Synthesis of mono- and 1,3-disubstituted allenes from propargylic amines *via* palladium-catalysed hydride-transfer reaction†

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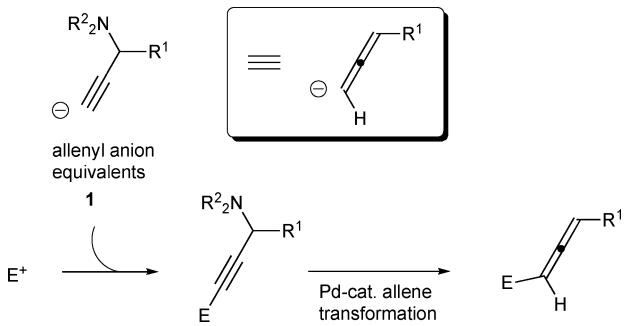
Mono- and 1,3-disubstituted allenes were synthesized from the corresponding propargylamines *via* palladium-catalysed hydride-transfer reaction. In the current transformation, propargylic amines can be handled as allenyl anion equivalents and introduced into various electrophiles to be transformed into allenes under palladium-catalyzed conditions.

Introduction

Allenes have extraordinary properties, such as the axial chirality of the elongated tetrahedron and their higher reactivity than alkenes; hence, they have received attention not only as an attractive building block for organic synthesis, but also as a potent functional group for improvement of biologically and pharmacologically active compounds.[1] Therefore, the development of a simple protocol for the introduction of an allenic moiety into the existing backbone of the molecule is still an important requirement.[2,3] Allenes can be generally prepared from propargyl alcohol derivatives by S_N2'-type displacement with organocopper species.[4] Other preparation methods have also been reported, namely the homologation of 1-alkynes,[5] the stereoselective reduction of alkynes,[6] asymmetric allylation,[7,8] β-elimination by Horner–Emmons–Wadsworth reaction[9] or reaction of sulfinyl radicals,[10] palladium-catalyzed hydrogenolysis,[11] coupling reactions of allenylstannanes[12] and allenylindiums,[13] and indium-mediated reactions of propargyl bromides with aldehydes.[14] We recently found a novel protocol for the synthesis of allenes from propargylamines by a palladium-catalysed hydride-transfer reaction.[15] In this transformation, propargylamines can be handled as an allenyl anion equivalent and introduced into various electrophiles to be transformed into allenes. Although this transformation can be utilized for various electrophiles, including heterocycles[16] and conjugated compounds,[17] only monosubstituted allenes were synthesized. In this paper, we provide a full account of our previous results on the simple protocol for the synthesis of monosubstituted allenes,[15] together with new findings on the synthesis of 1,3-disubstituted allenes from 1-substituted propargylamines as substituted allenyl anion equivalents (Scheme 1).



Scheme 1 Design of substituted allenyl anion equivalents and the palladium-catalyzed allene transformation.

Results and discussion

We first examined the synthesis of phenylallene **3a** from *N*,*N*-diisopropyl-3-phenylprop-2-ynylamine **2a** under various catalytic conditions. The results are summarized in Table 1. The allene formation reaction of *N*,*N*-diisopropyl-3-phenylprop-2-ynylamine **2a** proceeded in the presence of $Pd_2dba_3{\cdot}CHCl_3/Ph_3P$ catalyst at 80 °C in dioxane, giving phenylallene **3a** in only 9% yield after 8 h (entry 1). Although $(PhO)_3P$, bis(diphenylphosphino)ethane (dppe), and bis(diphenylphosphino)ferrocene (dppf) were not effective for the current transformation (entries 2–4), 1,2-bis(diphenylphosphino)carborane **4**[4b,18] gave **3a** in 58% yield (entry 5). Since a carborane framework involves three-center two-electron bonding[19] and is thus known as an electron-deficient cluster,[20] we thought that the electron-deficient phosphine ligands would be effective for this transformation. Finally, we found that $(C_6F_5)_3P$ was the best ligand for the current transformation (entry 7), and phenylallene **3a** was obtained quantitatively when the reaction was carried out in the presence of $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mol%) at 100 °C (entry 8). $Pd(OAc)_2$ was also an effective catalyst (entries 9 and 11). Although $(C_6F_5)_3P$ was essential for the hydride-transfer reaction under palladium(0)-catalysed conditions (entry 10), the reaction also proceeded without any phosphine ligands in the presence of $Pd(OAc)_2$ catalyst (entry 12).

