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Tashiro, Masashi
Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Mataka, Shuntaro
Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Tsuzuki, Hirohisa
Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Matsumoto, Junici
Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University

他

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Reduction of Chlorophenols, Chlorobenzoic Acids, and 5-Chlorosalicylic Acid with Raney Co-Al Alloy in 10%NaOH Solution

Masashi TASHIRO*, Shuntaro MATAKA*
Hirohisa TSUZUKI*, Jun-ichi MATSUMOTO**
Kouji NAKAYAMA***, and Tadashi YONEMITSU****

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Reduction of chlorophenols (**1a-1f**), chlorobenzoic acids (**3a-3g**), and 5-chlorosalicylic acid (**5**) was carried out with Raney Co-Al alloy in an alkaline solution under various conditions in order to find best conditions for formation of phenol (**2**), benzoic acid (**4**), and salicylic acid (**6**) from the corresponding chlorinated compounds. It was found that **2, 4**, and **6** were obtained in good yield from **1a-1f**, **3a-3g**, and **5** by the reduction with Raney Co-Al alloy in 10% NaOH solution, respectively. Although **3b** was not reduced by the treatment with Raney Co-Al alloy in 10% Na_2CO_3 solution, but in a mixture of 10% NaOH and 10% Na_2CO_3 solutions with the same alloy, **4** was formed in good yield from **3b**. This finding suggests that the reduction in the mixed alkaline solutions should be a convenient method for the preparation of deuteriated aromatic compounds from the corresponding chlorinated ones since NaOD solution is more expensive than Na_2CO_3 solution.

It has been previously reported that bromophenols[1] and bromobenzoic acids[2] could be easily reduced with Raney Alloys such as Ni-Al and Cu-Al in an alkaline solution to give phenol and benzoic acid in good yield, respectively. It was also found that when bromophenols and bromobenzoic acids were treated with Raney Cu-Al alloy in 10% NaOD-D_2O solution, the desired deuteriated phenols[3] and deuteriated benzoic acids[4] were obtained in good yield and in high isotopic purity, respectively. However, the similar reduction with Raney Ni-Al alloy afforded low purity of the deuteriated phenols[3] and benzoic acids[4], respectively. The reduction of chlorophenols and chlorobenzoic acids with Raney Ni-Al alloy in an alkaline solution afforded the expected phenol and benzoic acid in good yield. However, the reaction with Raney Cu-Al alloy did not afford any product under the same conditions.

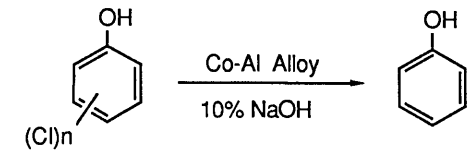
The above results promoted us to investigate about the reduction of chlorinated aromatic compounds, which are usually more available and cheaper than bromo derivatives, with Raney Co-Al alloy in order to find the best reaction conditions for preparation of deuteriated aromatic compounds.

INTERDISCIPLINARY GRADUATE SCHOOL OF ENGINEERING SCIENCES, KYUSHU UNIVERSITY 39, KASUGA 816 JAPAN
*Department of Molecular Science and Technology
**Department of Industrial Chemistry, Saga University
***Faculty of Pharmaceutical Science, Johsai University
****Department of Industrial Chemistry, Kyushu Sangyo University

Results and Discussion.

The Reduction of chlorophenols (**1a-1f**) was carried out with Raney Co-Al Alloy in 10% NaOH solution and the results are summarized in **Table 1**.

