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Dehalogenation of Organic Compounds. 4[1]. Dechlorination of Pentachlorophenol and 1,2,4-Trichlorobenzene with Transition Metal-Promoted Alkoxyborohydrides

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Abstract: Metal-promoted $NaBH_4$ and $NaBH_2(OCH_2CH_2OCH_3)_2$ dechlorinations were carried out on the aromatic chloro compounds pentachlorophenol and 1,2,4-trichlorobenzene. The best results were obtained by dropwise addition of $NiCl_2$ in solution to $NaBH_2(OCH_2CH_2OCH_3)_2$ and the substrate in THF solutions.

Over the last 30 years there has been a growing concern about environmental hazards due to exposure to chemicals.[2] Halogenated organic compounds are important industrial chemicals which include solvents, pesticides, herbicides and polymers. For example, pentachlorophenol was marketed widely as a wood preservative, insecticide, and herbicide. It is also fungicidal toward wood-destroying fungi and kills termites.[3] Some pesticides are now known to be carcinogenic to humans.[4] Compounds such as Dieldrin, Lindane, Mirex, Kepone, pentachlorophenol, polychlorinated biphenyls (PCBs), and DDT, although having demonstrated utility, are persistent environmental pollutants requiring safe and effective means of disposal.[5] Dechlorination of these pollutants has centered on such methods as incineration,[6] plasma incineration,[7] microbiological[8] as well as other chemical methods.[9] Unfortunately, these methods have limitations. For example, incineration generates HCl and detectable amounts of dioxins.[10] Thus, it is desirable to develop low temperature rapid dehalogenations for organic compounds for use prior to their safe incineration. Hydride reducing agents such as $LiAlH_4$ and $NaBH_4$ typically have not been very active in dechlorinations.[11] However, combination of these reactive hydrides with transition metal salts to generate M(0) species appeared to offer a more promising approach to dechlorination.[1c,12]

Dehalogenation of pentachlorophenol, 1:

1 was dechlorinated using several dehalogenating systems. The conditions used and results achieved are shown in *Table 1.* Neither tetraethyleneglycol (TEG)/KOH[9a] nor $NaBH_4$/TEG/KOH[1] were effective for the dechlorination of 1 at low temperatures (e.g., 68 °C, see Entries 1 and 2). However, 1 was partially reduced (35%) after treatment with $NaBH_2(OCH_2CH_2OCH_3)_2$/ THF at 68 °C for 2 h (Entry 3). The product obtained in this dechlorination was phenol (35%). This dehalogenation was enhanced by the dropwise addition of a $NiCl_2$ (1 equiv per Cl present in 1) solution in 2-methoxyethanol to a solution of 1/$NaBH_2(OCH_2CH_2OCH_3)_2$

/THF over a period of 2 h (Entry 4). Under these conditions 98% of 1 was reduced after 2 h at 68 °C. Phenol (77.8%) was the major product and cyclohexanol (20%) was also obtained (Table 1, Entry 4). The use of more $NiCl_2$ gives 100% dechlorination. Complete dechlorination of 1 to phenol is noteworthy at such mild conditions. The phenoxide form of 1 is present in this media and by the time a monochlorophenoxide is produced (an electron rich aromatic system) slow dechlorination is expected.

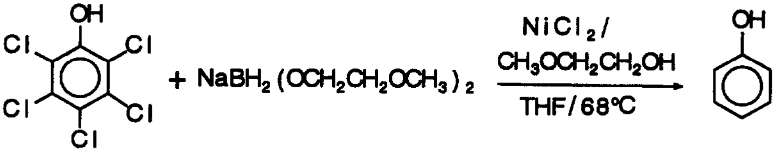

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Table 1. Dechlorination of Pentachlorophenol

Entry	Reagents (Mol Ratios)[a]	Temp. (°C)	Time (h)	Dechlorination (Mol%)[a]
1	TEG/KOH	68	168	0
	(46/5)	100	168	22
2	$NaBH_4$/TEG/KOH	68	168	0
	(2/46/5)	100	168	26
3	$NaBH_2(OCH_2CH_2OCH_3)_2$/	68	1	28
	THF (4/80)		2	35
			24	36
4[b]	$NaBH_2(OCH_2CH_2OCH_3)_2$/	68	1	68[c]
	$NiCl_2$/THF (4/5/80)		2	98[c]

[a] All ratios are relative to one mole of pentachlorophenol. [b] A solution of $NiCl_2$ (1 equiv per Cl present in 1) in 2-methoxyethanol was continuously added to the reaction mixture by the use of a syringe pump. [c] Phenol was the major product and also some cyclohexanol was produced.