We next examined various 3-phenylprop-2-ynylamines (**2a–f**), which were readily prepared from iodobenzene and the corresponding propargylic amines by Sonogashira coupling in 64–92% yields. As shown in Table 2, the allene transformation reaction of *N*,*N*-diethyl-3-phenylprop-2-ynylamine **2b** proceeded in the presence of $Pd_2dba_3{\cdot}CHCl_3/(C_6F_5)_3P$ catalyst at 100 °C in dioxane, giving phenylallene **3a** in only 12% yield after 24 h (entry 2). Although *N*,*N*-dibenzyl-3-phenylprop-2-ynylamine **2c** gave **3a** in 40% yield, the reaction of *N*,*N*-diisobutyl-3-phenylprop-2-ynylamine **2d** afforded **3a** in 76% yield (entries 3 and 4). The

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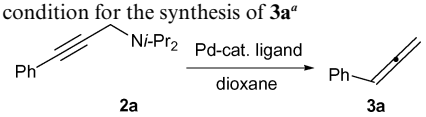
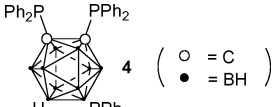
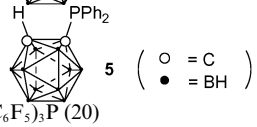
† Electronic supplementary information (ESI) available: Additional experimental information. See DOI: 10.1039/b718298h

Table 1 Optimisation of hydride-transfer reaction condition for the synthesis of **3a**[a]



2a **3a**

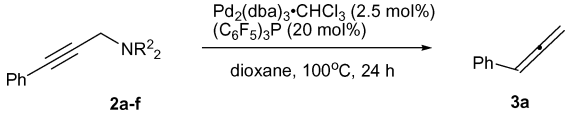
Entry	Catalyst (mol%)	Ligand (mol%)	Time/h	Yield (%)[b]
1	$Pd_2dba_3{\cdot}CHCl_3$ (5)	Ph_3P (20)	8	9
2	$Pd_2dba_3{\cdot}CHCl_3$ (5)	$(PhO)_3P$ (20)	25	16
3	$Pd_2dba_3{\cdot}CHCl_3$ (5)	dppe (10)	24	3
4	$Pd_2dba_3{\cdot}CHCl_3$ (5)	dppf (10)	27	16
5	$Pd_2dba_3{\cdot}CHCl_3$ (5)	 (10)	9	58
6	$Pd_2dba_3{\cdot}CHCl_3$ (5)	 (20)	9	20
7	$Pd_2dba_3{\cdot}CHCl_3$ (5)	$(C_6F_5)_3P$ (20)	31	79
8[c]	$Pd_2dba_3{\cdot}CHCl_3$ (2.5)	$(C_6F_5)_3P$ (20)	24	>99
9[c]	Pd_2dba_3 (2.5)	$(C_6F_5)_3P$ (20)	24	99
10[c]	Pd_2dba_3 (2.5)	None	24	5 (95)[d]
11[c]	$Pd(OAc)_2$ (5)	$(C_6F_5)_3P$ (20)	24	95
12[c]	$Pd(OAc)_2$ (5)	None	24	61 (31)[d]

4 (○ = C, ● = BH)

5 (○ = C, ● = BH)

[a] All reactions were carried out in dioxane at 80 °C using a vial tube. [b] Yields were determined by GC analysis using hexadecane as an internal standard. [c] The reaction was carried out at 100 °C. [d] The amount of recovered **2a** is indicated in parentheses.

