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A facile method for the dechlorination of mono- and dichlorobiphenyls using Raney Ni–Al alloy in dilute aqueous solutions of alkali hydroxides or alkali metal carbonates

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ABSTRACT

Raney Ni–Al alloy in a dilute aqueous alkaline solution of NaOH, KOH, CsOH, LiOH, or $Ca(OH)_2$ or of alkali metal carbonates such as Na_2CO_3, K_2CO_3 becomes a very powerful reducing agent and dechlorinates the polychlorobiphenyl(PCB) congeners mono- and dichlorobiphenyls effectively to afford biphenyl and/or phenylcyclohexane, respectively. The reactions are run under mild conditions *without the use of organic solvents*. The reductive dechlorination of dichlorobiphenyls with a Raney Ni–Al alloy under ultrasonication was investigated, also.

1. Introduction

Much attention has been focused on the remediation of environmental pollution caused by chlorinated organic compounds such as polychlorinated biphenyls (PCBs), which have been utilized extensively in transformer oils, heat-exchanger fluids and carbonless copy paper for several decades. PCBs are hazardous substances and are long-lived, once released into the biosphere.[1] Although nowadays the use and production of PCBs are severely restricted, it has been estimated that the total world production from the 1930s to the 1980s was between one and two million tons. Since PCBs exhibit a high degree of chemical and biological stability, due to low degradation by reductive and oxidative enzymatic pathways, and also exhibit lipid solubility, they have accumulated in the environment, especially along the food chains. Possible adverse effects on wildlife and human health have been reported such as, in the gravest cases, induction of skin lesions and tumours.[1] It has been reported that PCBs have been detected in animal and human lipid-rich tissues and secretions, including mother-milk.[1] Therefore, it is very important to develop effective methods, which could be used to reductively dechlorinate these recalcitrant compounds. To the best of our knowledge, the destruction of PCBs has usually been carried out by normal and plasma incineration.[2] A few chemical methods are known to transform PCBs and congeners through dechlorination. They are photochemical dechlorination,[3] electrolytic reduction,[4] sodium, potassium or calcium-based reduction,[5] transition metal-promoted reductive dechlorination with sodium borohydride or sodium alkoxyborohydride,[6] Raney Ni-mediated dechlorination using excess amounts of silyl hydride as an additional reductant,[7] iron-promoted reduction[8] and dechlorination with an excess amount of sodium borohydride at elevated temperatures.[9] Additionally, the Pd/C–Et_3N mediated catalytic hydrodechlorination has become of interest.[10] Some disadvantages can be noted for most of these documented processes. The combustion of PCBs usually produces corrosive HCl gas and detectable amounts of highly toxic chlorinated dioxins.[2] Photochemical methods require UV irradiation. Thus, the efficiency of dechlorination is low and the method is not of general practicability.[3] Transition metal-promoted reductive dechlorination needs stoichiometric or even an excess amount of transition metal.[6,7] Also, in some cases, complete dechlorination cannot be achieved.[5] Harsh reaction conditions such as elevated temperatures are necessary for many of the processes.[7–9] Alkali metals as reductants, such as sodium and potassium, are troublesome to handle.[5] All of the reactions using chemical reductants have been carried out in organic solvents such as methanol and *N*,*N*-dimethylformamide, some of which have considerable toxicity. A generally practical dechlorination method for PCBs and congeners has not yet appeared.

Raney Ni–Al alloy, which is commercially available, cheap and easy to handle, has been widely employed as a starting material for preparing Raney Ni catalyst and as a reductant in 10–25% aq NaOH solution in organic synthesis.[11] In continuation of our work on the dehalogenation of aromatic halides with Raney Ni–Al alloy in

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aqueous media,[12] we turned our attention to the development of a convenient and practical method for the disposal of PCBs. In a preliminary communication, we have reported previously that Raney Ni–Al becomes a very strong reducing agent in dilute aqueous alkaline solutions and reduces monochlorobiphenyls easily to give biphenyl and/or phenylcyclohexane. The method is carried out under mild conditions and in the absence of organic solvents.[13] These successful results prompted us to develop a more convenient and practical method for the disposal of PCBs. An obvious advantage of this method is that water is employed as the solvent and proton source. No organic solvent is used. The reduction is carried at atmospheric pressure. No special apparatus is required.

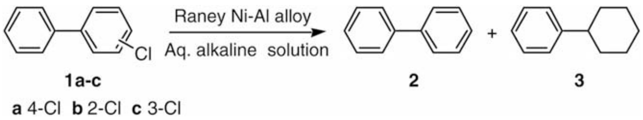
In this paper, we wish to give a detailed report on the reductive dechlorination of a series of pure PCB congeners, mono- and dichlorobiphenyls with Raney Ni–Al alloy in dilute basic aqueous solutions. The effects of the nature, the concentration and the amount of the alkaline and alkali metal carbonate solution, the amount of the Raney Ni–Al alloy used, the reaction temperature and the order of addition of the reagents on the dechlorination are investigated.

2. Dechlorination of monochlorobiphenyls 1a–c (Scheme 1)

2.1. Effects of the concentration of the aq NaOH solution, the amount of the Raney Ni–Al alloy used, the reaction temperature and the order of adding the reagents

Two methods were employed. Method A: the Raney Ni–Al alloy was added gradually to a mixture of **1** in an alkaline solution; Method B: an alkaline solution was added dropwise to a mixture of **1** and Raney Ni–Al alloy in water. As a model reaction, the dechlorination of 4-chlorobiphenyl (**1a**), which among the PCB congeners is known to be one of the most difficult to be dechlorinated,[3a,d] was examined under various reaction conditions, as shown in Table 1. At first, the effect of the concentration of the aq NaOH solution on the dechlorination of **1a** was investigated. When using method A with 1.0 g Raney Ni–Al alloy for 1 mmol of substrate, the reaction time could be greatly shortened (8 h→3 h) upon decreasing the concentration of the aq NaOH solution (5 wt %→0.5 wt %). In a dilute NaOH solution, phenylcyclohexane (**3**) was afforded in addition to biphenyl (**2**). Here, dechlorination and hydrogenation of one of aromatic rings occurred at the same time (Table 1, runs 2–4 vs 1). In the case of a 10 wt % aq NaOH solution, complete dechlorination was not achieved. Interestingly, 0.2 g of Raney Ni–Al alloy per 1 mmol of substrate was enough for a complete dechlorination of **1a** when using a 0.1 wt % NaOH solution. Dechlorination was incomplete under otherwise identical conditions, when using a 0.5 wt % aq NaOH solution (Table 1, run 5 vs 6). In a more concentrated, aq NaOH solution, e.g., in 5 wt % aq NaOH, the reduction was found to be slow (8 h), and only the dechlorinated product, biphenyl (**2**), was afforded in good yield (Table 1, run 2).

