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Reduction of diphenylacetylene using Al powder in the presence of noble metal catalysts in water

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ABSTRACT

Diphenylacetylenes can be reduced to the corresponding diphenylethanes (**2**) in water in excellent yield using Al powder and Pd/C at 60 °C for 3 h in a sealed tube. In addition, the complete reduction of both aromatic rings required 80 °C for 15 h with Al powder in the presence of Pt/C. However, the nature of hydrogenated product formed was found to be strongly influenced by the reaction temperature, time, volume of water and the amount of catalyst being employed.

1. Introduction

Hydrogenation of aromatic alkynes to the corresponding alkenes and alkanes is of great interest in synthetic organic chemistry. This is one of the most widely used chemical reactions with many industrial applications in the petro, food and pharmaceutical industries. Styrene is an industrially and commercially valuable material. Phenylacetylene reduced by semi-hydrogenation is a process of great industrial importance[1,2] because phenylacetylene is a poisoning impurity in styrene feedstocks, and leads to deactivation of the styrene polymerization catalyst. The hydrogenation of phenylacetylene proceeds under relatively mild conditions and the desired product is the intermediate (styrene). Thus, this methodology is a very convenient tool for the evaluation of process design[2,3] and testing the efficiency of hydrogenation catalysts.[4–7] This is why a substantial amount of literature is available featuring both homogeneous[8–10] and heterogeneous[11–17] selective processes for the semi-hydrogenation of alkynes.

Catalytic hydrogenation using hydrogen gas or hydride transfer agents is commonly employed for this transformation. Various hydrogenation reactions have been studied, for which the active catalysts commonly employed include systems based on the metals Pd,[18–20] Rh,[21,22] Ru,[23–25] Ni,[26] Pt,[27,28] Ir,[29] Os,[30] V,[31] Fe,[32] and Nb.[33] There is particular interest in the use of Pd given its excellent performance in the selective hydrogenation of alkynes.[34] Recently, transition-metal nanoparticles in catalysis have drawn much attention due to their high efficiency and unique properties. Palladium nanoparticles possessing high catalytic activity and controllable particle size have also attracted attention.[35] Moreover, the use of ruthenium nanoparticles for the semi-hydrogenation of alkyne and platinum-ruthenium nanoparticles for the selective hydrogenation of phenylacetylene has been reported.[36,37] The selective reduction of phenylacetylene was also investigated with AlMgO particles which were used as an alternative to water-reactive generator of hydrogen.[38] The partial hydrogenation of 3-hexyne was observed using low-loadings of palladium mono- and bimetallic catalysts.[39] A Hantzsch amido dihydropyridine has been used as a transfer hydrogenation reagent for α,β-unsaturated ketones.[40]

Catalytic hydrogenation is widely considered to be an environmentally benign process and both heterogeneous and homogeneous alternatives are popular in industry.[41–47] Nowadays, heterogeneous catalysts are being used for the selective reduction of condensed *N*-heterocycles using water as both a solvent and a hydrogen source.[48] Based on the application of Raney-type Ni–Al alloy in aqueous medium, the selective reduction of ketones and reductive amination of carbonyl compounds has been reported.[49,50] More recently, the application of a heterogeneous catalyst in

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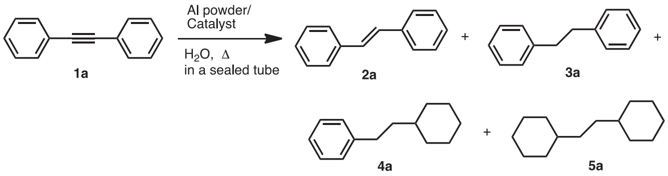
combination with microwave irradiation has been employed as an environmentally benign tool for some contemporary organic synthesis.[51,52]