Table 2 Effects of amine substituents (R^2) on the allene transformation reaction[a]



2a-f **3a**

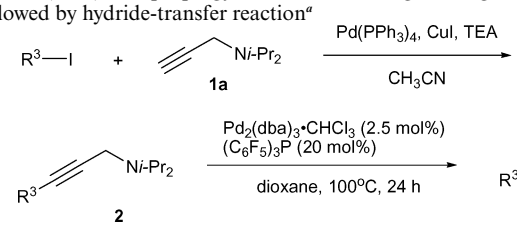
Entry	**2**	R^2	Yield of **3a** (%)[b]
1	**2a**	*i*-Pr	>99
2	**2b**	Et	12
3	**2c**	Bn	40
4	**2d**	*i*-Bu	76
5	**2e**	Cy	99
6	**2f**	–CH(Me)$CH_2CH_2CH_2$CH(Me)–	43

[a] The reaction was carried out in the presence of $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mol)/$(C_6F_5)_3P$ (20 mol%) in dioxane at 100 °C for 24 h in a vial tube. [b] Yields were determined by GC analysis using hexadecane as an internal standard.

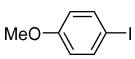
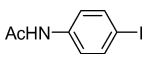
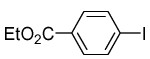
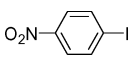
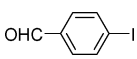
best result was also obtained in the case of *N*,*N*-dicyclohexyl-3-phenylprop-2-ynylamine **2e**, and **3a** was obtained in 99% yield (entry 5). The use of the cyclic amine **2f** was not effective for this transformation reaction (entry 6).

Now that an optimum condition for allene formation was established, we investigated the synthesis of various allenes (**3a–g**) from the corresponding iodides with *N*,*N*-diisopropylprop-2-ynylamine **1a** through Sonogashira coupling followed by hydride-transfer reaction (Table 3). The reactions of **2a** and **2g**, which were prepared from iodobenzene and 1-iodonaphthalene by Sonogashira coupling in 86 and 98% yields, respectively, were complete after 24 h to give allenybenzene **3a** and 1-allenylnaphthalene **3b** in >99 and 67% yields, respectively (entries 1 and 2). The propargylic amines, which have an electron-donating group, such as MeO (**2h**) and AcNH (**2i**), substituted on the aromatic ring of molecules, underwent the allene formation reaction to give **3c** and **3d** in 99% and 74% yields, respectively (entries 3 and

Table 3 Synthesis of monosubstituted allenes **3a–g** from various aromatic iodides (R^3–I) and propargylic amine **1a** through Sonogashira coupling followed by hydride-transfer reaction[a]



1a **2** **3**

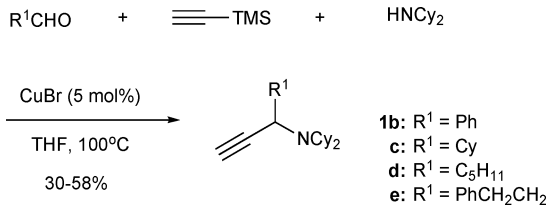
Entry	R^3–I	**2** (yield, %)[b]		**3** (yield, %)[c]	
1	Ph–I	**2a**	86	**3a**	>99
2		**2g**	98	**3b**	67
3		**2h**	95	**3c**	99
4		**2j**	89	**3d**	74
5		**2j**	99	**3e**	96
6		**2k**	95	**3f**	75
7		**2l**	60	**3g**	66

[a] All reactions were carried out in dioxane at 100 °C using a vial tube. [b] Isolated yield. [c] Yields were determined by GC analysis using hexadecane as an internal standard.

4). The electron-deficient propargylic amines **2j–l** also underwent the allene formation reaction: the reaction of **2j**, prepared from

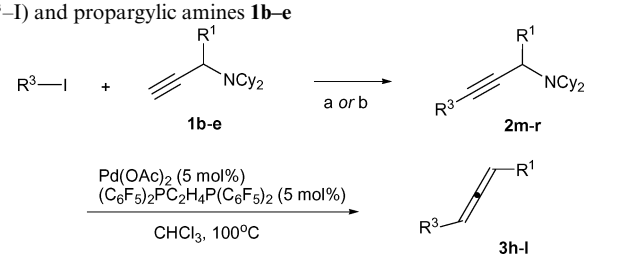
ethyl 4-iodobenzoate in 99% yield, proceeded smoothly to give the corresponding allene **3e** in 96% yield (entry 5). The reactions of propargylic amines **2k** and **2l** gave **3f** and **3g** in 75% and 66% yields, respectively (entries 6 and 7).

