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The First Complete Dechlorination of 1,1,1-Trichloro-2,2-Bis(4-Chlorophenyl) Ethane (P,P'-DDT) Using Metal-Promoted Alkoxyborohydride in a Protic Solvent

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THE FIRST COMPLETE DECHLORINATION OF 1,1,1-TRICHLORO-2,2-BIS(4-CHLOROPHENYL) ETHANE (P,P′-DDT) USING METAL-PROMOTED ALKOXYBOROHYDRIDE IN A PROTIC SOLVENT

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Abstract: The reaction in situ of sodium borohydride with 2-methoxyethanol in 2-propanol in the presence of catalytic amount of $NiCl_2{\cdot}6H_2O$ generates a powerful dechlorinating system which dechlorinates 1,1,1-trichloro-2,2-bis (4-chlorophenyl)-ethane (DDT) to 1,1-diphenylmethoxymethane(80%) and 1-(*p*-chlorophenyl)-1-phenylethane(10%) in 6 hours at 82-84 °C .

Environmental and toxicological effects of man-made organic compounds have been a serious concern over the last decades.[1] Chlorinated organic compounds are commonly used as solvents and industrial chemicals which include pesticides, herbicides, insecticides and polymers.[2] They have become widely distributed in the environment as a result of industrial discharges and overuse in the fields.[3] Organochlorine insecticides and the most important of them

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"DDT", although having outstanding applications are persistent environmental pollutants requiring safe and effective means of disposal.[4] Resistance to degradation and a tendency to accumulate in animal tissues[5] has resulted in control manufacture, use and disposal of these toxic compounds.[6] For example, DDT which caused liver cancer in both mice and rats, has been banned in the United States from 1972.[7]

DDT (**1**), one of the most important early pesticides, was first prepared by Zeidler in 1874.[8] Its powerful insecticidal properties were discovered in 1939 by Muller of the Swiss Geigy Company.[9] DDT was found to be effective against wide variety of disease-bearing and agricultural insects and widely used by the year 1969. DDT and many of its derivatives are persistent insecticides in that they are not readily degraded in the environment. The stability of this chlorinated organic pesticide coupled with its high solubility in fatty tissues, causes it to a concentrate in food chain.[10] Many examples have been documented on the concentration of organochlorine compounds along food chains.[11]

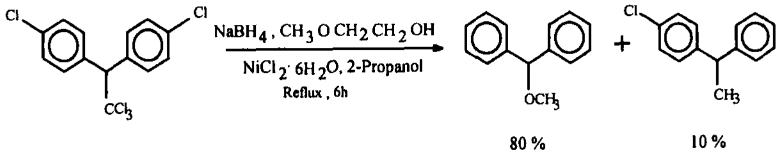
Many dechlorination methods have been suggested for disposal of these materials from the environment. Dechlorination of these pollutants has centered on such methods as incineration[12], plasma incineration[13], wet oxidation[14] and other chemical methods.[15] Unfortunately these methods have limitations. Thus it is desirable to develop low temperature rapid dehalogenations for organic compounds which can be used prior to their safe incineration. Hydride reducing agents such as $LiAlH_4$ and $NaBH_4$ typically have not been very active in dechlorinations.[16] However, combination of these reactive hydrides with transition metal salts to generate M(0) species appeared to offer a more promising approach to dechlorination.[17]

Previously, Ni-promoted $NaBH_4$ and $NaBH_2(OCH_2CH_2OCH_3)_2$ in THF have been used to dechlorinate some chlorinated aromatic[18,19] and also aliphatic[20] compounds. These methods need high amount of metal salts and also high hydride/chloride ratio. Since dechlorination of DDT by the use of these methods was not successful, we have developed the first methodology for achieving complete dechlorinated product of DDT(a chlorinated aromatic-aliphatic compound). In addition to its simplicity, use of inexpensive materials and safety, this method has two important advantages: the use of low amount of metal salt and also low hydride/chloride ratio in comparison with previous methods.

