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A Direct Synthesis of Trisubstituted Allenes from Propargyl Alcohols via Oxaphosphetane Intermediates

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Nagatoshi Nishiwaki received his Ph. D. in 1991 from Osaka University. He worked at Professor Ariga's group in Department of Chemistry, Osaka Kyoiku University as assistant professor (1991-2000) and as associate professor (2001-2008). From 2000 to 2001, he joined to Karl Anker Jørgensen's group at Århus University in Denmark. He worked at Center for Collaborative Research, Anan National College of Technology as associate professor from 2008 to 2009. Then, he moved to School of Environmental Science and Engineering, Kochi University of Technology in 2009, and he is a professor from 2011. His research interests comprise synthetic organic chemistry using nitro compounds, heterocycles (synthesis, ring transformation, 1,3-dipolar cycloaddition, application as tools in organic synthesis), pseudo-intramolecular reaction, and solid supported palladium catalysts.

Abstract

A direct synthetic method for trisubstituted allenes from propargyl alcohol is provided; the synthesis proceeds *via* an oxaphosphetane intermediate. Functional groups such as formyl and pyridyl exhibited a degree of tolerance during reaction without any protection. The alcohol dimethylated at the propargyl position afforded two structural isomers, allene and 1,3-diene. The product ratio was considerably influenced by the solvent. Allene was predominantly obtained when the reaction was conducted in cyclohexane, and the ratio was inverted by changing the solvent to dichloromethane. The prepared (2-pyridyl)allene served as a substrate for the copper(I) catalyzed cyclization reaction to afford 3,3-dimethylindorizine-2-one.

