Rhodium-catalyzed allylation of styrenes with allyl tosylate

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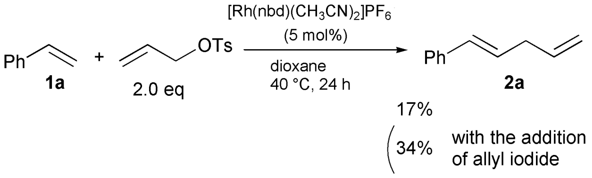
Rhodium-catalyzed allylation of styrene with allyl tosylate gave 1-phenylpenta-1,4-diene, and various styrene derivatives were also allylated yielding 1,4-dienes or 1,5-dienes.

The palladium-catalyzed arylation of alkenes, the Heck reaction, has proven to be a versatile method for the formation of carbon–carbon bonds.[1] In contrast, the analogous reaction of alkenes with allyl compounds is far more limited in its application, except for intramolecular metallo-ene reactions,[2] and remains a challenge in organic synthesis. Although a few examples of the transition metal-catalyzed allylation of alkenes have been reported,[3–5] to our knowledge, a reaction yielding simple allylation products, *i.e.* 1,4-dienes, is yet to be discovered. For example, strained alkenes such as norbornene† react with allyl compounds in the presence of various transition metal catalysts, however, these reactions do not afford 1,4-dienes because of stereochemical problems.[3] The palladium-catalyzed allylation of activated olefins with allylstannane and allyl chloride gives not mono-allylation products, but double allylation products selectively.[4] Mitsudo *et al.* reported ruthenium-catalyzed reactions of allyl carbonates with *N,N*-dimethylacrylamide, in which only 1,3-dienes were obtained in moderate yields.[5] Herein we wish to report the rhodium-catalyzed simple allylation of styrene derivatives with allyl tosylate.[6]

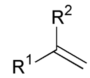
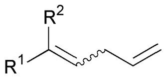
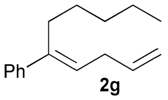
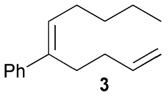
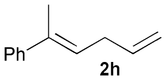
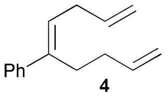
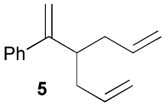
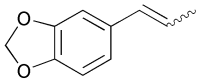
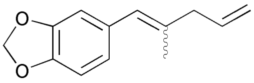
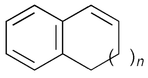
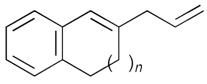
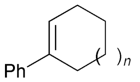
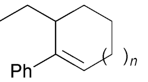
When styrene (**1a**) was treated with two equivalents of allyl tosylate in the presence of a catalytic amount of [Rh(nbd)(CH_3CN)$_2$]PF_6 (nbd = norbornadiene‡) in dioxane at 40 °C, 1-phenylpenta-1,4-diene **2a** was produced in 17% yield (eqn. (1)). Allyl tosylate and styrene were not recovered, and no other product was identified. No allylation product was formed using typical allylating agents such as allyl acetate, allyl carbonate and allyl iodide. Palladium complexes such as Pd(PPh_3)$_4$, Pd_2(dba)$_3$·$CHCl_3$, [Pd(CH_3CN)$_4$](BF_4)$_2$, or various Lewis acids were ineffective as catalysts for the allylation reaction. The yield of **2a** was improved up to 34% by the addition of allyl iodide (40 mol%). In contrast, the addition of other allylic compounds such as allyl bromide, allyl acetate, or allyl phosphate, decreased the yield slightly. Other organic and inorganic iodides like *n*-propyl iodide, *tert*-butyl iodide and potassium iodide also hindered the reaction to some extent. Furthermore, amounts of allyl iodide less than or exceeding 40 mol% were less effective on the yield of **2a**.



(1)

Although satisfactory yield was not obtained in the allylation of *non-substituted* styrene, the reactions of several substituted styrenes gave allylation products in higher yields as illustrated in Table 1. The allylation of 1,1-diphenylethylene **1b** afforded **2b** in 51% yield (run 1). The yield of **2b** increased to 74% with the addition of allyl iodide (run 2). The electron-rich alkene **1c** was so reactive that the product **2c** was obtained in 80% yield

Table 1 Rhodium-catalyzed allylation of styrene derivatives with allyl tosylate[a]

Run	Styrene derivatives **1**	Products, yield (%)[b]
	 **1b-h**	 **2b-f**
1	**1b**; R^1, R^2 = Ph	**2b**, 51
2[c]	**1b**	**2b**, 74
3	**1c**; R^1, R^2 = p-$CH_3OC_6H_4$	**2c**, 80
4	**1d**; R^1 = Ph, R^2 = p-$CH_3OC_6H_4$	**2d**, 73 (53:47)[d]
5	**1e**; R^1 = Ph, R^2 = o-$CH_3OC_6H_4$	**2e**, 33 (66:34)[d]
6	**1f**; R^1, R^2 = p-ClC_6H_4	**2f**, 26
7	**1g**; R^1 = Ph, R^2 = n-C_5H_{11}	 **2g**  **3** 82 (**2g**:**3** = 43:57)
8	**1h**; R^1 = Ph, R^2 = CH_3	 **2h**  **4**  **5** 42 (**2h**:**4**:**5** = 71:29:0)
9[c]	**1h**	63 (**2h**:**4**:**5** = 0:52:48)
10	 **1i** (E:Z = 84:16)	 **2i**, 16 (E:Z = 75:25)
		
