Raney Ni–Al alloy mediated hydrodehalogenation and aromatic ring hydrogenation of halogenated phenols in aqueous medium

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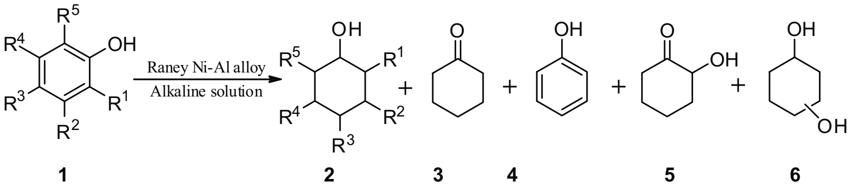
Raney Ni–Al alloy in a dilute aqueous alkaline solution has been shown to be a very powerful reducing agent and is highly effective for the reductive dehalogenation of polyhalogenated phenols and aromatic ring hydrogenation of phenols to the corresponding cyclohexanols.

Keywords: Raney Ni-Al alloy, phenols, reduction, detoxification, aqueous alkaline solution, cyclohexanols

Phenols represent an important group of refractory organic pollutants. They are detected in a variety of industrial and agricultural wastewaters, as they have been utilised widely in a number of important industrial processes. Their toxicity, strong odour, and persistency in the environment, once released to the biosphere, and their suspected carcinogenicity and mutagenicity[1] make these molecules especially troublesome pollutants. A lot of effort has been devoted to the development of new, cost-effective and eco-friendly procedures for the disposal of phenols. In the case of chlorinated phenols, detoxification processes have concentrated on incineration,[2] aerobic and anaerobic biodegradation,[3] microwave[4] and ultrasound[5] assisted hydrodechlorination, electrochemical reduction,[6] treatment with hydrazine and formic acid,[7] photocatalysis,[8] oxidative destruction,[9] and reductive transformation over metal catalysts under a hydrogen atmosphere.[10-12] However, incineration of residues from waste water results in the a large consumption of energy and in the formation of highly toxic by-product such as dioxins. In the case of bioremediation, both aerobic and anaerobic biodegradation need specific environmental conditions.

From a synthetic chemical point of view, a hydrodehalogenation and hydrogenation of toxic halogenated phenols leading to more eco-friendly cyclohexanols should be quite interesting. Significant research effort has been undertaken towards the development of new, cost-effective and eco-friendly syntheses of cyclohexanol derivatives, which are key intermediates for the preparation of useful functional polymers.[13] Thus, cyclohexanol is a key feedstock for ε-caprolactam and adipic acid in the production of nylon. A newly patented process for the production of cyclohexanol is the hydrogenation of benzene to cyclohexene with subsequent hydration.[14] Partial hydrogenation of benzene remains problematic, however. The conversion of phenol to cyclohexanol is still used and this process constitutes the most important industrial process incorporating a hydrogenation of a monocyclic arene.[15] Nevertheless, the total or partial hydrogenation of the aromatic ring in phenols represents a challenge for the industry. Typically, the catalytic transformations are carried out under high pressures and reaction temperatures with homogeneous or heterogeneous Rh and Ru catalysts. The use of Pd, Pt, Ni, and Co based catalysts has also been described.[10-12] Recently, the hydrogenation of arenes using Pd, Rh and Ru nanoparticles as catalysts has been investigated extensively.[16] Several shortcomings have been noted for these reported methods that make it more difficult to employ the procedures both in the laboratory and on an industrial scale. These include the expense of some of the reductants, the severe conditions for the transformation necessitating special apparatus such as autoclaves, and the not always straightforward procedures to make nanoparticle catalysts.

