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Site-Selective Deuterated-Alkene Synthesis with Palladium on Boron Nitride

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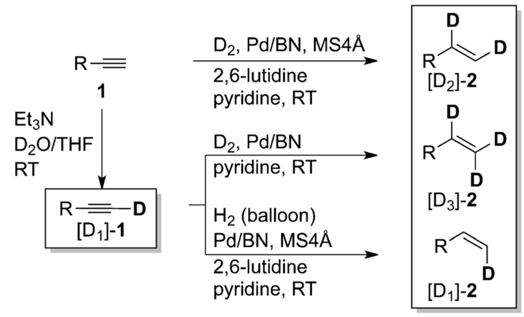
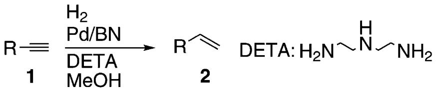
Deuterium (^2H or D)-labeled compounds are utilized in various scientific fields,[1–5] and many deuterium-labeling methods have therefore been developed.[6–14] Deuterium-labeled alkenes are widely available as starting materials for the construction of a wide variety of deuterated target compounds because of their remarkable features as building blocks. Although direct H–D exchange reactions of unlabeled alkenes with a deuterium source are regarded as the most straightforward approach to the synthesis of deuterated alkenes ([D_n]alkenes), the site- and regioselective introduction of the desired number of deuterium atoms with high deuterium efficiency remains challenging.[9] Among the stepwise syntheses of [D_n]alkenes,[10] the site-selective reductive deuteration of an alkyne or [D_1]alkyne can be useful for the synthesis of the desired [D_n]alkene.[11–14] [D_1]- and [D_2]alkenes could be prepared from terminal propargylic compounds by using homogeneous metal hydride or deuteride reagents ([Cp_2ZrHCl] or [Cp_2ZrDCl]; Cp = cyclopentadienyl,[11] boron,[12a] and aluminum[12b] reagents) followed by an aqueous workup by using D_2O or H_2O. Deuterated 4-methoxystyrene analogues were efficiently synthesized from 4-ethynylanisole by homogeneous Rh-catalyzed semi-deuterogenation under an atmosphere of H_2 or D_2.[13] *cis*-Deuterated alkenes were prepared by use of the Lindlar catalyst for partial reductive deuteration of 1,2-disubstituted alkynes by using D_2 gas generated by the electrolysis of D_2O in a special flow reactor (H-cube).[14] Although these methods enable the incorporation of the desired number of deuterium atoms into suitable alkynes, an efficient and widely applicable method for the synthesis of monosubstituted [D_n]alkene compounds from monosubstituted aromatic and aliphatic alkynes remains challenging because of the ready over-reduction of in situ generated alkenes to alkanes. We now report a new deuterium-labeling method for terminal alkynes, which yields [D_1]alkynes, and the highly selective and systematic synthesis of terminal [D_1]-, [D_2]-, and [D_3]alkenes from unlabeled terminal alkynes or [D_1]alkynes by palladium on boron nitride catalyzed[15] partial reduction (semihydrogenation[16] or semideuterogenation) with H_2 or D_2 gas (Scheme 1).



Scheme 1. Regioselective preparation of deuterated alkenes by using the Pd/BN catalyst under a D_2 or H_2 atmosphere.

Theoretically, terminal alkynes (**1**) can be transformed into the [D_2]alkene by deuterogenation with D_2 gas on a heterogeneous palladium catalyst such as Pd/C. However, the generated [D_2]alkenes are easily and further deuterogenated to [D_4]alkane derivatives, even when using the Lindlar catalyst.[17–19] Moreover, D_2 gas is quite expensive and not easily obtainable because of the complicated acquisition process, on account of limited production as a consequence of its combustible nature and import restrictions because it is considered a strategic material.

We have developed an efficient semihydrogenation of monosubstituted alkynes to alkenes by using Pd/BN (boron nitride supported Pd catalyst) in the presence of an appropriate amine such as diethylenetriamine [DETA; Eq. (1)][15] and D_2 gas generated by the method described in reference [8] [Pd/C in D_2O, the cheapest deuterium source, is stirred under an atmosphere of H_2 at room temperature; Eq. (2)]. However, in contrast to our expectations, the Pd/BN-catalyzed deuterogenation of 4-ethynylanisole (**1a**) in the presence of DETA in MeOH at room temperature under in situ generated D_2 gas gave the [D_3]alkene ([D_3]-**2a**) in low D efficiencies [Eq. (3)]. This result indicated that the Pd/BN-catalyzed *cis*-addition of D_2 gas to the alkyne (**1a**) proceeded after the preliminary H–D exchange reaction of the relatively acidic unlabeled alkyne (**1a**) to the corresponding [D_1]alkyne ([D_1]-**1a**) because the D content at the *cis*-positions of [D_3]**2a** was nearly equal.



