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Highly regioselective hydroselenation of inactivated terminal alkynes using diselenide–$Ph_2P(O)H$ mixed systems under visible-light irradiation

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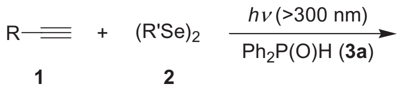
ABSTRACT

Upon visible-light irradiation, we could achieve a highly regioselective hydroselenation of inactivated terminal alkynes to give 1-(organylseleno)-1-alkenes by using diselenide–$Ph_2P(O)H$ mixed systems. The photoinduced hydroselenation presented in this study is advantageous as it does not involve the handling of oxygen-sensitive and foul-smelling selenols.

In recent years, the chemistry of organoselenium compounds has attracted a lot of interest as they can be used in a variety of applications such as biological active agents, functionalized molecules for electronic materials, and synthetic intermediates.[1] Among organoselenium compounds, vinyl selenides are useful intermediates for the synthesis of various vinyl and carbonylcompounds.[2] One of the most straightforward methods for the synthesis of vinyl selenides is the hydroselenation of alkynes with selenols.[3] The hydroselenation of alkynes has been studied under a variety of reaction conditions such as Michael-type addition,[4] radical addition,[4c,d,5] and transition-metal-catalyzed addition[6] of selenols to alkynes. Their regio- and/or stereoselectivities can be controlled by the choice of reaction conditions. However, these methods sometimes suffer from drawbacks such as the unpleasant smell of selenols and the rapid oxidation of selenols to their corresponding diselenides by atmosphericoxygen.[7] Therefore, developing a method for the hydroselenation of alkynes without using selenols as the selenium source is strongly desired. Thus, we focused on the use of diorganyl diselenides instead of selenols, because the diselenides are stable under an oxidizing atmosphere and do not have a foul smell. The hydroselenation of 'activated alkynes' (electron-deficient alkynes having electron-withdrawing groups such as carbonyl and aryl groups) using diselenides has already been achieved by mixing diselenides and alkynes with appropriate reductants through ionic reaction pathway.[8] In contrast, effective hydroselenation of inactivated alkynes (relatively electron-rich alkynes) using diselenides and reductant has not been achieved hitherto.[9] Herein, we report a highlyregioselective hydroselenation of inactivated alkynes **1** under visible-light irradiation by using a diselenide–$Ph_2P(O)H$ mixed system. The above reaction affords vinyl selenides **4** (Eq. (1)).



(1)

The photoinduced hydroselenation of alkynes with selenols via the formation of radicals is a useful and convenient method for the synthesis of vinyl selenides. If hydroselenation is performed using diselenides instead of selenols, it is essential to first reduce the diselenides to selenols. Moreover, in order to carry out hydroselenation as described above, high concentrations of starting material and neutral reaction conditions are needed. However, existing methods for the reduction of diselenides to selenols generally require acidic or basic conditions and/or large quantities of solvent.[10] Therefore these existing methods are not suitable for hydroselenation with diselenides via the formation of radicals. Thus, we investigated the hydroselenation of alkynes with diselenides by combining it with the reduction of diselenides using hydrogensources.

First, we examined the reaction of 1-octyne (**1a**) (1.0 mmol) with diphenyl diselenide (**2a**) (0.20 mmol) in the presence of

