



Full paper/Mémoire

Reduction of aromatic compounds with Al powder using noble metal catalysts in water under mild reaction conditions



Ummey Rayhan, Hyeokmi Kwon, Takehiko Yamato*

Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga-shi, Saga 840-8502, Japan

ARTICLE INFO

Article history:

Received 18 August 2013

Accepted after revision 23 September 2013

Available online 20 February 2014

Keywords:

Reduction of aromatic compounds

Al powder

Noble metal catalysts

Water

Cyclohexane ring

ABSTRACT

In water, Al powder becomes a powerful reducing agent, transforming in cyclohexyl either one or both benzene rings of aromatic compounds such as biphenyl, fluorene and 9,10-dihydroanthracene under mild reaction conditions in the presence of noble metal catalysts, such as Pd/C, Rh/C, Pt/C, or Ru/C. The reaction is carried out in a sealed tube, without the use of any organic solvent, at low temperature. Partial aromatic ring reduction was observed when using Pd/C, the reaction conditions being 24 h and 60 °C. The complete reduction process of both aromatic rings required 12 h and 80 °C with Al powder in the presence of Pt/C.

© 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

The reduction of aromatic ring is a useful and important technique for obtaining a variety of cyclohexane derivatives. Because of the stabilization of the aromatic ring by resonance hybridization, aromatic hydrocarbons are seldom hydrogenated at room temperature over base metals and palladium catalysts [1]. However, at elevated temperatures and pressures, most aromatic hydrocarbons are hydrogenated without difficulty over nickel and cobalt catalysts [2–4]. Over ruthenium and particularly, over rhodium and platinum, benzene and its derivatives are hydrogenated at considerable rates, even at room temperature [5–7]. Previously reported methods for developing cyclohexane rings from arenes are classified into two types of reactions:

- one is the reduction with greater than stoichiometric amounts of reducing agents, such as LiAlH₄, borane derivatives [8–11], or dissolving metals (Birch reduction) [12,13]. These reagents are moisture-sensitive and the

reaction should be conducted under anhydrous, strongly reducing and basic conditions. These reaction conditions cannot be tolerated by some co-existing functional groups, such as esters and ketones. Moreover, large amounts of metal waste are produced from the reducing agents in these reactions;

- another one is hydrogenation with a transition metal catalyst, which is a simple, convenient and sustainable method [14,15]. Although some homogeneous catalysts promote arene hydrogenation efficiently [16,17], the presence of residual metal in the products makes the industrial application of this method difficult. On the other hand, the hydrogenation of arenes through the use of heterogeneous metals (Ni, Rh, Ru, Pt and Pd) [15] has some advantages, such as easy handling, lesser metal contamination in the products and reusability, which would make it suitable for industrial production.

Catalytic hydrogenation of organic compounds with catalysts and hydrogen gas is one of the most useful methods in the field of organic synthesis [18–20]. It was reported by Tashiro's group that aromatic compounds were reduced to the corresponding cyclohexane products in high yields, by using Raney Ni–Al [21]. Recently, Maegawa et al. reported the convenient reduction of

* Corresponding author.

E-mail address: yamatot@cc.saga-u.ac.jp (T. Yamato).

aromatic compounds by a hydrogenation procedure based on the use of heterogeneous platinum group catalysts. Rh/C is the most effective catalyst for the hydrogenation of the aromatic ring, which can be conducted in *i*PrOH under neutral conditions and at ordinary to medium H₂ pressures (< 10 atm) [22]. They also reported the solvent-free and solid-phase hydrogenation of various reducible functionalities, which was effectively catalyzed by heterogeneous palladium on carbon (Pd/C) [23]. Palladium catalysts embedded on molecular sieves (MS3A and MS5A) were also developed for chemoselective hydrogenation [24].

Wang et al. developed polymeric mesoporous carbon graphitic nitrides (mpg-C₃N₄) and ordered mesoporous graphitic carbon nitrides (ompg-C₃N₄), which were used to prepare palladium catalysts (Pd@C₃N₄). These catalysts demonstrated excellent activity and selectivity for hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline under mild temperatures (30–50 °C) and H₂ pressure (1 bar) [25]. A green approach was reported about the hydrogenation of bisphenol A (BPA) utilizing a special Ru catalyst in water medium [26]. Utilization of water as a chemical reagent is an essential aspect of green chemistry [27]. Water has many advantages as a solvent for organic reactions from the aspects of cost, safety, operation simplicity, and environmental concerns as compared to the use of an organic solvent [28–30].

