

Catalytic Chemoselective and Stereoselective Semihydrogenation of Alkynes to E-Alkenes Using the Combination of Pd Catalyst and Znl₂

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Supporting Information



ABSTRACT: An efficient E-selective semihydrogenation of internal alkynes was developed under low dihydrogen pressure and low reaction temperature from commercially available reagents: Cl₂Pd(PPh₃)₂, Zn⁰, and ZnI₂. Kinetic studies and control experiments underline the significant role of ZnI_2 in this process under H₂ atmosphere, establishing that the transformation involves syn-hydrogenation followed by isomerization. This simple and easy-to-handle system provides a route to E-alkenes under mild conditions.

he semihydrogenation of alkynes to alkenes is a remarkable transformation of paramount importance in synthetic fine chemistry.¹ While reduction with Z-selectivity is readily achieved through catalytic hydrogenation under H₂ atmosphere with heterogeneous catalysts such as Lindlar's catalyst,² obtaining E-selectivity requires Birch-type conditions³ which often lack functional-group compatibility (see Scheme 1a). To overcome this constraint, hydrosilylation/ desilylation strategies and related trans-hydrometalations have been developed (Scheme 1b), although stoichiometric waste is produced.⁴ In the same vein, catalytic *E*-selective semihydrogenations of alkynes using hydrogen-transfer chemistry or molecular hydrogen have been also explored.⁵ Yet, this transformation remains challenging because most transition metal-catalyzed semihydrogenations of C-C triple bonds occur through cis-selective processes and E-alkenes are only obtained upon isomerization of the initially formed Z-alkenes. In such a situation, over-reduction of the alkene is a major limitation. Hydrogen transfer semireductions of alkynes have been completed using chromium reagents⁶ or transition-metal catalysts such as Ir,⁷ Ni,⁸ Co,⁹ Ru,¹⁰ and Pd¹¹ (Scheme 1c). The use of molecular H₂ has been also reported employing different catalytic systems (Scheme 1d). While the metal-free $HB(C_5F_5)_2$ /pentafluorostyrene system required high temperatures and pressures of H₂ (140 °C and 50 bar),¹² Co-,¹³ Fe-,¹⁴ and Ru-catalysts¹⁵ were disclosed to achieve trans-selective alkyne semihydrogenations under lower temperatures and pressures of H₂ (below 90 °C and below 10 bar).

Atmospheric pressure of H₂ can be also used. Dinuclear Ircomplexes¹⁶ and an Ag-Ru bimetallic complex¹⁷ were described to be efficient under 1 atm of H₂. Recently, propargylic alcohol derivatives can be transformed to E-allylic Scheme 1. Selective Semihydrogenation of Alkynes to E-Alkenes



alcohols with Ru-catalyst^{15b} and a ruthenium hydride catalyst was reported to require only 10 equiv of H₂.¹⁸ Finally, the heterogeneous combination of Pd₃Pb/SiO₂ and RhSb/SiO₂