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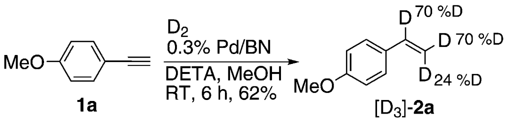
$$H_2 \xrightarrow[D_2O,\ RT,\ 24\ h]{10\%\ Pd/C} D_2 \qquad (2)$$



(3)

The H–D exchange reaction of the unlabeled alkyne to a [D$_1$]alkyne derivative ([D$_1$]-**1**) has generally been performed by the formation of metal acetylide by using relatively strong bases (e.g., *n*BuLi[20] or a Grignard reagent[21]) and subsequent workup by using deuterium sources, such as D_2O and MeOD. The acidic protons in DETA and MeOH may cause the reverse D–H exchange reaction, resulting in the low D incorporation observed.[22] Therefore, the reaction was carried out under aprotic conditions by using a Et_3N/D_2O/THF solvent system. Reactions under these conditions proceeded effectively and various aromatic and aliphatic alkynes were deuterated with excellent D incorporations and isolated in high yields at room temperature (Figure 1).[23]

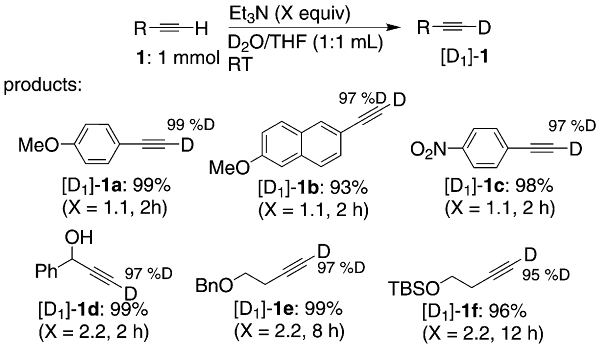


Figure 1. Synthesis of [D$_1$]alkyne compounds.

The acidic protons of DETA and MeOH can also decrease the D efficiency of Pd/BN-catalyzed semideuterogenation of [D$_1$]alkynes ([D$_1$]-**1**) to [D$_3$]alkenes ([D$_3$]-**2**) with D_2 [see q. (3)], as is the case for the preparation of [D$_1$]alkynes ([D$_1$]-**1**, Figure 1). Consequently, pyridine was chosen as the solvent to maintain the D efficiency of the reaction. As a result, compounds [D$_3$]-**2** were effectively prepared from [D$_1$]-**1** with high D efficiencies and isolated in near quantitative yields with an extremely low catalyst loading (0.03 mol %) of Pd/BN (Figure 2). Because Pd/BN is an extremely mild catalyst for hydrogenation, the totally chemoselective semihydrogenation of alkynes in the presence of nitro, benzyl ether, benzyl alcohol, and *tert*-butyldimethylsilyl (TBS) ether functionalities is possible.[15] Therefore, the present Pd/BN-catalyzed semideuterogenation of [D$_1$]alkynes in pyridine gave various aromatic and aliphatic [D$_3$]alkenes, but left the other reducible functionalities intact ([D$_3$]-**2c**, [D$_3$]-**2d**, [D$_3$]-**2e**, and [D$_3$]-**2f**).

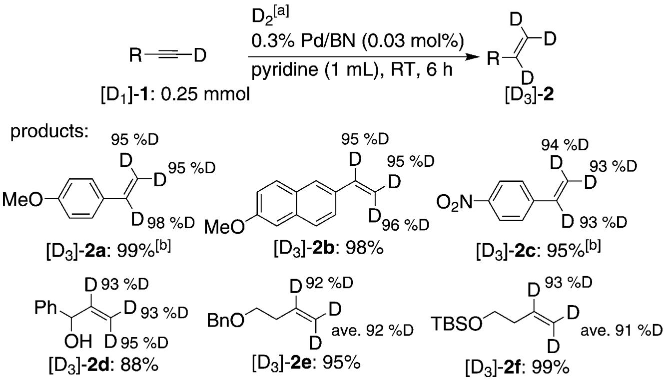
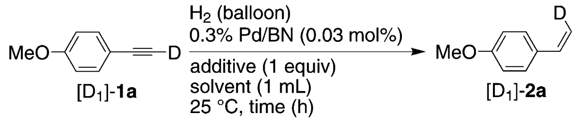
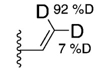
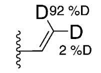
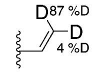
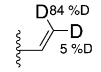
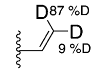
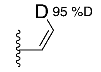
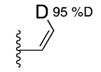


Figure 2. Preparation of [D$_3$]alkenes: [a] Prepared by the method reported in reference [8]. [b] 0.06 mol % of 0.3 % Pd/BN was used.