Table 1 Reduction of Chlorophenols (**1a-1f**) with Raney Co-Al Alloy in 10%NaOH Solution at 70℃.[a)]



1 **2**

a: 2-Cl d: 2,4-Cl_2
b: 3-Cl e: 2,4,6-Cl_3
c: 4-Cl f: 2,3,4,6-Cl_4

Run	Substrate	Alloy (g)	Alkali (ml)	Time (h)	Yield of **2** (%)[b)]
1	**1a**	1	10	1	70
2	**1b**	1	10	1	70
3	**1c**	1	10	1	71
4	**1d**	2	20	2	65
5	**1e**	3	30	2	70
6	**1f**	4	40	2	70

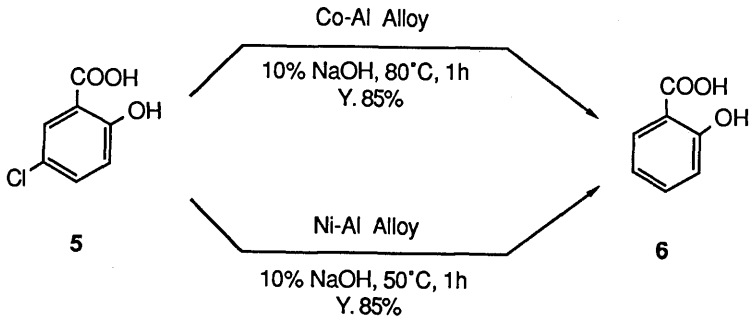
a) Ten mmol of **1** was used. b) Isolated yields are shown.

Data in **Table 1** show that Raney Co-Al alloy as well as Ni-Al alloy can reduce chlorophenols to give **2** in good yields, respectively. It was found that one gram of the alloy per one chlorine atom of **1a-1f** should be used to obtain the reduced product **2** in good yield.

The reduction of chlorobenzoic acids (**3a-3g**) with Raney Co-Al alloy was carried out under various conditions and the results are summarized in **Table 2**.

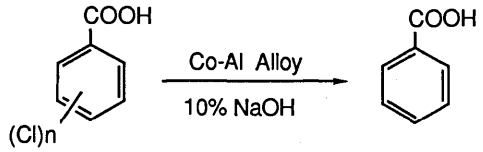
As is shown in **Table 2, 3a-3g** as well as **1a-1f** were reduced by treatment with Raney Co-Al alloy in an alkaline solution to give benzoic acid (**4**) itself in good yield. It should be noted that chlorobenzoic acids such as **3b** and **3e** could be reduced in a mixture of 10% NaOH and 10% Na_2CO_3 solutions but the reduction did not occur in 10% Na_2CO_3 solution.

It was also found that 5-chlorosalicylic acid (**5**) could be reduced by treatment with Raney Co-Al alloy as well as Ni-Al alloy in 10%NaOH solution (**Scheme 1**).



Scheme 1

Table 2 Reduction of Chlorobenzoic Acids (**3a-3g**) with Raney Co-Al Alloy in an Alkaline Solution at 80℃ for 2 h.[a)]



a: 2-Cl　e: 3,4-Cl_2
b: 4-Cl　f: 3,5-Cl_2
c: 2,3-Cl_2　g: 2,4,6-Cl_3
d: 2,5-Cl_2

Run	Substrate	Alloy (g)	Alkaline (ml)	Yield of **4** (%)[b)]
1	**3a**	0.7	10%NaOH(10)	84
2	**3b**	0.1	10%NaOH(10)	82
3	**3b**	0.4	10%Na_2CO_3(10)	no reaction
4[c)]	**3b**	0.3	10%NaOH(5) 10%Na_2CO_3(5)	89
5	**3c**	0.7	10%NaOH(15)	93
6	**3d**	0.6	10%NaOH(15)	91
7	**3e**	0.8	10%NaOH(10)	81
8[c)]	**3e**	0.8	10%NaCO(5) 10%Na_2CO_3(5)	81
9	**3f**	0.6	10%NaOH(15)	84
10	**3g**	1.2	10%NaOH(15)	80

a) The amount of **3** used was 1.5mmol.　b) Isolated yields are shown.
c) Reaction time; 1 h, temp.; 50℃.

