Catalytic Hydrogenation

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[Pd(Ar-BIAN)(alkene)]-Catalyzed Highly Chemo-, Regio-, and Stereoselective Semihydrogenation of 1,2-Allenyl Phosphonates and Related Compounds**

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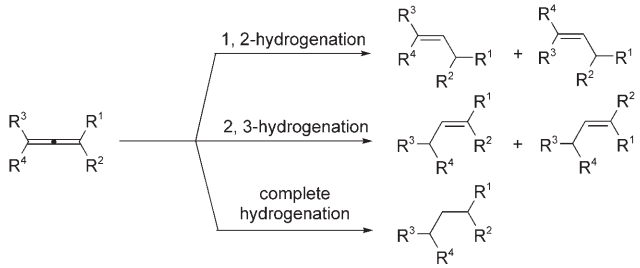
Allenes are an important class of compounds with many applications in organic chemistry.[1,2] However, the hydrogenation of allenes is challenging, as there are issues of chemo-, regio-, and stereoselectivity to be addressed (Scheme 1).[2d] Only a very limited number of studies in this area have been reported, and the selectivity in the reported cases is low.[3]



Scheme 1. The hydrogenation of allenes.

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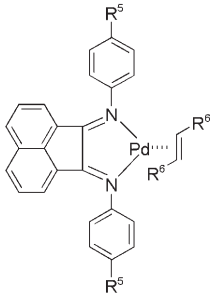
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



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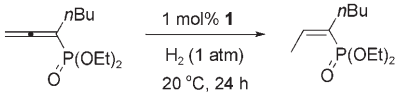
1a: R^5 = Me, R^6 = CN
1b: R^5 = OMe, R^6 = COOMe

One of the authors and co-workers have previously reported the hydrogenation of alkynes catalyzed by [Pd(Ar-BIAN)(alkene)] complexes **1** (Ar-BIAN = bis(arylimino)acenaphthene) to afford *Z*-alkenes in excellent yields with high stereoselectivity.[4] Herein we report a highly chemo-, regio-, and stereoselective hydrogenation of 1,2-allenyl phosphonates to give di- or trisubstituted (*Z*)-1-alkenyl phosphonates with the same catalysts. Such trisubstituted alkenes are otherwise difficult to obtain.

We first chose the 1,2-allenyl phosphonate **2a** as the model substrate to study the solvent effects of the reaction at 20 °C. In most solvents, such as diethyl ether, dioxane, *N*,*N*-dimethyl formamide, dimethyl sulfoxide, CH_2Cl_2, CH_3CCl_3, toluene, CH_3NO_2, CH_3OH, AcOH, and Et_3N, the hydrogenation did not proceed. Fortunately, when the reaction was conducted in CH_3CN or THF, only the trisubstituted (*Z*)-1-alkenyl phosphonate (*Z*)-**3a** was formed, in excellent yield with excellent chemo-, regio-, and stereoselectivity (Table 1,

Table 1: [Pd(Ar-BIAN)(alkene)]-catalyzed hydrogenation of **2a** under various conditions.[a,b]



2a (*Z*)-**3a**

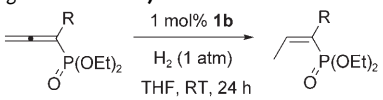
Entry	Solvent	Catalyst	*T* [°C]	Yield [%]
1	CH_3CN	**1a**	20	92
2	THF	**1a**	20	94
3	THF	**1a**	30	94
4	THF	**1a**	50	92
5	THF	**1b**	20	94

[a] The reaction was carried out at the temperature stated with **2a** (0.2 mmol) and **1a** or **1b** (1 mol%) in 3 mL of solvent under H_2 (1 atm) for 24 h. [b] The chemo-, regio-, and stereoselectivities were determined by ^{1}H NMR spectroscopic analysis of the crude reaction product.

entries 1 and 2). As the yield in THF was slightly higher than that in CH_3CN, THF was chosen as the solvent for this reaction. When we increased the reaction temperature, no obvious changes were observed (Table 1, entries 3 and 4). It was also found that the activity of catalyst **1b** was the same as that of **1a** for the hydrogenation of **2a** (Table 1, entry 5).