On the other hand, in case of method B, Raney Ni–Al alloy was found to be even more effective. More **3** was formed as compared to when using method A (Table 1, runs 7–12 vs 1–6). The reductive dechlorination accelerated with a decrease of the OH^- concentration of the aq NaOH solutions (Table 1, runs 7–10). The ratio of **3** tended to increase with an increase of the amount of Raney Ni–Al alloy used (Table 1, run 4 vs 5). It is noteworthy that in method A, only **2** was formed when the reaction was performed in a 5 wt % NaOH solution. When using method B, however, a mixture of **2** and **3** was obtained upon adding dropwise a 10 wt % aq NaOH solution to the reaction mixture (Table 1, run 2 vs 8). These results reveal that the order of addition of the reagents affects the reductive dechlorination of **1a**. However, an attempt to completely reduce **1a** (5 mmol, 942 mg) with 0.5 g of Raney Ni–Al alloy failed. Compound **1a** (20%) remained unreacted, even though the reduction was found to run to completion very quickly with 1.0 g of the Raney Ni–Al alloy in 0.2 wt % aq NaOH solution (Table 1, run 12 vs 13).



Scheme 1.

Furthermore, the dechlorination of **1a** at lower temperature (60 °C) under ultrasonication was examined. It should be noted that a mixture of **2** and **3** was obtained, when performing the reaction in a 0.5 wt % aq NaOH solution according to method A or when carrying out the experiment according to method B by adding dropwise a 1 wt % aq NaOH solution to the reaction mixture (Table 1, runs 3 and 10). Compound **2** was afforded as the sole product in 86% yield, when adding a 0.2 wt % aq NaOH solution according to method B (Table 1, run 16). Without ultrasonic irradiation, the dechlorination did not proceed until completion and some **1a** remained unreacted even after 6 h (Table 1, run 17). These results indicate that ultrasonication accelerates the reductive dechlorination of **1a**.

2.2. Effect of the nature of the alkaline solution

Regarding the experimental handling of the reactions, method B is more useful than method A, since adding dropwise an aq NaOH solution to the reaction vessel is more convenient than adding the Raney Ni–Al alloy to the reaction solution. Therefore, the dechlorination of **1a** in alkaline solutions other than aq NaOH was investigated using method B (Table 2). It is noteworthy that the use of Raney Ni–Al alloy in 1 wt % aq KOH or CsOH solutions led to strongly reducing agents, comparatively stronger than using the alloy in other alkaline aqueous solutions under otherwise identical conditions. Compound **3** was obtained selectively and in high yields (89–91%) (Table 2, runs 1 and 2). In case of adding 1 wt % aqueous solutions of $Ca(OH)_2$, LiOH and $Ba(OH)_2$, the ratio of **3** to **2** tended to decrease in that order (Table 2, runs 1–6). That is to say, the reducing ability of the Raney Ni–Al alloy exhibited upon dropwise addition of 1 wt % alkaline aqueous solutions follows the order: $KOH>CsOH>NaOH>Ca(OH)_2>Ba(OH)_2>LiOH$. When the reductive dechlorination was conducted by adding more dilute solutions such as 0.2 wt % KOH, CsOH and LiOH aqueous solutions, **1a** was converted to a mixture of **2** (main product) and **3** (minor product) (Table 2, runs 7–10). The dechlorination of **1a** was found to be incomplete when adding 0.2 wt % aq $Ca(OH)_2$ or 0.2 wt % aq $Ba(OH)_2$ solutions (Table 2, runs 11 and 12). From these results, it can be concluded that the strength of the base influences the reducing ability of the Raney Ni–Al alloy, and affects the dechlorination of **1a**.

2.3. Effect of the nature of the alloy; effect of using metal powders

From the above, it could be deduced that Raney Ni–Al alloy becomes a very strong reducing agent in 1 wt % aq NaOH solutions. With this information in hand, the behaviour of other alloys such as Co–Al, Cu–Al and Fe–Al alloys was examined in the dechlorination of **1a** (Table 3). The reaction was found to be slow with Co–Al and with Cu–Al alloy as compared to Raney Ni–Al alloy. In both cases, a complete dechlorination of **1a** could not be realized (Table 3, runs 2 and 3). With Fe–Al alloy, the reductive dechlorination hardly occurred at all. In the case of using Al (2.5 g for 5 mmol substrate) and Ni (2.5 g for 5 mmol substrate) or a combination of Al (2.5 g)

Table 1

Effects of the concentration of the NaOH solution, the amount of Raney Ni–Al alloy used, the reaction temperature and the method of addition in the dechlorination of **1a**[a]

Run	Ni–Al (g)	NaOH solution[b] (ml)	Method	Temp (°C)	Time (h)	Ratio[d] (%)		
						1a	**2**	**3**
1	5	10% NaOH (80)	A	90	8	46	54	0
2	5	5% NaOH (100)	A	90	8	0	100 (80)[e]	0
3	5	1% NaOH (400)	A	90	3	0	36	64
4	5	0.5% NaOH (800)	A	90	3	0	46	54
5	1	0.5% NaOH (800)	A	90	4	34	59	7
6	1	0.1% NaOH (800)	A	90	1	0	83	17
7	5	20% NaOH (40)/H_2O (40)	B	90	8	0	89	11
8	5	10% NaOH (50)/H_2O (50)	B	90	7	0	72	28
9	5	2% NaOH (200)/H_2O (200)	B	90	4	0	31	69
10	5	1% NaOH (400)/H_2O (400)	B	90	2	0	13	87
11	1	1% NaOH (400)/H_2O (400)	B	90	4	24	60	16
12	1	0.2% NaOH (400/) H_2O (400)	B	90	1	0	82	18
13	0.5	0.2% NaOH (400) H_2O (400)	B	90	4	20	75	5
14	5	0.5% NaOH (800)	A	60[c]	3	0	67	43
15	5	1% NaOH (400)/H_2O (400)	B	60[c]	2	0	47	53
16	1	0.2% NaOH (400)/H_2O (400)	B	60[c]	2	0	100 (86)[e]	0
17	1	0.2% NaOH (400)/H_2O (400)	B	60	6	48	47	5

[a] Compound **1a** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h.
[c] Under ultrasonic irradiation.
[d] GC ratio.
[e] Isolated yields in parentheses.

and Ni (2.5 g) for 5 mmol of substrate, the reduction did not take place, and **1a** remained unreacted. These results clearly show that only Ni–Al alloy is highly effective for the reduction of **1a**. In order to develop a reducing system catalytic in Ni, the dechlorination of **1a** using a combination of Raney Ni–Al alloy and Al metal was studied. The total amount of Al was kept at 2.5 g and a 1 wt % aq NaOH solution was added (Table 3, run 5). The Raney Ni–Al alloy was used in different combinations with Al. However, no satisfactory results were obtained and a catalytic system could not be found.

