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Organic Reaction in Water. Part 2. A New Method for Dechlorination of Chlorobiphenyls Using a Raney Ni-Al Alloy in Dilute Aqueous Alkaline Solution

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Abstract: Use of a Raney Ni-Al alloy in dilute aqueous alkaline solution gave rise to strong reducing power and chlorobiphenyls were reduced easily to biphenyl and/or phenylcyclohexane, respectively, *without any organic solvents.* © 1998 Elsevier Science Ltd. All rights reserved.

Much attention is focused on environmental pollution caused by chlorinated organic compounds such as polychlorobiphenyls (PCBs) because PCBs, which have been widely used as an insulator in transformer production, are hazardous and have half-life in the environment on the order of decades.[1,2] To the best of our knowledge, only a few methods, such as photochemical dechlorination,[3] electroreduction,[4] and dechlorination using sodium borohydride as a reductant in the presence of a catalytic or stoichiometric amount of a transitional metal,[5-7] have been reported for dechlorination of PCBs, and its congeners. However, the photochemical method requires UV irradiation, and all of these reactions must be carried out in organic solvents such as methanol and *N,N*-dimethylforamide, which have considerable toxicity. In continuation of our work on dehalogenation of aromatic halides with a Raney Ni-Al alloy in aqueous alkaline media,[8] we turned our attention to development of a convenient and practical method for the disposal of PCBs.

Herein, we wish to report the first finding that in dilute aqueous alkaline solution, *in the absence of any organic solvents*, a Raney Ni-Al alloy is effective for the dechlorination of PCBs congeners, monochlorobiphenyls **1a-c** in a simple operation. Two methods were employed; **A**: the Raney Ni-Al alloy was added gradually to a mixture of **1** and an alkaline solution; **B**: an alkaline solution was dropped slowly into a mixture of **1**, Raney Ni-Al alloy and water. The results are summarized in Table 1 and Scheme 1.

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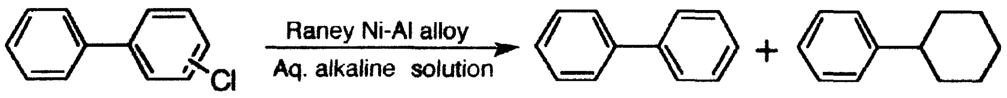

1 **2** **3**

a: 4-Cl **b**: 2-Cl **c**: 3-Cl

Scheme 1

Table 1. Dechlorination of **1a-c** in Aqueous Alkaline Solution.$^{a)}$

Run	Sub.	Ni-Al (g)	Alkaline Solution (ml)	Method	Temp (°C)	Time (h)	Ratio (%)$^{b)}$	
							2	3
1	**1a**	10	10% NaOH (80)	**A**	90	8	100 (84$^{d)}$)	0
2	**1a**	5	5% NaOH (100)	**A**	90	8	100 (80$^{d)}$)	0
3	**1a**	5	1% NaOH (400)	**A**	90	3	35	65
4	**1a**	5	0.5% NaOH (800)	**A**	90	3	46	54
5	**1a**	1	0.1% NaOH (800)	**A**	90	1	83	17
6	**1a**	5	2% NaOH (200) / H_2O (200)	**B**	90	4	31	69
7	**1a**	5	1% NaOH (400) / H_2O (400)	**B**	90	2	13	87
8	**1a**	5	1% NaOH (400) / H_2O (400)	**B**	60$^{c)}$	2	47	53
9	**1a**	5	1% KOH (400) / H_2O (400)	**B**	90	2	0	100 (89$^{d)}$)
10	**1a**	5	1% CsOH (400) / H_2O (400)	**B**	90	4	0	100 (91$^{d)}$)
11	**1a**	5	1% $Ca(OH)_2$ (400) / H_2O (400)	**B**	90	4	15	85
12	**1a**	5	1% LiOH (400) / H_2O (400)	**B**	90	4	41	59
13	**1a**	5	1% $Ba(OH)_2$ (400) / H_2O (400)	**B**	90	4	71	29
14	**1a**	1	0.2% NaOH (400) / H_2O (400)	**B**	90	1	82	18
15	**1a**	1	0.2% NaOH (400) / H_2O (400)	**B**	60$^{c)}$	2	100 (86$^{d)}$)	0
16	**1b**	5	1% NaOH (400) / H_2O (400)	**B**	90	2	30	70
17	**1b**	5	1% KOH (400) / H_2O (400)	**B**	90	2	0	100 (94$^{d)}$)
18	**1b**	1	0.2% NaOH (400) / H_2O (400)	**B**	90	1	76	24
19	**1b**	1	0.2% NaOH (400) / H_2O (400)	**B**	60$^{c)}$	2	100 (88$^{d)}$)	0
20	**1c**	5	1% NaOH (400) / H_2O (400)	**B**	90	2	38	62
21	**1c**	5	1% KOH (400) / H_2O (400)	**B**	90	2	0	100 (90$^{d)}$)
22	**1c**	1	0.2% NaOH (400) / H_2O (400)	**B**	90	1	78	22
23	**1c**	1	0.2% NaOH (400) / H_2O (400)	**B**	60$^{c)}$	2	100 (83$^{d)}$)	0

a) **1a-c** (5 mmol, 942 mg). b) GC ratio. c) Under ultrasonic irradiation. d) Isolated yields in parentheses.