[D$_1$]Alkenes ([D$_1$]-**2**) could be prepared by the Pd/BN-catalyzed semihydrogenation of [D$_1$]-**1** under an H_2 atmosphere. Although the semihydrogenation of [D$_1$]-**1a** by using the H_2/Pd/BN/pyridine combination gave [D$_1$]-**2a** with a satisfactory D content (92 %), a small amount of D (7 %) was introduced into the *E*-position relative to the aromatic ring on the terminal sp^2-carbon atom (Table 1, entry 1). The Pd/BN-catalyzed semihydrogenation in 2,6-lutidine as the solvent (Table 1, entry 2) failed. However, the use of only 1.0 equivalent of 2,6-lutidine (relative to the amount of [D$_1$]-**1a**) as an additive in pyridine (1 mL) efficiently suppressed D incorporation at the *E*-position (only 2 %, Table 1, entry 3). Other pyridine derivatives, such as 2-picoline, 2-methoxypyridine, and quinoline, were less effective inhibi-

Table 1. Optimization of [D$_1$]alkene preparation.



Entry	Additive	Solvent	Time [h]	Product	Yield [%]
1	–	pyridine	3		99
2	–	2,6-lutidine	6	–	n.r.
3	2,6-lutidine	pyridine	3		98
4	2-MeO-pyridine	pyridine	4		99
5	quinoline	pyridine	8		79
6	2-picoline[a]	pyridine	24		67
7	MS4 Å, 2,6-lutidine	pyridine	3		61
8	MS4 Å, 2,6-lutidine	pyridine	3		99[b]

[a] 2 Equivalents. [b] 0.1 mol % of Pd/BN catalyst was used.

tors of *E*-deuteration (Table 1, entries 4–6). Fortunately, the addition of 4 Å molecular sieves (MS4 Å) not only improved the D efficiency at the *Z*-position (up to 95% D), but also completely suppressed the incorporation of D at the *E*-position, resulting in isolation of $[D_1]$-**2a** in moderate yields (Table 1, entry 7). The semihydrogenation of $[D_1]$-**1a** could be forced to completion by use of a larger amount of Pd/BN (0.1 mol%), quantitatively yielding $[D_1]$-**2a** (Table 1, entry 8). The exact mechanistic role of the additives applied is not clear and, therefore, detailed investigations into the effect of 2,6-lutidine and MS4 Å are underway.

The Pd/BN-catalyzed semihydrogenation of $[D_1]$alkynes in pyridine in the presence of 2,6-lutidine and MS4 Å could be adapted to prepare various $[D_1]$alkenes ($[D_1]$-**2**) in high D efficiencies and yields (Figure 3). The nitro group and benzyl and TBS ethers are tolerated very well under the reaction conditions.

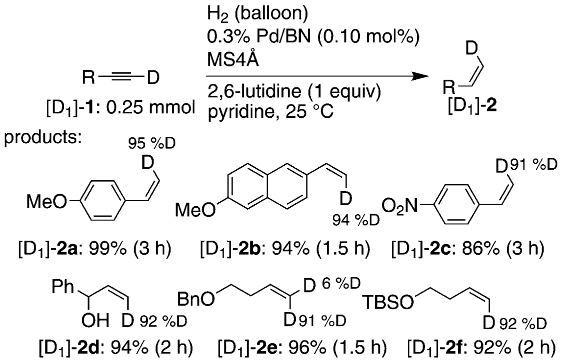


Figure 3. Syntheses of various $[D_1]$alkene compounds.

The preparation of $[D_2]$alkenes ($[D_2]$-**2**) was also accomplished starting from unlabeled alkynes (**1**) with the Pd/BN–MS4 Å–2,6-lutidine–pyridine system under an atmosphere of D_2 gas prepared by the method described in reference [8] instead of H_2 gas. Unfortunately, D incorporation at the undesired *Z*-position, relative to the aromatic ring, on the terminal sp^2-carbon atom was not completely suppressed because of the inevitable pyridine/2,6-lutidine-mediated H–D exchange reaction of **1** to $[D_1]$-**1** prior to the reductive semideuterogenation of **1** to $[D_2]$-**2** (Figure 4).

Lastly, we applied the systematic preparation methods for deuterated alkenes developed herein to the synthesis of deuterium-labeled allylsilanes, which are the key reactive reagents in the construction of deuterium-labeled frameworks of a wide variety of functionalized organic compounds. These deuterium-labeled materials may be synthesized by Sakurai–Hosomi allylation[24] or Hiyama cross-coupling,[25] and in the synthesis of physiologically significant heterocycles, such as tetrahydropyran[26] and tetrahydrofuran.[27] As shown in Scheme 2, dimethylphenylpropargylsilane (**1g**) underwent semideutrogenation by using the Pd/BN–MS4 Å–2,6-lutidine–pyridine system under a D_2 atmosphere, prepared as described in reference [8], to afford $[D_2]$-**2g** regioselectively with efficient D atom incorporation. After preparation of $[D_1]$-**1g** by the Et_3N-mediated H–D exchange reaction of unlabeled **1g** in D_2O/THF at 50 °C, the Pd/BN-catalyzed semihydrogenation and semideuterogenation gave $[D_1]$-**2g** and $[D_3]$-**2g**, respectively, in high yields and D efficiencies.