In the continuation of our work on the reduction of halogenated aromatic compounds,[17,18] we turned our attention to developing a convenient, eco-friendly and practical method for the hydrodehalogenation and hydrogenation of chloro- and bromophenols. It was found that Raney Ni–Al alloy in a dilute aqueous alkaline solution effectively reduces phenols to cyclohexanol. The reductions were carried by adding an aqueous alkaline solution dropwise to a suspension of a chlorophenol and Raney Ni–Al alloy (500 mg $mmol^{-1}$ of substrate) in water, when the resulting mixture was heated at 90 °C. The reactions are summarised in Table 1 and Schemes 1 and 2.



1 **2** **3** **4** **5** **6**

1: **a:** $R^1=R^2=R^3=R^4=H$, $R^5=OH$; **b**: $R^1=R^3=R^4=H$, $R^2=Cl$, $R^5=OH$; **c**: $R^2=R^4=H$, $R^1=R^3=Cl$, $R^5=OH$;
d: $R^1=R^4=H$, $R^2=R^3=Cl$, $R^5=OH$; **e**: $R^1=R^2=R^3=R^4=Cl$, $R^5=OH$; **f**: $R^1=R^2=R^3=R^4=Br$, $R^5=OH$;
g: $R^1=R^2=R^3=R^5=H$, $R^4=OH$; **h**: $R^2=R^3=R^5=H$, $R^1=Cl$, $R^4=OH$; **i**: $R^1=R^2=R^3=H$, $R^5=Me$, $R^4=OH$;
j: $R^1=R^5=R^3=H$, $R^2=Me$, $R^4=OH$; **k**: $R^2=H$, $R^1=R^3=R^5=Br$, $R^4=OH$; **l**: $R^1=R^2=R^4=R^5=H$, $R^3=OH$;
m: $R^1=R^2=R^5=H$, $R^4=Br$, $R^3=OH$; **n**: $R^1=R^2=R^5=H$, $R^4=Cl$, $R^3=OH$; **o**: $R^1=R^4=H$, $R^2=R^5=Br$, $R^3=OH$;
p: $R^1=R^2=R^4=R^5=Cl$, $R^3=OH$; **q**: $R^1=R^2=R^4=R^5=Br$, $R^3=OH$; **r**: $R^1=R^3=R^5=Cl$, $R^2=R^4=H$;
s: $R^1=R^2=R^3=R^4=R^5=Cl$; **t:** $R^1=R^2=R^4=R^5=Cl$, $R^3=Me$
2: **a:** $R^1=R^2=R^3=R^4=R^5=H$; **i**: $R^1=R^2=R^3=R^4=H$, $R^5=Me$; **j**: $R^1=R^2=R^3=R^4=H$, $R^2=Me$; **t**: $R^1=R^2=R^4=R^5=H$, $R^3=Me$;
6: **a:** 2-OH; **g**:3-OH; **l**:4-OH;

Scheme 1

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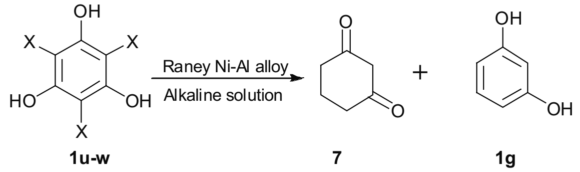

u: X=H; **v:** X=Br; **w:** X=Cl;

Scheme 2

When a 1wt% aq. KOH, CsOH or NaOH solution was added to a mixture of **1a** and Raney–Ni alloy in water, **1a** was reduced to give a mixture of cyclohexanol (**2a**), cyclohexanone (**3**), phenol (**4**), 2-hydroxycyclohexanone (**5**) and cyclohexane-1,2-diol (**6a**) (Table 1, runs 1, 2, 4 and 5). With a decrease of amount in Raney Ni–Al, the reaction progressed more slowly, with an increase in relative ratio of **6a** (Run 3). However, the reduction became sluggish, when even less alloy (200 mg mmol^{-1} of substrate) was employed, and unreacted **1a** (15.8%, according to GC measurement) was found to remain in the reaction mixture. With chlorinated and brominated catechols (**1b–f**), the reductive dehalogenation and ring hydrogenation progressed effectively to afford **6a** as the main product, along with small amounts of compounds **2a, 3, 4** and **5** (runs 6–10).

