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Dechlorination of 4-Chlorobiphenyl Using $NaBH_4$ at 120-310 °C in High Boiling Inert Solvents With and Without LiCl

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Abstract: Dechlorinations of 4-chlorobiphenyl with $NaBH_4$ in high boiling inert solvents from 120-310 °C were studied. Complete dechlorination occurred in $NaBH_4$/tetraglyme at 310 °C in one hour. Adding LiCl to $NaBH_4$ promoted dechlorination in di-, tri, and tetraglyme respectively at 120-135 °C. The rate was significantly enhanced when $NaBH_4$, LiCl, and glyme were prestirred at room temperature for 20 minutes before heating to 120-135 °C. At equivalent conditions, dechlorination rates followed the order: tetraglyme > triglyme > diglyme. 4-Chlorobiphenyl dechlorination failed using $NaBH_4$/diphenyl ether. In pentamethyldiethylenetriamine 3- and 4-N,N-dimethylaminobiphenyl was produced through a benzyne intermediate.

Chlorinated organic molecules, especially PCBs, represent a major environmental problem.[1] Chemical methods known for remediating chlorinated aromatic compounds include incineration,[2,3] wet air oxidation,[4] catalytic dehydrochlorination,[5] sodium-based reduction,[6,7] 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] silylhydride dechlorination,[14] amine-promoted titanium complex-catalyzed sodium borohydride dechlorination,[15] iron-promoted dechlorination,[16] and thermolysis over solid bases like $CaO/Ca(OH)_2$.[17] Sodium borohydride does not achieve aromatic dechlorinations,[18] except when using transition metal catalysts.[13,15] $NaBH_4$ is quite thermally stable. However, its use at high temperatures (120-350 °C) has largely been neglected. Instead, more expensive and reactive hydrides (e.g., $LiAH_4$, $NaBHEt_3$, $NaBH_2(OCH_2CH_2OCH_3)_2$, $LiB(NR_2)H_3$, and etc) have been used in more difficult organic reductions. Therefore, we investigated $NaBH_4$ at high temperatures for the dechlorination of 4-chlorobiphenyl. Di-, tri- and tetraglyme were used as high boiling solvents (162, 216, 275 °C, bps. respectively) due to their moderately high polarity, lack of acidic hydrogens, and ability to multiply chelate (solvate) Na^+.

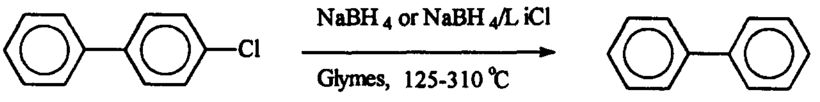
4-Chlorobiphenyl was slowly dechlorinated by $NaBH_4$/diglyme at 162 °C (reflux) (Table 1, Entry 1). Complete dechlorination had not occurred after 28 h. Faster rates were achieved using triglyme or tetraglyme at their boiling temperatures (Entries 2 and 3). Complete dechlorination of 4-chlorobiphenyl was achieved at 310 °C in 1 h using $NaBH_4$ in tetraglyme (Entry 4). Adding LiCl to $NaBH_4$/diglyme enhanced the dechlorination rate (Entry 5 vs 1). Formation of lithium borohydride[19,20] *in situ* might increase borohydride solubility due to more effective solvation of Li^+ versus Na^+. The dechlorination rate was greatly increased when the $NaBH_4$/LiCl/diglyme reaction mixture was stirred at room temperature before heating (Entry 6 vs 5). Even greater rate enhancements resulted when the temperature was lowered to 130 °C from 162 °C (Entry 7 vs 6). Complete 4-chlorobiphenyl dechlorination was achieved within 10 minutes (Entry 7). Replacing LiCl with LiBr lowered

Table 1. Dechlorination of 4-Chlorobiphenyl with NaBH$_4$ in Di-, Tri- and Tetraglyme

Entry	Reagents (Mol Ratios)[a]	Temp. (°C)	Time (h)	Disappearance (Mol%)[a]	Biphenyl (Mol%)[a]
1	NaBH$_4$/diglyme (20/168)	162	20	78	76
			28	96	95
2	NaBH$_4$/triglyme (20/133)	216	16	77	74
			22	100	97
3	NaBH$_4$/tetraglyme (20/109)	275	1	97	96
			10	97	96
4[b]	NaBH$_4$/tetraglyme (5/27.2)	310	0.5	88	80
			1	100	92
5	NaBH$_4$/LiCl/diglyme (20/20/168)	162	6	96	92
			7	100	98
6[c]	NaBH$_4$/LiCl/diglyme (20/20/168)	162	1/6	74	71
			0.5	100	98
7[c]	NaBH$_4$/LiCl/diglyme (20/20/168)	130	1/6	100	99
8[c]	NaBH$_4$/LiCl/diglyme (20/20/168)	100	2	22	20
9[d]	NaBH$_4$/LiCl/diglyme (20/20/168)	130	3	58	56
			12	99	98
10[c]	NaBH$_4$/LiCl/diglyme (5/5/42)	160	50	82	76
11[c]	NaBH$_4$/LiCl/diglyme (5/5/42)	130	5	86	85
			8	100	98

