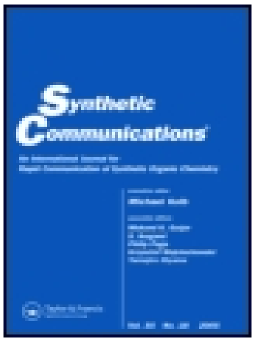

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DECHLORINATION OF PENTACHLOROPHENOL AND 1,2,4-TRICHLOROBENZENE USING $NaBH_4$ AND $NaBH_4$/LiCl AT 125-315 °C IN GLYME SOLVENTS

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Abstract: Dechlorinations of pentachlorophenol and 1,2,4-trichlorobenzene were achieved using $NaBH_4$ in tetraglyme at 290-315 °C and by $NaBH_4$/LiCl at 125-135 °C in diglyme, triglyme or tetraglyme after premixing at room temperature.

Chlorinated aromatic compounds represent a major environmental problem.[1] Many are converted into less dangerous organic products and eventually degraded by different microorganisms.[2] However, some chlorinated aromatic compounds are extremely persistent due to their slow degradation by reductive or oxidative enzymatic pathways.[3] Thus, it is desirable to develop rapid and efficient ways to dehalogenate these recalcitrant compounds. Known chemical methods for the remediation chlorinated aromatic compounds include incineration,[4] wet air oxidation,[5] catalytic dehydrochlorination,[6] sodium-based

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*To whom correspondence should be addressed reduction,[7] reaction with superoxide,[8] photolysis in the presence of hydrogen donors,[9] transition metal-promoted borohydride or alkoxyborohydride reductive dechlorination,[10,11] electrolytic reduction,[12] nickel-catalyzed hydrogenolysis,[13] silyhydride dechlorination,[14] amine-promoted titanium complex-catalyzed borohydride dechlorination,[15] iron-promoted dechlorination,[16] and thermolysis over solid bases like $CaO/Ca(OH)_2$.[17] Sodium borohydride, typically, has not dechlorinated chloroaromatic compounds,[18] except when transition metal catalysts are used.[13,15] Despite the fact $NaBH_4$ is very thermally stable, its use at high temperatures (120-350 °C) has largely been neglected by organic chemists. Instead, a large variety of more expensive and reactive hydrides (e.g., $LiAH_4$, $NaBHEt_3$, $NaBH_2(OCH_2CH_2OCH_3)_2$, $LiB(NR_2)H_3$, etc) have been extensively investigated and applied in functional group reductions.[19] Recently, we have conducted a study of the dechlorination of both 4-chlorobiphenyl and PCBs using $NaBH_4$ in various high boiling inert solvents at elevated temperatures.[20,21] 4-Chlorobiphenyl[20] and PCBs[21] were successfully dechlorinated using $NaBH_4$ at 290-310 °C or $NaBH_4/LiCl$ at 120-162 °C in glyme solvents. We now report that pentachlorophenol and 1,2,4-trichlorobenzene are readily dechlorinated under these same conditions.

Dechlorination of pentachlorophenol (PCP)

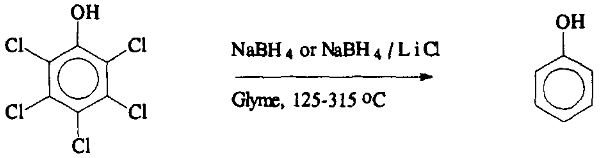
Pentachlorophenol (PCP) was dechlorinated using several different sodium borohydride dehalogenating systems. Example results are summarized in Table 1. PCP dechlorination was very slow (34% substrate disappeared in

128 h) when a 5.5-fold molar excess of $NaBH_4$ was used alone in diglyme at 162 °C (reflux) (Entry 1, Table 1). The dechlorination rate increased (but was still very slow) when lithium chloride was added (Entry 2). Only 79% of the PCP had disappeared within 96 h. Complete disappearance of PCP occurred before 32 h upon increasing the $NaBH_4$ to PCP ratio to 20 from 5.5 at 162 °C in diglyme (Entry 3). However, only 6% phenol was produced in this period. Dechlorination proceeded much more rapidly when $NaBH_4$, LiCl and PCP were prestirred at room temperature for 20 minutes in glyme solvents before heating to a reaction temperature of 130 °C (Entry 4). Pentachlorophenol had completely disappeared within 4 h but only 8% phenol had formed. The major product obtained after 36 h in this dechlorination was phenol (85%). Addition of a three-fold excess of LiCl (vs $NaBH_4$) and replacement of diglyme by tetraglyme enhanced the dechlorination rate (Entry 5) at 130 °C. PCP disappeared within 2 h producing a 12% yield of phenol. An 88% phenol yield was observed in 16 h.

Dechlorination was achieved at 315 °C in a sealed tube without added LiCl (Entry 6). Pentachlorophenol had completely disappeared within 2 h at 315 °C in tetraglyme. Phenol (72%) was the major product. Minor products present at this time were mono- and dichlorophenol (one monochlorophenol and two dichlorophenols were observed based on GC/MS).