We next investigated the hydrogenation of various 1,2-allenyl phosphonates **2b–j** (Table 2). It was surprising to note that **1a** failed to catalyze the hydrogenation of the methyl-substituted 1,2-allenyl phosphonate **2b** (Table 2, entry 1). As the lack of hydrogenation activity may result from the stronger coordination of the fumaronitrile ligand, we decided to attempt the reaction with palladium complex **1b**, which has a more labile alkene ligand. Indeed, **1b** catalyzed the partial hydrogenation reaction to afford alkene (*Z*)-**3b** in 91% yield (Table 2, entry 2). Therefore, the same conditions were used

Table 2: Hydrogenation of **2b–j**.[a,b]

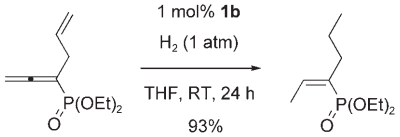


2 (*Z*)-**3**

Entry	Allene	R	Product	Yield [%]
1[c]	**2b**	Me	–	n.r.
2	**2b**	Me	(*Z*)-**3b**	91
3	**2c**	*t*Bu	(*Z*)-**3c**	90
4	**2d**	n-C_7H_{15}	(*Z*)-**3d**	94
5	**2e**	Ph	(*Z*)-**3e**	95
6	**2f**	p-$MeOC_6H_4$	(*Z*)-**3f**	99
7	**2g**	p-MeC_6H_4	(*Z*)-**3g**	93
8	**2h**	p-$NO_2C_6H_4$	(*Z*)-**3h**	90
9	**2i**	p-$MeO_2CC_6H_4$	(*Z*)-**3i**	93
10	**2j**	H	(*Z*)-**3j**	91

[a] The reaction was carried out at room temperature with **2** (0.2 mmol) and **1b** (1 mol%) in THF (3 mL) under H_2 (1 atm) for 24 h. [b] The chemo-, regio-, and stereoselectivities were determined by ^{1}H NMR spectroscopic analysis of the crude reaction product. [c] The reaction was conducted with **1a** (1 mol%) as the catalyst. n.r. = no reaction.

for the other substrates. Interestingly, the hydrogenation of **2k** under these conditions gave the (*Z*)-1-alkenyl phosphonate (*Z*)-**3k** in 93% yield as the only product, in which the isolated allylic C=C bond in **2k** had also been hydrogenated, but the conjugated electron-deficient carbon–carbon double bond remained (Scheme 2). The configuration of the C=C bond in the products **3** was determined by analysis of the ^{1}H-^{1}H NOESY spectra of (*Z*)-**3i**.

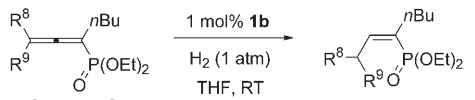


2k **3k**

Scheme 2. The hydrogenation of **2k**.

The hydrogenation of the 1,3-disubstituted 1,2-allenyl phosphonate **2l** and 1,3,3-trisubstituted 1,2-allenyl phosphonates **2m** and **2n** under the conditions indicated in Table 2 was also studied. Compounds (*Z*)-**3l**, (*Z*)-**3m**, and (*Z*)-**3n** were formed highly selectively in 92, 95, and 85% yield, respectively (Scheme 3).

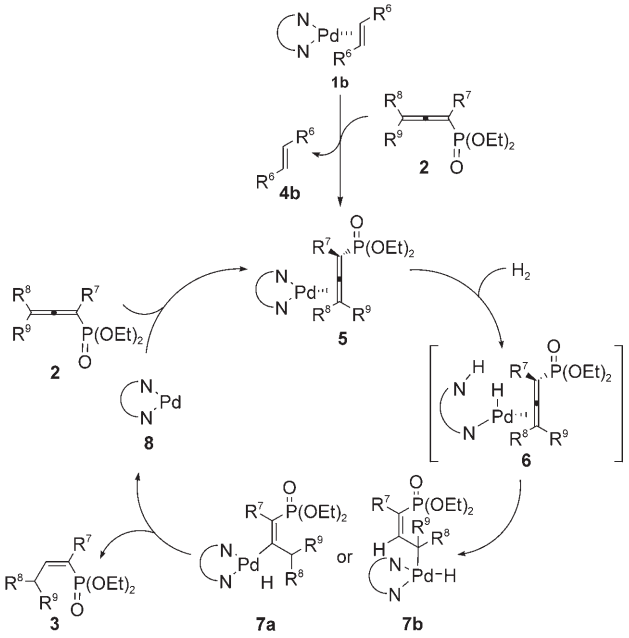
On the basis of these and previous results, a mechanism for this reaction is proposed in Scheme 4. The catalytic cycle starts with the loss of the alkene ligand from **1b**. Next, the more electron rich C=C bond in **2** coordinates to palladium in



2l: R^8 = *n*Pr, R^9 = H
2m: R^8 = Me, R^9 = Me
2n: R^8 = Me, R^9 = Et

(*Z*)-**3l**: R^8 = *n*Pr, R^9 = H, 92%
(*Z*)-**3m**: R^8 = Me, R^9 = Me, 95%
(*Z*)-**3n**: R^8 = Me, R^9 = Et, 85%

Scheme 3. The semihydrogenation of **2l–n**.