2.4. Effect of the amount of the aq NaOH solution used

When the volume of the 1 wt % aq NaOH solution was decreased (400 ml→50 ml), reaction times became longer (2 h→5 h). However, the ratio of **2** (13%→20%) to **3** (87%→80%) only changed slightly (Table 4, runs 1–3). It was found that the time of adding the NaOH solution had to be adjusted from 0.5 h to 1.5 h, when the volume of the 1 wt % NaOH solution was decreased further to 50 ml in order to accomplish the dechlorination of **1a**. Similarly, a decrease in the volume of a 0.2 wt % aq NaOH solution (400 ml→100 ml) led to the reaction time being prolonged (1 h→3 h). *The ratio of **2** (82%→86%) to **3** (18%→14%) exhibited a small change* (Table 4, runs 6 and 7). The dechlorination of **1a** could no longer be accomplished when the volume of the 0.2 wt % NaOH solution was reduced even further (Table 4, run 8).

Table 2

Effects of the nature of the alkaline solution in the dechlorination of **1a** (method B) at 90 °C[a]

Run	Ni–Al (g)	Alkaline solution[b] (ml)	Time (h)	Ratio[c] (%)		
				1a	**2**	**3**
1	5	1% KOH (400)/H_2O (400)	2	0	0	100 (89)[d]
2	5	1% CsOH (400)/H_2O (400)	4	0	0	100 (91)[d]
3	5	1% NaOH (400)/H_2O (400)	2	0	13	87
4	5	1% $Ca(OH0)_2$ (400)/H_2O (400)	4	0	15	85
5	5	1% LiOH (400)/H_2O (400)	4	0	41	59
6	5	1% $Ba(OH)_2$ (400)/H_2O (400)	4	0	71	29
7	1	0.2% NaOH (400)/H_2O (400)	1	0	82	18
8	1	0.2% KOH (400)/H_2O (400)	2	0	80	20
9	1	0.2% CsOH (400)/H_2O (400)	5	0	88	12
10	1	0.2% LiOH (400)/H_2O (400)	5	0	91	9
11	1	0.2% $Ca(OH)_2$ (400)/H_2O (400)	5	46	54	0
12	1	0.2% $Ba(OH)_2$ (400)/H_2O (400)	5	41	59	0

[a] Compound **1a** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h.
[c] GC ratio.
[d] Isolated yields in parentheses.

Table 3

Dechlorination of **1a** with different alloys (method B)[a]

Run	Alloy (g)	NaOH solution[b] (ml)	Time (h)	Ratio[c] (%)		
				1a	**2**	**3**
1	Ni–Al (5)	1% NaOH (400)/H_2O (400)	2	0	13	87
2	Co–Al (5)	1% NaOH (400)/H_2O (400)	5	84	16	0
3	Cu–Al (5)	1% NaOH (400)/H_2O (400)	5	64	36	0
4	Fe–Al (5)	1% NaOH (400)/H_2O (400)	5	94	6	0
5	Ni–Al (0.6)/Al (2.2)	1% NaOH (400)/H_2O (400)	5	42	50	8

[a] Compound **1a** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h.
[c] GC ratio.

Table 4

Effect of the volume of NaOH solution on the dechlorination of **1a** (method B)[a]

Run	Ni–Al (g)	NaOH solution[b] (ml)	Temp (°C)	Time (h)	Ratio[e] (%)		
					1a	**2**	**3**
1	5	1% NaOH (400)/H_2O (400)	90	2	0	13	87
2	5	1% NaOH (100)/H_2O (100)	90	3	0	17	83
3	5	1% NaOH (50)/H_2O (50)	90	5	21	26	53
4[c]	5	1% NaOH (50)/H_2O (50)	90	5	0	20	80
5[c]	5	1% NaOH (25)/H_2O (25)	90	7	31	21	48
6	1	0.2% NaOH (400)/H_2O (400)	90	1	0	82	18
7	1	0.2% NaOH (100)/H_2O (100)	90	3	0	86	14
8[c]	1	0.2% NaOH (50)/H_2O (50)	90	6	39	57	4
9	1	0.2% NaOH (400)/H_2O (400)	60[d]	2	0	100 (86)[f]	0
10	1	0.2% NaOH (100)/H_2O (100)	60[d]	4	0	100 (82)[f]	0

[a] Compound **1a** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h, unless stated otherwise.
[c] Added dropwise within 1.5 h.
[d] Under ultrasonication.
[e] GC ratio.
[f] Isolated yield in parentheses.

Table 5
Dechlorination of **1b**,**c** in an aq alkaline solution (method B)[a]

Run	Sub.	Ni–Al (g)	Alkaline solution[b] (ml)	Temp (°C)	Time (h)	Ratio[e] (%)	
						2	**3**
1[c]	**1b**	5	1% KOH (50)/H_2O (50)	90	4	0	100 (91)[f]
2[c]	**1b**	5	1% NaOH (50)/H_2O (50)	90	5	33	67
3	**1b**	1	0.2% NaOH (100)/H_2O (100)	90	3	84	16
4	**1b**	1	0.2% NaOH (100)/H_2O (100)	60[d]	4	100 (84)[f]	0
5[c]	**1c**	5	1% KOH (50)/H_2O (50)	90	4	0	100 (88)[f]
6[c]	**1c**	5	1% NaOH (50)/H_2O (50)	90	5	40	60
7	**1c**	1	0.2% NaOH (100)/H_2O (100)	60[d]	4	100 (80)[f]	0

[a] Compound **1a** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h, unless stated otherwise.
[c] Added dropwise within 1.5 h.
[d] Under ultrasonication.
[e] GC ratio.
[f] Isolated yield in parentheses.

Under ultrasonic irradiation, the reductive dechlorination also became slower as the volume of the 0.2 wt % aq NaOH solution was decreased. Here, **2** was formed as the sole product (Table 4, runs 9 and 10). These results could be important for the disposal of PCBs in larger-scale processes since the small volume of aqueous alkaline solution is more acceptable from the viewpoint of economic and environmental concerns.