Received: October 15, 2018

Table 1	. E-Selective	Semi-Hydro	genation of Alk	vnes: Optimizati	ion of Reaction	Conditions
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		H ₂ catalys Ph	(1 atm) t (5 mol %) dditive	A Ph		
		Ph solvent,	25 °C, 24 h	Phí 🗸		
		1	2	3		
entry	catalyst	solvent	additive (equiv)	1 (%)	2 (%) (E/Z)	3 (%)
1	$Pd(PPh_3)_4$	THF	-	0	63 (1.3/1)	37
2	$Pd(PPh_3)_4$	THF	MeZnI (2)	54	46 (5/1)	0
3	$Cl_2Pd(PPh_3)_2$	THF	MeZnI (2)	9	81 (64/1)	10
4	$Cl_2Pd(PPh_3)_2$	THF	Me_2Zn (0.2)	1	0	99
5	$Cl_2Pd(PPh_3)_2$	THF	$Me_2Zn (0.2) + ZnI_2 (2)$	4	83 (61/1)	13
6	$Cl_2Pd(PPh_3)_2$	THF	$Zn^{0}(3) + ZnI_{2}(2)$	2	86 (E)	12
7	$Cl_2Pd(PPh_3)_2$	Et ₂ O	$Zn^{0}(3) + ZnI_{2}(2)$	88	12 (5/1)	0
8	$Cl_2Pd(PPh_3)_2$	CH ₃ CN	$Zn^{0}(3) + ZnI_{2}(2)$	75	25 (2/1)	0
9	$Cl_2Pd(PPh_3)_2$	DMF	$Zn^{0}(3) + ZnI_{2}(2)$	21	75 (1.1/1)	4
10	$Cl_2Pd(PPh_3)_2$	THF	$Zn^{0}(3) + ZnCl_{2}(2)$	42	55 (1/3)	3
11	$Cl_2Pd(PPh_3)_2$	THF	$Zn^{0}(3) + ZnBr_{2}(2)$	2	85 (1/3.5)	13
12	$Cl_2Pd(PPh_3)_2$	THF	$Zn^{0}(3) + Zn(OTf)_{2}(2)$	0	62 (11.5/1)	38
13	$Cl_2Pd(PPh_3)_2$	THF	$Zn^{0}(3) + LiI(2)$	2	98 (2/1)	0
14	$Cl_2Pd(PPh_3)_2$	THF	$Zn^{0}(3) + MgI_{2}(2)$	82	18 (1/11)	0
15	$Cl_2Pd(PPh_3)_2$	THF	$Zn^{0}(3) + AlI_{3}(2)$	63	33 (1.5/1)	4
16	$Cl_2Pd(P^nBu_3)_2$	THF	$Zn^{0}(3) + ZnI_{2}(2)$	95	5 (nd)	0
17	$Cl_2Pd(PO^iPr_3)_2$	THF	$Zn^{0}(3) + ZnI_{2}(2)$	55	44 (20/1)	1
18	Cl ₂ Pd(dppp)	THF	$Zn^{0}(3) + ZnI_{2}(2)$	79	21 (4/1)	0
19	Cl ₂ Pd(xantphos)	THF	$\operatorname{Zn}^{0}(3) + \operatorname{ZnI}_{2}(2)$	95	5 (nd)	0
20	Pd-PEPPSI- ⁱ Pr	THF	$\operatorname{Zn}^{0}(3) + \operatorname{ZnI}_{2}(2)$	94	6 (nd)	0
21 ^b	$Cl_2Pd(PPh_3)_2$	THF	$\operatorname{Zn}^{0}(3) + \operatorname{ZnI}_{2}(1)$	0	96 (E)	4
D J	:1	J L., ITT NIMD	$b_{\mathbf{D}}$			

^aProduct distribution was determined by ¹H NMR analysis. ^bReaction time was 8 h.

was related to achieve *trans*-semireductions under 1 atm of H_2 at 25 °C.¹⁹

Our interest in semihydrogenation was instigated by the observation that zinc salts tamed the catalyst activity in the catalytic hydrogenation of alkenes.²⁰ We thus speculated that catalytic systems modified with zinc salt additives could allow for the partial hydrogenation of alkynes to alkenes with a subsequent *Z*-to-*E* isomerization. Herein we report the development of such a catalytic system competent for the semihydrogenation of internal alkynes to *E*-alkenes (Scheme 1).

We initiated our study by investigating the partial hydrogenation of diphenylacetylene 1 as model substrate (Table 1). First, a control experiment was performed with $Pd(PPh_3)_4$ in the absence of zinc additive: full conversion was observed but a mixture of alkane, Z- and E-alkenes was obtained (Table 1, entry 1). By contrast, adding MeZnI to the system (Table 1, entry 2) allowed for ~50% conversion with an encouraging E/Z ratio (5:1). In this transformation, the isomerization step without alkane formation is favored thanks to organozinc reagents. We then considered using $Cl_2Pd(PPh_3)_2$ as precatalyst and its in situ reduction by MeZnI. A noticeable improvement was observed: the E/Z ratio reached 64:1 while keeping alkane formation at 10% (Table 1, entry 3). On the other hand, when the reaction was conducted with Me₂Zn as a reducing agent (0.2 equiv), 1,2-diphenylethane 3 was the only product (Table 1, entry 4). However, the desired catalytic semihydrogenation was obtained upon addition of 2 equiv of ZnI₂ to the previous system: an excellent E-selectivity and a low proportion of 3 were obtained (Table 1, entry 5). Zn metal was then used as a reducing agent. E-stilbene 2 was delivered in 86% yield with limited alkane formation (Table 1, entry 6). We also screened different solvents under these conditions, but

no better results were obtained (Table 1, entries 7–9). Then, the influence of the counterion of the zinc salt was investigated. The use of anions such as Cl⁻ and Br⁻ was not selective (Table 1, entries 10 and 11), while softer donor anions provided good *E*-selectivities (Table 1, entries 6 and 12). However, alkane proportion was dramatically increased with the use of $Zn(OTf)_2$ (Table 1, entry 12). Metal salts with other maingroup cations were also considered. Replacing ZnI_2 by LiI or MgI₂ or AlI₃ diminished *E*-selectivity and/or conversion (Table 1, entries 13–15). Definitively, ZnI_2 emerged as the salt of choice to combine reactivity (full conversion) and selectivity (excellent *E*-stereoselectivity and low amounts of alkane).