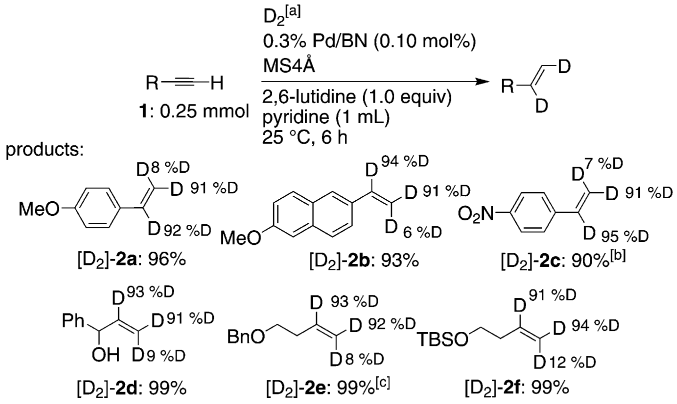
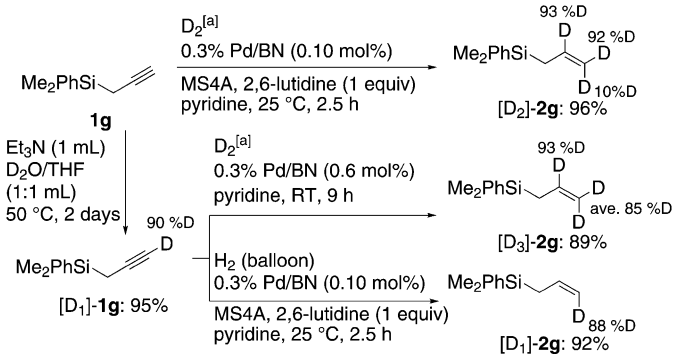


Figure 4. Preparation of $[D_2]$alkenes: [a] Prepared by the method reported in reference [8]. [b] 0.05 mol% of 0.3% Pd/BN was used. [c] 0.20 mol% of 0.3% Pd/BN was used.



Scheme 2. Synthesis of deuterated allylsilane derivatives: [a] Prepared by the method reported in reference [8].

In conclusion, we have developed a new Et_3N-mediated H–D exchange reaction of alkynes (**1**) to prepare $[D_1]$alkynes ($[D_1]$-**1**) in a mixture of D_2O and THF at room temperature and a method for the Pd/BN-catalyzed regioselective systematic preparation of various deuterated terminal alkenes from unlabeled alkynes or deuterated alkyne derivatives in excellent yields and with high D contents and regioselectivities. A variety of reducible functionalities, such as nitro groups, benzyl ethers, TBS ethers, and silanes, are well tolerated under the reaction conditions described and the wide variety of deuterated products obtainable by this method are expected to be useful building blocks for new deuterated materials including, but not limited to, deuterium-labeled drugs, deuterated polymers, and tracers.

Experimental Section

Typical procedure for the deuteration of alkynes (Figure 1): Et_3N (1.1 mmol) was added to a solution of an alkyne (1 mmol) in D_2O/THF (1:1 mL) at room temperature under an argon atmosphere and the reaction mixture was stirred for the appropriate duration, as indicated in Figure 1. The resulting mixture was diluted with Et_2O or hexanes (2 mL) and separated into two layers. The aqueous layer was then further extracted with Et_2O or hexanes (2 mL×2). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to give analytically pure product.

Typical procedure for the synthesis of [D$_3$]alkenes (Figure 2): A flask was charged with a mixture of the substrate (0.25 mmol) and Pd/BN (0.3 %; 0.03 mol % of the substrate) in pyridine (1 mL). After the reaction flask was depressurized, previously prepared D_2 (further details are provided in the Supporting Information) was allowed to flow into the reaction flask. After stirring for 6 h at room temperature, the resulting mixture was diluted with Et_2O or hexanes (5 mL) and then filtered through a pad of Celite. The filtrate separated into two layers and was treated with 1 M aqueous HCl (20 mL). The organic layer was separated and washed with H_2O (10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to give the analytically pure product.

Keywords: alkenes · alkynes · deuterium · palladium · regioselectivity

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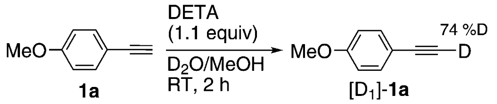

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