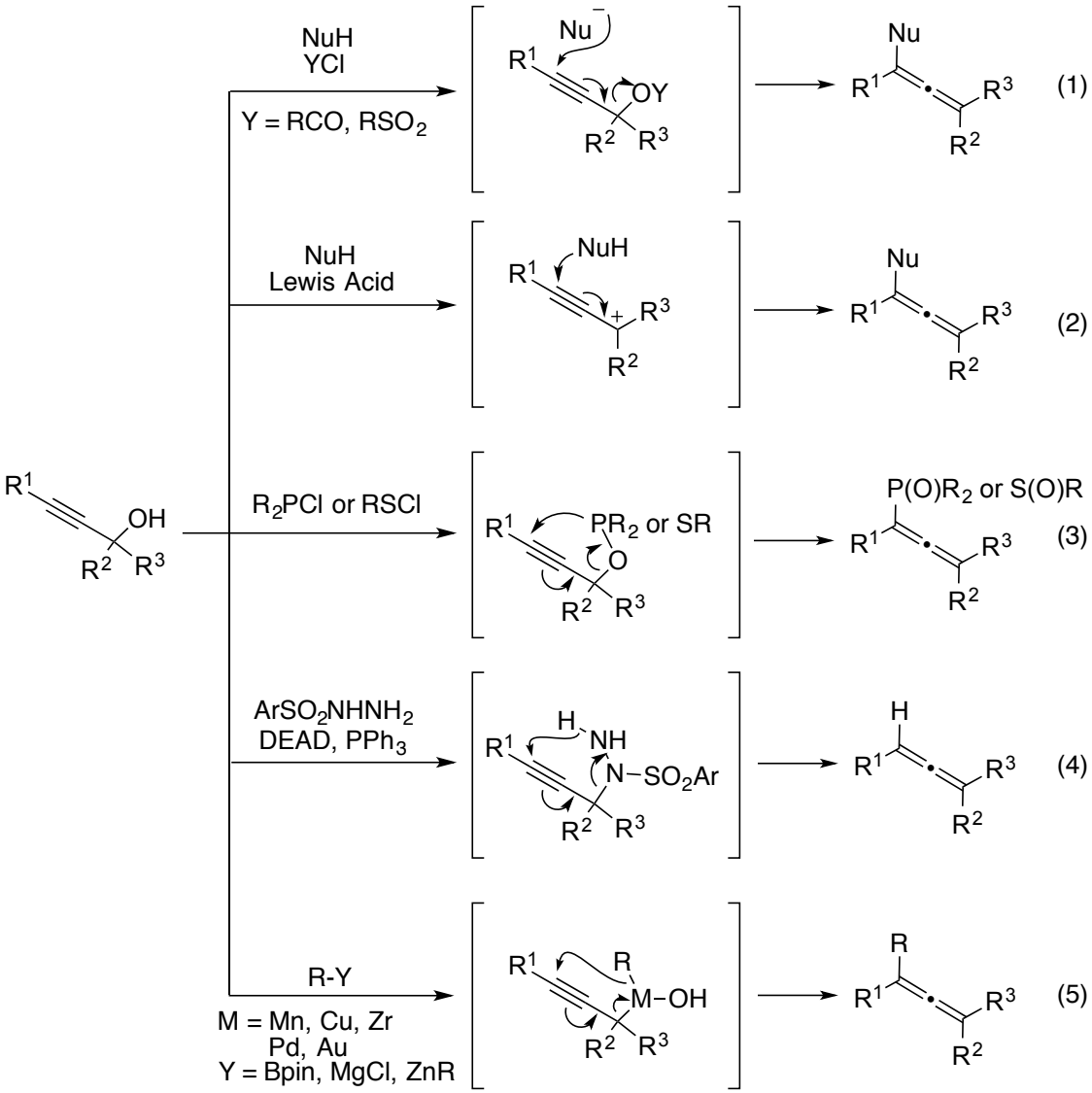
1. Introduction

The allene framework is often found as an important motif in natural products, and substituted allenes have been recognized as useful building blocks for construction of both carbo- and heterocyclic systems.[1] Many synthetic protocols for allenes have been developed, among which chemical transformations from readily available propargyl alcohols are commonly used methods (Scheme 1). The nucleophilic substitution of the hydroxy group in S_N2' fashion is the most common method for preparing substituted allenes, in which the hydroxy group is converted to ester function for a better elimination (Eq. 1).[2,3] In the case of neutral nucleophiles, the generation of a propargylic cation is effective upon treatment of propargyl alcohol with a Lewis acid (Eq. 2).[2,4] The migration of the heteroatoms or hydrogen is also acceptable. *O*-Phosphinylated- or O-sulfenylated propargyl alcohol facilitates the introduction of a heteroatom into the allene framework (Eq. 3).[2,5] Moreover, sulfonylhydrazine prepared by the Mitsunobu reaction furnished trisubstituted allenes as a result of 1,5-hydrogen shift (Eq. 4).[2,6] Although these protocols are certainly useful methods, additional experimental manipulations or the use of highly reactive regents are required, which sometimes prevent the synthesis of functionalized allenes. As an alternative approach, transition-metal-catalyzed synthesis is also developed, however, the products are sometimes contaminated with intrinsically toxic and expensive transition metals (Eq. 5).[2,7]

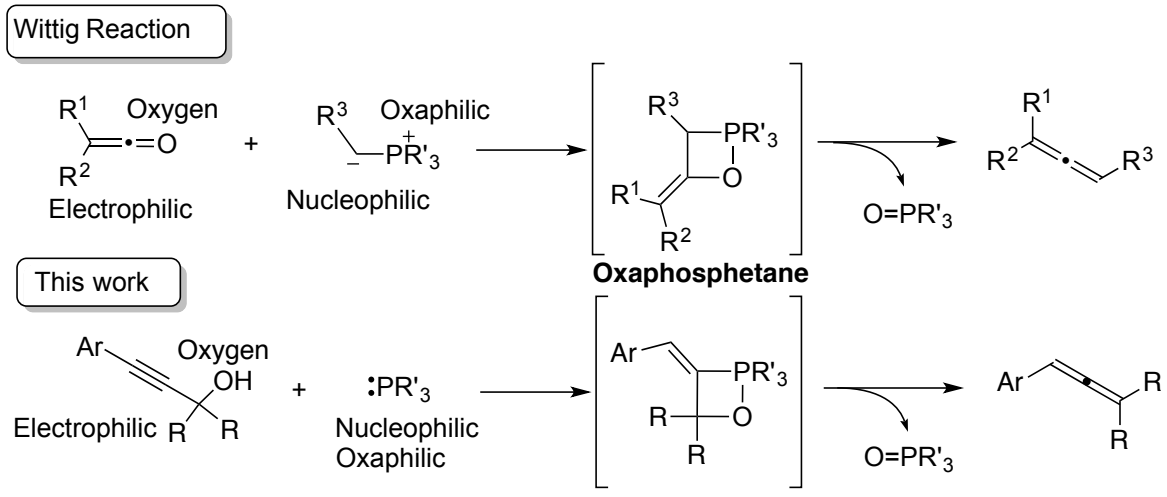
Additionally, allenes are also prepared by the Wittig reaction *via* the oxaphosphetane intermediate (Scheme 2).[2,8] In this reaction, unstable ketenes and reactive phosphine ylide should be used under basic conditions, which prevents the practical use of this method. In other words, allenes are promisingly synthesized if oxaphosphetane is constructed by an alternative method. From this viewpoint, we paid attention to propargyl alcohol because the oxygen atom and an electrophilic triple bond are considered to form an oxaphosphetane framework upon treatment with an oxaphilic and nucleophilic phosphine. Although there are numerous reports on the preparation of allenes, this protocol has not been reported except for only a few descriptions with a limited substrate scope.[8] These circumstances prompted us to study this reaction in detail, and functionalized allenes could be successfully prepared directly from propargyl alcohol under mild conditions even in the absence of a transition metal.