11	**1j**; n = 0	**2j**, 19
12	**1k**; n = 1	**2k**, 9
		
13	**1l**; n = 0	**2l**, 33
14	**1m**; n = 1	**2m**, 62
15	**1n**; n = 2	**2n**, 68

[a] Reaction conditions: **1** (0.5 mmol), allyl tosylate (1.0 mmol), [Rh(nbd)(CH_3CN)$_2$]PF_6 (0.025 mmol), dioxane, 40 °C, 24 h. [b] Isolated yields. [c] Allyl iodide (0.2 mmol) was added. [d] E/Z mixture (the stereochemistry cannot be determined).

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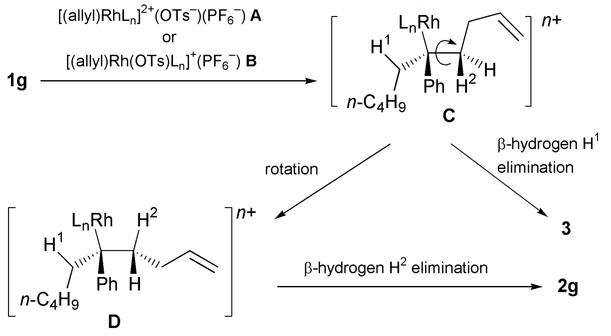

Scheme 1

(run 3). The reaction of 1-(*p*-methoxyphenyl)-1-phenylethylene **1d** also gave **2d** in high yield (run 4), whereas the *ortho*-substituted isomer **1e** was less reactive (run 5). By contrast, the reaction of the electron-poor alkene **1f** afforded **2f** in lower yield (26%, run 6). The α-alkyl-substituted styrenes **1g** and **1h** also reacted with allyl tosylate. In the reaction of **1g** the total yield of the allylated products was high (82%, run 7), although 1,5-diene **3** was yielded in addition to **2g**. The reaction of **1h** gave the monoallylated product **2h** and the diallylated **4**, generated by the allylation of a 1,5-diene product corresponding to **3** (run 8). When allyl iodide was added to the reaction of **1h**, diallylated products **4** and **5** were obtained in 63% yield (run 9). In contrast to the high reactivity of α-substituted styrenes, β-substituted styrenes were less reactive. The reactions of *Z*-stilbene, *E*-stilbene and β-methylstyrene did not give any allylated products. The electron-rich β-substituted styrene derivative **1i** barely reacted with allyl tosylate affording **2i** in only 16% yield (run 10). Indene **1j** was also allylated at the C-2 carbon (runs 11). The allylation reactions of the phenyl-substituted cyclic alkenes **1l–n** were also investigated. All the reactions gave only 1,5-dienes **2l–n** in satisfactory yields, in which no 1,4-diene was observed (runs 13–15).

Although little mechanistic information has been obtained for the Rh-catalyzed allylation of styrenes, we believe that the reaction proceeds *via* a mechanism similar to that of the palladium-catalyzed Heck arylation reaction. The likely intermediates for the allylation of **1g** are illustrated in Scheme 1. The oxidative addition of allyl tosylate with $[Rh(nbd)(CH_3CN)_2]PF_6$ gives the dicationic complex **A** or the complex **B**, in which tosylate anions weakly coordinate to rhodium, and with the insertion of **1g** to **A** or **B**, the rhodium organometallic intermediate **C** is afforded. In the reaction using allyl acetate or allyl iodide as the allylating agent, the coordination of acetate or iodide ions to rhodium is so strong that the insertion of an alkene does not take place. Subsequent β-hydrogen H^1 elimination in **C** affords 1,5-diene **3**. Since free rotation around the C(H^2)–C(Ph) bond in **C** is possible, alternate *syn*-β-hydrogen H^2 elimination in **D** also occurs, providing 1,4-diene **2g**. The 1,5-dienes were obtained selectively in reactions where free rotation around the C–C bond is not possible in the intermediate corresponding to **C** (runs 13–15). As the formation of **2j** and **2k** is not consistent with the mechanism shown in Scheme 1, the existence of another mechanism, *e.g.* a Friedel–Crafts type reaction, cannot be ruled out, although typical Lewis acids are ineffective in the present allylation reaction. Further investigation of the reaction mechanism and the application to other alkenes are in progress.

Notes and references

† The IUPAC name for norbornene is bicyclo[2.2.1]hept-2-ene.

‡ The IUPAC name for norbornadiene is bicyclo[2.2.1]hepta-2,5-diene.

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