**5**)	0.55 equiv	57%
5[c]	$Ph_2P(O)H$ (**2**) + $Ph_2P(O)OH$ (**5**)	0.75 equiv	72% (64%)

[a] Determined by ^1H NMR. The value in parentheses is isolated yield.
[b] Diphenylphosphine oxide (2.2 equiv) was employed.
[c] Both phosphorus reagents (1.1 equiv) were employed.

Table 7 represents the results of the direct synthesis of internal iodoalkenes from several silylalkynes. Aliphatic silylalkynes, such as 1-(trimethylsilyl)-1-octyne (**6a**) and 1-(trimethylsilyl)-1-dodecyne (**6b**) were converted to the corresponding internal iodoalkenes in excellent yields (entries 1, 2). In the case of several aromatic silylalkynes, the direct synthesis of α-iodostyrene derivatives was achieved successfully (entries 3–5).

Table 7
The direct synthesis of internal iodoalkenes from several TMS–alkynes[a]

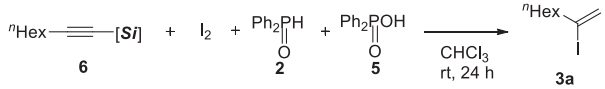


Entry	Silylalkyne		Product		Yield[b]
1	^{n}Hex—TMS	**6a**	^{n}Hex	**3a**	92%
2	^{n}Dec—TMS	**6b**	^{n}Dec	**3b**	99%
3	TMS	**6d**		**3d**	64%
4	TMS	**6h**		**3h**	94%
5	MeO—TMS	**6j**	MeO	**3j**	54%

[a] Reaction conditions: silylalkyne (0.30 mmol), I_2 (0.23 mmol), $Ph_2P(O)H$ (0.33 mmol), $Ph_2P(O)OH$ (0.33 mmol), $CHCl_3$ (0.6 mL).
[b] Isolated yield.

Amazingly, not only (trimethylsilyl) alkynes (TMS-alkynes) but other bulky silyl group-substituted alkynes were also suitable for the one-step desilylation and hydroiodination (Table 8). When *tert*-butyldimethylsilyl- (TBDMS-), dimethylphenylsilyl- (DMPS-), and triethoxysilyl-substituted alkynes were used, silylalkynes were converted to internal iodoalkenes (entries 2–4). On the other hand, in the case of 1-(triisopropylsilyl)-1-octyne, neither desilylation nor hydroiodination proceeded and the starting silylalkyne was recovered (entry 5). TBDMS–alkyne and DMPS–alkyne were usually desilylated by fluoride anion.[10a] The present method using iodine and phosphorus reagents is a novel method for desilylation of these silylalkyne in the absence of fluoride anion.

Table 8
Desilylative hydroiodination of several 1-silyl-1-octynes[a]

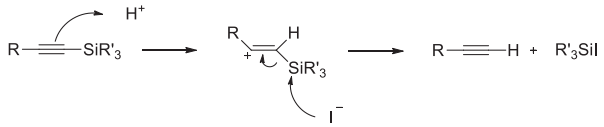


Entry	Silylalkyne		Yield of **3a**[b]
1	^{n}Hex—SiMe$_3$	**6a**	92%
2	^{n}Hex—Si^{t}BuMe$_2$	**9a**	62%
3	^{n}Hex—SiMe$_2$Ph	**10a**	71%
4	^{n}Hex—Si(OEt)$_3$	**11a**	72%
5	^{n}Hex—Si(^{i}Pr)$_3$	**12a**	0%

[a] Reaction conditions: silylalkyne (0.30 mmol), I_2 (0.23 mmol), $Ph_2P(O)H$ (0.33 mmol), $Ph_2P(O)OH$ (0.33 mmol), $CHCl_3$ (0.6 mL).
[b] Isolated yield.

In order to get insight into the reaction mechanism of the desilylative hydroiodination, time-dependent changes of desilylative hydroiodination of 1-(trimethylsilyl)-1-octyne were monitored by using ^1H NMR for 24 h. Formation of a constant amount of 1-octyne (3–5%) was observed during each measurement. Accordingly, a proposed pathway is shown in Scheme 4. First, protonation of a silylalkyne occurs to form the vinyl cation intermediate and next, the elimination of silyl group

took place by the attack of iodide anion to the Si atom to generate terminal alkyne and silyl iodide. Subsequently, the generated alkyne is consumed as a substrate for hydroiodination. The generated silyl iodide is used as an iodine source for the next step: hydroiodination of terminal alkyne.[5d]



Scheme 4.

