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Note

Nickel-catalyzed (*E*)-selective semihydrogenation of internal alkynes with hypophosphorous acid

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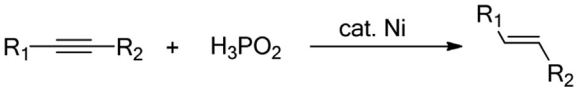
ABSTRACT

A facile Ni-catalyzed semihydrogenation of internal alkynes to (*E*)-alkenes using the cheap and easily handled hypophosphorous acid as a hydrogen donor was described. This reaction is featured by high reaction efficiency to produce the corresponding (*E*)-alkenes selectively.

1. Introduction

The transition metal catalyzed semihydrogenation of alkynes to alkenes with defined (*E*) or (*Z*)-configuration is an important transformation which is widely used in the preparation of synthetic intermediates, pharmaceuticals and natural products [1]. As exemplified by the famous Lindlar protocol, direct reductions of alkynes to (*Z*)-alkenes with good functional group tolerance are well known [2,3a–c]. However, in contrast, only few methods are known for the selective semihydrogenation of alkynes to (*E*)-alkenes [3]. Thus, the Birch-type reduction using NH_3 or amine as hydrogen donors can selectively produce (*E*)-alkenes. However, these reactions have to use a stoichiometric amount of alkali metals dissolving in amines which can damage the functional groups. Very recently, a selective (*E*)-alkene formation via semihydrogenation of alkynes mediated by ruthenium and silver heterogeneous catalysts was reported [3b,g]. Another example for selective generation of (*E*)-alkene was developed by Trost using a two-step process in which alkynes first underwent Ru-catalyzed *trans* hydrosilylation followed by the desilylation of the resulting alkenylsilanes with a fluoride. [4] Although this two-step protocol showed good functional group tolerance compared to the Birch reduction, the sacrifice of the expensive hydrosilane limits its general application. Therefore, the development of a more economical and greener method for the preparation of (*E*)-alkene is desirable.

Following our report on palladium-catalyzed selective hydrogenation of alkynes using formic acid as a reducing reagent [3a], herein, we described an effective selective Ni-catalyzed semihydrogenation of alkynes to (*E*)-alkenes using the easily handled hypophosphorous acid as hydrogen donor (Eq. (1)) [5]. This method reported herein features a high tolerance to a variety of functional groups and is a good complementary to the classic Birch reduction.



(1)

2. Result and discussion

Table 1 summarized the results for the reduction of diphenylacetylene using hypophosphorous acid catalyzed by metals. Although $RhCl(PPh_3)_3$ and palladium on carbon were ineffective at all (runs 1 and 2), under similar conditions at room temperature, palladium complexes (runs 3–5) could catalyze the semihydrogenation of diphenylacetylene to afford the (*Z*)-stilbene selectively. Nickel complexes were also effective for selective semihydrogenation of diphenylacetylene. Notably, however, being different from palladium and rhodium, nickel produced (*E*)-stilbene. Thus, under similar conditions, $NiCl_2(PPh_3)_2$ produced 5% yield of stilbene with a ratio of $E/Z = 60/40$. Complex $NiCl_2$dppp was

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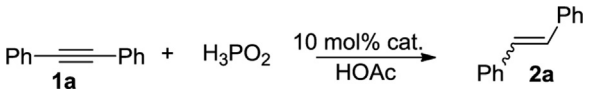
Table 1
Selective reduction of diphenylacetylene using hypophosphorous acid.[a]