Finally, we investigated the influence of the palladium ligand, but the results obtained with the simplest PPh₃ ligand were not improved. Indeed, a moderate conversion (44%) with a good *E*-selectivity was obtained with a less electron-donating ligand (Table 1, entry 17), while the uses of more electron-donating or bidentate ligands were detrimental (Table 1, entries 16, 18, and 19). With Pd complex bearing a NHC ligand, only 6% conversion of alkyne was observed (Table 1, entry 20). Conditions were fully optimized by diminishing the amount of ZnI₂ to 1 equiv (lower amounts offered erratic results) and setting the reaction time to 8 h (alkane formation was limited to 4%) (Table 1, entry 21).

We then considered the semihydrogenation of a range of substrates bearing a variety of functional groups to examine if the alkene formation could be sensitive to the electron density of the C–C triple bond. For some cases, the reactions had to be stopped before full conversion to prevent significant alkane formation (Scheme 2). Nonsymmetrical diphenylacetylenes having one ring substituted with one electron-donating group proceeded with excellent E/alkane ratios (2b–2e). The

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^{*a*}Product distribution was determined by ¹H NMR analysis.

transformation was compatible with chloride substitution as alkene 2f was obtained in a good yield with an acceptable E/alkane ratio (90:10). Nonsymmetrical diphenylacetylenes having one ring substituted with one electron-withdrawing group also proceeded in excellent yields and E/alkane ratios (2g-2i). Formation of CF₃-substituted stilbene 2j required 72 h of reaction time and 20 mol % of Pd catalyst to reach 89% yield and an excellent E/alkane selectivity (96:4). Conversely, introducing an electron-donating group (OMe) in para position on the other phenyl part to balance the CF3 electron-withdrawing effect led to a suitable yield (69%) and a decent E/alkane ratio (85:15) within only 7 h (2k). Compound 21 was obtained in a moderate yield, because of its low solubility in THF that needed the addition of dichloromethane, but the *E*/alkane selectivity was still excellent. Finally, nonsymmetrical heteroaryl derivatives were also good partners, as illustrated by the semihydrogenation delivering 2m and **2n**. A slight decrease in the E/Z selectivity (93.5:6.5) was observed for compound 2m, and this was attributed to competitive binding of nitrogen to the catalyst that could thwart the isomerization. Diene 20 formation required 20 mol % of Pd catalyst to reach 90% conversion with a total Eselectivity. Replacing one aryl moiety by an alkyl motif was also tolerated. Overhydrogenation was almost nonexistent (1%) and a good conversion with an excellent E-selectivity (97:3)

was obtained for alkene **2p**. Slightly worst results were observed for the formation of **2q**: *E*-selectivity was lower (E/Z ratio = 91:9) and alkane formation was slightly higher (9%). However, from 7-tetradecyne, no alkane was formed but the isomerization step was not efficient enough as a 34:66 E/Z ratio was detected for alkene **2r**. The semireduction of trimethylsilyl phenylacetylene gave only 10% of the corresponding *E*-vinyl silane. In the reaction medium, it was produced but it was directly transformed to ethylbenzene by Pd-catalyzed desilylation and subsequent hydrogenation of styrene.

To get more information about the transformation, monitoring studies were conducted on the semihydrogenation of diphenylacetylene (Figure 1). At the beginning (Figure 1), rapid formation of Z-stilbene was observed and reached a maximum after 4 h of reaction. In the same time, *E*-stilbene was also accumulated and a 1:1:1 mixture of alkyne/*E*/*Z* was observed after 4 h. During the following 3 h of reaction, the amount of *E*-stilbene increased steadily to reach 97% whereas both *Z*-stilbene and diphenylacetylene were totally consumed. Thus, the semihydrogenation of diphenylacetylene into *E*stilbene was achieved within 7 h. These studies lend clear evidence that *E*-alkene formation with our new catalytic conditions involving the combination of ZnI₂ and Pd⁰ complex is achieved through a pathway entailing semihydrogenation



Figure 1. Monotoring studies: from diphenylacetylene toward *E*-stilbene. (Proportion was determined by GC analysis.)

and subsequent isomerization. Alkane formation was only detected after 6 h of reaction when the amount of *E*-stilbene reached 75%. Furthermore, monitoring studies on isomerization and over-reduction conducted, respectively, from Z-stilbene and *E*-stilbene (see the Supporting Information) suggest that 1,2-diphenylethane 3 arises essentially from the reduction of *E*-stilbene.

