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# Organic reaction in water. Part 3:[1] A facile method for reduction of aromatic rings using a Raney Ni–Al alloy in dilute aqueous alkaline solution under mild conditions

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## Abstract

Reduction of aromatic rings such as phenol, naphthalenes, biphenyls, acenaphthene, and acenaphthylene was smoothly performed using a Raney Ni–Al alloy in dilute aqueous alkaline solution *without any organic solvents* at 90°C under atmospheric pressure, and the corresponding reduced compounds were obtained in high yields. © 2000 Elsevier Science Ltd. All rights reserved.

The reduction of aromatic rings is carried out by a variety of methods, including heterogeneous or homogeneous catalytic hydrogenation, metal hydride reaction, dissolving metal reduction, and ionic hydrogenation.[2] Since hetereogeneous catalytic hydrogenation[3] is usually undertaken under forcing conditions (high pressure and/or elevated temperature) using a catalyst such as Raney Ni,[4] Pd,[5] Pt/$Al_2O_3$,[6] Ru[7] and Rh,[8] special apparatus such as an autoclave is generally necessary to achieve the reaction. On the other hand, although homogeneous catalytic hydrogenation can be carried out under milder conditions than those for heterogeneous hydrogenation, some atmospheric hydrogen pressure and an organic solvent are usually needed and, furthermore, a transition metal complex, which is very sensitive to air and moisture, must be employed.[2c,9] Similarly, since metal hydride reduction using, for example a borane catalyst[10] and LAH,[11] dissolving metal reduction such as Birch reduction,[12] and ionic hydrogenation, for example 1-ethyl-3-methylimidazolium chloride–$AlCl_3$,[13] also requires a moisture-sensitive reagent and an organic solvent, the reaction procedures are considerably tedious. In these methods, there is little consideration given to the environment as they require the use of an organic solvent. Accordingly, as a result of our extensive efforts to develop an environmentally-friendly method with a cheap reagent in a simple operation, we have now found that by a novel combination of a Raney Ni–Al alloy[14] and dilute aqueous alkaline solution *without any organic solvents*, a strong reducing power is attained to reduce an aromatic ring under mild conditions.

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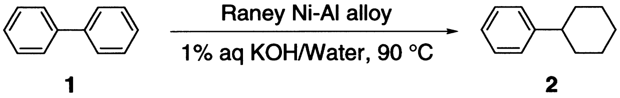
In a preliminary work, reduction of biphenyl **1** was performed under various conditions. In the method employed, an aqueous KOH solution was dropped slowly into a mixture of **1**, Raney Ni–Al alloy and water.[15] The results are summarized in Table 1 and Scheme 1. The reaction time was shortened as the drop time of the aqueous alkaline solution was prolonged (Runs 1 and 2). On the other hand, when dropping the aqueous alkaline solution into the reaction vessel over 0.5 h, the reaction time was extended (7 h) and some of the unreacted substrate remained (yield: 5%). These results may suggest that the more dilute the concentration of the alkaline solution is, the stronger the reducing power is.[16] The requisite amount of the Raney Ni–Al alloy was 5 g when using 10 ml of the alkaline solution and 3.5 g when using 20 ml of the alkaline solution, respectively (Runs 5 and 6). Treatment of **1** with the Raney Ni–Al alloy (3.5 g) in 1% aq. LiOH/$H_2O$, NaOH/$H_2O$, $Na_2CO_3$/$H_2O$, and $Ba(OH)_2$/$H_2O$ as well as 1% aq. KOH/$H_2O$ also gave **2** in high yield. But, in 1% aq. CsOH/$H_2O$, $K_2CO_3$/$H_2O$, $NaHCO_3$/$H_2O$, and $Ca(OH)_2$/$H_2O$, the Raney Ni–Al alloy was ineffective for reduction of **1**.

Table 1

Reduction of biphenyl **1** with Raney Ni–Al alloy in dilute aqueous alkaline solution[a)]

| Run | Ni-Al (g) | Drop Time[b)] (h) | 1% aq KOH/Water (ml/ml) | Reaction Time[c)] (h) | Isolated Yield (%) |
|---|---|---|---|---|---|
| 1 | 5 | 1 | 50/50 | 5 | 94 |
| 2 | 5 | 1.5 | 50/50 | 3 | 95 |
| 3 | 5 | 1.5 | 25/25 | 4 | 93 |
| 4 | 5 | 1.5 | 10/10 | 4 | 91 |
| 5 | 5 | 1.5 | 5/5 | 6 | 91 |
| 6 | 3.5 | 1.5 | 10/10 | 6 | 94 |

a) **1**: 5 mmol. b) Drop time is that 1% aq KOH was added dropwise to reaction vessel. c) The drop time is not included in the mentioned time.

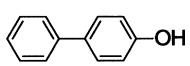
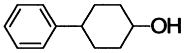
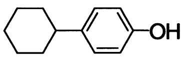
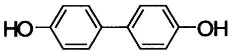
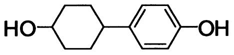
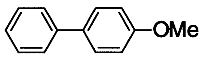
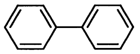
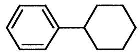
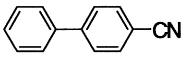
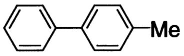
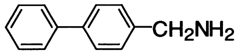
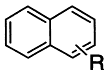
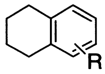
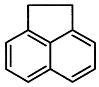
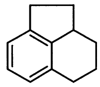
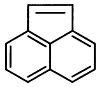
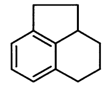
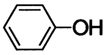
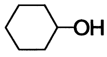
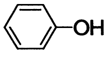
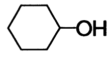
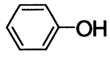
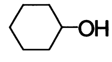


Scheme 1.