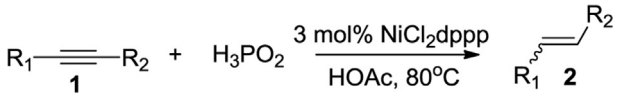
Run	Catalyst	Tem. (°C)	H_3PO_2 (equivs)	Time (h)	GC Yield (*E*/*Z*)
1	$RhCl(PPh_3)_3$	25	5	24	0%
2	Pd/C	25	5	24	0%
3	$Pd_2(dba)_3$	25	5	24	33% (1:99)
4	$PdCl_2(PPh_3)_2$	25	5	24	46% (1:99)
5	$Pd(PPh_3)_4$	25	5	24	48% (1:99)
6	$NiCl_2(PPh_3)_2$	25	5	24	5% (60:40)
7	$NiCl_2$dppp	25	5	24	91% (90:10)
8	$NiCl_2$dppp	50	5	1	16% (56:44)
9	$NiCl_2$dppp	80	5	1	91% (98:2)
10	$NiCl_2$dppp	100	5	1	93% (97:3)
11[b]	$NiCl_2$dppp	80	1	1	67% (86:14)
12[b]	$NiCl_2$dppp	80	3	1	94% (97:3)
13[c]	$NiCl_2$dppp	80	3	4	98% (98:2)

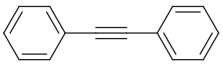
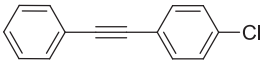
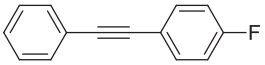
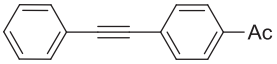
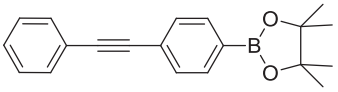
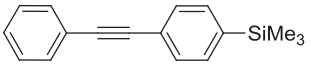
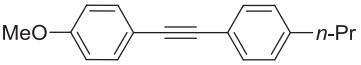
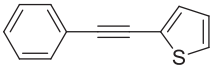
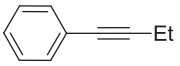
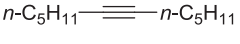
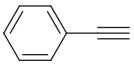
[a] Condition: a mixture of diphenylacetylene (0.2 mmol), H_3PO_2 50% aqueous solution and a catalyst in 0.5 mL of acetic acid was allowed to react at the temperature shown in the table. dppp = $Ph_2P(CH_2)_3PPh_2$.
[b] 5 mol% $NiCl_2$dppp.
[c] 3 mol% $NiCl_2$dppp.

a more effective catalyst which could give better selectivity and higher yield of (*E*)-stilbene. Thus, in the presence of 10 mol% $NiCl_2$dppp, the semireduction with 5 equivs H_3PO_2 at room temperature for 24 h gave the desired product (*E*)-stilbene in 91% yield with 90% selectivity (run 6). After optimizing the reaction conditions by changing temperature and catalyst loading, it was found that 98% yield of stilbene could be obtained with a ratio of *E*/*Z* = 98/2 by simply heating the reaction mixture of diphenylacetylene with 50% H_3PO_2 aqueous solution at 80 °C for 4 h in the presence of 3 mol % $NiCl_2$dppp (run 13). It is noted that acetic acid seems to be the solvent of choice because other solvents such as DMSO, DMF, dioxane, THF, toluene and hexane only gave low yields of the products.

By using the optimized conditions described in Table 1, other internal alkynes could also be smoothly converted to the corresponding (*E*)-alkenes. As shown in Table 2, this Ni-catalyzed reaction was effective for various aromatic internal alkynes bearing both electron-donating and electron-withdrawing groups. Worth noting was that this reaction had a wide functional group tolerance. Thus, functional groups such as chloro (run 2), fluoro (run 3), carboxyl (run 4), and methoxy (run 7) all were compatible. Especially, trimethylsilyl group which was easily hydrolyzed [3a] also survived and the corresponding product (*E*)-alkenes **2f** was produced in 82% yield with 99:1 selectivity under the catalytic conditions (run 6). Boronic ester group was also tolerant with this nickel-catalyzed semihydrogenation and the corresponding (*E*)-alkene was produced in good yield with high selectivity (>99:1) (run 5). In the presence of 3 mol% $NiCl_2$dppp, 1,4-bis(2-phenylethynyl)benzene can be readily converted to the corresponding (*E*,*E*)-product **2h** in moderate yield (run 8). In addition, **2i** could also be obtained highly selectively from the corresponding 2-(2-phenylethynyl)thiophene (run 9). It was noted that 20% over reduced alkane was also generated although similar over reduction products were hardly detected in other cases. An alkyl–aryl internal alkyne 1-(pent-1-ynyl)benzene also produced the corresponding product efficiently (run 10). Only a moderate yield of the product was obtained from an alkyl–alkyl internal alkyne dodec-6-yne (run 11) in which the hydration side product was generated in a large amount. Finally, terminal