Synthesis of 1,3-disubstituted allenes was examined using the 1-substituted propargylamines as substituted allenyl anion equivalents. The 1-substituted propargylamines **1b–e** were prepared from the corresponding aldehydes, trimethylsilylacetylene, and dicyclohexylamine *via* a CuBr-catalysed three-component coupling reaction (Scheme 2).[21,22] We examined the introduction of substituted allenes into organic iodides, such as iodohexadecane and iodobenzene, through the anionic substitution or Sonogashira coupling reaction followed by the palladium-catalysed hydride-transfer reaction. The results are summarized in Table 4. The nucleophilic substitution of iodohexadecane with the lithium acetylide of **1b–e** proceeded in THF at 0 °C to give the corresponding allene precursors **2m–p** in 58–87% yields (entries 1–5). The allene formation reaction of **2m**, which has an aromatic group at R^1, proceeded in the presence of $Pd(OAc)_2$ (5 mol%) and $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$ (5 mol%) in $CHCl_3$ at 100 °C, giving nonadeca-1,2-dienylbenzene **3h** in 53% yield (entry 1). $Pd_2(dba)_3{\cdot}CHCl_3$ and other phosphine ligands, such as $P(C_6F_5)_3$, PPh_3, $P(OPh)_3$, and bis(diphenylphosphino)ethane, were not effective for this transformation. Although the transformation reaction of **2n** gave nonadeca-1,2-dienylcyclohexane **3i** in



Scheme 2 Synthesis of 1-substituted propargylamines **1b–e** from aldehydes, trimethylsilylacetylene, and dicyclohexylamine.

Table 4 Synthesis of 1,3-disubstituted allenes **3h–l** from various iodides (R^3–I) and propargylic amines **1b–e**

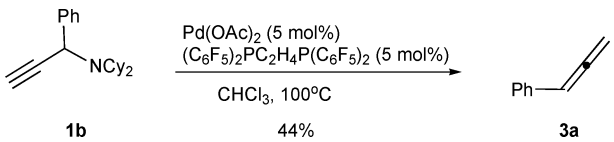


Entry	R^3	**1**	**2** (yield, %)[a]		**3** (yield, %)[b]	
1	$C_{16}H_{33}$	**1b**	**2m**	58	**3h**	53
2	$C_{16}H_{33}$	**1c**	**2n**	81	**3i**	45
3	$C_{16}H_{33}$	**1d**	**2o**	87	**3j**	73
4	$C_{16}H_{33}$	**1e**	**2p**	73	**3k**	72
5	CH_3	**1e**	**2q**	84	**3l**	63
6	Ph	**1d**	**2r**	95	**3m**	26

[a] The allene precursors **2m–q** were prepared as follows: Method a: the substitution reaction of iodoalkanes with lithium acetylides (entries 1–5); Method b: the allene precursor **2r** was prepared by Sonogashira coupling of iodobenzene with **1d** (entry 6). [b] All reactions were carried out in the presence of $Pd(OAc)_2$ (5 mol%) and $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$ (5 mol%) in $CHCl_3$ at 100 °C using a vial tube. Reaction progress was monitored by TLC.

moderate yield (entry 2), the allene precursors **2o** and **2p**, which have an aliphatic functional group at R^1, gave the corresponding allenes **3j** and **3k** in higher yields (entries 3 and 4). *N*,*N*-Dicyclohexyl-1-phenylhex-4-yn-3-ylamine **2q** also underwent the allene formation reaction to give hexa-3,4-dienylbenzene **3l** in 63% yield (entry 5). However, *N*,*N*-dicyclohexyl-1-phenyloct-1-yn-3-ylamine **2r** prepared by Sonogashira coupling reaction of iodobenzene with **1d** afforded octa-1,2-dienylbenzene **3m** in 26% yield (entry 6). Aromatic substituents at R^1 and/or R^3 were not suitable for the current 1,3-disubstituted allene formation: *N*,*N*-dicyclohexyl-1,3-diphenylprop-2-ynylamine (**2s**, $R^1 = R^3 = Ph$), derived from **1b** and iodobenzene, gave 1,3-diphenylpropa-1,2-diene in only 10% yield (data not shown).