Surprisingly, treatment of resorcinol (**1g**) with Raney Ni–Al alloy (500 mg mmol^{-1} substrate) in the presence of a 1% aq. KOH or aq. CsOH solution did not produce the expected cyclohexane-1,3-diol (**6e**), but gave **2a** in 85 and 82% yields (runs 11 and 12). A minor amount of cyclohexane-1,3-diol (**6e**) was also obtained, albeit with compounds **2a** and **3**, when a smaller amount of Raney Ni–Al alloy (300 mg mmol^{-1} and 400 mg mmol^{-1}, respectively) was employed (runs 13 and 14). Compound **2a** was also obtained as the main product, albeit with a small amount of **4**, when the reaction was carried out in the presence of a 1wt% aq. $Ca(OH)_2$ solution (run 16). Again, the hydrogenation progressed less readily with a decrease of Raney Ni–Al alloy (200 mg/mmol substrate), and **1g** was still detected in the reaction mixture (at a ratio of 15.6%, according to GC analysis) even after the mixture had been heated for 10 h. Under similar reaction conditions, treatment of 2-methyl-resorcinol (**1i**) and 5-methylresorcinol (**1j**) with Raney Ni–Al alloy did not afford the desired cyclohexane-1,3-diols, but produced the corresponding 2-methylcyclohexanol (**2i**, *syn*/*anti* = 1.0/4.2) and 3-methylcyclohexanol (**2j**, *syn*/*anti* = 1.0/3.8) as the sole products in good yields (runs 18 and 19). Tribromoresorcinol (**1k**) was easily reduced to give **2a** as the sole product (run 20). Treatment of a mixture of hydroquinone (**1l**) and Raney Ni–Al alloy with a 1wt% aq. KOH, NaOH, CsOH or $Ca(OH)_2$ solution afforded cyclohexane-1,4-diol (**6l**) in 80–86% isolated yields (runs 21, 22, 24 and 25). Even when the amount of Raney Ni–Al alloy was reduced (400 mg/mmol substrate), compound **6l** was afforded selectively (yield: 80%, run 23). With a further decrease in the amount Raney Ni–Al alloy that was used (300 mg mmol^{-1} substrate), the reduction became sluggish and residual **1l** could be detected in the reaction mixture (in a ratio of 12.8%, GC analysis), even after the mixture was heated at 90 °C for 8 h. In the case of the chloro- and bromo substituted hydroquinones **1m–q**, cyclohexane-1,4-diol **6l** was isolated in good yield (yield 71–83%, *syn*/*anti* = 1.0/2.2, runs 26–29). Moreover, 1,3,5-trichlorophenol (**1r**) and 1,2,3,4,5-pentachlorophenol (**1s**), which are highly toxic persistent organic pollutants, were found to be dehydrochlorinated and hydrogenated effectively to afford cyclohexanol (**2a**) in good yields (Table 1, Runs 30 and 31). Similarly, tetrachlorophenol (**1p)** was dechlorinated

Table 1 Reduction of phenol (**1**)[a]