In the above-mentioned literature, different aspects of aromatic ring reduction were discussed. In present study, we investigated the reduction of aromatic compounds using Al powder with Pd/C, Rh/C, Pt/C and Ru/C in water under atmospheric pressure at lower temperature. Biphenyl, fluorene, and 9,10-dihydroanthracene were selected because they were employed as model compounds in pioneering works [21,22,31]. To the best of our knowledge, there is no literature referring to any partial and complete aromatic ring reduction technique utilizing Al powder with these catalysts at lower temperature in water. In this article, we developed new method for partial and complete aromatic ring reduction using Al powder with commercially available Pd/C and Pt/C, respectively.

2. Experimental

2.1. Materials and apparatus

All melting points are uncorrected. ¹H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in CDCl₃ with Me₄Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ20M spectrometer. Mass spectra were obtained on a Shimadzu GC–MS–QP5050A Ultrahigh Performance Mass Spectrometer AOC-20I, 100 V using a direct-inlet system. GLC analyses were performed with a Shimadzu gas chromatographer GC-2010.

2.2. General procedure for the reduction of aromatic compounds

To the mixture of substrate (20 mg, 0.13 mmol) (Wako), Al powder (500 wt%) (53–150 μm, 99.5%) (Wako) and Pt/C,

Pd/C, Ru/C and Rh/C (20 mg) (4.5 mol% metal) was added water (0.5 mL) (Wako distilled water). After heating at 60–80 °C for 12–24 h, the mixture was cooled to room temperature. The solution was diluted with 1 mL of water and then stirred overnight at room temperature in a sealed tube. After 24 h, the solution was extracted with diethyl ether (2 mL × 3) following the reported procedures [32]. The organic layer was combined, dried with MgSO₄, filtered through a cotton layer and concentrated in vacuum to give the corresponding hydrogenated product. The yields were determined by GLC analysis by using the standard compound (1,2,3,4-tetrahydronaphthalene) and the products were identified by GC–MS.

3. Results and discussion

In our present research work, we tried to reduce biphenyl without using any alkaline solution, isopropyl alcohol or any extra hydrogen pressure at lower temperature. To acquire the optimized reaction conditions (i.e. catalysts, reaction time and temperature), hydrogenation of biphenyl was carried out using Al powder at 60 °C for 12 h in water in the sealed tube; hydrogenation was not initiated. Prolonging the reaction time (24 h) and increasing the reaction temperature at 120 °C (12 h) afforded the same results. Hydrogenation proceeded in the presence of a co-catalyst (Pd/C, Rh/C, Pt/C or Ru/C); and the results are shown in Table 1 (Scheme 1).

The benzene rings of biphenyl were reduced to afford a mixture of cyclohexylbenzene (**2a**) and cyclohexylcyclohexane (**3a**) in 10 and 84% yield, respectively, along with the recovery of biphenyl (**1a**) in 6% yield at 60 °C using Pt/C. Consequently, we have succeeded in reducing both benzene rings of biphenyl (**1a**) to obtain cyclohexylcyclohexane (**3a**) in quantitative yield by increasing the reaction temperature to 80 °C (Table 1; entry 3). When Pd/C and Rh/C were used as co-catalysts under the same reaction conditions, the partial reduction of biphenyl (**1a**) afforded cyclohexylbenzene in 54–60% yield (**2a**) along with the recovery of the starting compound (**1a**) (Table 1; entries 4,5,7). In the case of Ru/C, only 35% of the compound **2a** was observed under the used reaction conditions. Thus, it

Table 1
Reduction of biphenyl (**1a**) by using Al powder in H₂O in the presence of a co-catalyst^{a,b}.

Entry	Co-catalyst	Temp (°C)	Yield [%] ^d		
			2a	3a	Recovery 1a
1	None	60	0	0	100
2	Pt/C	60	10	84	6
3	Pt/C	80	0	100	0
4	Pd/C	60	54	0	46
5	Pd/C	80	59	22	19
6	Ru/C	80	35	39	26
7	Rh/C	80	60	11	29
8 ^c	Pd/C	60	91	5	4
9 ^c	Rh/C	60	7	90	3

^a Substrate: 20 mg (0.13 mmol), co-catalyst: 4.5 mol% (metal), Al powder: 100 mg (500 wt%), H₂O: 0.5 mL.

^b Conditions: time, 12 h.

^c Conditions: time: 24 h.

^d The yields were determined by GLC.

Download English Version:

<https://daneshyari.com/en/article/170389>

Download Persian Version:

<https://daneshyari.com/article/170389>

[Daneshyari.com](https://daneshyari.com)