On the other hand, the utilization of water as a chemical reagent is an essential aspect of Green Chemistry.[53] Water as a solvent for organic reactions has many advantages over the use of other organic solvents including cost, safety, simplicity of operation and most importantly its benign environmental character.[54–56] More recently, water has been used as a stoichiometric H or D atom donor for tetrahydroxydiboron-mediated palladium-catalyzed transfer hydrogenation and deuteriation of alkenes and alkynes.[57] In addition, hydrogenations and deuterium labeling has been carried out with Al-based metal alloys under aqueous conditions.[58] Here in this study, we illustrate a simple reduction method for diphenylacetylene using commercially available Al powder in the presence of noble metal catalysts (Pt/C, Pd/C, Ru/C or Rh/C) in water in a sealed tube.

2. Results and discussion

In order to achieve a more environmentally friendly chemical process, the reduction of diphenylacetylene (Scheme 1, **1a**) was carried out using Al powder in the presence of a noble metal catalyst in water in a sealed tube. Besides the expected product 1,2-diphenylethane (Scheme 1, **3a**), a mixture of stilbene (Scheme 1, **2a**), cyclohexylphenylethane (Scheme 1, **4a**) and 1,2-dicyclohexylethane (Scheme 1, **5a**) was obtained upon reduction. The relative distribution of the products formed was found to depend on the reaction conditions employed. Consequently, the effects of the reaction temperature, time, amount of catalyst and required volume of water for the reduction of diphenylacetylene (**1a**) were investigated.



Scheme 1. Reduction of diphenylacetylene (**1a**) by using Al powder and noble metal catalyst in H_2O.

An initial attempt to reduce diphenylacetylene (**1a**) using only Al powder in water in a sealed tube failed. However, when the reduction was carried out using Al powder and Pd/C at 60 °C for 3 h, diphenylethane (**3a**) was isolated in good yield (Table 1, entry 2). On increasing the reaction time, diphenylacetylene (**1a**) gradually underwent further reduction and as a result, the intermediate product (**3a**) was transformed into **4a** over a longer reaction time (Table 1, entry 3).

The reduction of diphenylacetylene (**1a**) was conducted at 60 °C to evaluate the effect of the reaction time at 60 °C using Al powder and Pd/C. When **1a** was subjected to reduction over 3 h, the product (**3a**) was found in the highest yield (97%) (Table 2, entry 2). On increasing the reaction time, the amount of the reduction product (**3a**) was not found to increase, rather over a longer reaction time of more than 4 h, the product (**3a**) started to transform into **4a** (Table 2, entry 4).

Table 1
Reduction of diphenylacetylene (**1a**) using Al powder and noble metal catalyst in H_2O[a,b]

Entry	Catalyst	Time (h)	Yield[c] (%) **3a**	**4a**	Recovery **1a**
1	Al Powder+Pt/C	3	20	0	80
2	Al Powder+Pd/C	3	95	0	5
3	Al Powder+Pd/C	6	94	6	0
4	Al Powder	6	0	0	100
5	Ni–Al	3	91	0	9

[a] Substrate: 0.11 mmol, Ni–Al: 100 mg (500 wt %) (Wako), Al powder: 100 mg (500 wt %) (Wako), Catalyst: 4.5 mol % (metal) (Wako), H_2O: 0.5 mL (Wako).
[b] Conditions: temp: 60 °C.
[c] The yields were determined by GLC.

Table 2
Reduction of diphenylacetylene (**1a**) using Al powder and Pd/C in H_2O[a,b]

Entry	Time (h)	**2a**	**3a**	Yield[c,d] (%) **4a**	**5a**	Recovery **1a**
1	2	0	52	0	0	48
2	3	0	97[84]	0	0	3
3	4	0	100	0	0	0
4	5	0	97	3	0	0

[a] Substrate: 20 mg (0.11 mmol), Al powder: 100 mg (500 wt %), Catalyst: 4.5 mol % (metal), H_2O: 0.5 mL.
[b] Conditions: temp: 60 °C.
[c] The yields were determined by GLC.
[d] The isolated yields are shown in a square bracket.