Reduction using a Raney Ni–Al alloy was mainly developed by Papa and Schwenk et al. and this method is well-known.[17] However, the conventional method which is carried out by adding a Raney Ni–Al alloy to 10% aq. NaOH solution at 90°C is very dangerous because hydrogen gas is vigorously generated, and in the reduction of alkali-insoluble compounds, an organic solvent such as EtOH and toluene and a considerable amount of the Raney Ni–Al alloy are required.[18] Furthermore, biphenyl was hardly reduced by this procedure.[19] In comparison with the conventional method, there are some advantages to our method as it is very safe and operationally easy even at 90°C because hydrogen gas generates very gently as a dilute alkaline solution is added to a mixture of water and the Raney Ni–Al alloy. In addition, our method has a stronger reducing power and the reduction of alkali-insoluble compounds could be performed smoothly in the absence of organic solvents.

Under these optimized conditions, reduction of other aromatic compounds was carried out by using the Raney Ni–Al alloy in 1% aq. KOH/$H_2O$ *without any organic solvents* at 90°C under atmospheric pressure (Table 2). In the case of 4-phenylphenol, 4-phenylcyclohexanol and 4-cyclohexylphenol were obtained (Entry 1). The reduction of biphenol afforded 4,4′-dihydroxycyclohexylbenzene (Entry 2). Interestingly, the stereoisomer of the obtained 4-phenylcyclohexanol and 4,4′-dihydroxycyclohexylbenzene was only the *trans* form (Entries 1 and 2). The methoxy group on biphenyl was reduced under these conditions, and cyclohexylbenzene was mainly formed (Entry 3). In the case of a cyano group, reduction of the cyano group only proceeded

Table 2
Reduction of aromatic compounds with Raney Ni–Al alloy in dilute aqueous KOH solution[a)]

| Entry | Substrate | Temp./°C | Time/h[b)] | Product | Isolated Yield/% |
|---|---|---|---|---|---|
| 1 |  | 90 | 3.5 |  (*trans*)[c)]<br> | 60<br>30 |
| 2 |  | 90 | 4.5[e)] |  (*trans*)[f)] | 93 |
| 3 |  | 90 | 25.5[d)] | <br> | 4<br>69 |
| 4 |  | 90 | 25.5 | <br> | 9<br>71 |
| |  | | |  | |
| 5 | R=H | 90 | 3.5 | R=H | 91 |
| 6 | R=1-OMe | 90 | 3.5 | R=H<br>R=1-OMe | 11<br>59 |
| 7 | R=1-OH | 90 | 3.5 | R=1-OH | 93 |
| 8 | R=2-OH | 90 | 3.5[g)] | R=2-OH | 57 |
| 9 |  | 90 | 6.5 |  | 93 |
| 10 |  | 90 | 6.5 |  | 94 |
| 11 |  | 90 | 2.5 |  | 93 |
| 12 |  | 60,)))[h)] | 1.5 |  | 86 |
| 13 |  | 60 | 2.5 |  | 93 |

a) Substrate: 5 mmol, Raney Ni-Al alloy: 3.5 g, 1% aq KOH/$H_2O$=10/10 ml. b) The time (90 min) of dropping 1% aq KOH solution to the reaction vessel is included in the mentioned time. c) m.p. 119-120 °C (lit.[20] 118-118.5 °C). d) Substrate (12%) was recovered. e) 1% aq KOH/$H_2O$=100/100 ml. f) m.p. 223.5-224.5 °C (lit.[21] 222.5-223.5 °C). g) Substrate (34%) remained. h) Under ultrasonication.

(Entry 4). In the case of naphthalenes, the corresponding tetrahydronaphthalenes were obtained (Entries 5–8). Reduction of 2-naphthol was more difficult than that of 1-naphthol. Furthermore, acenaphthene and acenaphthylene were also reduced, respectively (Entries 9 and 10). In the case of phenol, reduction took place easily at a lower temperature (60°C) to give cyclohexanol in high yield. Ultrasonication accelerated the reaction (Entries 12 and 13).

The greatest advantage of our method compared with other methods is that the reaction is operationally simple and safe in aqueous media under mild conditions (90°C and atmospheric pressure) and hydrogen gas is not necessary because the proton source is water. Furthermore, the Raney Ni–Al alloy is inexpensive. Recently, in view of environmental concerns, organic reactions in water *without any organic solvents* have been receiving attention.[22] Therefore, our method is quite interesting and provides a simple and effective procedure for reduction of aromatic rings.

## References

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14. Raney Ni–Al alloy (Ni: 50%) was purchased from the Kishida Chemical Company.
15. **A typical procedure is described as follows**: 1% aq. KOH solution (10 ml) was gradually dropped into a mixture of **1** (5 mmol, 650 mg), Raney Ni–Al alloy (3.5 g) and water (10 ml) for 1.5 h at 90°C under atmospheric pressure. After the reaction mixture was stirred for 4.5 h, the mixture was cooled to room temperature. The insoluble materials were filtered off with Celite and the residue was washed with ethyl acetate. The filtrate was extracted with ethyl acetate and the organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated in vacuo to afford **2** (639 mg, 94%) (Run 6).
16. When using a 5% aq. KOH solution under the same conditions as Run 4 in Table 1, the yield of **2** was 40%, but **1** was recovered (55%).
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19. When the reduction was undertaken by adding a Raney Ni–Al alloy over 1.5 h to a mixture of 10% aq. NaOH (10 ml) *without any organic solvents* and **1** (5 mmol) at 90°C, **1** was recovered (95%) (**2**: 2%). Furthermore, although the reaction was carried out by adding the Raney Ni–Al alloy at 60°C and then heating up the mixture to 90°C, the reaction did not proceed (**1** was recovered quantitatively).
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