Ruthenium-Catalyzed Transfer Hydrogenation of Alkynes by Tributylamine

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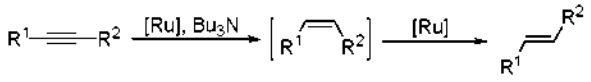
Received May 21, 2009, Accepted August 2, 2009

Key Words: Alkenes, Alkynes, Ruthenium catalyst, Transfer hydrogenation, Tributylamine

In contrast to conventional reduction methods, which frequently require a high hydrogen pressure and hazardous reducing agents, transition metal-catalyzed transfer hydrogenation has some unique advantages in its simplicity and avoidance of cumbersome reducing agents.[1,2] Many hydrogen donors combined with a variety of transition metal catalysts so far have been developed for such a transfer hydrogenation.[1] Among them, in connection with this report, several transition metals revealed a catalytic activity to the transfer of hydrogen from trialkylamines.[3] For example, Tsuji *et al.* have reported that aldehydes react with allylic acetates in the presence of a ruthenium catalyst along with triethylamine to give homoallylic alcohols and the hydrogen source for the products is triethylamine.[3e] It is also reported that diphenylacetylene is used as a sacrificial hydrogen acceptor in a ruthenium-catalyzed synthesis of esters from aldehydes and alcohols.[4] During the course of our ongoing studies on ruthenium catalysis, we recently found an unusual type of transfer hydrogenation between ketones (or secondary alcohols) and primary alcohols (or aldehydes) accompanied by carbon-carbon bond formation under a ruthenium-catalyzed redox shuttle.[5-8] Under these circumstances, herein we report a ruthenium-catalyzed transfer hydrogenation of alkynes to *trans*-alkenes by a trialkylamine (Scheme 1).[9]

The results of several attempted transfer hydrogenation of diphenylacetylene (**1a**) under various conditions are listed in Table 1. Treatment of **1a** in dioxane in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$ along with Bu_3N afforded *trans*-stilbene (**2a**) in 87% yield with concomitant formation of *cis*-stilbene (**3**) (2% yield) with complete conversion of **1a** (run 1). Performing the reaction for a longer reaction time (15 h) gave **2a** as the sole reduction product (run 2). The amount of $RuCl_2(PPh_3)_3$ affected the distribution of reduced products, a smaller amount of $RuCl_2(PPh_3)_3$ even under a larger amount of Bu_3N resulting in preferential formation of **3** (run 3). This result clearly indicates that $RuCl_2(PPh_3)_3$ plays a role for the selectivity of **2a** to **3**. Lower reaction temperature resulted in lower yield and selectivity of reduced products (run 4). The reaction proceeds even in the absence of Bu_3N, however, the yield and selectivity of products were lower than those when the reaction was carried out in the presence of Bu_3N (run 5). The reduction seems to be due to transfer hydrogenation from

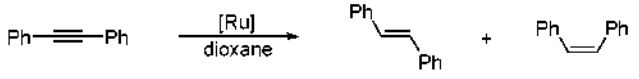


Scheme 1

dioxane to **1a**. It is known that dioxane has been used as a hydrogen donor in transition metal-catalyzed transfer hydrogenation.[10] From the activity of several ruthenium precursors examined, $RuCl_2(PPh_3)_3$ is revealed to be the catalyst of choice and other catalyst precursors such as $RuH_2(PPh_3)_4$, $RuCl_2(=CHPh)(PCy_3)_2$, $RuCl_3nH_2O/3PPh_3$ and $Ru_3(CO)_{12}$ resulted in either lower yield or lower selectivity of products (runs 6-9).

After the reaction conditions have been established, a series of diarylalkynes **1** were employed to investigate the reaction scope and several representative results are summarized in Table 2.[11] With diarylalkynes (**1a-g**) having electron donating and withdrawing substituents, the reductive isomerized diaryl alkenes (**2a-g**) were formed in the range of 60 - 86% yields. Here again, *cis*-alkenes were scarcely produced. The product yield was not significantly affected by the position of the substituent on the aromatic ring, whereas the electronic nature of that had some relevance to the product yield. 2-(Phenylethynyl) naphthalene (**1h**) was also reductively isomerized under the employed conditions to give (*E*)-2-styrylnaphthalene (**2h**) in 74% yield. With diaryl alkyne **1i**, which has heteroaryl group, the corresponding *trans*-alkene **2i** was also produced and the product yield was lower than that when compared to the reaction with previously described diaryl alkynes (**1a-h**). The reaction proceeds likewise with diaryl alkynes (**1j** and **1k**) having electron donating and withdrawing substituents at both aromatic rings

Table 1. Reductions under several conditions[a]