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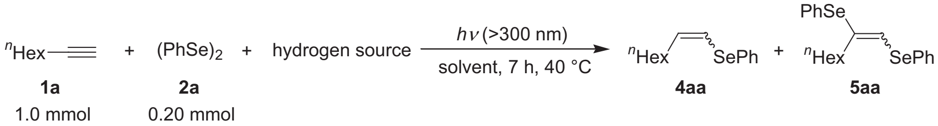
several hydrogen sources upon photoirradiation with a tungsten lamp (500 W) through a sealed Pyrex tube ($h\nu$ >300 nm) (Table 1). When 0.24 mmol of diphenylphosphine oxide (**3a**) was used as the hydrogen source, 0.15 mmol of 1-(phenylseleno)-1-octene (**4aa**) (77%) was obtained and 0.18 mmol of selenophosphine oxide ($PhSe–P(O)Ph_2$) was detected by ^{31}P and ^{77}Se NMR[11] (entry 1). Under theseconditions, the bisselenated compound (**5aa**) was also obtained as a byproduct, because **2a** could also add to alkynes under photoirradiation.[12] Use of diphenylphosphine (**3b**) instead of **3a** also afforded **4aa** in good yields (entry 2). However, the complex mixture also contained hydrophosphination[13] and phosphinoselenation[14] products of **1a**. On the other hand, diethyl phosphite (**3c**) did not promote the desired hydroselenation (entry 3). Tris(trimethylsilyl)silane (**6a**) caused the hydroselenation of **1a**, along with the formation of the corresponding selenosilane ($PhSe–Si(SiMe_3)_3$), whichwas detected using ^{29}Si and ^{77}Se NMR (entry 4).[15] However, **6a** also caused undesired bisselenation resulting in the formation of **5aa** in measurable yield. In contrast, the reaction with another hydrosilane, such as triethylsilane (**6b**), gave only **5aa** (entry 5). Tri-*n*-butyltin hydride (**7**), a typical hydrogen source, afforded the hydroselenation product in moderate yield with good selectivity (entry 6). When **7** was used as hydrogen source, a byproduct bearing a selenium-heteroatom bond, selenostannane ($PhSe–Sn^nBu_3$) was detected by ^{77}Se and ^{117}Sn, ^{119}Sn NMR.[16,17] 1,4-Cyclohexadiene (**8**) was found to be an unsuitable hydrogen source for hydroselenation, as it afforded **4aa** in poor yields and the bisselenated product **5aa** in large amounts (entry 7). These results clearly indicated that **3a** was the most appropriate hydrogen source for this hydroselenation reaction. Next, the effects of the $(PhSe)_2$/hydrogen source molar ratios, concentration of the starting materials, and solvent on the reaction were investigated. The hydroselenation product **4aa** was obtained selectively in excellent yield when 2.0 equiv of **3a** were used (entry 8). Although **4aa** was obtained in high yields when $CHCl_3$ was used as the solvent, the selectivity was reduced (entry 9). When hydroselenation was conducted in low concentrations of the solvent, theyields of the desired product decreased (entries 10 and 11).

Next, we investigated the substrate scope of this hydroselenation reaction (Table 2).[18] Hydroselenation of an aliphatic alkyne, 1-octyne (**1a**), using bis(*p*-methylphenyl) diselenides (**2b**) and 2.0 equiv of **3a** proceeded regioselectively to afford 1-(*p*-methylphenylseleno)-1-octene (**4ab**) in good yields with preferential *cis*-stereoselectivity (entry 2). In contrast, hydroselenation using bis(*p*-trifluoromethylphenyl) diselendes (**2c**) proceeded only slightly under the same conditions (entry 3). After the reaction, diselenide (**2c**) wascompletely consumed leaving behind large amounts of *p*-trifluoromethylbenzeneselenol. It is known that the photoinduced hydroselenation of alkynes with selenols is accelerated in the co-presence of small amounts of diselenide.[5] Therefore, we examined the hydroselenation of **2c** under milder reducing conditions (i.e., 1.2 equiv of $Ph_2P(O)H$ and $CHCl_3$ (0.1 mL)), so as to not consume the diselenide entirely. Carrying out the reaction in the presence of $CHCl_3$ as the solvent significantly improved the yield of 1-(*p*-trifluoromethylphenylseleno)-1-octene (**4ac**). When other diaryl diselenides (**2d–g**) were employed for the hydroselenation, 1-(arylseleno)-1-octenes (**4ad–ag**) were obtainedin good yields under mild conditions (entries 5–8). This hydroselenation reaction could also be applied to other aliphatic alkynes, such as 6-chloro-1-hexyne (**1b**) and 5-methyl-1-hexyne (**1c**) (entries 9–12). Diselenides bearing a 1- or 2-naphthyl group (**2h–i**) could also be used for this hydroselenation, although longer reaction times were required (entries 11 and 12). Aromatic alkynes can also be employed in this hydroselenation reaction (entry 13). The use of di-*n*-butyl diselenide (**2j**) successfully gave the corresponding adduct having an *n*-butylseleno group. This result was noteworthy because butaneselenol is difficult to handle and has a particularly bad smell (entry 14).[7] The hydroselenation of an internal alkyne (4-octyne, **1e**) or an alkene (1-decene,**9**) was not effec tive (entries 15 and 16).