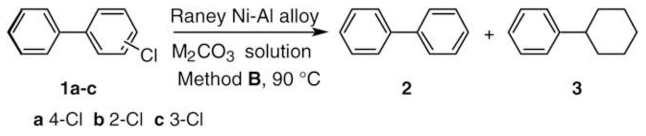
2.5. Dechlorination of monochlorobiphenyls 1b and 1c

Raney Ni–Al alloy is also effective in the reduction of 2-chloro and 3-chlorobiphenyls (**1b**,**c**) when using method B (Table 5). Compound **3** was afforded selectively and in high yields, when a 1 wt % aq KOH solution was added dropwise to a mixture of chlorobiphenyl and Raney Ni–Al alloy. On the other hand, a mixture of **2** (main product) and **3** (minor product) was produced upon using a 1 wt % aq NaOH solution. When the reduction was performed by adding a 0.2 wt % aq NaOH solution, **2** was obtained as the major product, together with **3**. Under ultrasonication at 60 °C, **1b**,**c** were dechlorinated easily and **2** was obtained as the sole product in 83–88% yield. An effect of the volume of the aq NaOH solutions was observed similar to that with **1a**: the reaction time increased with decreasing volume, i.e., with decreasing amount of the aq NaOH solution.

3. Dechlorination of monochlorobiphenyls 1a–c with Raney Ni–Al alloy in dilute aqueous solutions of alkali metal carbonates (Scheme 2)

3.1. Effects of the nature, the concentration and the amount of the aqueous alkali metal carbonate solutions and the amount of Raney Ni–Al alloy used

Based on the findings described above, we decided to investigate the behaviour of the Raney Ni–Al alloy in much more weakly basic solutions such as in dilute aqueous alkali metal carbonate solutions, with reductions carried out according to method B (Table 6). Similar to what we observed for dilute aq alkaline solutions, the reducing capability of the Raney Ni–Al alloy was enhanced greatly with a decrease in the concentration of the alkali carbonate in aq Na_2CO_3 solutions (10 wt %→1 wt %), giving a raise in product yield of **3** (21%→71%) (Table 6, runs 1–4). The reduction of the volume of a 1 wt % aq Na_2CO_3 solution (100 ml→50 ml) resulted in the reaction time being lengthened (4 h→6 h) (Table 6, runs 2 and 6). Rather surprisingly, when the volume of a 0.2 wt % Na_2CO_3 solution was reduced (400 ml→100 ml), a complete dechlorination could no longer be accomplished. This result differs from that observed for the dechlorination of **1a** with a 0.2 wt % NaOH solution (method B). It is particularly noteworthy that in a 1 wt % aq K_2CO_3 solution, the reducing power of the Raney Ni–Al alloy is stronger than in other aqueous metal carbonate solutions. Here, **3** was formed selectively in 89% yield (Table 6, runs 5 and 6). When performing the reaction in 1 wt % aq Cs_2CO_3 or Li_2CO_3 solutions, a mixture of **2** (main product) and **3** (minor product) was obtained (Table 6, runs 7 and 8). Hence, the reducing power of the Raney Ni–Al alloy in 1 wt % alkali metal carbonate solutions shows the trend: $K_2CO_3 > Na_2CO_3 > Cs_2CO_3 > Li_2CO_3$. The ratio of **3** is seen to increase with an increase of the amount of the Raney Ni–Al alloy. These results clearly indicate that the nature of alkali metal carbonate plays an important role in the reductive dechlorination of **1a**. Interestingly, dechlorination of **1a** was readily accomplished with Raney Ni–Al (1.0 g/5 mmol substrate) in the more dilute, 0.2 wt % aq Na_2CO_3 solution, while the reduction was sluggish in the more concentrated, 1 wt % Na_2CO_3 solution (Table 6, run 9 vs 10). Under ultrasonic irradiation at 60 °C, the dechlorination of **1a** was incomplete, when a 0.2 wt % aq Na_2CO_3 solution was added (Table 6, runs 9 and 10). Here, the relatively low reaction temperature might be the reason. In fact, 90% of **1a** remained unreacted,



Scheme 2.

Table 6
Effects of the nature, concentration and volume of the alkali metal carbonate solution and the amount of Raney Ni–Al alloy used for the dechlorination of **1a** (method B)[a]

Run	Ni–Al (g)	Metal carbonate solution[b] (ml)	Temp (°C)	Time (h)	Ratio[e] (%)		
					1a	**2**	**3**
1	5	10% Na_2CO_3 (100)/H_2O (100)	90	5	0	79	21
2	5	1% Na_2CO_3 (400)/H_2O (400)	90	2	0	28	72
3	5	1% Na_2CO_3 (100)/H_2O (100)	90	4	0	30	70
4[c]	5	1% Na_2CO_3 (50)/H_2O (50)	90	6	0	29	71
5	5	1% K_2CO_3 (400)/H_2O (400)	90	2	0	0	100 (93)[f]
6[c]	5	1% K_2CO_3 (50)/H_2O (50)	90	5	0	0	100 (89)[f]
7	5	1% Cs_2CO_3 (400)/H_2O (400)	90	4	0	75	25
8	5	1% Li_2CO_3 (400)/H_2O (400)	90	5	0	78	22
9	1	1% Na_2CO_3 (400)/H_2O (400)	90	4	23	65	12
10	1	0.2% Na_2CO_3 (400)/H_2O (400)	90	3	0	80	20
11	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	6	59	41	0
12	1	0.2% Na_2CO_3 (400)/H_2O (400)	60[d]	5	66	30	4
13	1	0.2% Na_2CO_3 (400)/H_2O (400)	60	5	90	10	0

[a] Compound **1a** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h, unless stated otherwise.
[c] Added dropwise within 1.5 h.
[d] Under ultrasonic irradiation.
[e] GC ratio.
[f] Isolated yield in parentheses.

when using a 0.2 wt % aq Na_2CO_3 solution at 60 °C without ultrasonication (Table 6, run 13). It must be noted that a reductive dechlorination of **1b**,**c** (5 mmol substrate) could no longer be accomplished, when the volume of the 0.2 wt % aq Na_2CO_3 solution was decreased further than 400 ml.

As expected, treatment of 2-chloro and 3-chlorobiphenyls (**1b**,**c**) with Raney Ni–Al alloy and using 1 wt % aq K_2CO_3 solution (method B) afforded **3** selectively and in high yields (90% and 91%) (Table 7, runs 1 and 5). With a 1 wt % aq Na_2CO_3 solution (method **B**), a mixture of **2** (main product) and **3** (minor product) was obtained. When the reaction was conducted with a 0.2 wt % aq Na_2CO_3 solution, **2** was afforded, albeit with **3** as a by-product. Similar effects of the overall amount of carbonate salt used in the reaction as regulated by the volume of the aq alkali carbonate solution used could be observed. Thus, it must be noted that the dechlorinations of **1b**,**c** were not complete, when the volume of a 0.2 wt % aq Na_2CO_3 solution was reduced even further than 400 ml (Table 7, run 8).