As a model reaction, dechlorination of 4-chlorobiphenyl (**1a**),which is known to be one of the most difficult to be dechlorinated among PCBs,[3a,d] was examined under various conditions. In the case of method **A**, as the concentration of the aqueous NaOH solution became more and more dilute, the reaction time was greatly shortened, and gave rise to strong reducing power to afford phenylcyclohexane (**3**), in which dechlorination and reduction of an aromatic ring occurred at the same time, in addition to biphenyl (**2**). In 5% aq or 10% aq NaOH solution, only dechlorination took place to give the biphenyl in good yield.

On the other hand, in the case of method **B**, reducing power is stronger than that in method **A**, and the formation of **3** was increased (Run 3, 4, 6 and 7). Increasing the temperature and the amount of the Raney Ni-Al alloy tended to increase the formation of **3** (Run 4,5,7 and 8). In the case of using 1.0 g of the Raney Ni-Al alloy for Run 4, **1a** remained unreacted (ratio: 24%) even though the reaction was carried out for 4 h. However, when a more dilute alkaline solution was employed (1→0.2%), the reduction was completed in only 1 h (Run 14). Furthermore, interestingly, dechlorination of **1a** selectively occurred at 60 °C under ultrasonic irradiation to afford the biphenyl in 80% yield (Run 15). Without ultrasonic irradiation, **1a** remained unreacted (ratio: 48%) even though the reaction was carried out for 6h. This means that ultrasonication accelerated dechlorination of **1a**.

From the results described above, it was found that the Raney Ni-Al alloy becomes a very strong reductant in dilute aqueous NaOH solution, especially in 0.5% aq and 1% aq NaOH solution, not only for the reductive dechlorination of **1a**, but also for the reduction of the aromatic ring of **2**. Moreover, the reaction is operationally simple and does not require elevated temperature, high pressure, hydrogen atmosphere, or any special apparatus. This procedure is expected to be very useful for the dehalogenation of aromatic halides and the reduction of aromatic compounds.

From the experimental standpoint, Method **B** is much more useful as compared with Method **A** since dropping the aqueous NaOH solution into the reaction vessel is more convenient than adding the Raney Ni-Al alloy powder to it. Therefore, the dechlorination of **1a** in other alkaline solutions in Method **B** was investigated. It is noteworthy that with the use of 1% aq KOH or CsOH solution, the reducing power is very strong in comparison with other alkaline solutions and **3** was reductively obtained in high yields (89-91%). In 1% aq $Ca(OH)_2$, LiOH, and $Ba(OH)_2$ solution, a mixture of **2** and **3** was formed and the ratio of **2** increased in this order. These results show that the nature of the alkaline solution plays an important role in the reduction of **1a**. Treatment of **1a** with the Raney Ni-Al alloy (1.0 g) in 0.2% aq KOH, CsOH or LiOH solution also afforded a mixture of **2** and **3**.

Similarly, in the case of using dilute aqueous NaOH solution (1 or 0.2%), the Raney Ni-Al alloy is also effective for the reduction of 2-chloro and 3-chlorobiphenyl (**1b,c**) to afford a mixture of **2** and **3** (Run 16-18 and 20-22). Under ultrasonication, **2** was obtained as the sole product in 83 and 88% yields, respectively (Run 19 and 23).

In conclusion, the strong reducing ability of the Raney Ni-Al alloy was observed for the first time. Treatment of chlorobiphenyls with the Raney Ni-Al alloy in dilute aqueous alkaline solutions *without using any organic solvents* afforded biphenyl and/or phenylcyclohexane. The reduced products are strongly dependent on the concentration and nature of the alkaline solutions, the amount of Raney Ni-Al alloy and the reaction temperature. This procedure was characterized by the ease and quickness of the reaction, simplicity to manipulate and mildness of the reaction conditions. Low cost is also one of the method's advantages. The Raney Ni-Al alloy is readily available commercially and is, of course, cheaper than the Raney Ni catalyst prepared from it. This procedure would turn out to be a convenient and practical method to dispose of PCBs. Further work on the reduction of PCBs is currently under way, and the results will be presented elsewhere.

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9. **A typical procedure is described as follow**: In method A, the Raney Ni-Al alloy (5.0 g) was gradually added to a mixture of **1a** (5 mmol, 942 mg) and 1% aq NaOH solution (400 ml) for 0.5 hour at 90 °C. After the reaction mixture was stirred for 3 hours, the mixture was cooled to room temperature. The insoluble materials were filtered off with Celite and the residue was washed with dichloromethane. The filtrate was extracted with dichloromethane 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 the ratio of 35: 65, respectively (Run 3). Compounds **2** and **3** were identified with the commercially available samples on the basis of their ^{1}H NMR spectra and GC retention time. On the other hand, in method **B**, 2% aq NaOH solution (200 ml) was gradually dropped to a mixture of **1a** (5 mmol, 942 mg), Raney Ni-Al alloy (5.0 g) and water (200 ml) for 0.5 hour at 90 °C. The reaction mixture was stirred for 4 hours and worked up as described above to give **2** and **3** in the ratio of 31:69, respectively (Run 6).