Dechlorination of DDT

DDT was subjected to several dechlorinating conditions. Reaction in situ of $NaBH_4$ and 2-methoxyethanol in presence of $NiCl_2{\cdot}6H_2O$ in 2-propanol generates, at reflux temperature (82-84°C), a powerful dechlorinating system that can dechlorinate DDT(**1**) to a completely dechlorinated product, 1,1-diphenyl methoxymethane (**2**), and monochlorinated derivative of DDT (**3**). Several $NaBH_4$-based systems used to dechlorinate DDT. The results are shown in the table. In the absence of $NiCl_2{\cdot}6H_2O$ or 2-methoxyethanol dechlorination is not successful (Entries 1-3). When $NiCl_2{\cdot}6H_2O$ and 2-methoxyethanol were used in combination, dechlorination was improved. However, complete dechlorination of DDT by this method is very sensitive to reagent ratios (Entries 4-10). When a low ratio (0.05 mole) of $NiCl_2 \cdot 6H_2O$ was used, dechlorination was promoted (comparing Entry 4 to Entry 3). When the ratio of $NaBH_4$/2-methoxyethanol was decreased, dechlorination dropped about 30% (Entry 5). The use of more $NiCl_2 \cdot 6H_2O$ (0.1 mole) caused further promotion in the dechlorination of DDT(Entry 5). Then the ratio of $NiCl_2 \cdot 6H_2O$ was kept fixed (0.1) and the ratio of $NaBH_4$ over 2-methoxyethanol was increased from 0.5 up to 0.7 (Entries 7-10). The best result (94% dechlorination) was obtained when this ratio was 0.6 (Entry 8). However, when anhydrous $NiCl_2$ was used, dechlorination percent was decreased (Entry 11). GC/MS spectrum shows that methoxy group was substituted for CCl_3 group in the major product (**2**). The mechanism of this reaction is under investigation.

Experimental Section: In a typical reaction, 200 mg (0.6 mmol) DDT was dissolved in 20 ml 2-propanol in a 100 ml round bottom three-neck flask . At reflux point (82-84°C) , 135 mg(3.6 mmol) $NaBH_4$ (powder) was added to the stirred solution. After 2-3 minutes (after complete distribution of powder in the solution) a solution of 14 mg (0.06 mmol) $NiCl_2 \cdot 6H_2O$ in 0.5 ml (6.0 mmol) 2-



(1) **(2)** **(3)**

Table- Dechlorination of DDT in 2-Propanol at Reflux (82-84°C)

Entry	Reagents(mole ratio)[a]	Time(h)	Products(mole%)		%Total Dechlorination[b]
			2	**3**	
1	$NaBH_4$ (6)	6	-	-	32
2	$NaBH_4$/ $NiCl_2 \cdot 6H_2O$ (6/ 0.1)	6	-	5	48
3[c]	$NaBH_4$/ $CH_3OCH_2CH_2OH$ (6/ 10)	6	-	5	51
4[c,d]	$NaBH_4$/ $CH_3OCH_2CH_2OH$/ $NiCl_2 \cdot 6H_2O$ (6/ 10/ 0.05)	6	10	63	72
5[c,d]	$NaBH_4$/ $CH_3OCH_2CH_2OH$/ $NiCl_2 \cdot 6H_2O$ (4/8 /0.05)	6	-	2	42
6[c,d]	$NaBH_4$/ $CH_3OCH_2CH_2OH$/ $NiCl_2 \cdot 6H_2O$ (4/ 8/0.1)	6	-	20	54
7[c,d]	$NaBH_4$/$CH_3OCH_2CH_2OH$/ $NiCl_2 \cdot 6H_2O$ (6/ 12/ 0.1)	6	43	44	83
8[c,d,e]	$NaBH_4$/$CH_3OCH_2CH_2OH$/ $NiCl_2 \cdot 6H_2O$ (6/ 10/ 0.1)	6	80	10	94
9[c,d,e]	$NaBH_4$/$CH_3OCH_2CH_2OH$/ $NiCl_2 \cdot 6H_2O$ (7/ 10/ 0.1)	6	70	25	91
10[c,d]	$NaBH_4$/ $CH_3OCH_2CH_2OH$/ $NiCl_2 \cdot 6H_2O$ (7/ 12/ 0.1)	6	26	61	81
11[c,d]	$NaBH_4$/$CH_3OCH_2CH_2OH$/ $NiCl_2$ (6/ 10/ 0.1)	6	13	71	78

[a] All ratios are relative to one mole of DDT. [b] These values refer to the total chlorine atoms removed as a percentage of total chlorine present in DDT. [c] The alkoxyborohydride was produced in situ. [d] A solution of $NiCl_2 \cdot 6H_2O$ (or $NiCl_2$) in 2-methoxyethanol was continuously added to the reaction mixture. [e] Some dichloro and trichloro derivatives were also produced.

methoxyethanol were added dropwise by a syringe in one minute. Because of heterogeneity of the system stirring should be done by an appropriate stirring bar roughly.

Preparation of GC/MS sample: At appropriate time intervals 0.2 ml of the reaction mixture was withdrawn by a syringe and immediately was added to 3-5 ml CH_2Cl_2 then the same volume of distilled water and few drops dilute H_2SO_4. After shaking, the organic layer was separated and its volume was reduced to 1 ml, then 1 μL of sample was injected to GC or GC/MS. Concentration ratios obtained by the area ratio method (assuming equal FID-sensitivity for all products).

Caution: DDT shows to be carcinogenic to both mice and rats.[7] It might be concentrated along food and accumulated in fatty tissues in the body.[10, 11]

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