3.2. Dechlorination of 1a in other basic salt solutions

The fact that Raney Ni–Al alloy is a very strong reducing agent in dilute aq solutions of alkali metal carbonates (see above) encouraged us to investigate its reactivity in other aq salt solutions (Table 8). In 1 wt % aq solutions of $(NH_4)_2CO_3$, $NaHCO_3$ and $KHCO_3$, the reductive dechlorination of **1a** was found to proceed very slowly (Table 8, runs 1–3). In 0.2 wt % aq solutions of $NaHCO_3$ and $KHCO_3$, and in 1 wt % aq solutions of NaOAc and NH_4Cl, very little reductive dechlorination occurred. These results clearly show that Raney Ni–Al alloy is a much stronger reducing agent in dilute aq solutions of NaOH, KOH, Na_2CO_3 and K_2CO_3 than in other basic salt solutions.

4. Dechlorination of dichlorobiphenyls with the Raney Ni–Al alloy in dilute aqueous alkaline solutions

4.1. Effects of the concentration of the aq NaOH solution, the amount of the Raney Ni–Al alloy used and the reaction temperature

Our success in the dechlorination of monochlorobiphenyls prompted us to test this powerful reducing system towards the PCB congeners dichlorobiphenyls (**4a**–**g**) (Tables 9 and 10 and Scheme 3). The reason for selecting dichlorobiphenyls as model compounds for PCBs in initial studies was based on their lower reactivity towards nucleophilic aromatic substitution (relative to the more highly chlorinated congeners).[14]

Therefore, these compounds pose the tougher challenge to dechlorination. Reaction conditions, which give good results in the dechlorination of dichlorobiphenyls might be expected to work well for the reductive dechlorination of commercial PCBs, too. 2,3-Dichlorobiphenyl (**4a**) was selected as a model substrate and various reaction conditions were investigated. First, the effect of the amount of aq NaOH solution per mmol of substrate was examined. The reaction time needed for complete dechlorination increased with a decrease in amount of 1 wt % or 0.2 wt % aq NaOH solutions used (Table 9, run 1 vs 2 and 4 vs 5). Complete dechlorination of **4a** could not be accomplished when the volume of the aq NaOH solution was reduced even further than 400 ml (runs 3 and 6). The ratios of the dechlorinated products formed were found also to depend on the amount of the Raney Ni–Al alloy used. The reducing ability of Raney Ni–Al alloy in a 1 wt % KOH solution is strong enough to convert **4a** to **3** selectively and in high yield (88%). Under ultrasonic irradiation, **4a** was dechlorinated reductively to afford a mixture of **2** (main product) and **3** (minor product). As expected, the amount of the Raney Ni–Al alloy had to be doubled for the dechlorination of **4a** in comparison to the monochlorobiphenyls. The reaction conditions found to be best for the dechlorination of **4a** were applied to the dechlorination of 2,4-, 2,5-, 3,4-, 3,5-, 3,3′- and 4,4′-dichlorobiphenyls (**4b**–**g**). Compounds **4b**–**g** were reductively dechlorinated to give a mixture of **2** and **3** in the case of adding dropwise a 1 wt % aq NaOH solution to a mixture of dichlorobiphenyl and Raney Ni–Al alloy in water. It must be noted that **4c**–**f** were dechlorinated to produce **3** as the dominant product, albeit with a trace amount of **2** (2–4%). These results clearly show that **4c**–**f** are more easily reduced than **4b**,**g** and are even more easily reduced than the monochlorobiphenyls, as determined by the product ratios found by GC. Treatment of **4a**,**b**,**d**,**f**,**g** with Raney Ni–Al alloy (1.0 g/2.5 mmol substrate) gave a mixture of **2** (main product) and **3** (minor product) in 0.2 wt % aq NaOH solution. Surprisingly, both **4c** and **4e**, which have a chloro atom at the *meta* position of one phenyl group, were dechlorinated to afford **3** (78–80%) as the main product, together with a small amount of **2** (20–22%) under identical reaction conditions (Table 9, runs 15 and 23). These results clearly indicate that **4c** and **4e** may be activated by a *meta*-positioned chloro atom. However, only small amounts of **3** are produced in the reductive dechlorination of 3,4-dichlorobiphenyl (**4d**), which has one *meta*-positioned chloro atom, and of 3,3′-dichlorobiphenyl (**4f**), which has one *meta*-positioned chloro atom on each aromatic ring, again under identical reaction conditions. These findings clearly show that the reductive dechlorination is strongly dependent upon the structure of dichlorobiphenyls. All compounds **4b**–**g** were converted to **3** selectively and in high yields (88–95%) by adding dropwise a 1 wt % aq KOH solution. Under ultrasonication, **4b**–**f** were dechlorinated to give a mixture of **2** and **3**, when a 0.2 wt % aq NaOH solution was added dropwise. However, the dechlorination of **4g** was not complete under the identical reaction conditions and **4g** (65%) remained unreacted. Indeed, it has been reported that **4g** is one of the most difficult PCB congeners to be dechlorinated.[14] Finally, it should be noted that two chloro atoms seemed to be replaced rapidly one after the other in the

Table 7
Dechlorination of **1b**,**c** in alkali metal carbonate solution using method B.[a]

Run	Sub.	Ni–Al (g)	Metal carbonate solution[b] (ml)	Time (h)	Ratio[d] (%)		
					1a	2	3
1[c]	**1b**	5	1% K_2CO_3 (50)/H_2O (50)	5	0	0	100 (91)[e]
2[c]	**1b**	5	1% Na_2CO_3 (50)/H_2O (50)	6	0	29	71
3	**1b**	1	0.2% Na_2CO_3 (400)/H_2O (400)	5	0	86	14
4	**1b**	1	0.2% Na_2CO_3 (100)/H_2O (100)	6	65	35	0
5[c]	**1c**	5	1% K_2CO_3 (50)/H_2O (50)	5	0	0	100 (90)[e]
6[c]	**1c**	5	1% Na_2CO_3 (50)/H_2O (50)	6	0	31	69
7	**1c**	1	0.2% Na_2CO_3 (400)/H_2O (400)	5	0	84	16
8	**1c**	1	0.2% Na_2CO_3 (100)/H_2O (100)	6	70	30	0

[a] Compounds **1b**,**c** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h, unless otherwise stated.
[c] Added dropwise within 1.5 h.
[d] GC ratio.
[e] Isolated yield in parentheses.