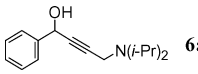
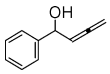
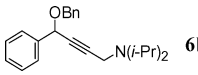
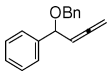
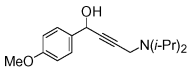
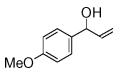
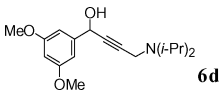
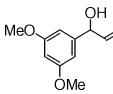
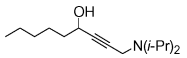
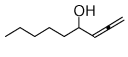
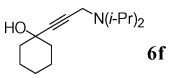
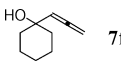
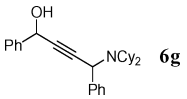
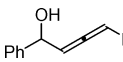
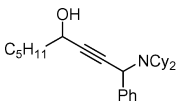
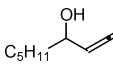
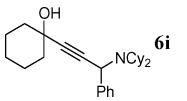
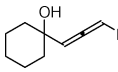
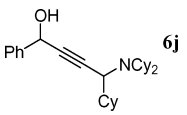
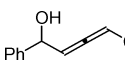
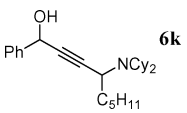
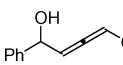
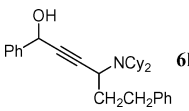
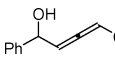
It should be noticed that the substituents at R^1 of the allene precursors **2** significantly affected the reaction yields: the allene formation reaction of *N*,*N*-dicyclohexyl-1-phenylprop-2-ynylamine **1b** in the presence of $Pd(OAc)_2$ (5 mol%) and $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$ (5 mol%) in $CHCl_3$ at 100 °C afforded phenylallene **3a** in 44% yield (Scheme 3), although **3a** was obtained from **2e** quantitatively (Table 2, entry 5).



Scheme 3 Synthesis of phenylallene **3a** from the precursor **1b**.

Recently, various transformations using allenylcarbinols have been reported, and hence development of a convenient synthesis of allenylcarbinols is an important issue in organic synthesis.[23–25] The allene formation reaction described above can be utilized for the synthesis of allenylcarbinols **7**. Various propargylic amines **1a–e** were readily introduced into various carbonyl compounds, and allene precursors **6a–f** were synthesized by the addition of the lithium acetylides of **1a–d** to aldehydes and a ketone. The results are summarized in Table 5. The allene formation reaction of **6a**, which was prepared from benzaldehyde and **1a**, proceeded in the presence of $Pd_2dba_3{\cdot}CHCl_3/(C_6F_5)_3P$ at 80 °C in dioxane, giving the corresponding allenylcarbinol **7a** in 64% yield after 13 h (entry 1). The benzyl ether **6b** afforded **7b** in a higher yield (91%; entry 2). The propargylic alcohols **6c–e** derived from 4-anisaldehydes, 3,5-dimethoxybenzaldehyde, and hexanal, respectively, underwent the transformation reaction to give the corresponding allenes **7c–e** in 56–92% yields (entries 3–5). The reaction of **6f** derived from cyclohexanone also proceeded to give **7f** in 86% yield (entry 6). Substituted allenylcarbinols **7g–l** were also synthesized from the corresponding substituted allene precursors **6g–l** prepared from propargylic amines **1b–d** and aldehydes or a ketone. The propargylic alcohol **6g** prepared from **1b** and benzaldehyde underwent the allene formation reaction in the presence of $Pd(OAc)_2$ (5 mol%) and $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$ (5 mol%) in $CHCl_3$ at 100 °C, giving 1,4-diphenylbuta-2,3-dien-1-ol **7g** in 48% yield (entry 7). Although the propargylic alcohol **6h** prepared from **1b** and hexanal gave **7h** in moderate yield (entry 8), the reaction yield increased in the case of the propargylic alcohol **6i** (prepared from **1b** and cyclohexanone), and the corresponding allnylcarbinol **7i** was obtained in 68% yield (entry 9). The propargylic alcohols **6j–l** also underwent the