Dehalogenation of 1,2,4-chlorobenzene:

The effects of several metal-promoted or catalytic dechlorinating systems were tested on 1,2,4-trichlorobenzene, 2. The conditions used and results obtained are summarized in *Table 2*. Treatment of 2 with TEG/KOH/$NaBH_4$/$CH_3OCH_2CH_2OH$ in the presence of a $PdCl_2$ catalyst produced 90% of dichloro compound, 3, after 41 h at 120 °C (Entry 1 and Eq. 2). The specific isomer was not determined. When a catalytic amount of $NiCl_2$ was used instead of $PdCl_2$, about 10% of 2 was converted to 3 after 112 h at 120 °C (Entry 2). The use of Rh/C with TEG/KOH/$NaBH_4$/$CH_3OCH_2CH_2OH$ under similar conditions at 120 °C gave about 10% of 3. Also, 50% of 2 isomerized to its more stable isomer, 1,3,5-trichlorobenzene, after 80 h (Table 2, Entry 3). Neither $NaBH_4$ /$CH_3OCH_2CH_2OH$/Rh/C nor SmI_2 /$CH_3OCH_2CH_2OH$ systems promoted dechlorination of 2 in 80 h at 120 °C.

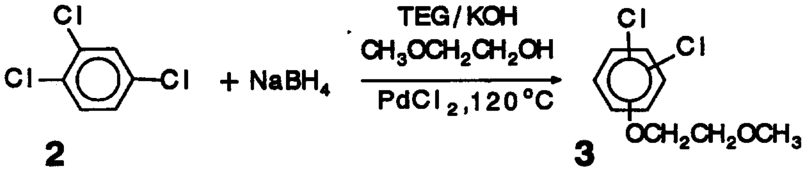

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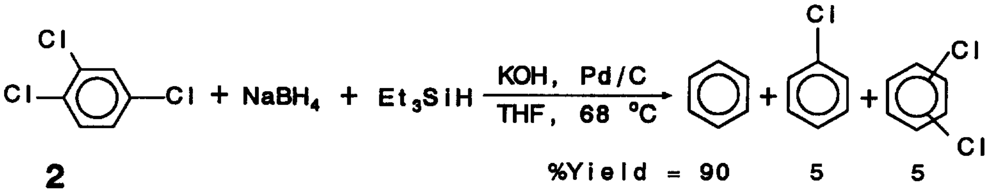
Table 2. Dechlorination of 1,2,4-Trichlorobenzene

Entry	Reagents (Mol Ratios)[a]	Temp. (°C)	Time (h)	Disappearance (Mol%)[b]
1	TEG/KOH/NaBH$_4$/CH$_3$OCH$_2$CH$_2$OH/ PdCl$_2$ (1/4/4/20/0.05)	120	168 168	90
2	TEG/KOH/NaBH$_4$/CH$_3$OCH$_2$CH$_2$OH/ NiCl$_2$ (1/4/4/20/0.05)	120	168 168	10
3	TEG/KOH/NaBH$_4$/CH$_3$OCH$_2$CH$_2$OH/ Rh/C (1/4/8/220/0.01)	120	80	60
4	Et$_3$SiH/Pd/C (1/0.02)	120	1/60 168	50 53
5	Et$_3$SiH/Pd/C (6/0.02)	50	1/60 168	70[c] 92[c]
6	Et$_3$SiH/KOH/NaBH$_4$/Pd/C/THF (1/0.5/1/0.02/24)	68	1/60 168	55 57
7	Et$_3$SiH/KOH/NaBH$_4$/Pd/C/THF (6/0.5/1/0.02/24)	68	1/60 168	87 95
8	NaBH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$/NiCl$_2$/THF (6/1/47)	68	2 168	80[d] 85[d]

[a] All ratios are relative to one mole of 1,2,4-trichlorobenzene.
[b] These values are based on the percent disappearance of the starting material.
[c] Benzene (28%), chlorobenzene (66%) and dichlorobenzene (6%) were obtained.
[d] Benzene (89%) and chlorobenzene (11%) were obtained.

When one equiv Et$_3$SiH was used in the presence of Pd/C, 50% of **2** was reduced to a mixture of chlorobenzene and two dichlorobenzene isomers in one min at 120 °C (Table 2, Entry 4). However, no further dechlorination occurred within 168 h. When a 6 mole excess Et$_3$SiH was used, 70% of **2** was reduced to benzene, chlorobenzene, and a small amount of dichlorobenzene in one min at 50 °C (Entry 5). After one week, 92% of **2** was reduced in this experiment to chlorobenzene (major), benzene and dichlorobenzene. Reduction of 1,2,4-trichlorobenzene with Et$_3$SiH/KOH/NaBH$_4$ in THF in the presence of Pd/C gave 55% chlorobenzene in one min at 68 °C (Entry 6). No further disappearance of **2** occurred after one week. Using a 6 mole excess of Et_3SiH gave an 87% conversion of **2** to benzene, chlorobenzene, and dichlorobenzene in one min (Entry 7, Eq. 3). After one week 95% of **2** was converted to benzene (major), chlorobenzene and dichlorobenzene. Dropwise addition of $NiCl_2$ (stoichiometric amount) in 2-methoxyethanol into the reaction mixture gave 80% reduction after 2 h at 68 °C (Entry 8). The major product was benzene in this experiment.



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(3)

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