The pathway for the present hydroselenation of alkynes using diselenides and diphenylphosphine oxide is discussed below. Although diselenides react smoothly with diphenylphosphine oxide to give the corresponding selenols and selenophosphine oxide, a small amount of diselenides remained.[6f] Previously, our group reported that the photoinduced hydroselenation of alkynes with benzeneselenol was catalyzed effectively by the addition of small amounts of diphenyl diselenide.[5] Based on our previous study, diselenides can catalyze the addition reaction of selenols to alkynes in the present hydroselenation reaction as well. On Table 2, entry 3, the hydroselenation did not proceed efficiently. In this case, ^{77}Se NMR measurements of the resulting mixture (formed after the reaction) indicated that the diselenide had been

Table 1

Hydroselenation of 1-octyne (**1a**) with diphenyl diselenide (**2a**) and several hydrogen sources



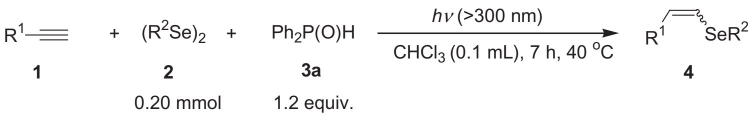
Entry	Hydrogen source	$(PhSe)_2$:hydrogen source[a]	Solvent	Yield of **4aa**[b,c]	Yield of **5aa**[b] (%)
1	$Ph_2P(O)H$ (**3a**)	1:1.2	None	77% [*E*/*Z* = 8/92]	6
2	Ph_2PH (**3b**)	1:1.2	None	74%	12
3	$(EtO)_2P(O)H$ (**3c**)	1:1.2	None	Trace	89
4	$(Me_3Si)_3SiH$ (**6a**)	1:1.2	None	32% [*E*/*Z* = 13/87]	31
5	Et_3SiH (**6b**)	1:1.2	None	0%	94
6	$^nBu_3SnH$ (**7**)	1:1.2	None	39% [*E*/*Z* = 15/85]	Trace
7	1,4-Cyclohexadiene (**8**)	1:1.2	None	13% [*E*/*Z* = 37/63]	78
8	$Ph_2P(O)H$ (**3a**)	1:2	None	93% (81%) [*E*/*Z* = 21/79]	0
9	$Ph_2P(O)H$ (**3a**)	1:1.2	$CHCl_3$ (0.1 mL)	93% (77%) [*E*/*Z* = 26/74]	4
10	$Ph_2P(O)H$ (**3a**)	1:2	$CHCl_3$ (0.5 mL)	54% [*E*/*Z* = 25/75]	0
11	$Ph_2P(O)H$ (**3a**)	1:2	C_6H_6 (0.5 mL)	35% [*E*/*Z* = 22/78]	0

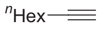
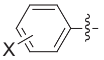
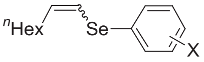
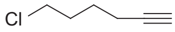
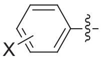
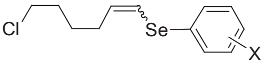
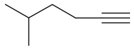
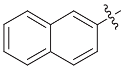
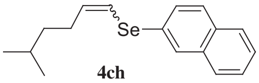
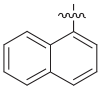
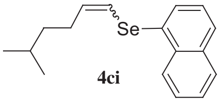
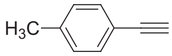
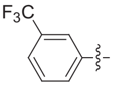
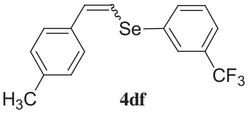
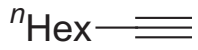
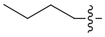
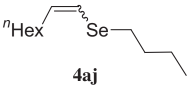
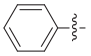
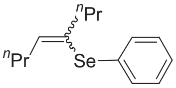
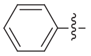
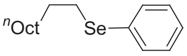
[a] Molar ratios.