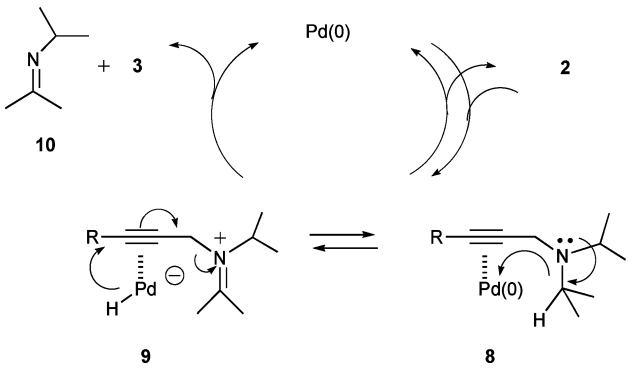
Table 5 Palladium-catalysed hydrogen transfer reaction of **6**[a]

entry	**6**	Time/h	Allenes **7**	Yield (%)[b]
1	 **6a**	13	 **7a**	64
2	 **6b**	23	 **7b**	91
3	 **6c**	14	 **7c**	92
4	 **6d**	14	 **7d**	70
5	 **6e**	12	 **7e**	56
6	 **6f**	9	 **7f**	86
7	 **6g**	8	 **7g**	48
8	 **6h**	23	 **7h**	42
9	 **6i**	43	 **7i**	68
10	 **6j**	24	 **7j**	38
11	 **6k**	23	 **7k**	36
12	 **6l**	24	 **7l**	47

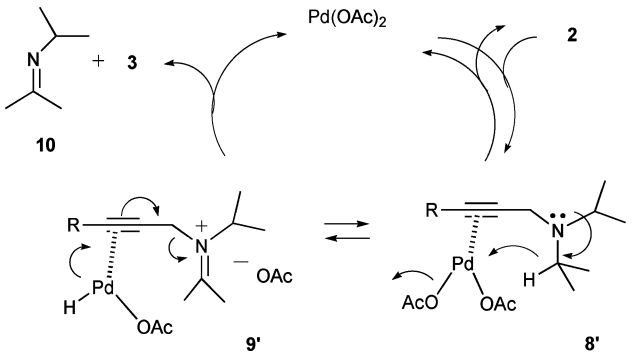
[a] The reactions were carried out in the presence of $Pd_2dba_3{\cdot}CHCl_3$ catalyst (2.5 mol%) and $(C_6F_5)_3P$ (10 mol%) in dioxane at 80 °C under Ar (entries 1–6), or $Pd(OAc)_2$ (5 mol%) and $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$ (5 mol%) in $CHCl_3$ at 100 °C (entries 7–12) under Ar. [b] Isolated yields.

allene formation to give the corresponding **7j–l** in 36–47% yields (entries 10–12).

The proposed mechanisms for palladium(0)- and palladium(II)-catalysed hydride-transfer reactions are shown in Schemes 4 and 5, respectively. In the case of palladium(0)-catalysed condition, π-coordination of Pd(0) with **2** at a carbon–carbon triple bond would form the complex **8**, and hydride transfer from the isopropyl carbon assisted by a lone pair electron of the nitrogen would generate the palladium anion species **9**. The migration of the hydride on palladium to the alkyne moiety of **9** followed by the rearrangement of the π-bond would give the allene **3** and the imine **10**, and regenerating palladium(0). Indeed, generation of cyclohexanone was observed in the reactions with propargylic dicyclohexylamines. Since electron-deficient phosphine ligands,



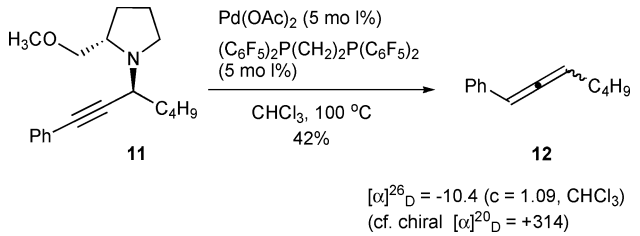
Scheme 4 Palladium(0)-catalysed mechanism.



