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A Pd(0)-Catalyzed Diamination of Terminal Olefins at Allylic and Homoallylic Carbons via Formal C−H Activation under Solvent-Free Conditions

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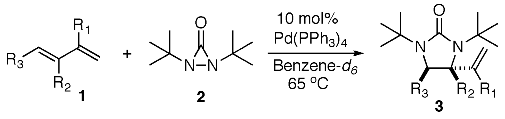
Diamination of olefins presents an attractive strategy for the synthesis of vicinal diamines, which are contained in various biologically active compounds as important functional moieties and are widely used in asymmetric synthesis as chiral control elements.[1] A number of metal-mediated[2,3] and -catalyzed diaminations have been developed.[4−6] Recently, we reported that conjugated dienes and trienes can be effectively diaminated with high regio- and stereoselectivity using di-*tert*-butyldiaziridinone (**2**)[7] as nitrogen source and $Pd(PPh_3)_4$ as catalyst (Scheme 1).[8] Herein we wish to report that terminal olefins can be diaminated at allylic and homoallylic carbons (Scheme 2).

Subjecting terminal olefins to the previous diamination conditions [10 mol % of $Pd(PPh_3)_4$ in C_6D_6 at 65 °C] (Scheme 1) gave no diamination products on the olefins. Instead, small amounts of diamination products at allylic and homoallylic carbons were observed. After much experimentation, it was found that this diamination process can be further improved by running the reaction without solvent and by slow addition of di-*tert*-butyldiaziridinone (**2**). For example, treating 4-phenyl-1-butene with 5 mol % of $Pd(PPh_3)_4$ and **2** (2.75 equiv, added slowly) at 65 °C for 7 h gave a clean diamination product (**5a**) in 90% yield (Table 1, entry 1). This diamination can be extended to a variety of terminal olefins, including monosubstituted (Table 1, entries 2−6) and 1,1-disubstituted olefins (Table 1, entries 7−11). In all of these cases, the reaction occurred at allylic and homoallylic carbons and essentially only one stereoisomer was obtained.[9,10] Diamination product **5** can be deprotected with TFA and concentrated HCl to give a free diamine (an example is shown in Scheme 3).

Bisdiamination can also occur for substrates bearing two terminal double bonds. For example, treating 1,9-decadiene with 10 mol % of $Pd(PPh_3)_4$ and **2** for 12 h led to the formation of a mixture (meso/DL) of bisdiamination products **8a** and **8b** in 61% yield (Scheme 4). X-ray structure of **8a** is shown in Figure 1. It appears that the first diamination has little effect on the stereochemistry of the second diamination. However, when the reaction was carried out with 1,7-octadiene, bisdiamination product **11** was obtained as a single diastereomer in 47% yield (Scheme 5), suggesting that the first diamination influences the stereochemical outcome of the second diamination. The stereochemistry of **11** was determined by X-ray structure (Figure 1). When the reaction was carried out with 5 mol % of $Pd(PPh_3)_4$ at 65 °C for 12 h, substantial amounts of compounds **10a** (14% yield) and **10b** (20% yield) were isolated. When isolated compounds **10a** and **10b** were subjected to the diamination conditions, both compounds were converted to compound **11**, suggesting that **10a** and **10b** are possible reaction intermediates toward **11**.

Scheme 1



Scheme 2

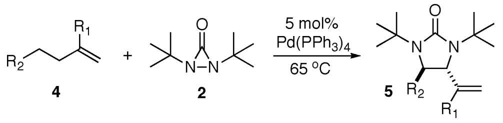
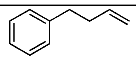
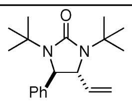
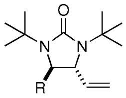
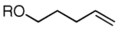
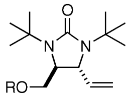
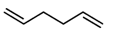
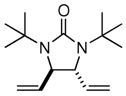
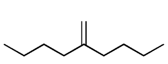
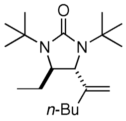
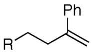
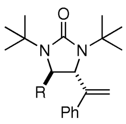
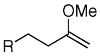
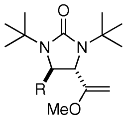


Table 1. Catalytic Diamination of Terminal Olefins[a]

Entry	Substrate (**4**)	Product (**5**)	Time	Yield (%)[d]
1[b]	 **4a**		7 h	90
2	 **4b**, R = Et		12 h	68
3	**4c**, R = n-C_6H_{13}		12 h	74
4	 **4d**, R = Bn		12 h	90
5	**4e**, R = n-C_6H_{13}		12 h	78
6	 **4f**		12 h	76
7	 **4g**		12 h	55
8	 **4h**, R = Me		12 h	83
9	**4i**, R = Et		12 h	92
10[c]	 **4j**, R = Ph		12 h	93
11[c]	**4k**, R = n-C_6H_{13}		12 h	64

[a] All reactions were carried out with olefin (1.6 mmol), $Pd(PPh_3)_4$ (0.08 mmol), and di-*tert*-butyldiaziridinone (4.4 mmol) (added by syringe pump at 0.4 mmol/h) at 65 °C under argon unless otherwise stated. [b] Di-*tert*-butyldiaziridinone (4.4 mmol) was added by syringe pump at 0.8 mmol/h. [c] These products are acid sensitive and were purified on less acidic silica gel (Iatrobeads 6RS-8060, Mitsubishi Kagaku Iatron, Inc., Japan). [d] Isolated yield based on the olefin.

