Hydrogenation of Halophenols to Cyclohexanols Using Raney Nickel–Aluminium Alloy in Saturated Ba(OH)2 Solution under Mild Conditions

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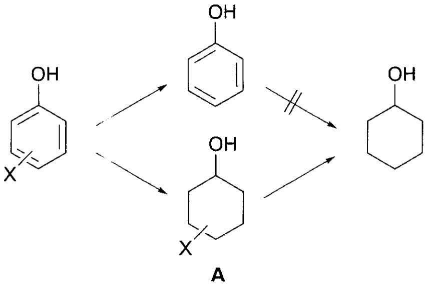
By use of Raney Nickel–Aluminium alloy in a saturated $Ba(OH)_2$ solution, halophenols are easily hydrogenated at mild temperatures and at atmospheric pressure, giving the corresponding cyclohexanols.

The preparation of cyclohexanols by the hydrogenation of phenols has been carried out under forcing conditions (high pressures and elevated temperatures) using catalysts such as Raney Ni,[1,2] Pd,[3] PtO_2,[4] Ru[5,6] and Rh.[7] Furthermore, in some cases side reactions occur together with hydrogenation of phenolic ring.[8] We report here that in a saturated $Ba(OH)_2$ solution, Raney Nickel–Aluminium alloy can reduce halophenols under mild conditions, to the corresponding cyclohexanols.†

In the reduction of halophenols with Raney Ni–Al alloy in a saturated $Ba(OH)_2$ solution at 60 °C at atmospheric pressure for 1 h, cyclohexanol was readily obtained in 42–91% yields (Table 1). The reduction of the phenolic ring proceeded independently of the number and the position of halogen atom(s) attached to the phenolic ring. Chlorophenols are more easily reduced than bromophenols. In particular, in the reduction of pentachlorophenol (run 9), cyclohexanol was obtained in 91% yield. The amount of Raney Ni–Al alloy shown in Table 1 is necessary; a complex mixture of products was obtained when the reaction was carried out using a smaller amount of the alloy. A saturated $Ba(OH)_2$ solution (0.275 mol dm^{-3}) is also necessary; the reduction of 2,4,6-tribromophenol using a less concentrated $Ba(OH)_2$ solution (0.1 mol dm^{-3}) gave a 3 : 95 : 2 mixture of cyclohexanol, phenol and unchanged tribromophenol.‡ Other aqueous bases such as aqueous NaOH or Na_2CO_3 solutions are unsatisfactory.§ The reduction of pentachlorophenol in an aqueous (10%) NaOH solution (2.8 mol dm^{-3}), yielded phenol (65%) as a main product and the expected cyclohexanol was obtained in only 20% yield. Similarly, the reduction in aqueous (0.625 mol dm^{-3}) Na_2CO_3 solution gave the expected cyclohexanol in only 10% yield, and pentachlorophenol was recovered in 79% yield.

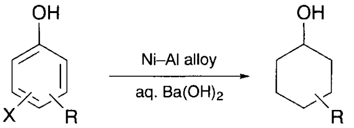


Scheme 1

The reduction of halo-3- and 4-methylphenol under ultrasonic irradiation produced 3- and 4-methylcyclohexanol in 75% and 93% yields, respectively.¶

When phenol itself was treated with Raney Ni–Al alloy in a saturated $Ba(OH)_2$ solution, only a trace amount of cyclohexanol was formed, together with recovery of unchanged phenol in an almost quantitative yield. This result suggests that at first

Table 1 Reduction of halophenols with Raney Ni–Al alloy in a saturated $Ba(OH)_2$ solution at 60 °C for 1 h



Run	Halophenol[a] X	Halophenol[a] R	$Ba(OH)_2$[b] /ml	Ni–Al alloy/g	Product R	Yield (%)
1	3-Br	H	60	8.0	H	54
2	4-Br	H	60	9.0	H	74
3	2,4-Br_2	H	60	10.0	H	65
4	2,4,6-Br_3	H	55	12.0	H	42
5	3-Cl-2,4,6-Br_3	H	130	16.5	H	62
6	2,3,4,6-Br_4	H	130	16.5	H	52
7	2,4,6-Cl_3	H	50	8.3	H	65
8	2,3,4,6-Cl_4	H	50	8.3	H	62
9	2,3,4,5,6-Cl_5	H	100	12.0	H	91
10[c]	2,4,6-Cl_3	3-Me	20	8.0	3-Me(*cis*) 3-Me(*trans*)	30 45
11[c]	2,6-Cl_2	4-Me	50	20.0	4-Me(*cis*) 4-Me(*trans*)	45 48

[a] Halophenol 6.5 mmol. halo-*m*-cresol 2.0 mmol, halo-*p*-cresol 5.0 mmol, $Ba(OH)_2$ solution saturated (0.275 mol dm^{-3}). [b] The amount of $Ba(OH)_2$ solution used was determined by the solubility for the corresponding halophenols. [c] Under ultrasonic irradiation.

the hydrogenation of the aromatic ring of the halogenated phenols occurs to afford the halogenated cyclohexanol **A** and then the halogen atom(s) of **A** is reductively removed to yield cyclohexanol (Scheme 1).

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Footnotes

† Typical procedure: Raney Ni–Al alloy (alloy/pentachlorophenol = 1.85 g mmol^{-1}, total amount = 12.0 g) was slowly added at 60 °C to a stirred mixture of pentachlorophenol (1.73 g, 6.5 mmol) and a saturated aqueous solution of $Ba(OH)_2$ (100 ml). After the reaction mixture had been stirred for 1 h, the mixture was cooled to room temp. and the insoluble materials were filtered off. The filtrate was acidified with conc. HCl to pH 1, extracted with CH_2Cl_2 (30 ml × 4), dried ($MgSO_4$), and evaporated *in vacuo* to afford 0.59 g (91%) of cyclohexanol.

‡ The ratio of products was analysed by GC.

§ $Mg(OH)_2$ and $Ca(OH)_2$ are poorly soluble in H_2O.

¶ The use of ultrasonic irradiation is for increasing the solubility of the substrate in a $Ba(OH)_2$ solution. In the case of halo-3-methylphenol, dehalogenated 3-methylphenol was obtained in 3% yield besides the expected 3-methylcyclohexanol.

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