It was observed that on increasing the reaction time, the yield of the desired compound (**3a**) was found to peak (97%) at 3 h. On increasing the reaction time further, the amount of product (**3a**) increased only very slightly. On the other hand, using Raney Ni–Al in dilute alkaline aqueous solution, benzophenone required a higher amount of catalyst compared to that used in this work,[59] Thus, the catalytic system developed here is more economical.

From Table 2, it was found that 60 °C for 4 h was the best conditions for the reduction of diphenylacetylene (**1a**) to diphenylethane (**3a**) when using Al powder and Pd/C. To explore the corresponding activity of other catalytic systems, the reduction was carried out under the same condition for 3h. In the case of Rh/C, we obtained a 27% yield, whilst for Ru/C, no reaction occurred. In Fig. 1, the pink colour indicates the starting compound diphenylacetylenes (DPA), the green colour represents our desired product 1,2-diphenylethane (DPE) and the blue colour for stilbene product.

In our previous study, a Pt/C catalyst with Al powder in water was found to be a stronger reducing agent for the reduction of aromatic rings.[60] Based on this information, the reduction of diphenylacetylene (**1a**) was examined with this catalyst in a sealed tube.

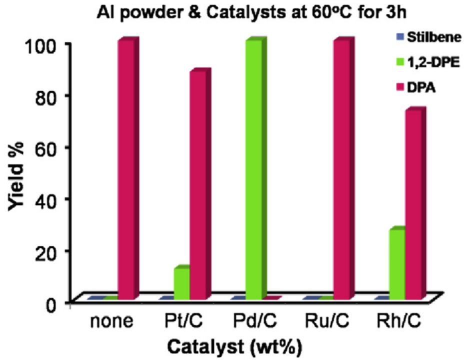


Fig. 1. Reduction of diphenylacetylene (**1a**) using Al powder and noble metal catalyst.

When the reduction of diphenylacetylene (**1a**) was carried out at 80 °C for 12 h using a Pt/C catalyst with Al powder in water, 37% of **5a** was observed along with 63% recovery of the starting compound (**1a**) (Table 3, entry 1). The reduction increased on increasing the reaction temperature up to 100 °C, but this temperature is not suitable when water is used as the solvent (Table 3, entry 2). Consequently, when using this catalyst, the reaction temperature was gradually decreased and a 91% yield of compound **5a** was obtained at 80 °C over 15 h. Thus Pt/C turned out to be the best catalyst and it

Table 3
Reduction of diphenylacetylene (**1a**) using Al powder and Pt/C in H_2O[a]

Entry	Temp(°C)	Time (h)	3a	Yield[b,c](%) 4a	5a	Recovery 1a
1	80	12	0	0	37	63
2	100	12	9	0	87	4
3	80	15	6	0	91[78]	3
4	80	18	7	0	92	1

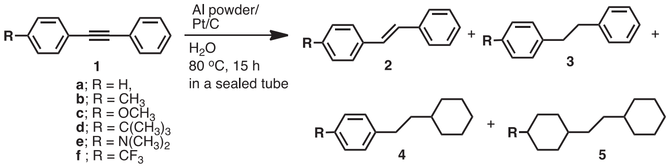
[a] Substrate: 20 mg, Al powder: 100 mg (500 wt %), catalyst: 4.5 mol % (metal), H_2O: 0.5 mL.

[b] The yields were determined by GLC.

[c] The isolated yields are shown in a square bracket.

is well-known that Pt/C can act as a more effective catalyst when used in the presence of Raney Ni–Al alloy and Al powder.[61] The intermediate product diphenylethane was also investigated under the same reaction conditions and it led to excellent yields via the reduction of both aromatic rings.