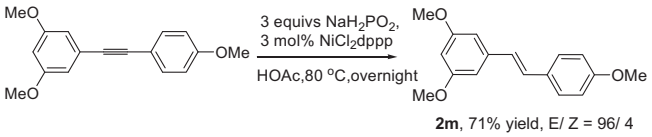
Table 2
Ni-catalyzed selective semihydrogenation of alkynes affording (*E*)-alkenes.[a]



Run	Substrate	Time (h)	GC yield (*E*:*Z*)	Isolated yield
1		4	**2a**, 98% (98:2)	85%
2		6	**2b**, 99% (98:2)	86%
3		4	**2c**, 95% (>99:1)	70%
4		6	**2d**, 96% (99:1)	80%
5		4	**2e**, 91% (>99:1)	73%
6[b]		48	**2f**, 90% (99:1)	82%
7		6	**2g**, 92% (99:1)	83%
8		4	**2h**, 70% (>99:1)[c]	–
9		28	**2i**, 80% (99:1)[d]	55%
10		4	**2j**, 82% (98:2)	23%[e]
11		6.5	**2k**, 44% (98:2)[f]	–
12		4	**2l**, Trace (–)[g]	–

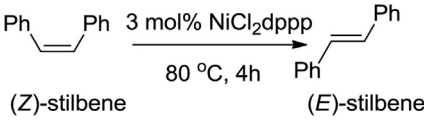
[a] Condition: a mixture of 0.2 mmol of an alkyne, 0.6 mmol of 50% aqueous H_3PO_2 solution and 3 mol% $NiCl_2$dppp was dissolved in 0.5 mL of acetic acid and heated at 80 °C until the alkyne was consumed.
[b] 40 °C.
[c] 23% yield of the partial reduction product remained.
[d] 20% yield of the over reduction alkane was produced. The product was isolated by a preparative GPC.
[e] A low isolated yield due to the low boiling point of the product.
[f] Yield determined by NMR. ca 48% yield of 6-dodecanone was formed.
[g] The hydration product acetophenone was produced predominantly.

alkynes such as phenylacetylene could not be used in the reaction because significant hydration, rather than hydrogenation, took place (run 12).



2m, 71% yield, E/ Z = 96/ 4 (2)

As shown in Eq. (2), the synthetic value of the present Ni-catalyzed semihydrogenation was further demonstrated by the efficient synthesis of precursors of resveratrol, the well-known bioactive natural products which have antitumor [6a,b], antibacterial [6c,d], antioxidation [6e], antiaging [6f,g], vascular protective, [6h] and metabolic regulation effects [6i,j]. Thus, by employing the Ni-catalyzed selective semihydrogenation, 3,5,4′-trimethoxydiphenylacetylene was smoothly converted to the corresponding (*E*)-alkene **2m** in 71% isolated yield selectively (Eq. (2)). Following the established procedures, [7] **2m** can be efficiently converted to the natural product resveratrol.