2. Results and Discussion

When propargyl alcohol **1a** was allowed to react with tributylphosphine in toluene at room temperature for 1 d, the desired allene **2a** was obtained in 48% yield (Table 1, Entry 1). The structure of **2a** was confirmed by observing the characteristic signal for the cumulene carbon at 200 ppm in the ^{13}C NMR spectrum. In this reaction, 1,3-diene **3a**[9] was also isolated in 17% yield. Although products **2a** and **3a** are structural isomers, interconversion between **2a** and **3a** did not occur upon treatment with tributylphosphine under the same conditions. Therefore, each product was formed through different reaction paths.



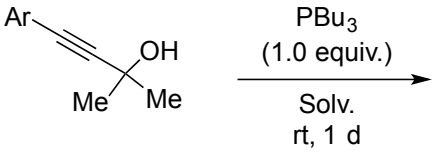
Scheme 1. Synthetic methods of allenes starting from propargyl alcohols



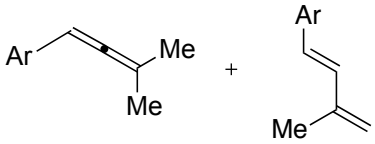
Scheme 2. Synthetic strategy of allenes *via* an oxaphosphetane intermediate

The product ratio **2a**/**3a** was considerably affected by the solvent (Table 1). When the reaction was conducted in non-polar solvents such as toluene, hexane, cyclohexane, and diethyl ether, allene **2a** was predominantly formed (Entries 1–4), and yield and selectivity of allene **2a** increased up to 70% and 83%, respectively, when cyclohexane was employed as a solvent (Entry 3). Notably, the ratio was inverted when the reaction was conducted in ethyl acetate or in a halogenated solvent such as dichloroethane and dichloromethane (Entries 5–7).

Table 1. Study on solvents



1a Ar = 4-$NO_2C_6H_4$

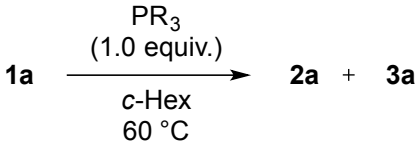


2a **3a**

Entry	Solvent	Yield (%)		Ratio	Recovery of
		2a	**3a**	**2a**/**3a**	**1a** (%)
1	PhMe	48	17	74/26	18
2	Hexane	57	18	76/24	6
3	*c*-Hex[a]	70	14	83/17	6
4	Et_2O	64	22	75/25	9
5	EtOAc	27	47	36/64	14
6	$ClCH_2CH_2Cl$	15	43	26/74	20
7	CH_2Cl_2	17	69	20/80	11

[a] Cyclohexane

Table 2. Study on phosphines

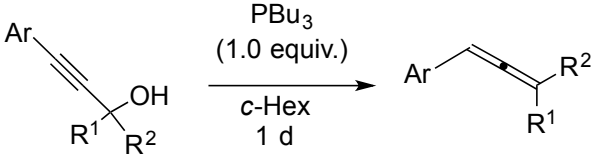


Entry	PR_3	Time (h)	Yield (%)		Ratio
			2a	**3a**	**2a**/**3a**
1	PBu_3	5	69	15	82/18
2	PEt_2Ph	5	68	17	80/20
3	$PEtPh_2$	5	40	3	93/7
4	$PEtPh_2$	24	58	5	92/8
5	PPh_3[a]	5	0	0	—

[a]At 100 °C

The reaction time could be shortened by conducting the reaction at 60 °C (Table 2, Entry 1). Thereafter, several kinds of phosphines were surveyed. Diethylphenylphosphine showed similar reactivity to tributylphosphine to afford allene **2a** (Entries 1 and 2). To our delight, ethyldiphenylphosphine considerably increased the selectivity of allene **2a**, although the yield decreased (Entry 3). This disadvantage was overcome by conducting the reaction over a longer period of time, which afforded allene **2a** with 58% yield and 92% selectivity (Entry 4). However, triphenylphosphine caused no reaction even at 100 °C, which is presumably due to the steric hindrance (Entry 5).

