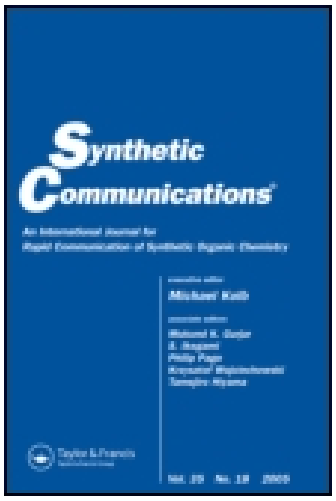

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THE NOVEL SELECTIVE REDUCTION OF THE CARBON-CARBON TRIPLE BOND USING $Pd(PPh_3)_4$ AS A CATALYST

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THE NOVEL SELECTIVE REDUCTION OF THE CARBON-CARBON TRIPLE BOND USING $Pd(PPh_3)_4$ AS A CATALYST

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ABSTRACT

A novel selective reduction system is reported in which compounds with terminal carbon-carbon triple bond and internal carbon-carbon triple bond were treated with $NaBH_4$-$Pd(PPh_3)_4$ in basic conditions and only the terminal C-C triple bond was reduced.

The reduction of carbon-carbon triple bonds is a particularly valuable reaction and is frequently used in organic synthetic chemistry.[1] The reduction of an alkyne can usually be stopped at the semihydrogenation stage because the alkene is more strongly bound than the alkyne, and competes effectively for the catalytic sites, blocking re-adsorption of the alkene, or displacing it.

Although various reduction reactions of alkynes have been reported in which the reagents such as $NaBH_4$[2], DIBAL-H[3], $LiAlH_4$[4] etc. are used widely, selective reduction has not been achieved. Suzuki *et al.* has reported the catalytic hydrogenation of alkynes using $NaBH_4$-$PdCl_2$ in the presence of

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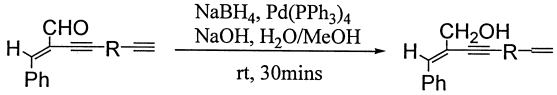
polyethylene glycol (PEG), in which reduction system both internal carbon-carbon triple bonds and terminal carbon-carbon triple bonds in the substrates were reduced unselectively.[5] Herein, we wish to report the preliminary results of a study focused on a new reduction system ($NaBH_4$-$Pd(PPh_3)_4$) in which the compounds with both internal carbon-carbon triple bonds and terminal carbon-carbon triple bonds are selectively reduced at the terminal carbon-carbon triple bond (Scheme). This reduction system has the advantages of faster rates and high regioselectivity, together with the easy handling.



1a-1d **2a-2d**

Scheme.

The typical procedure for the selective reduction of the compounds with both internal carbon-carbon triple bonds and terminal carbon-carbon triple bonds is described below. To a solution of 0.1 mol NaOH in 5 mL H_2O/MeOH (v:v = 1:1) was added successively $NaBH_4$ (75 mg, 2 mmol) and Pd $(PPh_3)_4$ (11.55 mg, 0.01 mmol), and the mixture stirred for 10 min at room temperature under nitrogen. The substrate (1 mmol) was added and the reaction mixture stirred for another 30 min. The resulting mixture was extracted with diethylether (3×25 mL). The combined extracts were dried (Na_2SO_4), the solvent was distilled off, and the residue was isolated by a column chromatography to afford olefins in 85–92% yield (Table 1).

Table 1. Results of the Reactions and the Spectral Data of Products

Substrate	R	Product	Yield (%)	Spectral Data of Products (%)
1a	C_3H_6	2a	90	δ_H: ($CDCl_3$, 300 MHz), 1.74 (m, 2H), 2.23 (m, 2H), 2.50 (t, 7.1 Hz, 2H), 4.28 (s, 2H), 5.05 (dd, 1.6 Hz, 10.2 Hz, 1H), 5.11 (dd, 1.7 Hz, 17.1 Hz, 1H), 5.86 (m, 1H), 6.73 (s, 1H), 7.29 ~ 7.87 (m, 5H); δ_C: ($CDCl_3$, 75 MHz), 19.9, 28.4, 33.5, 68.2, 77.3, 77.7, 78.1, 99.2, 116.2, 122.6, 128.7, 128.8, 129.1, 133.3, 136.8, 138.4; EI-MS (m/z): 226 (M^+, 12), 209 (base), 181 (21), 167 (32), 129 (18), 91 (7); (Found: C, 84.3; H, 8.1. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%).