Run	Substrate	Ni–Al/g	Alkaline solution[b]/mL	Time/h	Ratio/%[c]				
					2	**3**	**4**	**5**	**6**
1	**1a**	5	1%KOH (50)/H_2O (50)	5	8.0 (5.6)[d]	8.9 (6.5)[d]	25.1(19.1)[d]	6.3(4.6)[d]	51.7(45.6)[d,h]
2	**1a**	5	1% NaOH (50)/H_2O (50)	6	7.5	8.1	23.3	6.0	55.1
3	**1a**	3	1%NaOH (50)/H_2O (50)	8	4.6	3.3	24.3	5.9	61.9
4	**1a**	5	1% CsOH (50)/H_2O (50)	5	7.4	10.4	29.2	5.8	46.2
5	**1a**	5	1% $Ca(OH)_2$ (50)/H_2O (50)	6	3.0	7.4	28.4	3.1	58.1
6	**1b**	5	1%KOH (50)/H_2O (50)	5	5.8	7.3	21.4	5.9	59.6
7	**1c**	5	1%KOH (50)/H_2O (50)	5	5.1	6.8	24.8	4.9	58.4
8	**1d**	5	1%KOH (50)/H_2O (50)	6	5.5	7.2	26.3	4.1	56.9
9	**1e**	5	1%KOH (50)/H_2O (50)	7	4.9	8.1	22.8	3.7	60.5
10	**1f**	5	1%KOH (50)/H_2O (50)	5	8.3	8.1	24.7	6.9	52.0
11	**1g**	5	1%KOH (50)/H_2O (50)	4	100 (85)[d]	0	0	0	0
12	**1g**	5	1% NaOH (50)/H_2O (50)	4	100 (82)[d]	0	0	0	0
13	**1g**	4	1%NaOH (50)/H_2O (50)	5	88.5	0	2.5	0	9.0
14	**1g**	3	1%NaOH (50)/H_2O (50)	6	75.2	0	10.8	0	14.0
15	**1g**	5	1%CsOH (50)/H_2O (50)	4	100 (83)[d]	0	0	0	0
16	**1g**	5	1% $Ca(OH)_2$ (50)/H_2O (50)	4	94.2	0	5.8	0	0
17	**1h**	5	1%KOH (50)/H_2O (50)	5	100 (80)[d]	0	0	0	0
18	**1i**	5	1%KOH (50)/H_2O (50)	7	100 (81)[d,e]	0	0	0	0
19	**1j**	5	1%KOH (50)/H_2O (50)	6	100 (86)[d,f]	0	0	0	0
20	**1k**	5	1%KOH (50)/H^2O (50)	5	100 (81)[d]	0	0	0	0
21	**1l**	5	1%KOH (50)/H_2O (50)	4	0	0	0	0	100 (84)[d,g]
22	**1l**	5	1%NaOH (50)/H_2O (50)	4	0	0	0	0	100 (82)[d,g]
23	**1l**	5	1% CsOH (50)/H_2O (50)	5	0	0	0	0	100 (86)[d,g]
24	**1l**	5	1% $Ca(OH)_2$ (50)/H_2O (50)	5	0	0	0	0	100 (81)[d,g]
25	**1m**	5	1%KOH (50)/H_2O (50)	6	0	0	0	0	100 (83)[d,g]
26	**1n**	5	1%KOH (50)/H_2O (50)	7	0	0	0	0	100 (80)[d,g]
27	**1o**	5	1%KOH (50)/H_2O (50)	6	0	0	0	0	100 (78)[d,g]
28	**1p**	5	1%KOH (50)/H_2O (50)	6	0	0	0	0	100 (74)[d,g]
29	**1q**	5	1%KOH (50)/H_2O (50)	9	0	0	0	0	100 (71)[d,g]
30	**1r**	5	1%KOH (50)/H_2O (50)	4	100 (92)[d]	0	0	0	0
31	**1s**	5	1%KOH (50)/H_2O (50)	5	100 (90)[d]	0	0	0	0
32	**1t**	5	1%KOH (50)/H_2O (50)	4	100 (94)[d,i]	0	0	0	0

[a] **1** (10 mmol); [b] added dropwise within 1.0 h; [c] GC ratio; [d] isolated yields in parentheses; [e] *syn/anti*=1.0/4.2; [f] *syn/anti*=1.0/3.8; [g] *syn/anti*=1.0/2.2; [h] *syn/anti*=1.0/3.5; [i] *syn/anti*=1.0/4.0 (1HNMR ratio).

