Isomerization of Alkynes to 1,3-Dienes under Rhodium or Palladium Catalysis

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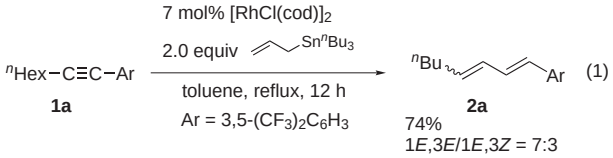
Abstract: Treatment of 1-aryl-1-octyne with allyltributylstannane under rhodium catalysis provided 1-aryl-1,3-octadiene in good yield. A combination of allyl acetate and a palladium catalyst also effected the isomerization of alkynes to 1,3-dienes.

Key words: rhodium, palladium, isomerization, alkynes, 1,3-dienes

Transition-metal-catalyzed isomerization of alkenes to other alkenes is a well-known process. In contrast, efficient isomerization of alkynes to 1,3-dienes is rare under transition-metal catalysis. Although the isomerization of 2-alkyn-1-one and 2-alkynoate proceeds smoothly,[1] there are a limited number of reports on the isomerization of simple alkynes.[2] Here we report a couple of new catalytic systems that realize the isomerization of simple alkynes to 1,3-dienes.

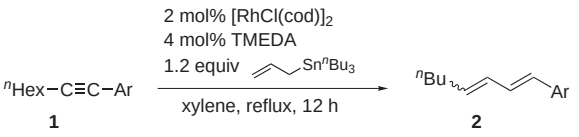
Treatment of 1-[3,5-bis(trifluoromethyl)phenyl]-1-octyne (**1a**) with allyltributylstannane (2.0 equiv) in the presence of 7 mol% of $[RhCl(cod)]_2$ in refluxing toluene for 12 hours provided 1-[3,5-bis(trifluoromethyl)phenyl]-1,3-octadiene (**2a**) in 74% yield (Scheme 1). The diene **2a** consisted of (1*E*,3*E*)-**2a** and (1*E*,3*Z*)-**2a** in a ratio of 7:3. Interestingly, the addition of allyltributylstannane is essential for the rhodium-catalyzed isomerization. Without the allylstannane, no reaction took place. Instead of allyltributylstannane, tributylmethallylstannane similarly promoted the reaction to yield **2a** in 58% yield. The use of other allylmetal reagents such as allylmagnesium chloride, allylzinc bromide, and allyltrimethylsilane resulted in the recovery of **1a**. Organostannanes including tributylstannane, tributylvinylstannane, 3-butenyltributylstannane failed to promote the isomerization.[3]



Scheme 1

After further optimization of reaction conditions, we could reduce the amounts of the rhodium catalyst and allyltributylstannane by using *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as an additive (Table 1). Specifically, treatment of **1a** with 1.2 equiv of allyltributylstannane, 2 mol% of $[RhCl(cod)]_2$, and 4 mol% of TMEDA in refluxing xylene for 12 hours furnished **2a** in 66% yield (entry 1). Other 1-aryl-1-octynes were converted into the corresponding 1-aryl-1,3-octadienes in reasonable yields. It is worth noting that the keto groups in **1e** and **1f** survived under the reaction conditions (entries 5 and 6). The ratios of (1*E*,3*E*)-**2** and (1*E*,3*Z*)-**2** were always 8:2 to 7:3.[4]

Table 1 Rhodium-Catalyzed Isomerization of Alkynes to 1,3-Dienes in the Presence of Allyltributylstannane



Entry	Ar	1	2	Yield (%)[a]
1	3,5-$(CF_3)_2C_6H_3$	**1a**	**2a**	66 (79:21)
2	Ph	**1b**	**2b**	84 (69:31)
3	4-$MeOC_6H_4$	**1c**	**2c**	72 (76:24)
4	2-MeC_6H_4	**1d**	**2d**	48 (71:29)
5	3-AcC_6H_4	**1e**	**2e**	68 (73:27)
6	4-AcC_6H_4	**1f**	**2f**	49 (77:23)

[a] 1*E*,3*E*/1*E*,3*Z* ratios in parentheses.