[b] Determined by ^1H NMR. Isolated yield is shown in parentheses.

[c] Yields are calculated based on molecular weight of **2a**.

Table 2
Hydroselenation of several alkynes (**1**) with several diselenide (**2**) and diphenylphosphine oxide (**3**)



Entry	**1**	R^2	**1**:**2**[a]	**4**	Yield of **4** [*E*/*Z*][b]
	 **1a**		5:1		
1[c]		X=H (**2a**)		X=H (**4aa**)	81% [*E*/*Z* = 21/79]
2[c]		=*p*-CH_3 (**2b**)		=*p*-CH_3 (**4ab**)	83% [*E*/*Z* = 18/82]
3[c]		=*p*-CF_3 (**2c**)		=*p*-CF_3 (**4ac**)	(10%)
4					90% [*E*/*Z* = 32/68]
5		=*p*-F (**2d**)		=*p*-F (**4ad**)	63% [*E*/*Z* = 14/86]
6		=*m*-CH_3 (**2e**)		=*m*-CH_3 (**4ae**)	85% [*E*/*Z* = 27/73]
7		=*m*-CF_3 (**2f**)		=*m*-CF_3 (**4af**)	65% [*E*/*Z* = 16/84]
8		=*m*-F (**2g**)		=*m*-F (**4ag**)	81% [*E*/*Z* = 18/82]
	 **1b**		5:1		
9		X=H (**2a**)		X=H (**4ba**)	77% [*E*/*Z* = 24/76]
10		=*p*-CH_3 (**2b**)		=*p*-CH_3 (**4bb**)	68% [*E*/*Z* = 7/93]
11[d]	 **1c**	 **2h**	5:1	 **4ch**	63% [*E*/*Z* = 25/75]
12[d]		 **2i**	5:1	 **4ci**	85% [*E*/*Z* = 12/88]
13	 **1d**	 **2f**	1.2:1	 **4df**	92% [*E*/*Z* = 39/61]
14[c,e]	 **1a**	 **2j**	5:1	 **4aj**	90% [*E*/*Z* = 29/71]
15	 **1e**	 **2a**	5:1	 **4ea**	(24%) [*E*/*Z* = 12/88]
16[c,f]	 **9**	 **2a**	5:1	 **10**	(14%)

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[a] Molar ratios.

[b] Isolated yields (NMR yields are shown in the parentheses). Yields are calculated based on molecular weight of **2**.

[c] $Ph_2P(O)H$ **3a** (0.4 mmol, 2.0 equiv) was used in the absence of solvent (condition of entry 8 in Table 2).

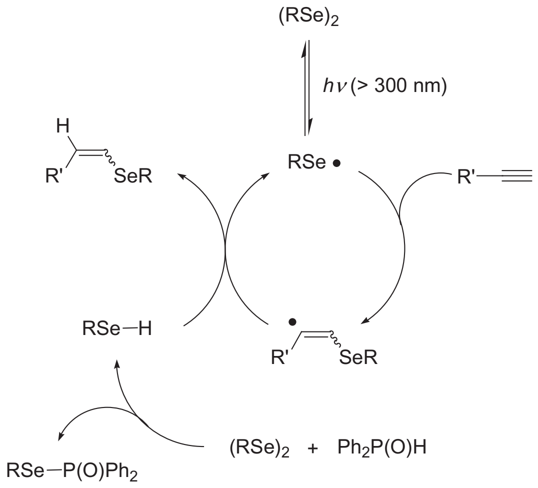
[d] Irradiated for 15 h.

[e] Stirred for 1 h beforeirradiation.