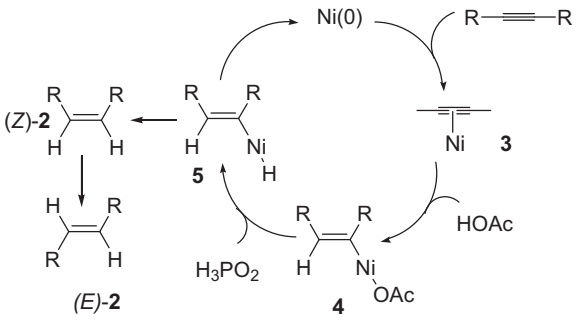


H_3PO_2	Solvent	Yield
2 equivs	HOAc	quantitative
-	HOAc	<1%
2 equivs	THF	quantitative

(3)

As to the mechanism for the generation of (*E*)-alkenes, it was assumed that (*Z*)-alkenes were initially generated which isomerized to the more stable (*E*)-alkenes by nickel catalysts. Indeed, as shown in Eq. (3), (*Z*)-stilbene was quantitatively converted to (*E*)-stilbene under the reaction conditions. It was noted that H_3PO_2 was essential for this isomerization and the isomerization hardly proceeded in the absence of H_3PO_2.

A proposed catalytic cycle was shown in Scheme 1. The Ni-catalyzed selective reduction of an alkyne to alkene took place via a catalytic cycle involving hydrometalation of the tripe bond with the combination of Ni(0) complex [8] and HOAc affording the alkenylnickel species **4** [3a], which was reduced by H_3PO_2 generating intermediate **5**. Subsequent reductive elimination of **5** and isomerization of (*Z*)-**2** produced (*E*)-**2** (Scheme 1).



Scheme 1. A proposed mechanism for Ni-catalyzed selective semihydrogenation of alkynes. Ligands were omitted for clarity.

3. Conclusion

In summary, a simple one-pot highly stereoselective Ni-catalyzed reduction of internal alkynes to (*E*)-alkenes using the cheap and environmental-friendly hypophosphorous acid was developed. This method featured high tolerance to a variety of functional groups and is a convenient method for the synthesis of (*E*)-alkenes.

4. Experimental section

4.1. A typical procedure for the Ni-catalyzed semihydrogenation of alkynes

Under N_2 atmosphere, a mixture 0.2 mmol of diphenylacetylene, 3 equivs 50% H_3PO_2 aqueous solution (65 μL), and 3 mol% $NiCl_2$dppp (3.3 mg) in 0.5 mL of AcOH was stirred at 80 °C for 4 h until diphenylacetylene was consumed as followed by GC. The volatiles were pumped off and the crude products were subject to purification by column chromatography on silica gel (silica gel size: 38–63 μm, 40 g; column size: 2 cm × 30 cm) using hexane as an eluent to obtain the pure **2a** in 85% yield (30.6 mg, *E*/*Z* = 98/2).

4.1.1. (E)-Stilbene (**2a**) [3a]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60–7.62 (m, 4H), 7.38 (t, 4H, *J* = 7.2 Hz), 7.25–7.29 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.50, 129.17, 128.90, 128.11, 126.95.

4.1.2. (E)-1-(4-Chlorophenyl)-2-phenyl-ethylene (**2b**) [3a]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.52 (m, 2H), 7.43–7.47 (m, 2H), 7.27–7.39 (m, 5H), 7.07 (d, 2H, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.95, 135.81, 133.16, 129.27, 128.87, 128.78, 127.91, 127.68, 127.35, 126.57.

4.1.3. (E)-1-(4-Fluorophenyl)-2-phenyl-ethylene (**2c**) [3c]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.51 (m, 4H), 7.37 (t, 2H, *J* = 7.0 Hz), 7.27 (t, 1H, *J* = 6.0 Hz), 7.00–7.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.28 (d, *J* = 247.8 Hz), 137.11, 133.46 (d, *J* = 2.9 Hz), 128.67, 128.44 (d, *J* = 1.9 Hz), 127.93 (d, *J* = 7.6 Hz), 127.63, 127.43, 126.40, 115.58 (d, *J* = 21.0 Hz).