Cyclododecyne (**1g**) underwent the rhodium-catalyzed isomerization to yield 1,3-dodecadiene (**2g**) with the aid of tributylmethallylstannane (Scheme 2). Similar treatment of cyclic allene **1h** provided 1,3-tridecadiene (**2h**, Scheme 2). Both of the products mainly comprised of the *E*,*Z* isomers, and no *E*,*E* isomers were detected. Unfortunately, the isomerization of an internal linear alkyne, 6-dodecyne, led to the formation of a mixture of conjugated dodecadienes. The reaction of 1-dodecyne provided a complex mixture containing no vinylic ^1H NMR signals.

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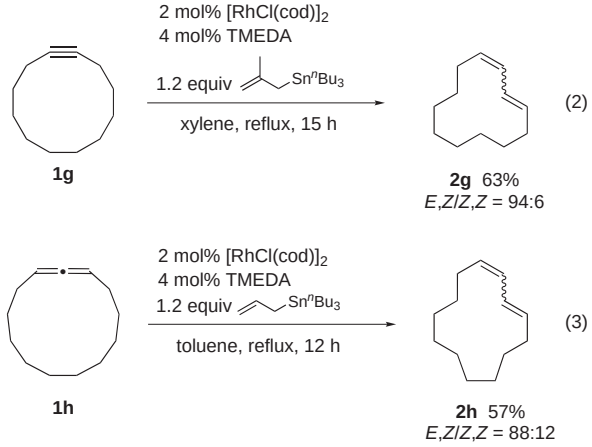
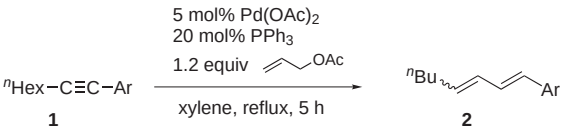


Scheme 2

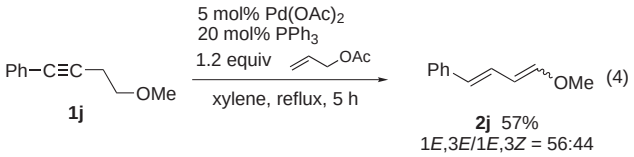
An alternative system for the isomerization utilizes a combination of palladium catalyst and allyl acetate. Heating a mixture of **1b**, 1.2 equiv of allyl acetate, 5 mol% of $Pd(OAc)_2$ and 20 mol% of PPh_3 in xylene for five hours afforded **2b** in 87% yield (Table 2, entry 1). Allyl acetate proved to enhance the efficiency of the reaction (entry 2). The exact role of allyl acetate is not clear at this stage. We are tempted to assume that an allylpalladium complex can be the actual catalyst. The palladium-catalyzed conditions usually provided the better yields of **2** than the rhodium-catalyzed reactions. Functional group compatibility was so satisfactory that the aldehyde moiety left untouched (entry 7). The palladium-catalyzed isomerization of homopropargyl methyl ether **1j** afforded dienyl ether **2j** (Scheme 3), whereas the rhodium-catalyzed system did not promote the isomerization.

Table 2 Palladium-Catalyzed Isomerization of Alkynes to 1,3-Dienes in the Presence of Allylacetate



Entry	Ar	1	2	Yield (%)[a]
1	Ph	**1b**	**2b**	87 (83:17)
2[b]	Ph	**1b**	**2b**	60 (83:17)
3	3,5-$(CF_3)_2C_6H_3$	**1a**	**2a**	97 (85:15)
4	4-$MeOC_6H_4$	**1c**	**2c**	53 (80:20)
5	2-MeC_6H_4	**1d**	**2d**	68 (84:16)
6	4-AcC_6H_4	**1f**	**2f**	90 (83:17)
7[c]	4-HC(=O)C_6H_4	**1i**	**2i**	73 (78:22)

[a] 1*E*,3*E*/1*E*,3*Z* ratios in parentheses.
[b] Performed in the absence of allyl acetate.
[c] 4-(1-Hexynyl)benzaldehyde was used.



Scheme 3

In summary, we have devised rhodium- and palladium-catalyzed isomerization reactions of alkynes to 1,3-dienes. The rhodium and palladium catalysts require allyltributylstannane and allyl acetate, respectively, to attain satisfactory results.