Table 3. Synthesis of other allene derivatives **2**

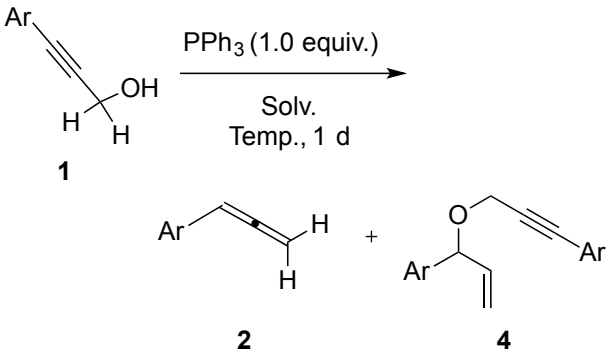


1 **2**

Entry	Ar	R^1	R^2		Temp. (°C)	Yield (%)
1	4-MeC_6H_4	Me	Me	**b**	60	0
2	4-MeC_6H_4	Me	Me	**b**	100	0
3	4-$CF_3C_6H_4$	Me	Me	**c**	100	14
4	4-$HCOC_6H_4$	Me	Me	**d**	60	14
5	4-$HCOC_6H_4$	Me	Me	**d**	100[a]	34
6	2-Pyridyl	Me	Me	**e**	60	37
7	4-$NO_2C_6H_4$	Ph	Ph	**f**	60	50[b]
8	4-$NO_2C_6H_4$	$Ph(CH_2)_2$	H	**g**	rt	cm[c]
9	4-$NO_2C_6H_4$	H	H	**h**	rt	cm[c]

[a] For 4 h. [b] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [c] A complex mixture was obtained.

Table 4. Synthesis of monosubstituted allenes



Entry	Ar		Solv.	Temp. (°C)	Yield (%)	
					2	**4**
1	4-$NO_2C_6H_4$	**h**	*c*-Hex[a]	60	0	42
2	4-$NO_2C_6H_4$	**h**	PhMe	60	trace	52
3	4-$NO_2C_6H_4$	**h**	1,4-Dioxane	60	24	0
4	4-$NO_2C_6H_4$	**h**	1,4-Dioxane	100	36	0
5	4-$HCOC_6H_4$	**i**	1,4-Dioxane	100	30	0

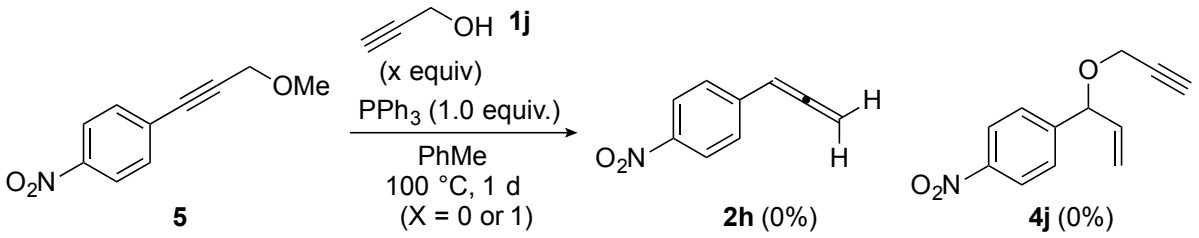
[a] Cyclohexane

Synthesis of other allene derivatives **2b–h** was studied under the optimized conditions in hand (Table 3). In each reaction, the formation of diene **3** was not observed. In the case of electron-rich propargyl alcohol **1b**, no reaction occurred due to the low electrophilicity of the ethynyl group even at 100 °C, which prevented the initial addition of a phosphine (Entries 1

