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Selective reduction of alkynes catalyzed by palladium acetate with sodium methoxide as the hydride source

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Abstract—Treatment of internal alkynes with sodium methoxide in the presence of $Pd(OAc)_2$ and PPh_3 in methanol for 48 h gave the reduction products, alkenes or alkanes in good chemical yields. This reaction proceeds through a palladium methanolate complex, followed by β-hydride elimination and reductive elimination. © 2003 Elsevier Science Ltd. All rights reserved.

One of the most useful synthetic applications of alkynes is the stereoselective reduction to (*E*)-alkenes by alkali metals in liquid ammonia or (*Z*)-alkenes by catalytic hydrogenation. The production of highly pure (*Z*)-alkenes is often a key-step for the synthesis of natural products,[1] for example pheromones.[2] The best method for the selective reduction of alkynes to the (*Z*)-alkenes is catalytic hydrogenation[3] using Lindlar's catalyst[4] or P-2 nickel.[5] In addition to these, new catalysts have been developed such as the Zn–Cu catalyst[6] and the $[(Ph_3P)CuH]_6$ catalyst.[7] In our study on the palladium catalyzed reaction of aryl iodides with diphenylacetylene, we noted that $Pd(OAc)_2$ with sodium methoxide can selectively reduce triple bonds to the corresponding double bonds and leave the aromatic ring unaffected.[8] We now report the $Pd(OAc)_2$–sodium methoxide mediated reduction of alkynes selectively to either alkenes or alkanes, depending on the choice of reaction conditions.

The results of this initial investigation are given in Table 1. The reactions were first studied using diphenylacetylene **1a** (0.5 mmol) with sodium methoxide (5 equiv.) in the presence of $Pd(OAc)_2$ (5 mol%) and PPh_3 (5 mol%) in methanol for 48 h whereby 1,2-diphenylethane **2a** was obtained in 92% yield (Table 1, entry 1). Reaction with unsymmetrically disubstituted alkynes **1b** and **1c** also gave the totally reduced products **2b** and **2c** in 80 and 57% yields, respectively (entries 2 and 3). This reaction was monitored by TLC until all starting material had disappeared. Similarly, both *cis*-stilbene and *trans*-stilbene under the same reaction conditions gave 1,2-diphenylethane **2a** in 88% yields, in both cases (entries 4 and 5).

Surprisingly when the reaction of **1a** was carried out under the same reaction conditions except in THF, only *cis*-stilbene **3a** was obtained in 80% yield (entry 6). Hydrogenation of **1c** under the same conditions for 72 h gave the alkene **3c** in 61% yield, nearly quantitative based on the recovered starting alkyne (entry 7). The ability to partially reduce in THF was further investigated by carrying out the reaction with *cis* and *trans* stilbene. No reduction of *cis* and *trans* stilbene was observed using THF as solvent (entries 8 and 9).

We have previously reported[9] that **1d** cyclized to **4d** without $Pd(OAc)_2$ catalyst. On the other hand, the reaction of **1d** with $NaOCH_3$ in the presence of 5 mol% of $Pd(OAc)_2$ at reflux for 48 h gave **3d** and the cyclization product **4d** in 50% and 17% yields, respectively (entry 10) (Scheme 1). Reaction of **1e** gave only the partially reduced product **3e** in 37% yield along with 32% of a dimer (entry 11). These results suggest that an electron-withdrawing group on the aromatic ring retards the reduction.

Keywords: palladium and compounds; β-hydride elimination; hydrogenation.

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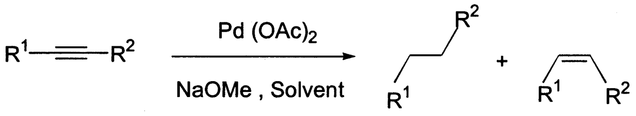
Table 1. Palladium-catalyzed reduction of diarylacetylenes



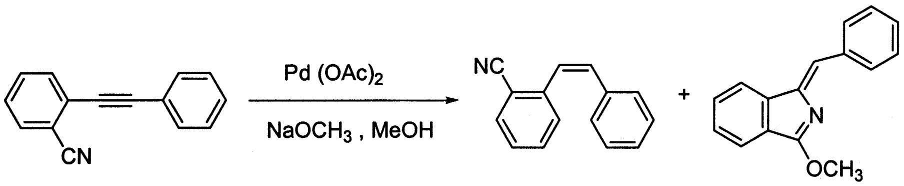
1 2 3

1 a : $R^1 = R^2 = Ph$
1 b : $R^1 = o\text{-}CH_3OC_6H_4, R^2 = Ph$
1 c : $R^1 = p\text{-}CH_3OC_6H_4, R^2 = Ph$
1 d : $R^1 = o\text{-}CNC_6H_4, R^2 = Ph$
1 e : $R^1 = R^2 = p\text{-}CF_3C_6H_4$