Scheme 4. A possible mechanism for this reaction.

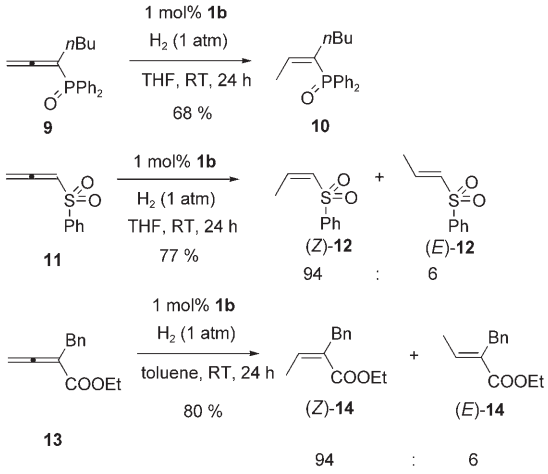
place of the alkene ligand to form a [Pd(Ar-BIAN)(allene)] complex **5**. In analogy with the mechanism for alkyne hydrogenation studied by one of us and co-workers,[4c] we propose the heterolytic hydrogen cleavage of **5** to afford the monohydridopalladium complex **6**, which may undergo highly stereoselective hydropalladation to generate the palladium hydride **7a** or **7b** after transfer of the N–H hydrogen atom to Pd.[5] The final product **3** is produced by reductive elimination from **7a** or **7b**. Meanwhile, the catalytically active [Pd(Ar-BIAN)(allene)] species **5** is regenerated through the interaction of **8** with the starting allene. On the basis of the stereoselectivity observed, we reason that the reaction most likely proceeds via the intermediate **7a**, in which the mutual *trans* orientation of the palladium and phosphonate moieties may determine the stereoselectivity.

This protocol was successfully extended to allenes substituted with other functionalities, namely, the 1,2-allenyl phosphine oxide **9**, the 1,2-allenyl sulfone **11**, and the 2,3-allenoate **13** (Scheme 5). In these cases the semihydrogenation also proceeds with very high chemo-, regio-, and stereoselectivity. Note that toluene should be used as the solvent for the 2,3-allenoate **13**.

In conclusion, we have demonstrated a novel, highly chemo-, regio-, and stereoselective [Pd(Ar-BIAN)(alkene)]-catalyzed hydrogenation of 1,2-allenyl phosphonates[6,7] and other 1,2-allenyl compounds to form di- or trisubstituted (*Z*)-1-alkenyl phosphonates, sulfones, and esters in excellent yields. Further studies in this field are being carried out in our laboratories, including investigations into synthetic applications of the reaction.

Experimental Section

Typical procedure: Catalyst **1b** (1 mg, 0.002 mmol), **2a** (46 mg, 0.2 mmol), and anhydrous THF (3 mL) were added to a Schlenk



Scheme 5. The semihydrogenation of some related compounds.

tube under a nitrogen atmosphere. The nitrogen atmosphere was replaced with a hydrogen atmosphere (1 atm), and the solution was stirred at 20 °C for 24 h. The reaction mixture was then filtered. Evaporation of the solvent and flash chromatography on silica gel (petroleum ether/diethyl ether 1:2) afforded (*Z*)-**3a** (44 mg, 94 %) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.24$ (dtq, $J = 0.9$, 7.2, 50.7 Hz, 1H), 4.13–3.96 (m, 4H), 2.22–2.12 (m, 2H), 2.03–1.98 (m, 3H), 1.48–1.38 (m, 2H), 1.35–1.23 (m, 8H), 0.88 ppm (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 142.2$ (d, $J_{PC} = 11.8$ Hz), 129.8 (d, $J_{PC} = 170.3$ Hz), 61.0 (d, $J_{PC} = 5.8$ Hz), 35.0 (d, $J_{PC} = 12.1$ Hz), 31.7 (d, $J_{PC} = 3.0$ Hz), 22.2, 16.3 (d, $J_{PC} = 4.4$ Hz), 16.2 (d, $J_{PC} = 2.6$ Hz), 13.8 ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 21.0$ ppm; IR (neat): $\tilde{\nu} = 1632$, 1444, 1391, 1245, 1026 cm^{-1}; MS: *m*/*z*: 234 (M^+, 9.87), 44 (100); HRMS (MALDI): *m*/*z* calcd for $C_{11}H_{23}O_3P^+$ [M^+]: 233.1385; found: 234.1400.

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