While a precise reaction mechanism awaits further study, a plausible catalytic cycle is shown in Scheme 6. The Pd(0) first inserts into the N−N bond of diaziridinone **2** to form a four-membered Pd(II) species (**12**),[11] which complexes with olefin **4** to form **13**. Upon removing an allylic hydrogen, complex **13** forms π-allyl Pd complex **14**,[12,13] which gives diene **15** and regenerates the Pd(0) catalyst after β-H elimination.[14] Subsequently, diene **15** complexes with **12** to form **17**, which is then converted into π-allyl

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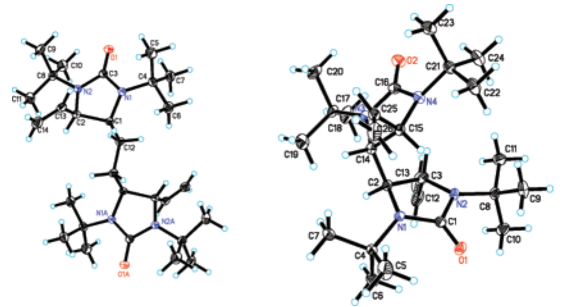
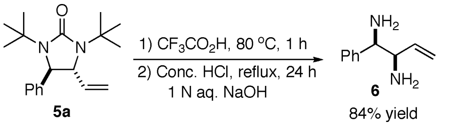


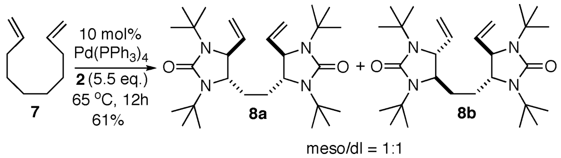
8a **11**

Figure 1. The X-ray structures of compounds **8a** and **11**.

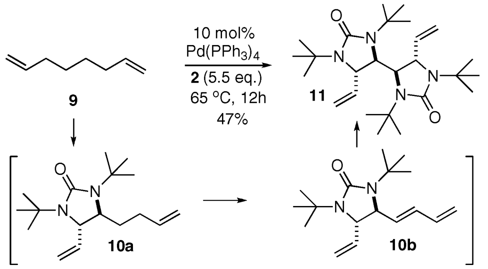
Scheme 3



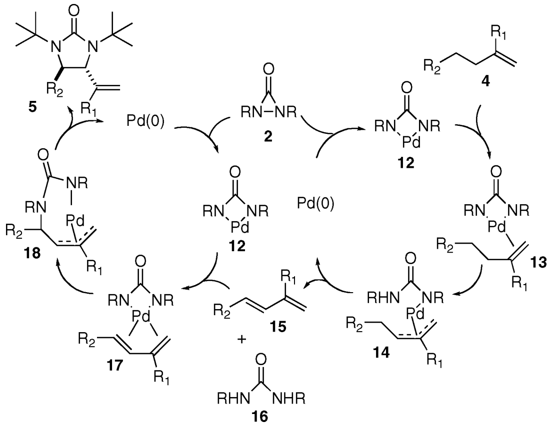
Scheme 4



Scheme 5



Scheme 6. A Proposed Catalytic Cycle for Diamination



Pd complex **18** after migratory insertion.[8,15] Finally, **18** undergoes reductive elimination to form product **5** and regenerate the Pd(0) catalyst.

In summary, a variety of terminal olefins have been effectively diaminated at allylic and homoallylic carbons via formal C−H activation[16] using di-*tert*-butyldiaziridinone (**2**) as nitrogen source and $Pd(PPh_3)_4$ as catalyst, giving the diamination products in good yields with high stereoselectivity. Bisdiamination can also be achieved for substrates bearing two terminal double bonds. This diamination uses readily available terminal olefins and is complementary to the previous diamination process of conjugated dienes. Further efforts will be devoted to studies of the reaction mechanism, search for a more effective catalytic process with different nitrogen sources and metal catalysts, and expansion of the substrate scope as well as the asymmetric process.

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Supporting Information Available: Diamination procedures, deprotection procedure, characterization and NMR spectra of **5**, **6**, **8a**,**b**, **10a**,**b**, and **11**, and the X-ray data of **8a**, **8b**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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