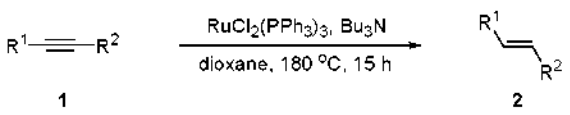


1a **2a** **3**

Run	Ruthenium catalyst	Conv.[b] (%) of **1a**	Yield[b] (%)	
			2a	**3**
1	$RuCl_2(PPh_3)_3$	100	87	2
2[c]	$RuCl_2(PPh_3)_3$	100	89	trace
3[d]	$RuCl_2(PPh_3)_3$	100	16	48
4[e]	$RuCl_2(PPh_3)_3$	42	7	19
5[f]	$RuCl_2(PPh_3)_3$	30	7	18
6	$RuH_2(PPh_3)_4$	81	6	52
7	$RuCl_2(=CHPh)(PCy_3)_2$	100	57	26
8	$RuCl_3nH_2O/3PPh_3$	100	81	12
9	$Ru_3(CO)_{12}$	100	54	4

[a]Reaction conditions: **1a** (0.5 mmol), ruthenium catalyst (0.025 mmol), Bu_3N (0.2 mmol), dioxane (5 mL), 180 °C, for 5 h, under Ar. [b]Determined by GLC. [c]For 15 h. [d]$RuCl_2(PPh_3)_3$ (0.005 mmol). [e]At 120 °C. [f]In the absence of Bu_3N.

Table 2. Reduction of alkynes **1** to alkenes **2** under $RuCl_2(PPh_3)_3$/Bu_3N[a]



1 **2**

	Alkynes **1**		Isolated yield (%)
	R^1 =	R^2 =	
1a	Ph	Ph	83
1b	Ph	2-$CH_3C_6H_4$	84
1c	Ph	3-$CH_3C_6H_4$	84
1d	Ph	4-$CH_3C_6H_4$	86
1e	Ph	4-$CH_3OC_6H_4$	60
1f	Ph	2-FC_6H_4	78
1g	Ph	4-FC_6H_4	70
1h	Ph	2-Naphthyl	74
1i	Ph	3-Pyridyl	63
1j	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	89
1k	4-$CH_3C_6H_4$	4-FC_6H_4	72
1l	4-$CH_3OC_6H_4$	Hexyl	42[b]

[a]Reaction conditions: 1 (0.5 mmol), ruthenium catalyst (0.025 mmol), Bu_3N (0.2 mmol), dioxane (5 mL), 180 °C, for 15 h, under Ar. [b]Determined by ^1H NMR.

to give the corresponding diaryl alkenes (**2j** and **2k**) in similar yields. On the other hand, although the reaction proceeds with alkyl aryl alkyne **1l**, the isolation of pure *trans* alkene product from crude mixture met with failure since the product is exactly eclipsed with a small amount of several unidentifiable compounds on chromatographies.

As to the reaction pathway, although it is not yet fully understood, this seems to proceed *via* an initial transfer hydrogenation of alkyne by tributylamine as well as dioxane to form *cis*-alkene, which in turn triggers isomerization to give *trans*-alkene. We confirmed in a separate experiment that the yield of **2a** increased from 9% (1 h), 17% (2 h), 24% (3 h), 72% (4 h), to 87% (5 h), while that of **3** decreased from 45% (1 h), 46% (2 h), 57% (3 h), 10% (4 h), to 2% (5 h). Furthermore, we also confirmed that *cis*-stilbene was completely isomerized to *trans*-stilbene under $RuCl_2(PPh_3)_3$ (5 mol%)/dioxane/180 °C/5 h. These additional experiments along with the result of run 3 of Table 1 clearly show that **3** is initially formed by ruthenium-catalyzed transfer hydrogenation followed by ruthenium-catalyzed isomerization to **2a**. It is known that *cis*-alkenes are isomerized to *trans*-alkenes *via* a carbocation in the presence of a palladium catalyst.[12,13]

In summary, it has been shown that a variety of diaryl alkynes are converted into *trans*-alkenes under $RuCl_2(PPh_3)_3$/Bu_3N *via* initial transfer hydrogenation from Bu_3N to diaryl alkynes to form *cis*-alkenes and subsequent ruthenium-catalyzed isomerization.

Acknowledgments. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2008-331-C00176).

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11. General experimental procedure: To a 50 mL pressure vessel were added alkyne (0.5 mmol), $RuCl_2(PPh_3)_3$ (0.025 mmol), Bu_3N (0.2 mmol) and dioxane (5 mL). After the system was flushed with argon, the reaction mixture was allowed to react at 180 °C for 15 h. The reaction mixture was passed through a short silica gel column (ethyl acetate-hexane) to eliminate a ruthenium. Removal of the solvent left a crude mixture, which was separated by thin layer chromatography (silica gel, ethyl acetate-hexane mixture) to give *trans*-alkenes.
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