3. Conclusion

In conclusion, we have developed the hydroiodination of alkynes with iodine mediated by $Ph_2P(O)H$ or the combination of $(PhO)_2P(O)H$ and $Ph_2P(O)OH$. These methods are advantageous in terms of mild conditions, convenient operation, and tolerance to various functional groups for the preparation of internal iodoalkenes. Moreover, one-step synthesis of internal iodoalkenes from silylalkynes was achieved by the present system using iodine and phosphorus reagents. We hope that this hydroiodination is used in various stages of organic synthesis.

4. Experimental section

4.1. General comments

Oct-1-yn-1-yldiphenylphosphine oxide (**1c**),[23] ynone **1n**,[24] silylalkyne **6a**,[10a,25] **6b**,[10a,25] **6d**,[22] **6h**,[22] **6j**,[22] **9a**,[10a,26] **10a**,[10a,11e] **11a**,[10a,11e] and **12a**[10a,11e] were synthesized according to the literature. Other materials were obtained from commercial supplies. Alkynes were purified by distillation before use. Other materials were used without further purification. $CHCl_3$ was distilled and degassed before use. ^1H NMR spectra were recorded on JEOL JNM-ECX400 (400 MHz) FT NMR in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken on JEOL JNM-ECX400 (100 MHz) FT NMR in $CDCl_3$. ^{31}P NMR spectra were taken on JEOL JNM-ECX400 (162 MHz) FT NMR in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. Low resolution mass spectra were obtained on SHIMADZU GCMS-QP5000.

4.2. General procedure for the synthesis of internal iodoalkenes using I_2/$Ph_2P(O)H$ mixed system (method A)

Under a nitrogen atmosphere, diphenylphosphine oxide (60.6 mg, 0.3 mmol) was placed in a Schlenk tube at room temperature, followed by $CHCl_3$ (0.6 mL), iodine (38.1 mg, 0.15 mmol), and alkyne or alkene (0.2 mmol). The mixture was stood statically for 16 h at room temperature, and then MeOH or EtOH (5 mL) was added to quench the reaction. After a while, the crude solution turned colorless from pale purple and white solid of $Ph_2P(O)OH$ was precipitated. The precipitate was filtered, and the crude solution was purified by preparative TLC (silica gel). Eluant: **3a**, **3b**, **3d**–**g**, **3i**–**l**: hexane=100%; **3c**: hexane/AcOEt=1/1.

4.3. General procedure for the synthesis of internal iodoalkenes using iodine, $(PhO)_2P(O)H$, and $Ph_2P(O)OH$ (method B)

Under an inert gas atmosphere, diphenylphosphite (88.9 mg, 0.38 mmol) and diphenylphosphinic acid (82.8 mg, 0.38 mmol) were placed in a 10 mL flask at room temperature, followed by $CHCl_3$ (0.6 mL) and iodine (58.4 mg, 0.23 mmol). Then an alkyne (0.3 mmol) was added to the stirring mixture. The mixture was stirred for appropriate time at appropriate temperature (see Tables 4 and 5), and then MeOH (5 mL) was added to quench the reaction. The color of the crude solution changed from purple to colorless. After a short time, white solid precipitated. The precipitate was filtered, and then the solvent and MeI, which was generated from unreacted phosphorus iodide species and MeOH, were removed under reduced pressure. The crude product was purified by preparative TLC (silica gel) or silica gel column chromatography. (Eluent: hexane=100% for **3a**, **3b**, **3d**–**i**, **3k**, **3l**; hexane/$CHCl_3$=1:3 for **3m**).

*4.3.1. 2-Iodo-1-octene (**3a**).*[5d] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=6.9 Hz, 3H), 1.23–1.33 (m, 6H), 1.45–1.53 (m, 2H), 2.38 (t, J=7.3 Hz, 2H), 5.69 (d, J=0.9 Hz, 1H), 6.01 (d, J=0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.0, 29.1, 31.6, 45.4, 113.0, 125.2; MS (EI), m/z (%)=238 (M^+, 2), 111 (M^+–I, 19).