Table 8
Dechlorination of **1a** in an alkali metal carbonate solution using method B[a]

Run	Ni–Al (g)	Metal carbonate solution[b] (ml)	Time (h)	Ratio[c] (%)		
				1a	2	3
1	5	1% $(NH_4)_2CO_3$ (400)/H_2O (400)	5	58	42	0
2	5	1% $KHCO_3$ (400)/H_2O (400)	5	52	46	2
3	5	1% $NaHCO_3$ (400)/H_2O (400)	5	36	64	0
4	1	0.2% $KHCO_3$ (400)/H_2O (400)	6	90	10	0
5	1	0.2% $NaHCO_3$ (400)/H_2O (400)	5	91	9	0

[a] Compound **1a** (5 mmol, 942 mg).
[b] Added dropwise within 0.5 h.
[c] GC ratio.

Table 9
Dechlorination of **4a–g** in MOH solutions using method B[a]

Run	Sub.	Ni–Al (g)	Alkaline solution[b] (ml)	Temp (°C)	Time (h)	Ratio[e] (%)		
						4	**2**	**3**
1	**4a**	5	1% NaOH (100)/H_2O (100)	90	4	0	23	77
2	**4a**	5	1% NaOH (50)/H_2O (50)	90	5	0	25	75
3	**4a**	5	1% NaOH (25)/H_2O (25)	90	5	21	23	56
4[c]	**4a**	1	0.2% NaOH (400)/H_2O (400)	90	2	0	80	20
5[c]	**4a**	1	0.2% NaOH (100)/H_2O (100)	90	6	0	87	13
6	**4a**	1	0.2% NaOH (50)/H_2O (50)	90	6	38	56	6
7	**4a**	5	1% KOH (50)/H_2O (50)	90	4	0	0	100 (88)[f]
8[c]	**4a**	1	0.2% NaOH (100)/H_2O (100)	60[d]	6	0	89	11
9	**4b**	5	1% KOH (50)/H_2O (50)	90	3	0	0	100 (89)[f]
10	**4b**	5	1% NaOH (50)/H_2O (50)	90	5	0	12	88
11[c]	**4b**	1	0.2% NaOH (100)/H_2O (100)	90	3	0	70	30
12[c]	**4b**	1	0.2% NaOH (100)/H_2O (100)	60[d]	6	0	79	21
13	**4c**	5	1% KOH (50)/H_2O (50)	90	3	0	0	100 (93)[f]
14	**4c**	5	1% NaOH (50)/H_2O (50)	90	5	0	4	96
15[c]	**4c**	1	0.2% NaOH (100)/H_2O (100)	90	3	0	20	80
16[c]	**4c**	1	0.2% NaOH (100)/H_2O (100)	60[d]	6	0	69	31
17	**4d**	5	1% KOH (50)/H_2O (50)	90	3	0	0	100 (90)[f]
18	**4d**	5	1% NaOH (50)/H_2O (50)	90	3	0	4	96
19[c]	**4d**	1	0.2% NaOH (100)/H_2O (100)	90	3	0	75	25
20[c]	**4d**	1	0.2% NaOH (100)/H_2O (100)	60[d]	6	0	83	17
21	**4e**	5	1% KOH (50)/H_2O (50)	90	3	0	0	100 (95)[c]
22	**4e**	5	1% NaOH (50)/H_2O (50)	90	4	0	2	98
23[c]	**4e**	1	0.2% NaOH (100)/H_2O (100)	90	4	0	22	78
24[c]	**4e**	1	0.2% NaOH (100)/H_2O (100)	60[d]	6	0	72	28
25	**4f**	5	1% KOH (50)/H_2O (50)	90	3	0	0	100 (94)[f]
26	**4f**	5	1% NaOH (50)/H_2O (50)	90	5	0	3	97
27[c]	**4f**	1	0.2% NaOH (100)/H_2O (100)	90	3	0	79	21
28[c]	**4f**	1	0.2% NaOH (100)/H_2O (100)	60[d]	6	0	82	18
29	**4g**	5	1% KOH (50)/H_2O (50)	90	4	0	0	100 (89)[f]
30	**4g**	5	1% NaOH (50)/H_2O (50)	90	5	0	34	66
31[c]	**4g**	1	0.2% NaOH (100)/H_2O (100)	90	6	0	81	19
32[c]	**4g**	1	0.2% NaOH (100)/H_2O (100)	60[d]	6	65	13	22

[a] Compounds **4a–g** (2.5 mmol, 572 mg).
[b] Added dropwise within 1.5 h, unless stated otherwise.
[c] Added dropwise within 0.5 h.
[d] Under ultrasonication.
[e] GC ratio.
[f] Isolated yield in parentheses.

dechlorination of **4a–g**, since monochlorophenyls as possible intermediates could only be detected in small amounts (<3%), although some amount of dichlorobiphenyls **4a–g** remained unreacted at the time. Thus, intramolecular selectivities between two chloro atoms are low. It has been reported that a certain intramolecular selectivity could be observed in the following cases: 2-Cl>4-Cl in the dechlorination of **4b** using $NiCl_2/NaBH_4$ in DMF at room temperature; and 3-Cl>2-Cl (**4a**), 4-Cl>2-Cl (**4b**), 5-Cl>2-Cl (**4c**) and 3-Cl>4-Cl (**4d**) in the dechlorination of **4a–d** with $(Ph_3P)_2NiCl_2/NaBH_4$ in DMF at room temperature.[6f]

5. Dechlorination of dichlorobiphenyls with Raney Ni–Al alloy in dilute aqueous alkali metal carbonate solutions

5.1. Effects of the nature of the alkali carbonate, the concentration and the amount of the aqueous metal carbonate solution, the amount of the Raney Ni–Al alloy used and the reaction temperature

It was found that monochlorobiphenyls were dechlorinated easily with Raney Ni–Al alloy in a dilute aq Na_2CO_3 solution (see above). With this information in mind, we decided to examine the efficiency of this strongly reducing system towards dichlorobiphenyls (**4a–g**) (Table 10). As a model reaction, the dechlorination of **4a** was tested under various reaction conditions. As expected, when a decrease in amount of 1 wt % aq Na_2CO_3 solution, the reaction time increased for a complete dechlorination. Interestingly, the amount of the 0.2 wt % Na_2CO_3 solution could be reduced (400 ml → 100 ml per 2.5 mmol of substrate) in the dehalogenation of **4a**, even though this was not possible in the case of the complete dechlorination of the monochlorobiphenyls **1a–c** (method B), as described above. These findings can be attractive for the disposal of commercial PCBs at a larger-scale since it is expected that the higher chlorinated congeners can be dechlorinated more easily than dichlorobiphenyls. An increase of **3** was observed in the dehalogenation of **4a** when the amount of the Raney Ni–Al alloy was increased. Under ultrasonication, the reductive dechlorination could not be achieved. This is most likely due to the low reaction temperature. It should be noted that in a 1 wt % aq Na_2CO_3 solution, dichlorobiphenyls **4a–g** were reduced easily to give predominantly **3**, together with a trace amount of **2**, independently of the position of the chloro atoms. These results clearly show that **4a–g** are more easily dechlorinated with Raney Ni–Al alloy in dilute alkali metal carbonate solutions. Also, **4a–g** were reduced to **3** selectively and in high yields by adding dropwise a 1 wt % aq K_2CO_3 solution to the reaction mixture. Compounds **4a–g** were reduced to **2**, albeit with **3** as a by-product, when a 0.2 wt % aq Na_2CO_3 solution was employed. Again, the intramolecular selectivity between chloro atoms was low, and possible intermediates, monochlorobiphenyls, were detected only in trace amounts (GC ratio <3%) in the dechlorination of **4a–g** with Raney Ni–Al alloy in both 1 wt % and 0.2 wt % aq Na_2CO_3 solutions.