Scheme 5 Palladium(II)-catalysed mechanism.

such as 1,2-bis(diphenylphosphino)carborane **4** and $(C_6F_5)_3P$, were effective for the palladium(0)-catalysed allene transformation reaction, it is considered that these electron-deficient phosphine ligands should stabilize the anionic palladium intermediate **9** in the equilibrium between **8** and **9** to accelerate the generation of allenes **3** in the catalytic cycle. In the case of catalysis by palladium(II), a palladium(II) species would be the reactive intermediate in the catalytic cycle, as shown in Scheme 5. The coordination of $Pd(OAc)_2$ with **2** would form the complex **8′**, which comes to rapid equilibrium with the iminium ion complex **9′** assisted by a lone pair electron of the nitrogen. The hydride transfer from H–Pd–OAc to the alkyne moiety of **9′** followed by rearrangement of the π-bond would give the allenes **3** and the imine **10**, regenerating $Pd(OAc)_2$. It has been reported that the iminium ion can be generated by the insertion of palladium coordinated to the nitrogen lone pair into the carbon–hydrogen bond adjacent to nitrogen.[26] Since isopropyl and cyclohexyl groups (R^2 in Table 2) substituted on the nitrogen result in were effective for the reaction, it can be assumed that these substituents aid the formation of the stable iminium ion **9** (or **9′**) in the equilibrium, accelerating the catalytic cycle.

Furthermore, with the aim of synthesizing chiral allenes, we prepared the chiral propargylamine **11** from phenylacetylene, pentanal, and methoxymethylpyrrolidine according to the reported procedure by Knochel and co-workers.[21] As shown in Scheme 6, the transformation of **11** proceeded in the presence of $Pd(OAc)_2$ catalyst in $CHCl_3$, providing hepta-1,2-dienylbenzene **12** in 42% yield with a low ee.[27]



Scheme 6 Attempt to asymmetrically synthesise allene **12** from the chiral propargylamine **11**.

Conclusion

We have developed a novel synthesis of allenes using propargylic amines as an allenyl anion equivalent. The use of electron-deficient phosphine ligands, such as $(C_6F_5)_3P$, $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$ and 1,2-bis(diphenylphosphino)carborane **4**, is essential for the palladium-catalysed hydride-transfer reaction. Allenyl carbinols were prepared by the same route from propargylic aminoalcohols, and one may envision the extension of this preparation of allenes to other functionalities. Although mechanisms based upon either palladium(0) or palladium(II) could be envisaged, the hydride transfer from a C–H bond adjacent to nitrogen to an alkyne moiety *via* a hydride–palladium complex would give the allenes **3**. We believe that the current transformation could be influential not only in the development of new transition-metal-catalysed synthetic methods but also in the development of pharmacologically active allenes in organic synthesis.

Experimental

General procedures

^1H NMR, ^{13}C NMR, and ^{11}B NMR spectra were measured on a JEOL JNM-AL 300 (300 MHz) and VARIAN UNITY-INOVA 400 (400 MHz) spectrometers. Chemical shifts of ^1H NMR are expressed in ppm downfield from TMS as an internal standard ($\delta = 0.0$) in $CDCl_3$. Chemical shifts of ^{13}C NMR are expressed in ppm downfield from TMS as an internal standard ($\delta = 0.0$) in $CDCl_3$. Analytical thin layer chromatography (TLC) was performed on a glass plates (Merck Kieselgel 60 F_{254}, layer thickness 0.2 mm). Column chromatography was performed on silica gel (Merck Kieselgel 70–230 mesh). All reactions were carried out under argon atmosphere using standard Schlenk techniques. Most chemicals and solvents were analytical grade and used without further purification. IR spectra were recorded on a Shimadzu FT-IR 8200A spectrometer. Mass spectrometry data were collected on a Shimadzu LCMS-2010 EV spectrometer.