4.1.4. 1-[4-((1E)-2-Phenylethenyl)phenyl]ethanone (**2d**) [3a]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, *J* = 8.4 Hz), 7.61 (d, 2H, *J* = 8.4 Hz), 7.57 (d, 2H, *J* = 7.2 Hz), 7.41 (t, 2H, *J* = 7.6 Hz), 7.31–7.35 (m, 1H), 7.14–7.24 (m, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.42, 142.03, 136.73, 136.01, 131.50, 128.87, 128.79, 128.31, 127.48, 126.82, 126.50, 26.55.

4.1.5. (E)-4,4,5,5-Tetramethyl-2-(4-styrylphenyl)-1,3,2-dioxaborolane (**2e**) [3a]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, 2H, *J* = 8.0 Hz), 7.53 (d, 4H, *J* = 8.0 Hz), 7.37 (t, 2H, *J* = 8.0 Hz), 2.28 (d, 1H, *J* = 8.0 Hz), 7.10–7.21 (m, 2H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.02, 137.19, 135.17, 129.65, 128.72, 128.63, 127.81, 126.63, 125.81, 83.82, 24.93.

4.1.6. (E)-1-(4-Trimethylsilylphenyl)-2-phenyl-ethylene (**2f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.53 (m, 6H), 7.36 (t, 2H, *J* = 7.2 Hz), 7.26 (t, 1H, *J* = 7.6 Hz), 7.13 (d, 2H, *J* = 3.6 Hz), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.14, 140.04, 138.84, 138.45, 134.84, 130.03, 129.80, 128.77, 127.67, 126.92, 1.12.

4.1.7. (E)-1-(4-Fluorophenyl)-2-(4-propylphenyl)-ethylene (**2g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.46 (m, 4H), 7.16 (d, 2H, *J* = 8.0 Hz), 6.88–7.05 (m, 4H), 3.83 (s, 3H), 2.58 (t, 2H, *J* = 7.2 Hz),

1.56–1.69 (m, 2H), 0.95 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.13, 141.97, 135.11, 130.36, 128.80, 127.60, 127.26, 126.60, 126.16, 114.10, 55.35, 37.82, 24.57, 13.88.

*4.1.8. 1,4-Di-(E)-styrylbenzene (**2h**) [3a]*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.54 (m, 8H), 7.35–7.39 (m, 4H), 7.25–7.29 (m, 2H), 7.13 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.33, 136.71, 128.71, 128.60, 128.28, 127.66, 126.85, 126.52.

*4.1.9. 2-(E)-Styrylthiophene (**2i**) [3b]*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H, J = 7.6 Hz), 7.35 (t, 2H, J = 7.6 Hz), 7.19–7.27 (m, 3H), 7.08 (s, 1H), 7.01 (t, 1H, J = 4.0 Hz), 6.94 (d, 1H, J = 16.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.90, 136.98, 128.72, 128.35, 127.62, 126.31, 126.12, 124.36, 121.80.

*4.1.10. (E)-1-Phenylbut-1-en (**2j**) [9]*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.33 (m, 4H), 7.14–7.18 (m, 1H), 6.21–6.38 (m, 2H), 2.18–2.25 (m, 2H), 1.08 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.02, 132.66, 128.89, 128.50, 126.79, 125.96, 26.10, 13.68.

*4.1.11. (E)-1-(4′-Methoxyphenyl)-2-(3,5-dimethoxyphenyl)ethene (**2m**) [7]*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, 2H, J = 8.8 Hz), 6.89–7.07 (m, 4H), 6.66 (d, 2H, J = 2.4 Hz), 6.39 (t, 1H, J = 1.6 Hz), 3.83 (b, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.10, 159.42, 139.73, 129.96, 128.76, 127.82, 126.60, 114.17, 104.37, 99.65, 55.37, 55.33.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.09.023.

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