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Reduction of carbonyl groups to the corresponding methylenes with Ni–Al alloy in water

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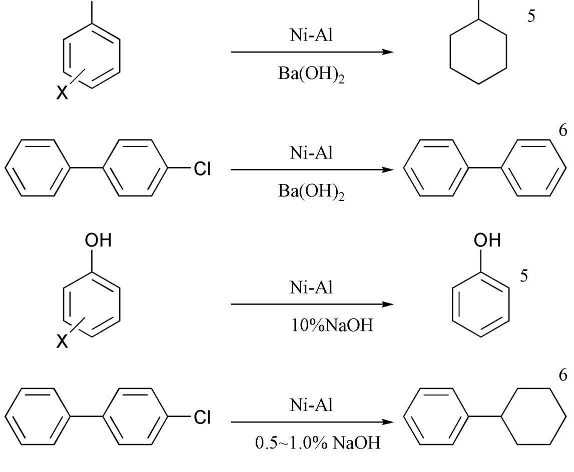
The reduction of carbonyl compounds 1a–h using Ni–Al alloy in water under reflux proceeded to give the corresponding methylene compounds 2a–h within 2 h in 89.0–99.8% relative yields.

The Clemmensen reduction[1] under acidic conditions and Wolf–Kishner reduction[2] under basic conditions are widely used for the reduction of carbonyl groups to the corresponding methylene units. A good review about the reduction of organic compounds with Ni–Al alloy in alkaline media[3] is available. In 1942, Papa *et al.*[4] reported that acetophenone and benzaldehyde were reduced to ethylbenzene and toluene by using Ni–Al alloy in 10% aq. NaOH solution, respectively. This method is carried out under basic conditions and thus the Wolf–Kishner reduction can not be applied for base sensitive substrates. The Clemmensen reduction is carried out under strongly acidic conditions and sometimes poisonous mercury must be used. Thus, the method is not suitable for acid sensitive precursors. It has been found that the reduction of halophenols[5] and 4-chlorobiphenyl[6] using Ni–Al alloy in highly dilute aq. NaOH alkaline solution or weakly basic Ba(OH)$_2$ solution afforded the reduced aromatic rings, respectively (Scheme 1). As shown in Scheme 1, it was found that the reduction of halophenols using Ni–Al alloy in 10% aq. NaOH solution afforded the phenol itself, however, the reaction of halophenols in saturated Ba(OH)$_2$ solution gave not phenol but cyclohexanol. Also 4-chlorobiphenyl was reduced to biphenyl itself by treating with Ni–Al alloy in 10% aq.

NaOH solution at 90 °C. However, when it was reduced in 0.5–1% aq. NaOH solution, cyclohexylbenzene was obtained.

The above results prompted us to investigate the reduction of carbonyl compounds with Raney alloys in only water without any organic solvent, or a base. Reduction of acetophenone **1a** was carried out in refluxing water with Ni–Al, Co–Al, Cu–Al, and Fe–Al alloys[7] for 2 h, the results are summarized in Table 1.



Scheme 1

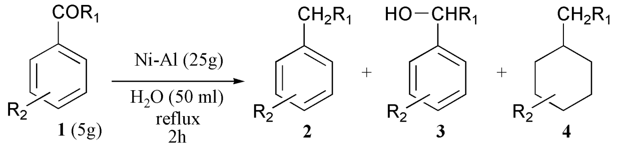
Table 1 Reduction of **1a** with alloy in water under reflux for 2 h[ab]

		Products		
		(Relative yield, %)		Recovered **1a**
Run	Alloy	**2a**	**3a**	(%)
1	Ni–Al	97.1	0.4	2.5
2	Co–Al	0.9	18.0	72.1
3	Cu–Al	(+)	20.1	79.9
4	Fe–Al	(+)	26.2	73.8

[a] **1a**: 5 g, Alloy: 25 g, Water: 50 ml. [b] Measured by GC-Mass.

Ni–Al alloy (50:50 composition) appears to be the best reducing system. The reduction of carbonyl compounds **1a–1h** with Ni–Al alloy was carried out in water under similar conditions as described below (Scheme 2), the results are summarized in Table 2.