General procedure for synthesis of 1-substituted propargylamines (1b–e) *via* CuBr-catalysed three-component coupling reaction

To a mixture of aldehyde (4.0 mmol), dicyclohexylamine (0.88 mL, 4.4 mmol) and CuBr (29 mg, 0.2 mmol) in THF (2 mL) was added trimethylsilylacetylene (0.85 mL, 6.0 mmol) under Ar, and the reaction mixture was stirred at 100 °C for 72 hours in a vial tube. Catalysts were removed by Celite filtration, and the solvent was evaporated under reduced pressure. Purification by silica gel

column chromatography with hexane–ethyl acetate (30 : 1) gave **1b–e** in 30–58% yields.

Typical procedure for the synthesis of propargylamines by Sonogashira coupling reactions

A mixture of iodobenzene (205 mg, 1.0 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), CuI (17 mg, 0.09 mmol), and **1a** (180 mg, 1.3 mmol) was dissolved in acetonitrile (5 mL) under Ar. Triethylamine (210 μL, 1.5 mmol) was added, and the mixture stirred at 60 °C for 6 h. The progress of the reaction was monitored by GC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with hexane–ethyl acetate (10 : 1) to give **2a** (185 mg, 86% yield).

General procedure for the synthesis of allene precursors 2m–q *via* substitution reaction of lithium acetylide of 1b–e with iodoalkanes (R^3–I)

To a mixture of **1b–e** (1.2 mmol) in THF (20 mL) was added n-BuLi (0.86 mL, 1.38 mmol) at 0 °C under Ar, and the reaction mixture was stirred for 30 min. Iodohexadecane (0.45 mL, 1.43 mmol) or iodomethane (0.09 mL, 1.45 mmol) was then added, and the reaction mixture allowed to warm to room temperature and stirred for 48 hours. The reaction was quenched with saturated aqueous ammonium chloride solution and the mixture was extracted with ether, dried over $MgSO_4$ anhydride, and then concentrated. The residue was purified by column chromatography on silica gel to give allene precursors **2m–q** in 58–87% yields.

General procedure for synthesis of allenes 3a–g from 2a–l *via* palladium-catalyzed hydride-transfer reaction

A mixture of **2** (0.4 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (0.01 mmol) and $(C_6F_5)_3P$ (0.08 mmol) in dioxane (2 mL) was stirred at 100 °C under Ar, and the progress of the reaction monitored by GC. When **2** was consumed, the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with hexane–ethyl acetate to give the allene **3**.

General procedure for synthesis of allenes 3h–m from 2m–r *via* palladium-catalyzed hydride-transfer reaction

A mixture of **2** (0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and $(C_6F_5)_2PC_2H_4P(C_6F_5)_2$ (15 mg, 0.02 mmol) in chloroform (2 mL) was stirred at 100 °C under Ar, and the progress of the reaction monitored by TLC. When **2** was consumed, the solvent was evaporated under the reduced pressure. The residue was purified by silica gel column chromatography with hexane–ethyl acetate to give the allene **3**.

General procedure for synthesis of allene precursors 6a–l by addition of lithium acetylides of 1a–e to various carbonyl compounds

To a solution of propargylamines **1** (2.0 mmol) in THF (20 mL) was added n-BuLi (1.38 mL, 2.2 mmol) dropwise at 0 °C under Ar and the reaction mixture was stirred for 30 min. Aldehydes or cyclohexanone were then added and the reaction mixture was allowed to reach room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl solution (20 mL), and the organic layer was washed with saturated aqueous NaCl solution (20 mL), dried over $MgSO_4$ anhydride, and concentrated. The residue was purified by silica gel column chromatography with hexane–ethyl acetate to give the allene precursors **6**.

General procedure for synthesis of allenes 7a–f from 6a–f *via* palladium-catalyzed hydride-transfer reaction

The procedure used was similar to that for the synthesis of allenes **3a–g** described above.

General procedure for synthesis of allenes 7g–l from 6g–l *via* palladium-catalyzed hydride-transfer reaction

The procedure used was similar to that for the synthesis of allenes **3h–m** described above.

Acknowledgements

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