



Controlled hydrogenation of diphenylacetylene using alkylammonium formate



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ABSTRACT

A simple and straightforward semihydrogenation of alkyne to alkene with triethanolamine and formic acid in the presence of PdCl₂ has been described. Although hydrogenation using formic acid as a hydrogenation source has been used in combination with amines previously, few reports are available concerning the associated reactivity. We demonstrated that reactivity changes depending on the type of amine used in the hydrogenation. Further, this reaction requires no strict time control, making it a useful tool in organic synthesis.

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Hydrogenation is widely used not only in laboratories but also in industry as a synthetic method.^{1–4} The process uses H₂ gas, HCl aq., formic acid, and alcohol as hydrogen sources in the presence of a metal catalyst such as Pd, Pt, Fe, Sn, Ru, Rh, and Ir.^{5–9} Although reactivity is usually controlled by the choice of ligand and additives, semihydrogenation of alkynes to alkenes remains a challenging and important issue. For instance, the classical approach using Lindlar catalysts suffers from selectivity issues of terminal alkynes and time control.^{10–13} The reactivity of hydrogenation using Lindlar catalysts is reduced through the addition of quinoline. However, there are few reports concerning controlling its reactivity through the addition of an appropriate amine. Recently, Sajiki and co-workers reported control of hydrogenation reactivity by changing the Pd carrier; semihydrogenation of alkynes was achieved using Pd/BN and diethylenetriamine.¹² Although most of these reactions use H₂ gas as the hydrogen source, the advantage of using formic acid is that it is easy to adjust its equivalent amount in the reaction. Using formic acid, the reaction mechanism and isomerization from the *cis* to the *trans* forms of the semihydrogenated products have been reported.^{14–17} Hydrogenation using formic acid as the hydrogen source in conjunction with amines such as ammonia,¹⁸ trimethylamine,^{18–20} and tributylamine²¹ have been described, but few reports on the associated reactivity are available. In the hydrogenation of carbonyl groups

using amine-formic acid salts, for example, we found that the reactivity changes greatly depending on the type of amine.^{22,23} As a next step, our present focus concerns the semihydrogenation of alkynes with these results in mind.

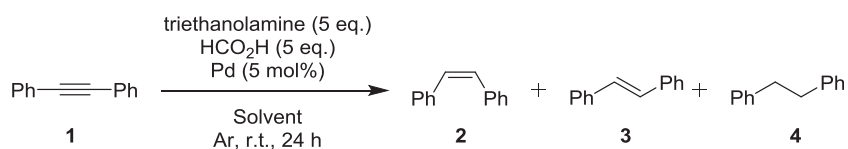
To determine the optimal reaction conditions for the semihydrogenation of alkynes, we first examined the hydrogenation of diphenylacetylene (**1**) with triethanolamine (5 eq.), formic acid (5 eq.), and Pd catalyst (5 mol%) in DMF at 30 °C (Table 1). When Lindlar catalyst and Pd(OAc)₂ were used, *cis*-stilbene (**2**) was obtained but in low yields (entries 1 and 2). Although we found that the reaction with PdCl₂ afforded **2**: *trans*-stilbene (**3**) = 14.5:1 in 93% yield, PdCl₂(CH₃CN)₂ and PdCl₂(PPh₃)₂ did not promote the reaction (entries 3–5). In the case of 20 eq. of triethanolamine and formic acid (entry 6), the yields of **2** and **3** were similar to those obtained in entry 3. The selectivity of **2** decreased at 50 °C (entry 7). When the choice of solvent was screened, acceleration of the reaction yet reduction in selectivity were observed when methanol was used (entry 8). In contrast, the reaction proceeded sluggishly in MeCN, THF, AcOEt, and CHCl₃ under the same conditions (entries 9–12). Overall, it is clear that the yield can be improved by selecting the solvent according to the reactivity of the substrate.

In general, amines suppress the catalytic activity of palladium by a coordination effect. We also know that PdCl₂ is not reduced without amine in preliminary experiments. To further investigate the effect of amine on hydrogenation, various amines were examined (Table 2). Although hydrogenation using ammonia

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Table 1
Optimization of the reaction conditions.



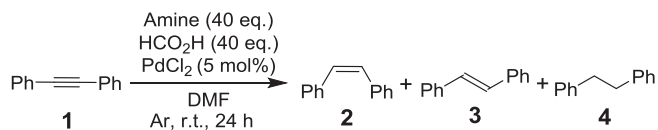
Entry	Pd	Solvent	Yield (%) ^a			
			2	3	4	1
1	Lindlar catalyst	DMF	36	0	0	64
2	Pd(OAc) ₂	DMF	23	1	4	67
3	PdCl ₂	DMF	87	6	3	0
4	PdCl ₂ (CH ₃ CN) ₂	DMF	34	2	1	62
5	PdCl ₂ (PPh ₃) ₂	DMF	7	0	0	91
6 ^b	PdCl ₂	DMF	85	6	4	0
7 ^c	PdCl ₂	DMF	74	14	8	0
8	PdCl ₂	MeOH	7	35	53	0
9	PdCl ₂	MeCN	32	2	2	62
10	PdCl ₂	THF	29	2	1	64
11	PdCl ₂	AcOEt	15	0	2	79
12	PdCl ₂	CHCl ₃	0	0	0	100

^a Determined by ¹H NMR analysis of crude reaction mixture.

^b 20 eq. of triethanolamine and formic acid were used.

^c The reaction was carried out at 50 °C.

Table 2
Effect of amines on hydrogenation.



Entry	Amine	Yield (%) ^a			
		2	3	4	1
1	NH ₃	6	0	0	88
2		9	9	79	0
3		0	0	95	0
4		0	0	95	0
5		0	0	93	0
6		0	0	98	0
7		67	8	4	16
8		0	0	98	0
9		41	18	37	0
10		54	9	34	0
11		75	4	18	0
12		81	8	4	0
13		3	7	85	0
14		57	7	34	0
15		77	6	13	0
16 ^b		0	0	97	0

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