Table 2 Reduction of trihydroxybenzene (**1u–w**)[a]

Run	Substrate	Ni–Al/g	Alkaline solution[b]/mL	Time/h	Yield/%[c]	
					7	**1g**
1	**1u**	5	1% KOH (50)/H_2O (50)	5	65.4 (48.9)[d]	34.6 (28.8)[d]
2	**1u**	5	1% NaOH (50)/H_2O (50)	5	63.8	36.2
3	**1u**	5	1% CsOH (50)/H_2O (50)	5	66.1	33.9
4	**1u**	5	1% $Ca(OH)_2$ (50)/H_2O (50)	7	58.1	41.9
5	**1v**	5	1% KOH (50)/H_2O (50)	7	60.3	39.7
6	**1w**	5	1% KOH (50)/H_2O (50)	8	58.6	41.4

[a]**1u–w** (10 mmol); [b]added dropwise in 1.0 h; [c]GC ratio; [d]isolated yields in parenthesis.

easily to give cyclohexanol (**2a**) in good yield under the reaction conditions (Table 1, Run 32).

Hydrogenation of trihydroxybenzenes with Raney Ni–Al alloy was also studied (Scheme 2 and Table 2). 1,3,5-Trihydroxybenzene (**1u**) (phloroglucinol), when reacted with Raney Ni–Al alloy (500 mg/mmol substrate) upon dropwise addition of a 1wt% aq. NaOH, KOH, CsOH or $Ca(OH)_2$ solution, did not give cyclohexane-1,3,5-triol, but a mixture of cyclohexa-1,3-dione (**7**) and resorcinol (**1g**) in a ratio of 65.4% to 34.8% (GC). Again, the reduction progressed less readily when a smaller amount of Raney Ni–Al alloy (400 mg/mmol substrate) was used, and **1u** could still be detected (15%, GC) at the end of the reaction, even after the reaction mixture had been heated at 90 °C for 12 h. Similarly, the tribromo and trichloro derivatives **1v** and **1w** could also be reduced upon treatment with Raney Ni–Al alloy in an aq. KOH solution to produce a mixture of **7** and **1g**.

In conclusion, we have developed a new and efficient method for the reduction of bromo- and chlorophenols as well as of dihydroxybenzenes and halogenated dihydroxybenzenes using commercially available Raney Ni–Al alloy in a dilute alkaline aqueous solution. No organic solvents were used in the reactions. Catechols were easily reduced to afford a mixture of cyclohexanol (**2a**), cyclohexanone (**3**), phenol (**4**), 2-hydroxycyclohexanone (**5**), and cyclohexan-1,2-diol (**6**). Resorcinols could be converted to cyclohexanol in high yield. Hydroquinones could be transformed to cyclohexane-1,4-diol in good yield. The advantages of the process lie in the ease of manipulation, the short reaction time necessary, and the mildness of the reaction conditions. Raney Ni–Al alloy is commercially readily available and is, of course, cheaper than the Raney Ni catalyst made from it. From an environmental stand-point, chlorinated and brominated phenols and mixtures thereof with the corresponding parent compounds are converted to the less toxic and often useful cyclohexanols.

Experimental

General

IR spectra were measured with Nicolet FT-IR 360, JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^1H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^1H at 270 MHz and ^{13}C at 67.8 MHz). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer [electron impact mode (EI), 70 eV or fast atom bombardment (FAB)] and with a GC-MS 6890[GC]/HP MS5973 combination. An HP-5 GC column from Agilent was used [50 m × 0.25 mm × 0.25 mm; injector temperature: 300 °C; detector temperature: 280 °C; starting temperature 80 °C, holding time 3 min, temperature rising rate: 10 °C/min; final temperature 300 °C; holding time 10 min, carrier gas: helium].

The Raney-Ni alloy [Ni/Al 50:50wt%] was acquired commercially from Jinzhou Catalyst Company (16, Wenshengli, Linhe, Jinzhou 12100, P.R. China).The halogenated phenols were purchased from Sino-Pharma Chemical Reagent Co., Ltd., Shanghai 200001, China.