[f] Irradiated for 24 h.

converted completely to selenol and selenophosphine oxide and no diselenide was detected. On the other hand, when the hydroselenation proceeded well, small amounts of diselenides were detected. Therefore, it appears that in order for the hydroselenation reaction to proceed well, small amounts of diselenides were needed during the reaction. Since the rate of diselenide reduction with diphenylphosphine oxide depends on the substituent in the diselenide, tuning the reaction conditions is important for this reaction. On the basis of these considerations, a plausible reaction pathway for the hydroselenation is shown in Scheme 1. First, visible-light irradiation triggers homolytic cleavage of the Se–Se single bond in the unreacted diselenide,[19] generating the corresponding seleno radicals. Next, attack of the seleno radical on the terminal carbon of alkynes leads to vinyl radical intermediates. The vinyl radicals are captured by selenols[20] to produce hydroselenation products[21] along with regeneration of the seleno radicals. Moreover, $Ph_2P(O)SeR$, which is generated as a by-product, does not add to alkynes. This is in contrast to the addition reaction of unoxidized Ph_2PSePh and alkynes.[14] This is also an important reason that makes the present hydroselenation system so simple.

In conclusion, we have developed a highly regioselective hydroselenation of inactivated terminal alkynes by using novel diselenide–$Ph_2P(O)H$ mixed systems. It has been found that regulation of the reducing conditions can control the desired hydroselenation. The method for the hydroselenation of alkynes discussed in this study is user-friendly because it does not involve the use of selenols.



Scheme 1. A plausible reaction pathway for hydroselenation using the diselenide–Ph$_2$P(O)H mixed systems.

Acknowledgments

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Supplementary data

Supplementary data (general comments, spectral and analytical data, and copies of ^{1}H NMR,^{13}C NMR, and ^{77}Se NMR spectra of vinyl selenides) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.07.127.

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16. *Spectral data of PhSe–Sn^{n}Bu$_3$*: ^{77}Se NMR (CDCl$_3$) δ −27 (with 4 satellites $J_{\text{Se–117Sn}}$ = 957 Hz, $J_{\text{Se–119Sn}}$ = 999 Hz); ^{117}Sn NMR (CDCl$_3$) δ 66.6 ppm (with 2 satellites $J_{\text{117Sn–Se}}$ = 957 Hz); ^{119}Sn NMR (CDCl$_3$) δ 65.6 ppm (with 2 satellites $J_{\text{119Sn–Se}}$ = 999 Hz).
17. It was reported that selenostannane was synthesized from diphenyl diselenide and tri-*n*-butyltin hydride. See, Crich, D.; Hwang, J.-T.; Gastaldi, S.; Recupero, F.; Wink, D. J. *J. Org.Chem.* **1999**, *64*, 2877.
18. *General Procedure for Photoinduced Hydroselenation of Alkynes or Alkenes with Diselenides and Diphenylphosphine Oxide:* Diphenylphosphine oxide (48.5 mg, 0.24 mmol), diselenide (0.20 mmol), alkyne or alkene (1.0 mmol), and chloroform (0.10 mL) were placed in a sealed Pyrex glass tube under nitrogen. The mixture was irradiated with a tungsten lamp (500 W) for 7 h. After the reaction, purification of the crude product was performed by preparative TLC or silica gel column chromatography using hexane as eluent.
19. When the reaction was conducted in dark condition, only trace amount of **4** was obtained.
20. In the reaction system, adequate amount of selenol and diphenylphosphine oxide are present. Selenols are known as effective hydrogen source for the carbon-centered radicals (the rate constant $k = 2.1 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$, Newcomb, M. Choi, S.-Y. Horner, J. H. *J. Org, Chem.* **1999**, *64*, 1225). Although the capturing ability of carbon-centered radicals of diphenylphosphine oxide has not been investigated directly, this ability of other P–H bond compound (dicyclohexylphosphine) has been known ($k = 2.5 \times 10^3\ \mathrm{M^{-1}\,s^{-1}}$, Franz, J. A. Suleman, N. K.Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19). Based on these rate constants, we assume that selenols are almost the only hydrogen source to vinyl radicals.
21. Once-formed **(*Z*)-4** cannot isomerize to **(*E*)-4** under photoirradiation (λ >300 nm).