*4.3.2. 2-Iodo-1-dodecene (**3b**).*[5c] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.9 Hz, 3H), 1.20–1.32 (m, 14H), 1.46–1.52 (m, 2H), 2.37 (t, J=7.4 Hz, 2H), 5.67 (d, J=0.9 Hz, 1H), 6.00 (d, J=1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.2, 29.1, 29.30, 29.31, 29.5, 29.6, 31.9, 45.3, 112.8, 125.1.

*4.3.3. (E)-2-Iodo-1-(diphenylphosphinyl)-1-octene (E)-(**3c**).* Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=6.7 Hz, 3H), 1.21–1.40 (m, 6H), 1.52–1.68 (m, 2H), 2.74 (t, J=7.3 Hz, 2H), 6.95 (d, J_{H-P}=18.6 Hz, 1H), 7.38–7.57 (m, 6H), 7.70–7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 27.9, 29.2, 31.4, 50.0 (d, J_{C-P}=13.2 Hz), 128.2 (d, J_{C-P}=111.1 Hz), 128.6 (d, J_{C-P}=12.3 Hz), 131.3 (d, J_{C-P}=9.9 Hz), 131.6 (d, J_{C-P}=10.7 Hz), 131.7 (d, J_{C-P}=2.5 Hz), 133.0 (d, J_{C-P}=107.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.7; HRMS (EI) Calcd for $C_{20}H_{24}OPI$: 438.0609, Found: 438.0613.

*4.3.4. (1-Iodoethenyl)benzene (**3d**).*[5b] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.08 (d, J=1.9 Hz, 1H), 6.46 (d, J=1.9 Hz, 1H), 7.21–7.38 (m, 3H), 7.45–7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.4, 127.3, 128.1, 128.8, 132.1, 141.6; MS (EI), m/z (%)=230 (M^+, 6), 103 (M^+–I, 100).

*4.3.5. 5-Chloro-2-iodo-1-pentene (**3e**).*[27] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.99 (qin, J=6.8 Hz, 2H), 2.57 (t, J=7.0 Hz, 2H), 3.55 (t, J=6.4 Hz, 2H), 5.76 (d, J=1.5 Hz, 1H), 6.12 (d, J=1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 42.1, 43.0, 109.7, 127.0; MS (EI), m/z (%)=230 (M^+, 13), 103 (M^+–I, 22), 67 (M^+–I–Cl, 100).

*4.3.6. 2-Iodooctane (**3f**).*[28] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7.3 Hz, 3H), 1.20–1.55 (m, 8H), 1.55–1.68 (m, 1H), 1.79–1.91 (m, 1H), 1.92 (d, J=7.4 Hz, 3H), 4.19 (Se, J=7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.5, 29.0, 29.8 31.0, 31.7, 43.0; MS (EI), m/z (%)=240 (M^+, 1), 113 (M^+–I, 23).

*4.3.7. (Z)-4-Iodo-4-octene (**3g**).*[29] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J=7.4 Hz, 3H), 0.91 (t, J=7.4 Hz, 3H), 1.38–1.58 (m, 4H), 2.07 (q, J=7.3 Hz, 2H), 2.41 (t, J=7.1 Hz, 2H), 5.44 (t, J=6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 13.7, 21.7, 22.5, 38.3, 47.1, 109.6, 134.8; MS (EI), m/z (%)=238 (M^+, 20).

*4.3.8. 1-(1-Iodoethenyl)-4-methylbenzene (**3h**).*[30] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 6.01 (d, J=1.4 Hz, 1H), 6.40 (d, J=1.4 Hz, 1H), 7.08 (d, J=8.2 Hz, 2H), 7.38 (d, J=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 107.6, 126.4, 126.4, 127.9, 128.8, 138.8; MS (EI), m/z (%)=244 (M^+, 6), 117 (M^+–I, 100).