Entry	Substrate	Solvent	Time (h)/temp. (°C)	**2** (Yield,[a] %)	**3** (Yield,[a] %)
1	**1a**	MeOH	48 (25)	**2a** (92%)	
2	**1b**	MeOH	48 (25)	**2b** (80%)	
3	**1c**	MeOH	48 (25)	**2c** (57%)	
4	*cis*-Stilbene	MeOH	48 (25)	**2a** (88%)	
5	*trans*-Stilbene	MeOH	48 (25)	**2a** (88%)	
6	**1a**	THF	24 (25)		**3a** (80%)
7	**1c**	THF	72 (25)		**3c** (61%)
8	*cis*-Stilbene	THF	48 (25)	No reaction	
9	*trans*-Stilbene	THF	48 (25)	No reaction	
10	**1d**	MeOH	48 (65)		**3d** (50%)[b]
11	**1e**	MeOH	48 (65)		**3e** (37%)

[a] Yields refer to isolated yields. All of the compounds gave satisfactory ^1H and ^{13}C NMR spectral data.

[b] Another product **4d** was obtained in 17% yield.



1d **3d**, 50% **4d**, 17%

Scheme 1.

We previously proposed[8] a mechanism for this reduction, as shown in Scheme 2. This mechanism involves first a palladium methanolate **4** proceeding through β-hydride elimination[10] to give adduct **5**. Next, addition of **5** to the alkyne **1** gives σ-vinylpalladium adduct **6** which exchanges one ligand with sodium methoxide to give **7**. Adduct **7** proceeds via β-hydride elimination to give adduct **8**. Finally, adduct **8** undergoes reductive elimination to give product **3**. The proposed mechanism implies that the hydrogens come from the α-hydrogens of methanol.

In conclusion, we have demonstrated that the reactions of internal alkynes with sodium methoxide in the presence of $Pd(OAc)_2$ and PPh_3 in methanol give either (*Z*)-alkenes or alkanes in good yields. When the solvent was changed to THF, the reductions stop at the alkene stage. We have also found that β-hydride elimination of palladium methanolate provides an alternative route for hydrogenolysis of organopalladiums. This paper proposes a useful application where internal alkynes are stereoselectively reduced to either (*Z*)-alkenes or alkanes.

Acknowledgements

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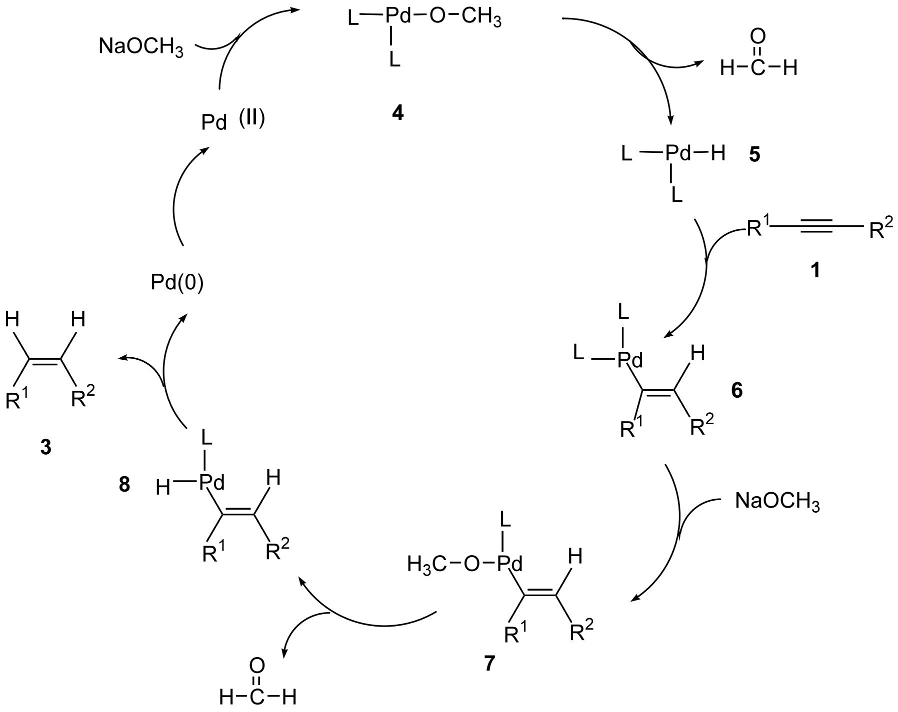

Scheme 2.

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