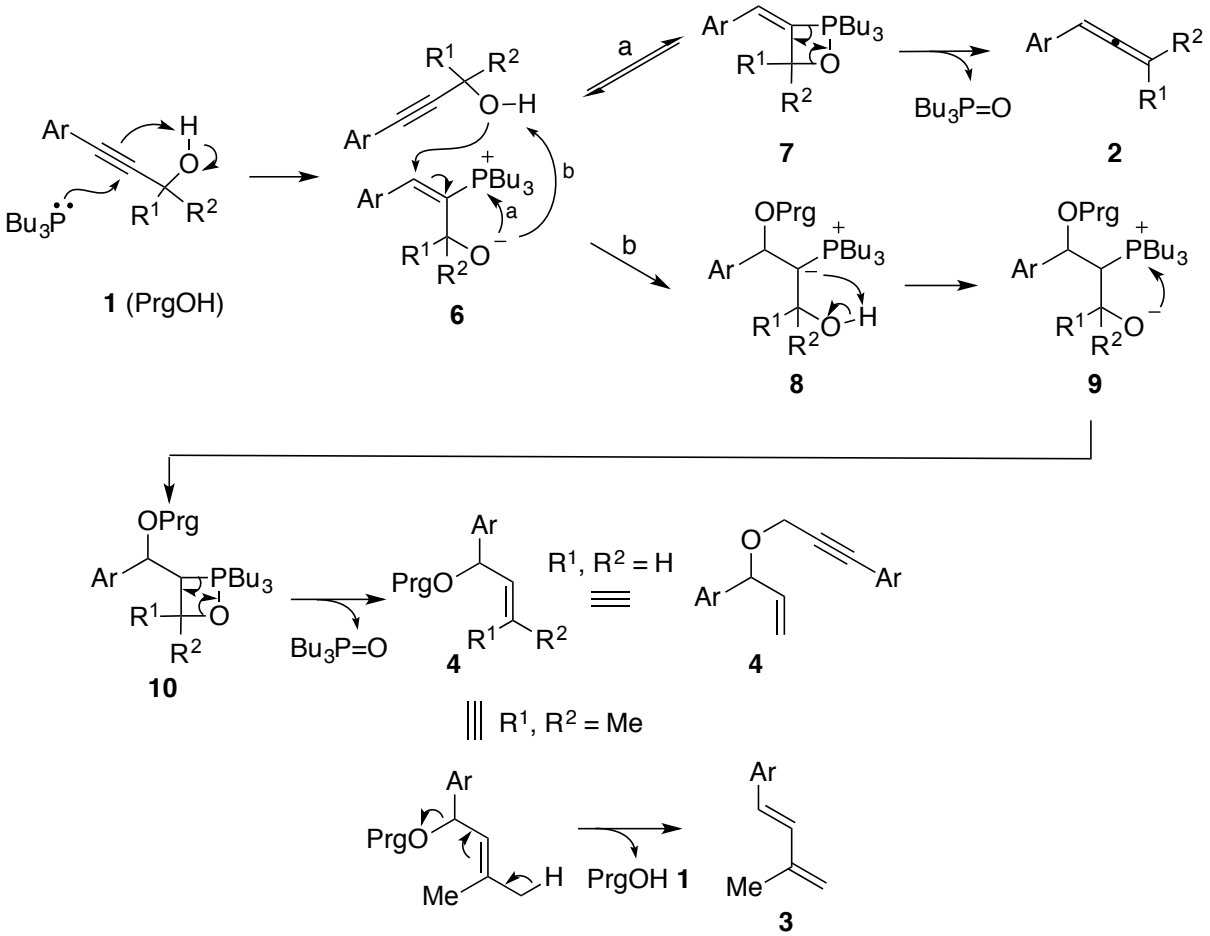
and 2). However, electron-poor propargyl alcohols **1c–e** underwent a reaction to afford the corresponding allenes **2c–e** possessing a functional group such as 4-trifluoromethylphenyl, 4-formylphenyl, and 2-pyridyl group (Entries 2–6). It is noteworthy that the highly reactive formyl group of **1d** exhibits a degree of tolerance during the reaction without any protection in a single step. It was possible to modify the substituents at the propargyl position, and triarylated allene **2f** could be synthesized when diphenyl substituted alcohol **1f** was used (Entry 7). However, propargyl alcohols **1g** and **1h** yielded only a complicated mixture due to side reactions under the employed conditions (Entries 8 and 9). Since the formed allenes **2g** and **2h** are highly reactive, they underwent the further reactions with reactive tributylphosphine.

In order to synthesize monosubstituted allene by this protocol, reaction conditions were investigated using **1h** as a model substrate and by using less reactive triphenylphosphine instead of tributylphosphine (Table 4). When the reaction was conducted at 60 °C, dimerization of **1h** predominantly proceeded to afford allyl propargyl ether **4h** (Entries 1 and 2). This undesired dimerization was suppressed by conducting the reaction in the polar solvent, 1,4-dioxane, to afford allene **2h**,[10] which resulted in an increase to the yield at higher temperatures (Entries 3 and 4). This method was applicable to alcohol **1i**, leading to the formation of formyl substituted allene **2i**[10] without detectable dimer **4i** (Entry 5).

To realize the role of the hydroxy group in this reaction, *O*-methylated substrate **5** was employed (Scheme 3). When propargyl ether **5** was heated with triphenylphosphine (x = 0), no reaction was observed at all, which indicates that the hydroxy group is crucial for the formation of allene **2**. Furthermore, ether **5** was quantitatively recovered even when the reaction was conducted in the presence of propargyl alcohol **1j** (x = 1), and the corresponding allyl propargyl ether **4j** was not detected. The hydroxy group was found to be also necessary for the formation of ether **4**.