[a] All ratios are relative to one mole of 4-chlorobiphenyl. Biphenyl was the only dechlorination product. [b] The reaction was conducted in a sealed tube. [c] The reaction mixture was stirred at room temperature for 30 minutes before heating. [d] The reagents were added at 130 °C (no premixed process at room temperature).

the rate (100%, 2.5 h). Complete dechlorinations were also obtained in 10 min. using LiCl-promoted NaBH$_4$ at 130 °C in both tri- and tetraglyme (not listed). However, lowering the reaction temperature to 100 °C decreased the dechlorination rate (Entry 8). Reaction temperatures ranging from 120 to 135 °C were optimum. Adding LiCl or NaBH$_4$ to preheated (especially boiling) diglyme solutions greatly lowered dechlorination rates (Entry 9 vs 7) no matter which reagent was added first. The rate was not effected by increasing the time (e.g., 20 min, 40 min, 1 h) used to prestir reagents and glyme at ambient temperature. LiBH$_4$ should be generated in glyme solvents *in situ* at lower temperatures. Biphenyl was the only product detected in all of these reactions (Eq. 1).

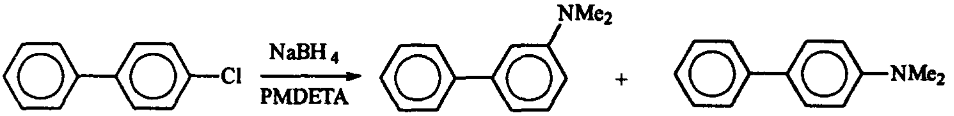


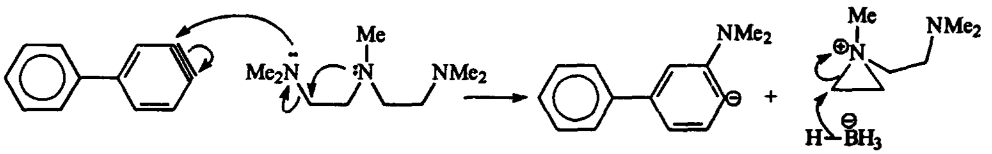
(1)

Attempts to reduce the high borohydride to substrate ratios required for high dechlorination yields were only successful after it was discovered that great rate enhancements occurred by first prestirring $NaBH_4$/LiCl in glymes at room temperature and then heating to 120 to 135 °C (Entry 11 vs 10).

Dechlorinations of 4-chlorobiophenyl in tri- and tetraglyme exhibited similar trends to those observed in diglyme except that even faster rates were obtained. A few examples of this solvent effect appear in Table 2. The rate in $NaBH_4$ (only)/tetraglyme at 162 °C (Entry 2, Table 2) was faster than that in triglyme (Entry 1, Table 2) at the same $NaBH_4$/substrate ratio. The rates were faster in both tetraglyme and triglyme than in diglyme (see Entry 1, Table 1) at the same conditions (same volumes of solvent was used accounting for the difference in moles of solvent). The same dependence of rate on solvent was observed in LiCl/$NaBH_4$ systems (compare Entry 11, Table 1 with Entries 3 and 4, Table 2). This interesting observation probably occurs because tetraglyme solvates lithium and sodium cations more favorably (less increase in entropy for six oxygens to coordinate Li^+ or Na^+; chelate effect) than triglyme and diglyme, respectively. This effect may increase $NaBH_4$ solubility or more effectively solvent-separate the ion pairs enhancing BH_4^- reactivity. A complex temperature dependence of NaBH4 solubility in diglyme is known.[20]

4-Chlorobiphenyl was not dechlorinated using $NaBH_4$ in diphenyl ether (DPE) at temperatures from 100-300°C after long reaction times under nitrogen. At 300 °C the solubility of $NaBH_4$ was negligible in DPE. When LiCl was added at 259 °C, 4-chlorobiphenyl was slowly converted (88%, 49 h) to a mixture of high boiling biphenyl arylethers produced by DPE cleavage followed by nucleophilic aromatic substitution of phenoxide for chlorine or, more likely, by benzyne formation reaction with phenoxide. In pentamethyldiethylenetriamine (PMDETA), $NaBH_4$ did not dechlorinate 4-chlorobiphenyl at temperatures from 150-250 °C although $NaBH_4$ was consumed in reactions with solvent. At 275 °C, substrate slowly disappeared. No biphenyl was formed. Instead the 4- and 3-isomers of N,N-dimethylaminobiphenyl were formed in a 1 to 1 ratio. Without $NaBH_4$ this reaction did not occur. Nucleophilic attack by PMDETA on a benzyne intermediate accounts for this result.