Subsequently, the reduction of substituted diphenylacetylenes was examined to afford compounds **3** and **5**. Following exposure of the substituted diphenylacetylenes to reduction, under the established standard conditions, 4-methyldiphenylacetylene (**1b**) gave the product **3b** with a yield of 68% along with recovery of the starting compound (**1b**), which is probably due to steric hindrance (Table 4, entry 2). Interestingly, given in the presence of the bulky group, 4-methoxydiphenylacetylene (**1c**) gave a 53% yield of stilbene product (**2c**) whereas 4-*tert*-butyl-diphenylacetylene (**1d**) and 4-trifluorodiphenylacetylene (**1f**) produced a negligible amount of the stilbene products (**2d**) and (**2f**) along with the corresponding diphenylethane derivatives. In case of an electron-donating group, a complete reduction of the alkyne group occurred for 4-dimethylaminodiphenylacetylene (**1e**) under the conditions used (Table 4, entry 5). The outcome of the reduction depends on the substituents present in the diphenylacetylene (see Scheme 2).



Scheme 2. Reduction of substituted diphenylacetylenes (**1**) using Al powder and Pt/C in H_2O.

We also explored the substituent effects on diphenylacetylenes (**1**) to observe a wider picture of the reduction products obtained using the above catalysts under the same reaction conditions. In the case of 4-methyldiphenylacetylene (**1b**) and 4-*tert*-butyldiphenylacetylene (**1d**), a completely reduced products (5b) and (5d) were obtained in low yield, namely 36% and 10%, respectively along with the other products due to the steric hindrance of the respective methyl and *tert*-butyl groups (Table 5, entries 2 and 4). Only 4-*N*,*N*-dimethylaminodiphenyl-acetylene (**1e**) afforded a quantitative yield for the alkyne group reduction product **3e** which may be due to the electron donating nature of the substituent. In the case of 4-methoxydiphenylacetylene (**1c**), a 48% yield of compounds **5c** and **5a** (7%) was achieved (Table 5, entry 3). This result strongly suggests that the present system not only reduces the aromatic ring but also cleaves the polar C–O bond. On the other hand, a 78% reduction occurred with the formation of compounds **3f** (7%) and **4f** (15%) in the case of 4-trifluoromethyldiphenylacetylene (**1f**) (Table 5, entry 6).

One of the most important advantages of this method is that the reaction can be carried out in water which amongst all its important environmental properties, is both readily available and cheap. In addition, water serves as an economic source of hydrogen and as a result, no extra hydride or hydrogen gas addition is required. It is noteworthy that this is also accomplished without the need of the presence of any strong base. Moreover, the noble metal catalyst most likely readily adsorbs hydrogen and thereby ensures the effective hydrogenation of the substrates. In addition, the reaction does not produce any harmful waste materials and the only byproduct that forms is non-toxic $Al(OH)_3/Al_2O_3$ that can be filtered and used in other hydrogenation processes.

Table 4
Reduction of substituted diphenylacetylenes (**1**) using Al powder and Pd/C in H_2O[a,b]

Entry	R	2	Yield[c,d] (%) 3	Recovery 1
1	**1a**	0	100	0
2	**1b**	0	68	32
3	**1c**	53	37	10
4	**1d**	16	36	48
5	**1e**	0	100[90]	0
6	**1f**	19	41	40

[a] Substrate: 0.11 mmol, Al powder: 100 mg (500 wt %), H_2O: 0.5 mL.

[b] Conditions: temp: 60 °C, time: 3 h.

[c] The yields were determined by GLC.

[d] The isolated yields are shown in a square bracket.

Table 5
Reduction of substituted diphenylacetylenes (**1**) using Al powder and Pt/C in H_2O[a,b]

Entry	R	3	Yield[c] (%) 4	5	Recovery 1
1	**1a**	6	0	91	3
2	**1b**	25	34	36	5
3	**1c**	25	4(**4a**)	7(**5a**)+48	0
4	**1d**	13	77	10	0
5	**1e**	100	0	0	0
6	**1f**	7	15	78	0

[a] Substrate: 20 mg, Ni–Al: 100 mg (500 wt %), Al powder: 100 mg (500 wt %), Pt/C: 4.5 mol % (metal), H_2O: 0.5 mL.