Scheme 3. Study on the hydroxy group propargyl alcohols **1** by the reaction using *O*-methylated substrate **5**



Scheme 4. A plausible mechanism for formation of **2**, **3** and **4**

On the basis of these results, a plausible mechanism for the formation of allene **2** and 1,3-diene **3** is proposed (Scheme 4). This reaction was initiated by nucleophilic attack of a phosphine to the alkynyl moiety to afford betaine intermediate **6** (route a), which serves as a common intermediate for all products. Adding anionic oxygen to phosphonium moiety affords oxaphosphetane **7**, from which phosphine oxide is eliminated leading to allene **2**. However, when alcohol **1** attacks **6**, betaine **9** is formed *via* **8** (route b). After cyclization of **9**, elimination of phosphine oxide yields allyl propargyl ether 4 (R^1, R^2 = H) *via* oxaphosphetane **10**. When substituents of **4** (R^1 and R^2) are methyl groups, deprotonation accompanied by the elimination of alcohol **1**, successively occurs to furnish diene **3**.

In non-polar solvents, such as cyclohexane, betaine **6** is not stabilized enough, which facilitates the intramolecular cyclization prior to intermolecular addition of alcohol **1** to afford allene **2** predominantly. When bulky phosphine is employed, the approach of alcohol **1** to betaine **6'** was prevented, which resulted in the predominant formation of allene **2a** *via* route a (Figure 1).

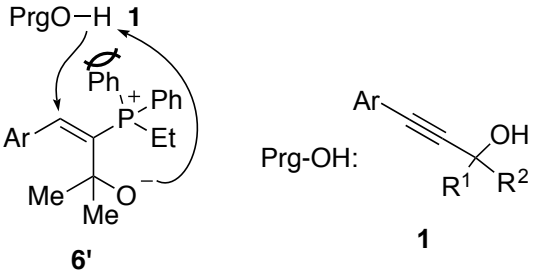
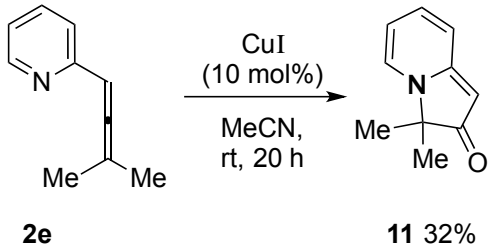
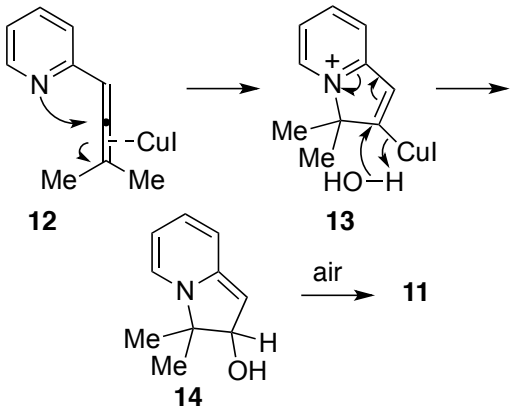


Figure 1. Effect by the substituents of the phosphine

This method facilitates the synthesis of functionalized allenes **2**, among which pyridylallene **2e** served as a precursor of indolizinone **11**.[11] When a solution of **2e** in acetonitrile was stirred at room temperature for 1 day in the presence of copper(I) iodide, copper–catalyzed cyclization readily proceeded to afford indolizinone **11** with a moderate yield (Scheme 5). Although other mechanism including radical species is also possible, a plausible mechanism is shown in Scheme 6. The activated allene moiety by copper is attacked by the ring nitrogen to form a five-membered ring **13**. After protonation and hydroxylation by a water, the resultant **14** is oxidized by air to afford indolizinone **11**.



Scheme 5. Synthesis of indolidinone **11** from pyridylallene **2e**



Scheme 6. A plausible mechanism for forming **11**

3. Conclusion

We provided a direct synthesis of functionalized allenes **2** from easily available propargyl alcohols **1** upon treatment with phosphine, which proceeded *via* oxaphosphetane intermediate. This method does not require the use of any transition metal, thereby avoiding the contamination of the products. Moreover, functional groups such as trifluoromethyl, formyl and pyridyl groups exhibited a degree of tolerance during the reaction without any protection. These features are advantageous for practical use.

In addition to allenes **2**, electron-deficient diene **3a** and allyl propargyl ether **4h** were also formed. These products could be synthesized with high selectivity by changing the solvents. Furthermore, indolizinone **11** was synthesized from pyridylallene **2e** by copper-catalyzed cyclization.