Table 10
Dechlorination of **4a–g** using method B[a]

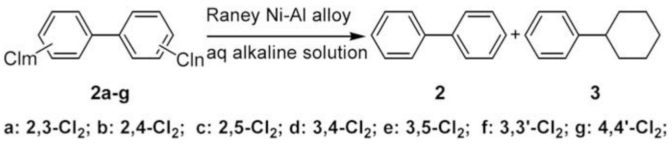
Run	Sub.	Ni–Al (g)	M_2CO_3 solution[b] (ml)	Temp (°C)	Time (h)	Ratio[e] (%)		
						4	**2**	**3**
1[c]	**4a**	5	1% Na_2CO_3 (100)/H_2O (100)	90	4	0	13	87
2	**4a**	5	1% Na_2CO_3 (50)/H_2O (50)	90	5	0	16	84
3	**4a**	5	1% K_2CO_3 (50)/H_2O (50)	90	3	0	0	100 (88)[f]
4[c]	**4a**	1	0.2% Na_2CO_3 (400)/H_2O (400)	90	3	0	77	23
5[c]	**4a**	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	5	0	81	19
6[c]	**4a**	1	0.2% Na_2CO_3 (100)/H_2O (100)	60[d]	5	73	17	0
7[c]	**4a**	1	0.2% Na_2CO_3 (100)/H_2O (100)	60	5	82	18	0
8	**4b**	5	1% K_2CO_3 (50)/H_2O (50)	90	3	0	0	100 (92)[f]
9	**4b**	5	1% Na_2CO_3 (50)/H_2O (50)	90	5	0	7	93
10[c]	**4b**	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	4	0	64	36
11	**4c**	5	1% K_2CO_3 (50)/H_2O (50)	90	3	0	0	100 (87)[f]
12	**4c**	5	1% Na_2CO_3 (50)/H_2O (50)	90	5	0	5	95
13[c]	**4c**	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	5	0	66	34
14	**4d**	5	1% K_2CO_3 (50)/H_2O (50)	90	3	0	0	100 (90)[f]
15	**4d**	5	1% Na_2CO_3 (50)/H_2O (50)	90	4	0	3	97
16[c]	**4d**	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	4	0	53	47
17	**4e**	5	1% K_2CO_3 (50)/H_2O (50)	90	3	0	0	100 (92)[f]
18	**4e**	5	1% Na_2CO_3 (50)/H_2O (50)	90	4	0	4	96
19[c]	**4e**	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	4	0	16	84
20	**4f**	5	1% K_2CO_3 (50)/H_2O (50)	90	3	0	0	100 (90)[f]
21	**4f**	5	1% Na_2CO_3 (50)/H_2O (50)	90	4	0	8	92
22[c]	**4f**	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	3	0	56	44
23	**4g**	5	1% K_2CO_3 (50)/H_2O (50)	90	5	0	0	100 (93)[f]
24	**4g**	5	1% Na_2CO_3 (50)/H_2O (50)	90	6	0	11	89
25[c]	**4g**	1	0.2% Na_2CO_3 (100)/H_2O (100)	90	5	0	72	28

[a] Compounds **4a–g** (2.5 mmol, 572 mg).
[b] Added dropwise within 1.5 h, unless stated otherwise.
[c] Added dropwise within 0.5 h.
[d] Under ultrasonic irradiation.
[e] GC ratio.
[f] Isolated yield in parentheses.

In the reductions using very dilute alkaline (0.2 wt % NaOH, Table 9, run 24) or alkali carbonate solutions (0.2 wt % Na_2CO_3, Table 10, run 19), **4e** shows the largest proportion of phenylcyclohexane (**3**). It may be due to the chloro functions positioned so close to each other and to the remaining phenyl substituent that they reinforce the polarization within the phenyl group through the field effect and thus facilitate the approach of the molecule to the catalyst and perhaps even the hydrogenation itself.

6. Reaction mechanism

Although the reaction mechanism of the dechlorination is not totally clarified yet, it can be proposed that aluminium metal of the Raney Ni–Al alloy reacts with the basic solution, e.g., with the aq NaOH solution, and produces a reactive form of hydrogen and highly porous nickel metal on the catalyst's surface. The actual hydrodechlorination may well operate as a mixture of ionic and radical pathways as has been suggested for the hydrodechlorination of chloroarenes over another supported nickel catalyst.[15] In the case of an ionic pathway the basicity of the solvent would exert an effect that would overlie the effect of the base on the production of the catalytic surface (see below) (Fig. 1).



Scheme 3.

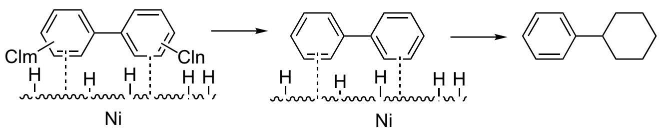
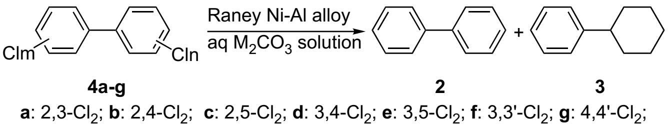


Figure 1.

Mono- and dichlorobiphenyls, which are p-electron rich, are adsorbed on the surface of the active nickel metal, and reaction with the reactive form of hydrogen occurs at the catalyst's surface. We have noted that in dilute aq NaOH, KOH, Na_2CO_3 and K_2CO_3 solutions, Raney Ni–Al alloy becomes a stronger reductant than in more concentrated alkaline solutions. The reasons for this may be a solution-dependent particle size distribution of active nickel metal, which plays an important role in the reductive dechlorination reaction, and a different surface porosity of the catalyst, although both of these still need to be substantiated. In the case of using a 10 wt % aq NaOH solution, the Raney Ni–Al alloy reacts more uncontrolled with the NaOH solution and gives off hydrogen gas, which escapes unreactedly from the reaction vessel. In fact, an effervescence of hydrogen gas was observed in that case (Scheme 4). On the other hand, it has been reported that 2 N NaOH



Scheme 4.

can partly deactivate[16] the catalytic surface of Raney Ni–Al so that not all of the catalyst is used effectively for the dechlorination.