(*continued*)

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Table 1. Continued

Substrate	R	Product	Yield (%)	Spectral Data of Products (%)
1b	C_4H_8	2b	92	δ_H: ($CDCl_3$, 300 MHz), 1.63 (m, 2H), 2.13 (m, 2H), 2.49 (t, 6.7 Hz, 2H), 4.28 (s, 2H), 5.03 (dd, 1.1 Hz, 11.1 Hz, 1H), 5.09 (dd, 1.8 Hz, 18.0 Hz, 1H), 5.84 (m, 1H), 6.74 (s, 1H), 7.29 ~ 7.88 (m, 5H); δ_C: ($CDCl_3$, 75 MHz), 20.4, 28.6, 28.8, 33.9, 68.1, 77.3, 77.7, 79.1, 99.3, 115.4, 122.6, 128.6, 128.8, 129.1, 133.2, 136.8, 139.1; EI-MS (m/z): 241 (M^+, 11), 223 (base), 181 (14), 141 (13), 129 (10); (Found: C, 84.7; H, 8.2. $C_{17}H_{20}O$ requires C, 85.0; H, 8.4%).
1c	C_5H_{10}	2c	88	δ_H: ($CDCl_3$, 300 MHz), 1.48 (m, 2H), 1.65 (m, 2H), 2.09 (m, 2H), 2.48 (t, 6.9 Hz, 2H), 4.28 (s, 2H), 4.99 (dd, 1.5 Hz, 10.3 Hz, 1H), 5.06 (dd, 1.6 Hz, 16.4 Hz, 1H), 5.83 (m, 1H), 6.72 (s, 1H), 7.28 ~ 7.88 (m, 5H); δ_C: ($CDCl_3$, 75 MHz), 20.3, 20.5, 29.0, 29.1, 34.3, 68.3, 77.9, 78.1, 79.0, 99.6, 115.1, 122.6, 128.7, 128.8, 129.1, 133.3, 136.8, 139.5; EI-MS (m/z): 255 (M^+, 22), 237 (base), 223 (16), 195 (13), 155 (31), 141 (26), 129 (18); (Found: C, 85.2; H, 8.6. $C_{18}H_{22}O$ requires C, 85.0; H, 8.7%).
1d	C_6H_{12}	2d	85	δ_H: ($CDCl_3$, 300 MHz), 1.45 (m, 6H), 1.65 (m, 2H), 2.10 (m, 2H), 2.48 (t, 6.9 Hz, 2H), 4.28 (s, 2H), 5.00 (dd, 1.1 Hz, 10.0 Hz, 1H), 5.07 (dd, 1.6 Hz, 17.2 Hz, 1H), 5.85 (m, 1H), 6.73 (s, 1H), 7.29 ~ 7.89 (m, 5H); δ_C: ($CDCl_3$, 75 MHz), 20.5, 29.1, 29.3, 29.4, 29.5, 34.4, 68.2, 77.3, 77.7, 78.2, 99.6, 115.0, 122.6, 128.6, 128.8, 129.1, 133.1, 136.8, 139.6; EI-MS (m/z): 268 (M^+, 36), 251 (base), 237 (16), 209 (13), 195 (14), 155 (20), 141 (15); (Found: C, 84.6; H, 8.8. $C_{19}H_{24}O$ requires C, 85.0; H, 9.0%).

In a comparison experiment, three substrates which possess only one carbon-carbon triple bond (1e, 1f, 1g) were treated under the same conditions. Compounds with a terminal carbon-carbon triple bond (1e, 1f) were reduced in good yield and the compound with an internal carbon-carbon triple bond (1g) was not be reduced (Table 2).

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Table 2. Results of the Reactions

No.	substrate	product	yield (%)
1e	Ph—≡	Ph—=	90
1f	Ph-CH_2-CH_2-≡	Ph-CH_2-CH_2-=	95
1g	Ph—≡—Ph	Ph—=—Ph	—

Mechanistic studies and application of the present reduction method are now in progress.

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