4. Experimental

General

The melting points were determined on SRS-Optimelt Automated Melting Point System, and are uncorrected. All the reagents and solvents were commercially available and used as received. The ^{1}H NMR spectra were measured on a Bruker Ascend-400 at 400 MHz with tetramethylsilane as an internal standard. The ^{13}C NMR spectra were measured on a Bruker Ascend-400 at 100 MHz, and assignments of ^{13}C NMR spectra were performed by DEPT experiments. The high-resolution mass spectra were measured on an AB SCIEX Triple TOF 4600. The IR spectra were recorded on a JASCO FT/IR-4200 spectrometer.

General method for preparation of allenes 2

To the suspension of propargyl alcohol **1a** (41.0 mg, 0.2 mmol) in cyclohexane (2 mL), tributylphosphine (50 μL, 0.2 mmol) was added. A resultant mixture was stirred for 1 d at room temperature, and the solvent was removed *in vacuo*. The residue was subjected to silica gel column chromatography (hexane/ethyl acetate = 95/5) to afford allene **2a** (26.5 mg, 0.14 mmol 70%) as a pale-yellow oil.

When other propargyl alcohols were used, the reaction was conducted in a same way.

3-Methyl-1-(4-nitrophenyl)-1,2-butadiene (2a)

IR (ATR, cm^{-1}) 1952, 1517, 1340; ^{1}H NMR ($CDCl_3$, 400

MHz) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 6.05 (sep, *J* = 2.8 Hz, 1H), 1.85 (d, *J* = 2.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 205.4 (C), 146.1 (C), 143.4 (C), 126.9 (CH), 123.9 (CH), 100.4 (C), 91.7 (CH), 19.9 (CH_3); HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{11}H_{11}NNaO_2$ 212.0682; found 212.0675.

3-Methyl-1-{(4-trifluoromethyl)phenyl}-1,2-butadiene (2c)

Colorless oil. IR (ATR, cm^{-1}) 1955; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.00 (sep, *J* = 2.8 Hz, 1H), 1.83 (d, *J* = 2.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.2 (C), 139.9 (C), 128.1 (C), 126.6 (CH), 125.3 (CH), 124.2 (q, J_{C-F} = 269.8 Hz), 99.8 (C), 91.8 (CH), 20.0 (CH_3); HRMS (ESI-TOF) *m/z* $[M+K]^+$ Calcd for $C_{12}H_{11}F_3K$ 251.0444; found 251.0447.

3-Methyl-1-(4-formylphenyl)-1,2-butadiene (2d)

Colorless oil. IR (ATR, cm^{-1}) 1951, 1693, 1602; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.95 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.04 (sep, *J* = 3.2 Hz, 1H), 1.84 (d, *J* = 3.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 205.0 (C), 191.6 (CH), 142.9 (C), 134.6 (C), 130.1 (CH), 127.0 (CH), 99.9 (C), 92.3 (CH), 19.9 (CH_3); HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{13}O$ 173.0960; found 173.0956.

3-Methyl-1-(2-pyridyl)-1,2-butadiene (2e)

Pale-yellow oil. IR (ATR, cm^{-1}) 1958; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (br d, *J* = 4.8 Hz, 1H), 7.50 (ddd, *J* = 8.0, 8.0, 1.2 Hz, 1H), 7.57 (d, *J* = 8.0, 1.2 Hz, 1H), 7.57 (d, *J* = 8.0, 4.8 Hz, 1H), 6.10 (sep, *J* = 3.2 Hz, 1H), 1.77 (d, *J* = 3.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 205.1 (C), 156.0 (C), 149.3 (CH), 136.0 (CH), 121.2 (CH), 120.8 (CH), 99.7 (C), 94.3 (CH), 20.0 (CH_3); HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{10}H_{11}N$ 146.0964; found 146.0964.

1-(4-Nitrophenyl)-3,3-diphenylpropanediene (2f)

Although the formation of allene **2f** was confirmed by measuring HRMS and IR spectra of the reaction mixture, it could not be isolated even after several attempts because of the instability. IR (ATR, cm^{-1}) 1927; HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{21}H_{15}NNaO_2$ 336.0995; found 336.0984.

1,5-Bis(4-nitrophenyl)-4-oxahept-6-ene-1-yne (4h)

Yellow oil. IR (ATR, cm^{-1}) 1518, 1345; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 4H), 5.89 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.40 (d, *J* = 10.0 Hz, 1H), 5.13 (d, *J* = 7.2 Hz, 1H), 4.46 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.6 (C), 147.4 (C), 147.3 (C), 136.4 (CH), 132.5 (CH), 129.2 (C), 127.6 (CH), 123.7 (CH), 123.5 (CH), 119.2 (CH2), 89.9 (C), 84.7 (C), 80.9 (CH), 56.4 (CH_2); HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{18}H_{14}N_2NaO_5$ 361.0794; found 361.0804.