7. Conclusion

In conclusion, it was found that Raney Ni–Al alloy in dilute solutions of alkali hydroxides and alkali metal carbonates becomes a powerful reducing agent. This is especially true in 0.5 wt % aq NaOH, KOH, Na_2CO_3 and K_2CO_3 solutions. A series of PCB congeners, mono- and dichlorobiphenyls, were reduced facilely to biphenyl (**2**) and/or phenylcyclohexane (**3**) under mild reaction conditions. *No organic solvents were used in the reactions*. The dechlorinated products strongly depended upon the concentration and the nature of the aq alkaline and alkali metal carbonate solutions, and the amount of the Raney Ni–Al alloy used. When adding dropwise a 1 wt % aq alkaline solution to the chlorinated biphenyl in water, a dependence of the dechlorination on the basicity of the metal hydroxide was found: $KOH>CsOH>NaOH>Ca(OH)_2>LiOH>Ba(OH)_2$. In the case of adding a 1 wt % aq alkali metal carbonate solution to the chlorinated biphenyl in water, the ease of dechlorination was found to show the following trend: $K_2CO_3>Na_2CO_3>Cs_2CO_3>Li_2CO_3$. The effects of the amount of aq alkaline and alkali metal carbonate solutions used, reaction temperature and the order of addition of reagents were discussed above. Overall, this dechlorination is operationally simple. No harsh reaction conditions such as elevated temperatures, high pressures, a hydrogen atmosphere, an inert gas atmosphere or special apparati are required. Moreover, this procedure offers the practical convenience of obviating the need of handling inflammable and toxic organic solvents. From the environmental protection point of view, this process shows potential advantages in reducing the adverse impact of solvent disposal on the environment. Hence, this procedure is environmentally benign for the potential treatment of toxic PCBs. We believe that the Raney Ni–Al alloy in dilute aqueous alkaline and alkali metal carbonate solutions provides another very useful technique for the reductive dehalogenation of aromatic halides and for the hydrogenation of aromatic compounds, a technique that is characterized by the ease and quickness of the reaction, simplicity of manipulation and mildness of reaction conditions. Convenience and low costs are also advantages of this method. Raney Ni–Al alloy is readily available commercially and is, of course, cheaper than the Raney Ni catalyst made from it. It is expected that this procedure would have potential application for the disposal of toxic PCBs in certain cases in the industry such as where relatively small volumes of material is contaminated by PCBs in relatively high concentrations. Needless to say that the spent nickel needs to be recycled.[17a] Efficient nickel recycling from larger amounts of aqueous medium such as by use of ion exchange resin has been forwarded by other authors,[17] the technology of which is also used in electroplating.

8. Experimental section

8.1. General

4-Chlorobiphenyl (**1a**), Raney Ni–Al (Wako), Co–Al (Wako), Cu–Al (Wako) and Fe–Al (Wako) (50:50, wt %) were readily available commercially and used as received. 3,3′- and 4,4′-Dichlorobiphenyls (**4f,g**) were prepared via homocoupling reaction of 3- and 4-chloroiodobenzene catalyzed by $Pd(OAc)_2$ in DMF, according to the method reported.[18] All other mono- and dichlorobiphenyls were synthesized via Gomberg–Bachman reaction between an aryl diazonium salt and benzene as described in the literature.[19] The reductive dechlorination was monitored by a Shimadzu GC-17A gas chromatograph (Column: J & W Scientific DB-1, 30 m×0.25 mm×0.25 mm), equipped with a capillary column (stationary phase: dimethylpolysiloxane), using a hydrogen flame ionization detector. The relative ratio was calculated on the basis of the peak area of the GC (assuming equal FID-sensitivity for all substrates).

8.2. Dechlorination of monochlorobiphenyls (1a–c)

A typical procedure is described as follows:

Method A. Within 0.5 h and at 90 °C, Raney Ni–Al alloy (5.0 g) was added in small portions to a mixture of **1a** (5 mmol, 942 mg) in a 0.5 wt % aq NaOH solution (400 ml). Afterwards, the reaction mixture was stirred for 3 h (monitored by GC). Then, the mixture was cooled to room temperature. The insoluble materials were filtered off over Celite and the residue was washed with dichloromethane (3×15 ml). The filtrate was extracted with dichloromethane (3×25 ml), and the organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated in vacuo to afford a mixture of biphenyl (**2**) and phenylcyclohexane (**3**) in a ratio of 46:54 (Table 1, run 4).

Method B. Within 0.5 h and at 90 °C, a 1 wt % aq NaOH solution (400 ml) was added dropwise to a mixture of **1a** (5 mmol, 942 mg) and Raney Ni–Al alloy (5.0 g) in water (400 ml). The reaction mixture was stirred for 2 h at 90 °C. Thereafter, the reaction mixture was subjected to a work-up procedure described above to give **2** and **3** in a ratio of 13:87 (Table 1, run 10).

8.3. Dechlorination of monochlorobiphenyls (1a–c) under ultrasonication

A typical procedure is as follows: according to method B, a 0.2 wt % aq NaOH solution (400 ml) was added dropwise to a mixture of **1a** (5 mmol, 942 mg), and Raney Ni–Al alloy (1.0 g) in water (200 ml) within 0.5 h at 60 °C and under ultrasonication (*Ultrasonic Multi Cleaner W-115, HONDA*). The reaction mixture was stirred and irradiated simultaneously for 2 h and then subjected to the work-up procedure described above to give **2** (670 mg, yield 87%) and **3** in a ratio of 13:87 (Table 1, run 16).[19c]

8.4. Dechlorination of dichlorobiphenyls (4a–g)

A typical procedure is as follows: according to method B, a 0.2 wt % aq Na_2CO_3 solution (100 ml) was added dropwise to a mixture of **4a** (2.5 mmol, 572 mg) and Raney Ni–Al alloy (1.0 g) in water (100 ml) within 0.5 h and at 90 °C. The reaction mixture was stirred for 5 h at 90 °C (monitored by GC) and then subjected to the work-up described above to give **2** and **3** in a ratio of 81:19 (Table 10, run 5).

Compounds **2** and **3** were compared with commercially available samples and on the basis of their ^1H NMR spectra and GC retention times.

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