Then, to understand the role of ZnI_2 better, several experiments were conducted. ³¹P NMR (162 MHz in CDCl₃) analysis evidenced that the peak for Cl₂Pd(PPh₃)₂ shifted from 23.73 ppm to 13.31 ppm upon the addition of ZnI₂ (see the Supporting Information). By comparison, freshly prepared I₂Pd(PPh₃)₂²¹ presented a signal at 13.11 ppm. This suggests that chlorine exchange by iodine occurs and delivers I₂Pd(PPh₃)₂. This precatalyst was then used for other control experiments (Table 2). First, by introducing I₂Pd(PPh₃)₂

instead of $Cl_2Pd(PPh_3)_2$ when only Zn^0 was present, 45% conversion was obtained within 24 h but low E/Z selectivity was observed (Table 2, entry 1). By contrast only 5% conversion was observed with $Cl_2Pd(PPh_3)_2$ (Table 2, entry 2). Seemingly, $I_2Pd(PPh_3)_2$ precatalyst is more easily reduced and the presence of ZnI₂ allows to regain a high transformation (Table 2, entry 3). In fact, ZnI_2 appears to be involved at two levels: the Pd^0 generation through $I_2Pd(PPh_3)_2$ formation and the E-selective semihydrogenation kinetics. As isomerization and over reduction are involved in this catalytic process, specific experiments with E- and Z-stilbenes were then conducted to acquire more information about these steps. In a first experiment, H₂ atmosphere was removed and no reaction was observed (Table 2, entry 4). Then two reactions were conducted on Z-stilbene under H₂ atmosphere using Me₂Zn as a reducing agent. In the presence of ZnI_2 , a mixture of E-stilbene and 1,2-diphenylethane 3 was obtained in 84/16 ratio (Table 2, entry 5), whereas, in the absence of ZnI_2 , only compound 3 was obtained (Table 2, entry 6).

Finally, suppressing the precatalyst resulted in a strong drop in the Z-stilbene isomerization (Table 2, entry 7). At last, alkane formation from *E*-stilbene was also investigated and ZnI₂ appears to significantly reduce alkene hydrogenation (Table 2, entries 8 vs 9). Overall, the newly developed catalytic *E*-selective semihydrogenation of alkynes can be explained through a *syn*-hydrogenation/isomerization pathway. First ZnI₂ interacts with the Pd^{II} precatalyst to deliver I₂Pd(PPh₃)₂, which is reduced to Pd⁰. Note that ZnI₂ can also dramatically modify the nature of Pd species and, a "cocktail system" of mononuclear Pd and/or clusters and/or nanoparticles could be envisioned in the absence of any further information concerning its specific structure.²² Preliminary studies conducted in the presence of Hg⁰ suggest the existence of heterogeneous species in our "cocktail system".²³ Hence, this

Table 2. Control Experiments: Role of ZnI₂^{*a*}

		conditions				
		substrate Ph + Ph + Ph + Ph + Ph + Ph + Ph	+ Ph´ Ph	∽_Ph 3		
entry	substrate	conditions	$(\%)^a$	E- 2 (%) ^a	Z-2 (%) ^a	3 (%) ^a
1		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv)	55	23	22	0
2	Ph	H ₂ (1 atm), Cl ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv)	5	-	-	-
3	Ph	H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv), ZnI ₂ (1 equiv)	100	85	1	14
4	Ph	I ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv.), ZnI ₂ (1 equiv.)	0	-	-	-
5	5 Ph	H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %) Me ₂ Zn (12 mol %), ZnI ₂ (1 equiv)	100	84	0	16
6		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol%), Me ₂ Zn (12 mol %)		0	0	100
7		$\mathrm{H_{2}}\left(1\mathrm{atm} ight),\mathrm{Zn^{0}}\left(3\mathrm{equiv} ight),\mathrm{ZnI_{2}}\left(1\mathrm{equiv} ight)$		18	82	0
8		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %), Me ₂ Zn (12 mol %)	100	0	0	100
9	Ph	H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %) Zn ⁰ (3 equiv), ZnI ₂ (1 equiv)	30	70	0	30

^aProduct distribution was determined by ¹H NMR analysis.

"cocktail system" activates H_2 and Z-alkene is liberated, and then rapidly converted to *E*-alkene. The combination of Pd⁰ and ZnI₂ is essential to promote isomerization without alkane formation.

In conclusion, we have developed a catalytic process for the semihydrogenation of internal alkynes with excellent *E*-selectivity. Monitoring studies and control experiments underline the significant role of ZnI_2 in this process, establishing that the transformation involves *syn*-hydrogenation, followed by isomerization under a H_2 atmosphere. Finally, this simple and easy-to-handle system constitutes a route to *E*-alkenes under mild conditions. Further studies are currently under investigation to determine the role of ZnI_2 more precisely and to elucidate the structure of the active catalytic species.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b03295.

Experimental data, product characterizations, and spectral data for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank to Université de Carthage for financial support (to R. Maazaoui).

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(23) Two experiments were conducted in the presence of Hg⁰ (~2 mmol). When mercury was directly added at the beginning to the reaction mixture no conversion was observed after 6 h. In a second experiment, reaction was carried out normally within 2 h (conversion \approx 40%) and then Hg⁰ was added. No further evolution was observed during the following 20 h.