[b] Conditions: temp: 80 °C, time: 18 h.

[c] The yields were determined by GLC.

2.1. Proposed reaction mechanism

The reaction mechanism for the reduction is not yet fully clear. It can be proposed that in the presence of Pt/C, the Al powder reacts with water producing a reactive form of hydrogen that gets adsorbed on the catalyst's surface. Also, we have noted that when Al powder and Pt/C were combined with Raney Ni–Al alloy as a co-catalyst, the system becomes a much more potent reducing agent in water. Here, the solvent water may play an important role in the creation of the catalytic surface (Fig. 2).[62]

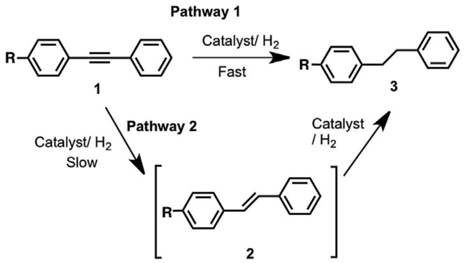


Fig. 2. Proposed reaction pathways for the reduction of diphenylacetylenes.

Based on the GC–MS analysis, a detailed reaction pathway for the reduction of diphenylacetylenes can be proposed.[61] In pathway **1** the triple bond is reduced to single bond directly and in pathway **2** the single bond is afforded through the intermediate product stilbene (**2**). The intermediate product **2** only forms when a bulky substituent is introduced (Table 4), which makes the pathway **2** relatively slower. So, we can assume that pathway **1** is the faster route compared to pathway **2**. It may be concluded here that the approach of the diphenylacetylenes towards the catalyst's surface is very important in terms of achieving a high yield of the product.

3. Conclusion

It was found that the alkyne diphenylacetylene could be converted to the corresponding diphenylethane using Al powder in the presence of Pd/C in H_2O in a high yield. Furthermore, both the aromatic rings were also reduced in high yield with Al powder in the presence of Pt/C in H_2O under mild reaction conditions in a sealed tube. Without using any organic solvents, Al powder in the presence of the catalyst in water turns out to be a powerful reducing agent. The nature of the reduction products greatly depends on the reaction temperature, time, volume of water and the amount of catalyst employed. This novel approach is characterized by the ease and speed of the reaction, the simplicity of the manipulation and the mildness of the reaction conditions. Moreover, the convenience and low costs associated with the process are worth highlighting.

4. Experimental

4.1. General

4.1.1. Materials and apparatus. All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on Shimadzu GC–MS-QP5050A Ultrahigh Performance Mass Spectrometer AOC-20I, 100 V using a direct-inlet system. G.L.C. analyses were performed by Shimadzu gas chromatograph, GC-2010.

4.1.2. General procedure for reduction of aromatic compounds. The mixture of substrate (20 mg, 0.11 mmol) (Wako), Al powder (500 wt %) (53–150 μm, 99.5%) (Wako) and Pt/C, Pd/C, Ru/C or Rh/C (20 mg) (4.5 mol % metal) were added to water (0.5 mL) (Wako distilled water). After heating the mixture at 60–80 °C for 3–15 h, it was cooled to room temperature. The solution was then diluted with 1 mL water and stirred overnight at room temperature in a sealed tube. After 24 h, the solution was extracted with diethyl ether (3×2 mL) as per the reported procedures.[63] The combined organic layers were, dried over $MgSO_4$ and filtered through a cotton layer followed by being concentrated in vacuum to give the corresponding hydrogenated product. The yields were determined by GLC analysis using the standard compound (1,2,3,4-tetrahydronaphthalene), and the products were identified by GC–MS.

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Supplementary data

Supplementary data (Details of the GC and GC–MS data.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2016.09.021.

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