The typical procedure was the following. To a mixture of **1a** (5.00 g, 41.6 mmol) in 50 mL of water at room temperature was



a: R$_1$ = -CH$_3$, R$_2$ = -H; **b**: R$_1$ = -CH$_2$CH$_3$, R$_2$ = -H; **c**: R$_1$ = -CH$_2$CH$_2$CH$_3$, R$_2$ = -H; **d**: R$_1$ = -CH(CH$_3$)$_2$, R$_2$ = -H; **e**: R$_1$ = -CH$_3$, R$_2$ = 4-CH$_3$-; **f**: R$_1$ = -CH$_3$, R$_2$ = 3-CH$_3$-; **g**: R$_1$ = -CH$_3$, R$_2$ = 2-CH$_3$-; **h**: R$_1$ = -C$_6$H$_5$, R$_2$ = -H

Scheme 2

Table 2 Reduction of **1** with alloy in water under reflux for 2 h[ab]

		Products		
Run	Ketone	(Relative yield %)		
1	**1a**	**2a** (99.0)	**3a** (1.0)	**4a** (+)
2	**1b**	**2b** (98.6)	**3b** (1.4)	**4b** (+)
3	**1c**	**2c** (89.0)	**3c** (2.0)	**4c** (9.0)
4	**1d**	**2d** (96.2)	**3d** (3.8)	
5	**1e**	**2e** (99.8)	**3e** (0.2)	
6	**1f**	**2f** (93.1)	**3f** (6.9)	
7	**1g**	**2g** (99.8)	**3g** (0.2)	
8	**1h**	**2h** (99.8)	**3h** (0.2)	

[a] **1a**: 5 g, Alloy: 25 g, Water: 50 ml. [b] Measured by GC-Mass.

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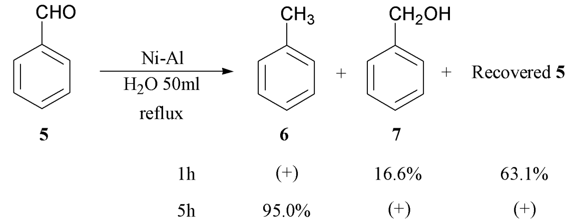
added Ni–Al alloy (25.0 g, Ni: 50%) in one portion. The reaction mixture was stirred vigorously under reflux for 2 h. During the reaction, the pH of solution remained close to neutral. The mixture was extracted with ether (10 mL × 3 times). The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated. The **2a** was obtained in a 99.8% yield (4.41 g). The hydrocarbon products can also be isolated by simple steam distillation.

As shown in Table 2, the reduction of ketones **1a**–**g** with Ni–Al alloy in water afforded corresponding methylene compounds **2a**–**g** in good yields (89–99.8%), respectively, with small amount of alcohols **3a**–**g**. The reduction of acetophenone **1a**, propiophenone **1b**, butyrophenone **1c**, and isobutyrophenone **1d** under similar conditions shown in Table 2 afforded the corresponding alkylbenzenes **2a**–**d** in excellent yields. The formation of a small amount of alcohols **3** in these reactions suggests that they are the *de facto* intermediates *en route* to the formation of **2**. When **3a** was treated with Ni–Al alloy in water under similar conditions to those described above, expected **2a** was obtained in good yield.

Surprisingly, it was found that **1a** was reduced to **2a** in excellent yield, even at room temperature over a 24 h period. Also, reduction of acetyltoluenes **1e**–**g** and benzophenone **1h** afforded the corresponding ethyltoluenes **2e**–**g** and diphenylmethane **2h** with a small amount of intermediate alcohol products **3e**–**h**.

The formation of **4a**–**c** under the moderate reaction conditions used is a very interesting phenomenon since usually reduction of an aromatic ring with Raney Ni catalyst needs high pressure and high temperature to proceed.

Similar reduction of benzaldehyde **5** afforded benzyl alcohol **7** and/or the desired toluene **6** according to the reaction time used (Scheme 3). A longer reaction time is necessary for the formation of **6** in good yield.



Scheme 3

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7 It should be noted that sometimes commercial Ni–Al alloy has varying reactivities. The reactivities of the batch should be tested before the reductions.