Reduction of chlorophenols

A 1wt% aq. KOH solution (100 mL) within 1.0 h and at 90 °C was added dropwise. To a suspension of **1a** (10 mmol, 1.10 g), and Raney Ni–Al alloy (5.0 g) in water (50 mL) After being heated for 5 h at 90 °C, the mixture was cooled to room temperature and filtered through Celite. The residue was washed with ethyl acetate. The filtrate was neutralised with aq. hydrochloric acid, and the resulting mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$. After removal of the solvent, a mixture of cyclohexanol (**2a**), cyclohexanone (**3**), phenol (**4**), 2-hydroxy cyclohexanone (**5**), and cyclohexan-1,2-diol (**6**) in a ratio of 8.0: 8.9: 25.1: 6.3: 51.7 was obtained (Table 1, Run 1).

For final identification, the compounds were separated by column chromatography on silica gel, when mixtures of structures were obtained from the reactions. All of the compounds, **2a**, **3**, **3**, **4**, **5** and **6** were compared with authentic samples and their structures were also assigned on the basis of ^1H NMR, IR and GC-MS spectroscopic data.

2-Methylcyclohexanol (**2i,** *a mixture of* syn *and* anti-*isomers*):[18] ν_{max} (neat/cm^{-1}) 3365 (bs, OH), 2930, 2870, 1450, 1062, 1045, 1030, 978, 917, 840; δ_H (400 MHz, $CDCl_3$) 1.02–1.88 (12H, m), 2.04 (1H, s, OH), 3.14 (0.81 H, dt, *J* = 4.0 and 9.2 Hz, C*H*OH, *anti*-isomer), 3.84 (0.19 H, quintet, *J* = 2.6 Hz, C*H*OH, *syn*-isomer); δ_C (67.8 MHz, $CDCl_3$) for *syn*-isomer: 20.6, 24.5, 28.8, 30.9, 32.5, 35.8, 71.1; for *anti*-isomer: 18.5, 25.2, 25.7, 33.6, 35.5, 40.2, 76.5; MS (EI, 70 eV) *m/z* (%) 114 (M^+) (38), 96 (100), 81 (88), 68 (64), 58 (58).

3-Methylcyclohexanol (**2j,** *a mixture of* syn *and* anti-*isomers*):[18] ν_{max} (neat/cm^{-1}) 3380 (bs, OH), 2940, 2880, 1452, 1105, 1045, 1030, 1000, 945, 935; δ_H (400 MHz, $CDCl_3$) 0.94–1.80 (12H, m), 2.02 (1H, s, OH), 3.25 (0.80H, m, C*H*OH, *anti*-isomer), 3.76 (0.20H, m, C*H*OH, *syn*-isomer); δ_C (67.8 MHz, $CDCl_3$) for *syn*-isomer: 20.2, 22.2, 26.6, 33.2, 34.4, 41.6, 66.6; for *anti*-isomer: 22.5, 24.4, 31.6, 34.3, 35.6, 44.9, 70.6; MS (EI, 70 eV) *m/z* (%) 114 (M^+) (3.7), 96 (100), 81 (62), 71 (62).

4-Methylcyclohexanol (**2t,** *a mixture of* syn *and* anti-*isomers*):[18] ν_{max} (neat/cm^{-1}) 3370 (bs, OH), 2920, 1450, 1358, 1185, 1047, 980; δ_H (400 MHz, $CDCl_3$) 0.86–1.78 (12H, m), 2.02 (1H, s, OH), 3.42 (0.78H, m, C*H*OH, *anti*-isomer), 3.84–3.88 (0.22H, m, C*H*OH, *syn*-isomer); δ_C (67.8 MHz, $CDCl_3$) for *syn*-isomer: 21.6, 29.0 (2C), 31.1, 32.2 (2C), 66.9; for *anti*-isomer: 21.6, 31.4 33.0 (2C), 35.3 (2C), 70.6; MS (EI, 70 eV) *m/z* (%) 114 (M^+) (5.5), 96 (100), 81 (95), 70 (38), 57 (55).

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