Acknowledgment

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References and Notes

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(2) Isomerization of propargyl ethers: (a) Hirai, K.; Suzuki, H.; Morooka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, *21*, 3413. (b) Isomerization of perfluoroalkylalkynes: Wang, Z.; Lu, X. *Tetrahedron* **1995**, *51*, 11765. (c) Isomerization as a side reaction: Kadota, I.; Shibuya, A.; Lutete, L. M.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4570. (d) Ruthenium-catalyzed isomerization: Shiotsuki, M.; Ura, Y.; Ito, T.; Wada, K.; Kondo, T.; Mitsudo, T. *J. Organomet. Chem.* **2005**, *689*, 3168.

(3) The role of allyltributylstannane is not clear at this stage. The formation of chlorotributylstannane was confirmed upon mixing equimolar amounts of $[RhCl(cod)]_2$ and allyltributylstannane in refluxing xylene.

(4) (a) **General Procedure for Rhodium-Catalyzed Isomerization of Alkynes.**
$[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol) was placed in a 20 mL reaction flask under argon. TMEDA (2.3 mg, 0.02 mmol, dissolved in 2 mL of xylene), alkyne **1b** (93 mg, 0.50 mmol, dissolved in 2 mL of xylene), and allyltributylstannane (199 mg, 0.6 mmol, dissolved in 2 mL of xylene) were sequentially added at ambient temperature. After being stirred for 12 h at 140 °C, the reaction mixture was cooled to ambient temperature, and HCl (6 M, 5 mL) was added. After being stirred for additional 1 h, the product was extracted with hexane (2 ×10 mL). The combined organic phase was dried over Na_2SO_4. Evaporation followed by silica gel column purification afforded 1,3-diene **2b** (78.2 mg, 0.42 mmol, 84%). The obtained **2b** showed the identical spectra in the literature, see: Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972. (b) **General Procedure for Palladium-Catalyzed Isomerization of Alkynes.**
$Pd(OAc)_2$ (5.6 mg, 0.025 mmol) and PPh_3 (26 mg, 0.10 mmol) were placed in a 20 mL reaction flask under argon.

Allyl acetate (60 mg, 0.60 mmol, dissolved in 2 mL of xylene) and alkyne **1a** (161 mg, 0.50 mmol) were sequentially added at ambient temperature. After being stirred for 5 h at 140 °C, the reaction mixture was filtered. Evaporation followed by silica gel column purification afforded 1,3-diene **2a** (156 mg, 0.49 mmol, 97%).
1,3-Diene **2a**: IR (neat): 2962, 2932, 1645, 1468, 1381, 1279, 1134, 986, 939, 893, 846, 684 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3 × 0.85 H), 0.96 (t, *J* = 7.5 Hz, 3 × 0.15H), 1.33–1.49 (m, 4 H), 2.20 (dt, *J* = 7.5, 6.5 Hz, 2 × 0.85 H), 2.35 (dt, *J* = 7.5, 6.0 Hz, 2 × 0.15 Hz), 5.70 (dt, *J* = 10.5, 7.5 Hz, 1 × 0.15 H), 5.99 (dt, *J* = 15.0, 7.5 Hz, 1 × 0.85 H), 6.16–6.26 (m, 1 H), 6.47 (d, *J* = 16.0 Hz, 1 × 0.85 H), 6.56 (d, *J* = 16.0 Hz, 1 × 0.15 H), 6.89 (dd, *J* = 16.0, 10.5 Hz, 1 × 0.85 H), 7.19 (ddd, *J* = 16.0, 11.0, 1.0 Hz, 1 × 0.15 H), 7.68 (s, 1 × 0.85H), 7.70 (s, 1 × 0.15H), 7.77 (s, 2 × 0.85 H), 7.80 (s, 2 × 0.15H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (1*E*,3*E* isomer) = 14.11, 22.45, 31.41, 32.81, 120.34–120.37 (m), 123.56 (q, *J* = 273 Hz), 125.86 (m), 126.76, 129.80, 132.06 (q, *J* = 33.2 Hz), 132.45, 139.65, 140.02; δ (1*E*,3*Z* isomer) = 14.17, 22.53, 28.11, 31.91, 120.58–120.64 (m), 126.08 (m), 127.97, 128.12, 128.91, 132.12 (q, *J* = 32.7 Hz), 136.76, 139.97; the signals for the carbons of CF_3 were not observed. Anal. Calcd for $C_{16}H_{16}F_6$ (%): C, 59.63; H, 5.00; Found: C, 59.70; H, 4.94.