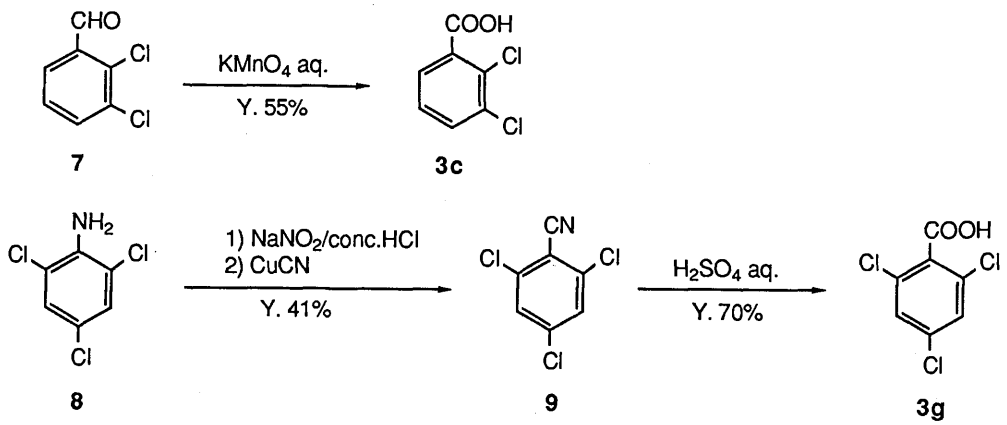
As described above, Raney Co-Al alloy can be used for the reduction of chlorinated aromatic compounds such as chlorophenols, chlorobenzoic acids, and 5-chlorosalicylic acid. These results suggest that deuteriated phenols, deuteriated benzoic acids, and deuteriated salicylic acids may be prepared from the corresponding chloro derivatives which are more available and cheaper than bromo derivatives by the reduction with Raney Co-Al alloy in NaOD-D_2O solution.

The preparation of deuteriated aromatic compounds by using the method described above is being progressed in our laboratory and the results will be reported in the near future.

Experimental Section

Materials.

The chlorinated aromatic compounds, except **3c** and **3g**, used in the present work were commercially available. Compounds, **3c** and **3g**, were prepared according to the reported or modified methods as shown in **Scheme 2**.



Scheme 2

Preparation of 3c.

To a warm solution of 7.0g (40 mmol) of 2,3-dichlorobenzaldehyde (**7**) in 150 ml of water was added dropwise in a period of 40 min at 70～80℃ under stirring a solution of 9.0g of $KMnO_4$ in 180 ml of water. After the stirring was continued for an additional 1 h, the reaction mixture was made alkaline with 10%NaOH solution to pH. 14 and filtered off to remove MnO_2 generated. The MnO_2 was washed with hot water and the washing was combined with the filtrate. The combined solution was acidified with conc. HCl to pH. 1. The precipitates formed were collected and washed with a small amount of cold water and then recrystallized from a mixed solvent of methanol and water (1/10 vol./vol.) to give 4.2 g (55%) of **3c** as colorless needles, mp 169—170℃; lit.,[5] mp 169—170℃.

Preparation of 2,4,6-trichlorobezonitril (9) and 2,4,6-trichlorobenzoic acid (3g).

The titled compound **9** was obtained from 2,4,6-trichloroaniline (**8**) by the reported method[6] as colorless needles (ethanol-water), mp 76℃, lit.,[6] 76—78℃.

Trichlorobenzoic acid (**3g**) was also obtained from **9** according to the reported method[7] as colorless needles (water), mp 160—161℃, lit.,[7] mp 160—161℃.

Reduction of Chlorinated Aromatic Compounds with Raney Co-Al Alloy in an Alkaline Solution. Typical Procedure.

To a stirred mixture of 345 mg (2 mmol) of **5** in 10 ml of 10% NaOH solution was gradually added 200 mg of Raney Co-Al alloy. After the reaction mixture was stirred at 80℃ for 1 h, it was cooled to room temperature. The Co powder produced and unchanged Raney Co-Al alloy were filtered off. The filtrate was acidified with con. HCl and extracted with diethyl ether. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuo to leave the residue which was recrystallized from water to give 235 mg (85%) of **6** as colorless needles, mp 158—159℃, lit.,[8] mp 158—159℃.

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