Dechlorination of 1,2,4-Trichlorobenzene

The dechlorination of 1,2,4-trichlorobenzene was also examined in several different sodium borohydride/glyme systems. Example results are



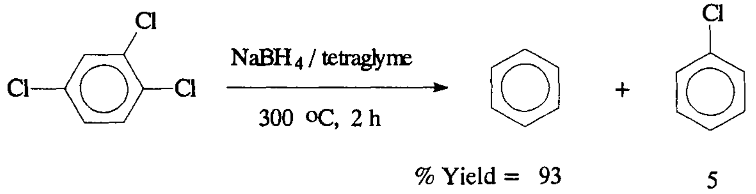
(1)

Table 1. Dechlorination of pentachlorophenol (PCP) with $NaBH_4$ or $NaBH_4/LiCl$ in glymes

Entry	Reagents (Mol Ratios)	Temp. (°C)	Time (h)	Disappearance (Mol%)[a]
1	substrate/$NaBH_4$/diglyme	162	128	34
	(1/5.5/42)			
	Cl/$NaBH_4$/diglyme			
	(1/1.1/8.4)			
2	substrate/$NaBH_4$/LiCl/diglyme	162	1	26.7
	(1/5.5/5.5/42)		16	33.7
	Cl/$NaBH_4$/LiCl/diglyme		48	51.1
	(1/1.1/1.1/8.4)		96	79.1
3	substrate/$NaBH_4$/LiCl/diglyme	162	1	29.5
	(1/20/20/84)		16	88.5
	Cl/$NaBH_4$/LiCl/diglyme		32	100[d]
	(1/4/4/16.8)			
4[b]	substrate/$NaBH_4$/LiCl/diglyme	130	1	58
	(1/20/20/84)		3	94
	Cl/$NaBH_4$/LiCl/diglyme		4	100[e]
	(1/4/4/16.8)		36	100[f]
5[b]	substrate/$NaBH_4$/LiCl/Tetraglyme	130	1	89
	(1/20/60/54)		2	100[g]
	Cl/$NaBH_4$/LiCl/tetraglyme		16	100[h]
	(1/4/12/11)			
6[c]	substrate/$NaBH_4$/Tetraglyme	315	2	100[i]
	(1/20/54.4)			
	Cl/$NaBH_4$/Tetraglyme			
	(1/4/10.9)			

[a] These values refer to the percent disappearance of the pentachlorophenol.

[b] The reaction mixture was stirred at room temperature for 20 min before being heated to 130 °C. [c] This reaction was conducted in a sealed tube. [d] A 6% yield of phenol was produced. [e] An 8% yield of phenol was produced. [f] Phenol was the major product (85% yield). [g] An 12% yield of phenol was produced. [h] Phenol was the major product (88% yield). [i] Phenol was the major product (72%).



(2)

Table 2. Dechlorination of 1,2,4-Trichlorobenzene with $NaBH_4$ or $NaBH_4/LiCl$ in glymes

Entry	Reagents (Mol Ratios)	Temp. (°C)	Time (h)	Disappearance (Mol%)[a]
1	substrate/$NaBH_4$/diglyme	162	48	14.5
	(1/12/42)		72	16.9
	Cl/$NaBH_4$/diglyme			
	(1/4/14)			
2	substrate/$NaBH_4$/LiCl/diglyme	162	2	8.5
	(1/12/12/42)		10	48.6
	Cl/$NaBH_4$/LiCl/diglyme		15	67.1
	(1/4/4/14)		20	81.6
			27	92.6
			40	100
3[b]	substrate/$NaBH_4$/LiCl/diglyme	130	0.5	66.8
	(1/12/12/42)		2	99.5
	Cl/$NaBH_4$/LiCl/diglyme		15	100[d]
	(1/4/4/14)			
4[b]	substrate/$NaBH_4$/LiCl/tetraglyme	130	0.5	90
	(1/12/36/42)		1	100
	Cl/$NaBH_4$/LiCl/diglyme		8	100[e]
	(1/4/12/14)			
5[c]	substrate/$NaBH_4$/tetraglyme	300	2	100[f]
	(1/12/27.2)			
	Cl/$NaBH_4$/tetraglyme			
	(1/4/9.1)			

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[a] These values refer to the mole percent disappearance of 1,2,4-trichlorobenzene. [b] The reaction mixture was stirred at room temperature for 20 minutes before being heated to 130 °C. [c] The reaction was conducted in a sealed tube. [d] Benzene (91%) and chlorobenzene (6%) were detected. [e] Benzene (92%) and chlorobenzene (4%) were detected. [f] Benzene (93%) and chlorobenzene (5%) were the products detected.

summarized in Table 2. Dechlorination was very slow (only 16.9% of the substrate had disappeared after 72 h) using $NaBH_4$ alone in diglyme at 162 °C (reflux) (Entry 1, Table 2). Addition of LiCl ($NaBH_4$/LiCl = 1) enhanced dechlorination but the reaction progress was still slow (Entry 2, 93% disappearance of 1,2,4-trichlorobenzene in 27 h). Only 6.4% of the substrate was reduced completely to benzene after 40 h at these conditions when all of the substrate had disappeared. The other products observed at this time were 1,4-, 1,3-, 1,2-dichlorobenzenes and chlorobenzene in yields of 29%, 8.5%, 5.3%, 39%, respectively. Prestirring $NaBH_4$, LiCl, diglyme and substrate at room temperature for 20 minutes and then heating to a reaction temperature of 130 °C significantly enhanced the dechlorination rate (Entry 3). 1,2,4-Trichlorobenzene was 99.5% removed within 2 hours and 91% yield of benzene was obtained after 15 hours (along with 6% of chlorobenzene). Addition of a three-fold excess of LiCl (vs $NaBH_4$) and the replacement of diglyme with tetraglyme resulted in complete disappearance of 1,2,3-trichlorobenzene within 1 h at 130 °C (Entry 4). A 92% yield of benzene and 4% chlorobenzene were obtained after 8 hours. 1,2,4-Trichlorobenzene completely disappeared within 2 h at 300 °C in a sealed tube (Entry 5, Eq. 2). Benzene (93%) and chlorobenzene (5%) were the only products detected.

Acknowledgments

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