*4.3.9. 1-(1-Iodoethenyl)-4-pentylbenzene (**3i**).* Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7.1 Hz, 3H), 1.28–1.38 (m, 4H), 1.54–1.65 (m, 2H), 2.60 (t, J=7.6 Hz, 2H), 6.03 (s, 1H), 6.43 (s, 1H), 7.11 (d, J=8.5 Hz, 2H), 7.42 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 14.0, 22.5, 31.0, 31.4, 35.5, 107.7, 126.4, 128.0, 128.2, 139.0, 143.9; MS (EI), m/z (%)=300 (M^+, 3), 173 (M^+–I, 100).

*4.3.10. 1-(1-Iodoethenyl)-4-methoxybenzene (**3j**).*[5a] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 5.99 (d, J=1.8 Hz, 1H), 6.37 (d, J=1.8 Hz, 1H), 6.82 (d, J=9.2 Hz, 2H), 7.46 (d, J=8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 107.4, 113.5, 125.7, 129.5, 134.3, 160.1; MS (EI), m/z (%)=260 (M^+, 3), 133 (M^+–I, 100).

*4.3.11. 1-Bromo-4-(1-iodoethenyl)benzene (**3k**).*[6d] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.08 (d, J=0.9 Hz, 1H), 6.45 (d, J=1.4 Hz, 1H), 7.36 (d, J=8.8 Hz, 2H), 7.42 (d, J=8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.7, 123.1, 128.0, 129.7, 131.4, 140.7; MS (EI), m/z (%)=310 (M^++2, 3), 308 (M^+, 3), 183 (M^++2–I, 56), 181 (M^+–I, 62), 102 (M^+–I–Br, 100).

*4.3.12. 1-(1-Iodoethenyl)-4-(trifluoromethyl)benzene (**3l**).*[31] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.18 (d, J=2.0 Hz, 1H), 6.54 (d, J=2.0 Hz, 1H), 7.54–7.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.0, 125.3 (q, J_{C-F}=3.8 Hz), 126.8 (q, J_{C-F}=271.9 Hz), 128.5, 129.3, 130.2 (q, J_{C-F}=149.8 Hz), 145.2; MS (EI), m/z (%)=298 (M^+, 6), 171 (M^+–I, 100).

*4.3.13. 1-Cyano-4-(1-iodoethenyl)benzene (**3m**).* Yellow paste; ^1H NMR (400 MHz, $CDCl_3$) δ 6.21 (d, J=1.8 Hz, 1H), 6.56 (d, J=2.3 Hz, 1H), 7.44 (d, J=8.2 Hz, 2H), 7.66 (d, J=9.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.7, 118.3, 128.7, 129.3, 132.1, 132.4, 147.5; HRMS (EI) calcd for C_9H_6NI: 254.9545, found: 254.9540.

*4.3.14. (Z)-3-Iodo-1-phenylnon-2-en-1-one (**3n**).*[9c] Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, J=6.4 Hz), 1.25–1.40 (m, 6H), 1.60–1.68 (m, 2H), 3.05 (t, 2H, J=7.3 Hz), 7.44–7.48 (m, 2H), 7.54–7.60 (m, 1H), 7.62 (s, 1H), 7.91 (d, 2H, J=8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 28.3, 29.9, 31.6, 42.1, 128.5, 128.7, 130.5, 133.2, 136.5, 137.9, 188.5; MS (EI), m/z (%)=342 (M^+, 1), 215 (M^+–I, 100).

4.4. General procedure for the synthesis of internal iodoalkenes from silylalkyne using iodine, $Ph_2P(O)H$, and $Ph_2P(O)OH$

Under a nitrogen atmosphere, diphenylphosphine oxide (66.7 mg, 0.33 mmol) and diphenylphosphinic acid (70.4 mg, 0.33 mmol) were placed in a Schlenk tube at room temperature, followed by $CHCl_3$ (0.6 mL), iodine (58.4 mg, 0.23 mmol), and alkyne (0.3 mmol). The mixture was stood statically for 16 h at room temperature, and then MeOH (5 ml) was added to quench the reaction. After a while, the crude solution turned colorless from pale purple and white solid of $Ph_2P(O)OH$ was precipitated. The precipitate was filtered, and the crude solution was purified by preparative TLC (silica gel).

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