Finally, these systems can quantitatively dechlorinate PCBs. For example, Aroclor 1016, a commercial PCB mixture, was 99% dechlorinated in 4 h at 130 °C using a substrate/$NaBH_4$/LiCl/tetraglyme mole ratio of 1/4/4/18.

Table 2. Dechlorination of 4-Chlorobiphenyl with $NaBH_4$ in Di-, Tri- and Tetraglyme

Entry	Reagents (Mol Ratios)[a]	Temp. (°C)	Time (h)	Disappearance (Mol%)[a]	Biphenyl (Mol%)[a]
1	$NaBH_4$/triglyme	162	2	94	
	(20/133)		2.5	100	98
2	$NaBH_4$/tetraglyme	162	1	85	
	(20/109)		1.5	100	98
3[b]	$NaBH_4$/LiCl/triglyme	130	1.5	89	
	(5/5/33)		2.5	100	98
4[b]	$NaBH_4$/LiCl/tetraglyme	130	1	93	91
	(5/5/27)		1.5	100	97

[a] All ratios are relative to one mole of 4-chlorobiphenyl. Biphenyl was the only dechlorination product. [b] The reaction mixture was stirred at room temperature for 30 minutes before heating.

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REFERENCES:

1. D'Itri, F. M.; Kamrin, M. A. *PCB's: Human and Environmental Hazards*; Ann Arbor Science Book;Boston, 1983.
2. Wentz, C. A. Hazardous Waste Management; Clark, B. J.; Morriss, J. M., Eds.; McGraw-Hill Chemical Engineer Series; McGraw-Hill: New York, 1989.
3. Exner, J. H. *Detoxification of Hazardous Waste*, Ann Arbor Science, Ann Arbor, MI, 1982, p. 185.
4. Baillod, R. C.; Lampartes, R. A.; Laddy, D. G. *Wet Oxidation of Toxic Organic Substance*, Purdue Industrial Waste Conference, West Lafayette, IN, May 1978.
5. Biros, F. J.; Walker, A. C.; Medbery, A. *Bull. Environ. Contam. Toxicol.*, **1970**, *5*, 317.
6. Oku, A.; Ysufuku, K.; Dataoka, H. *Chem. Ind.* 1978, 841.
7. Davies, W. A.; Prince, R. G. H. *Process Saf. Environ. Prot.* **1994**, *72*, 113.
8. Sugimoto, H.; Shigenobu, M.; Sawyer, D. T. *Environ. Sci. Technol.* **1988**, *22*, 1182.
9. Epling, G. A.; Florio, E. M.; Bourque, A. J. *Environ. Sci. Technol.* **1988**, *22*, 952.
10. Tabaei, S. M. H.; C. U. Pittman, Jr., *Tetrahedron lett.*, 34 (20), 3263-3266 **1993**
11. S. M. H. Tabaei; Pittman, Jr., C. U.; and Mead, K. T. *J. Org. Chem.* **1992**, *57*, 6669.
12. Zhang, S.; Rusling, J. F., *Environ. Sci. Technol.* **1993**, *27*, 1375
13. Roth, J. A.; Dakoji, S. R.; Hughes, R. C.; Carmody, R. E. *Environ. Sci. Technol.* **1994**, *28*, 80.
14. Romanova, Valentina S.; Parnes, Zinaida N.; Dulova, Vera G.; Volpin, Mark E. **Russ. RU** 2,030,377, *Izobreteniya* **1995**,(7) 135.
15. Liu, Y.; Schwartz, J.; Cavallaro, C. L., *Environ. Sci. Technol.* **1995**, *29*, 836.
16. Chuang, F.-W.; Larson, R. A.; Wessman, M. S., *Environ. Sci. Technol.* **1995**, *29*, 2460.
17. Yang, C.-M.; Pittman, C. U., *HAZARDOUS WASTE & HAZARDOUS MATERIALS*, v.13, No.4, **1996**.
18. Paderes, G. D.; Metivier, P.; Jorgensen, W. L. *J. Org. Chem.* **1991**, 56, 4718.
19. Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567-607.
20. Brown, H. C.; Mead, E. J.; Subba Rao, B. C. *J. Amer. Chem. Soc.*. **1955**, 77, 6209.

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