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The Novel Selective Reduction of the C-C Triple Bond

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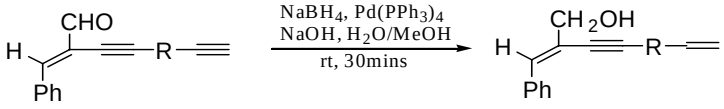
Abstract: A novel reduction system is reported here in which the compounds with terminal C-C triple bond and disubstituted C-C triple bond react with $NaBH_4/Pd(PPh_3)_4$ in a base condition and only terminal C-C triple bond is reduced.

Keywords: Selective reduction, C-C triple bond, $Pd(PPh_3)_4$.

Reduction of carbon-carbon triple bond is a valuable reaction and it plays an important role in the synthesis of a number of complicated natural products. Various methods of reduction of the C-C triple bond have been reported using the reduction reagents such as $NaBH_4$[1, 2] and DIBAL-H[3]. Under these reduction conditions, all C-C triple bonds are reduced. Recently, we have found a new reduction system ($NaBH_4/Pd(PPh_3)_4$) which reduces the terminal C-C triple bond selectively while the disubstituted one remains intact (**Scheme**).

Scheme



1a-1g **2a-2g**

The typical procedure for the selective reduction of the compounds with both disubstituted and terminal C-C triple bonds is described here. To a solution of NaOH (0.1 mol/L, 5 ml) in H_2O/MeOH (v:v = 1:1) were added successively $NaBH_4$ (37 mg, 1 mmol) and $Pd(PPh_3)_4$ (11.55 mg, 0.01 mmol) and the mixture was stirred for 10 mins in room temperature under nitrogen. The acetylenes (1 mmol) were added and the reaction mixture was stirred for another 30 mins, then the reaction mixture was extracted and the residue was purified by a column chromatography to afford olefins in 85-92% yield (**Table I**).

Table I

entry	substrate	R	t/h	product	yield (%)
1	**1a**	C_3H_6	0.5	2a	90
2	**1b**	C_4H_8	0.5	2b	92
3	**1c**	C_5H_{10}	0.5	2c	88
4	**1d**	C_6H_{12}	0.5	2d	85

In comparison, acetylenes such as **1e** and **1f** were also reduced to alkenes while diphenylacetylene **1g** was not reduced under the identical conditions (**Table II**). In conclusion, the reductive system of $NaBH_4/Pd(PPh_3)_4$ was efficient and effective to selectively reduce the terminal C-C triple bond.

Table II

entry	No.	substract	t/h	product	yield (%)
5	**1e**	Ph—≡	0.5	Ph—=	90
6	**1f**	Ph-CH_2-CH_2-≡	0.5	Ph-CH_2-CH_2-=	95
7	**1g**	Ph—≡—Ph	0.5	Ph—=—Ph	—

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