Synthesis of indolizinone 11

To the suspension of allene **2e** (43.6 mg, 0.3 mmol) and copper(I) iodide (5.7 mg, 0.03 mmol) in acetonitrile (3 mL) was stirred at room temperature for 20 h. The reaction mixture was washed with saturated sodium hydrogen carbonate aqueous solution (5 mL), extracted with ethyl acetate (5 mL × 3). Combined organic layer was dried over magnesium sulfate and evaporated *in vacuo*. The residue was washed with hexane (5 mL × 2) to afford 3,3-dimethylindolizin-2(3*H*)-one **11**[11] (15.2 mg, 0.094 mmol, 32%) as a brown oil. Further purification was performed with silica gel column chromatography (hexane/ethyl acetate = 95/5). IR (ATR, cm^{-1}) 1593, 1491; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (d, *J* = 6.8 Hz, 1H), 7.19 (dd, *J* = 8.0, 8.0, Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.28 (d, *J* = 8.0, 6.8 Hz, 1H), 4.94 (s, 1H), 1.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.0 (C), 163.1 (C), 137.4 (CH), 133.3 (CH), 116.4 (CH), 108.98 (C), 108.94 (CH), 86.4 (CH), 68.7 (C), 24.5 (CH_3); HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{10}H_{12}NO$ 162.0913; found 162.0908.

References

1. Reviews (a) A. Hoffmann-Röder, N. Krause *Angew. Chem. Int. Ed.* **2004**, *43*, 1196. (b) F. Lopez, J. L. Mascarenas *Chem. Soc. Rev*. **2014**, *43*, 2904. (c) C. S. Adams, C. D. Weatherly, E. G. Burke, J. M. Schomaker *Chem. Soc. Rev*. **2014**, *43*, 3136.
2. S. Yua, S. Ma *Chem. Commun*. **2011**, *47*, 5384.
3. Q. Lu, S. Greßies, F. J. R. Klauck, F. Glorius *Angew. Chem. Int. Ed.* **2017**, *56*, 6660.
4. (a) C. L. Ricardo, X. Mo, J. A. McCubbin, D. G. Hall. *Chem. Eur. J.* **2015**, *21*, 4218. (b) K. Huang, G. Sheng, P. Lu, Y. Wang *J. Org. Chem*. **2017**, *82*, 5294. (c) S. Jana, A. Dey, M. Singsardar, A. K. Bagdi, A. Hajra *J. Org. Chem.* **2016**, *81*, 9489.
5. (a) A. P. Boisselle, N. A. Meinhardt *J. Org. Chem*. **1962**, *27*, 1828. (b) C. J. M. Stirling, G. Smith *J. Chem. Soc. C*. **1971**, 1530.
6. (a) G. A. Myers, B. Zheng *J. Am. Chem. Soc.* **1996**, *118*, 4492. (b) Z. Yang, W. Hao, S. Wang, J. Zhang, B. Jiang, G. Li, S. Tu *J. Org. Chem*. **2015**, *80*, 9224.
7. (a) H. Jiang, X. Liu, L. Zhou *Chem. Eur. J.* **200**8, *14*, 11305. (b) M. Yoshida, T. Gotou, M. Ihara *Tetrahedron Lett.* **2004**, *45*, 5573. (c) L. Mao, K. J. Szabo, T. B. Marder *Org. Lett.* **2017**, *19*, 1204. (d) M. Sen, P. Dahiya, J. R. Premkumar, B. Sundararaju *Org. Lett*. **2017**, *19*, 3699.
8. (a) B. A. Trofimov, B. G. Sukhov, N. K. Gusarova, S. F. Malysheva, A. G. Mal'ki *Russ. J. Gene. Chem.* **2002**, *72*, 1141. (b) H. Jiang, W. Wang, B. Yin, W. Liu *Eur. J. Org. Chem*. **2010**, 4450.
9. J. Chen, C. Che *Angew. Chem. Int. Ed*. **2004**, *43*, 4950.
10. H. Nakamura, T. Kamakura, M. Ishiwkura, J. Biellmann *J. Am. Chem. Soc.* **2004**, *126*, 5958.
11. A. Kakehi, S. Ito, K. Watanabe, M. Kitagawa, S. Takeuchi, T. Hashimoto *J. Org. Chem.* **1980**, *45*, 5100.