# Catalytic Dechlorination of Organochlorine Compounds III. Lindane

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Nickel boride ($Ni_2B$), prepared in-situ by the reaction of sodium borohydride with alcoholic nickel chloride, has been used for the catalytic hydrogenation of olefins (BROWN and BROWN, 1963, BROWN, 1970, RUSSELL and HOY, 1971).

We found that in-situ preparation of $Ni_2B$ with the addition of excess $NaBH_4$ was effective in the extensive dechlorination of DDT (DENNIS and COOPER, 1975), heptachlor and chlordane (DENNIS and COOPER, in press). Similar systems have been used to reductively dehalogenate aromatic systems (EGLI, 1968) and as a site specific method for deuteration (BOSIN, et al., 1973). This catalytic system was found to rapidly and completely dechlorinate lindane (the gamma isomer of 1,2,3,4,5,6 - hexachlorocyclohexane) to benzene, cyclohexene, cyclohexane and chloride ions. In a similar reduction of lindane described by Bieniek et al. (1970), lindane, $Co_2B$ and an excess of $NaBH_4$, in various solvents, produced tetrachlorocyclohexane as the major product.

The $Ni_2B$ reduction was carried out by adding 15 mmol of $NaBH_4$ dropwise, as a 5M solution, to 30 ml of methanol containing 1 mmol lindane and 0.5 mmol $NiCl_2 \cdot 6H_2O$. After thirty minutes the reaction mixture was analyzed by gas chromatography using 10% Carbowax 20M on 80/100 HP Chrom W in a 6' x 1/8" column. Further identification of products was made using a DuPont 490-B gas chromatograph/mass spectrometer. The amount of chloride produced in the dechlorination of lindane in various systems was determined by potentiometric titration as described earlier (DENNIS and COOPER, 1975).

Ethanol and 2-propanol were found to promote the reduction as well as methanol. However, addition of water to the mixture was found to hinder the reaction as shown in Table 1.

A yield of between 94 and 100% of the expected amount of chloride (6 mmol) was found in all solvents when at least 10 mmol of $NaBH_4$ were reacted with 1 mmol of lindane and 0.5 mmol of $NiCl_2$. In each case benzene was the major reaction product, but the product composition varied with solvents as shown in Table II.

Bulletin of Environmental Contamination & Toxicology,
Vol. 18, No. 1 © 1977 by Springer-Verlag New York Inc.

## TABLE I.

Production of Chloride in the Dechlorination of 1 mmol of Lindane in 25 ml 2-Propanol/Water Mixtures with 10 mmol $NaBH_4$ and 0.5 mmol $NiCl_2$

| $H_2O$ (% by vol.) | Chloride Produced (mmol) |
|---|---|
| 0.0 | 5.66 |
| 3.8 | 5.07 |
| 10.7 | 3.92 |
| 16.6 | 3.92 |
| 100.0 | 0.00 |

## TABLE II.

Product Composition in mole % from Reaction of 1 mmol of Lindane with 15 mmol $NaBH_4$ and 0.5 mmol of $NiCl_2$

| Solvent | Benzene | Cyclohexene | Cyclohexane |
|---|---|---|---|
| Methanol | 73% | 16% | 11% |
| Ethanol | 61% | 35% | 4% |
| 2-Propanol | 79% | 18% | 3% |

Using NaOH in methanol, lindane produced the expected isomeric trichlorobenzenes. However, using $NaBH_4$ in methanol, in the absence of $Ni_2B$, the trichlorobenzenes were not observed. Compounds containing four and five chlorine atoms were observed using gas chromatography/mass spectrometry but have not been identified. From this data it appears that the reduction of the lindane by the $Ni_2B/NaBH_4$ system does not proceed through the trichlorobenzene intermediates. The $Ni_2B/NaBH_4$ system shows potential for the chemical degradation of lindane and should be studied in more detail

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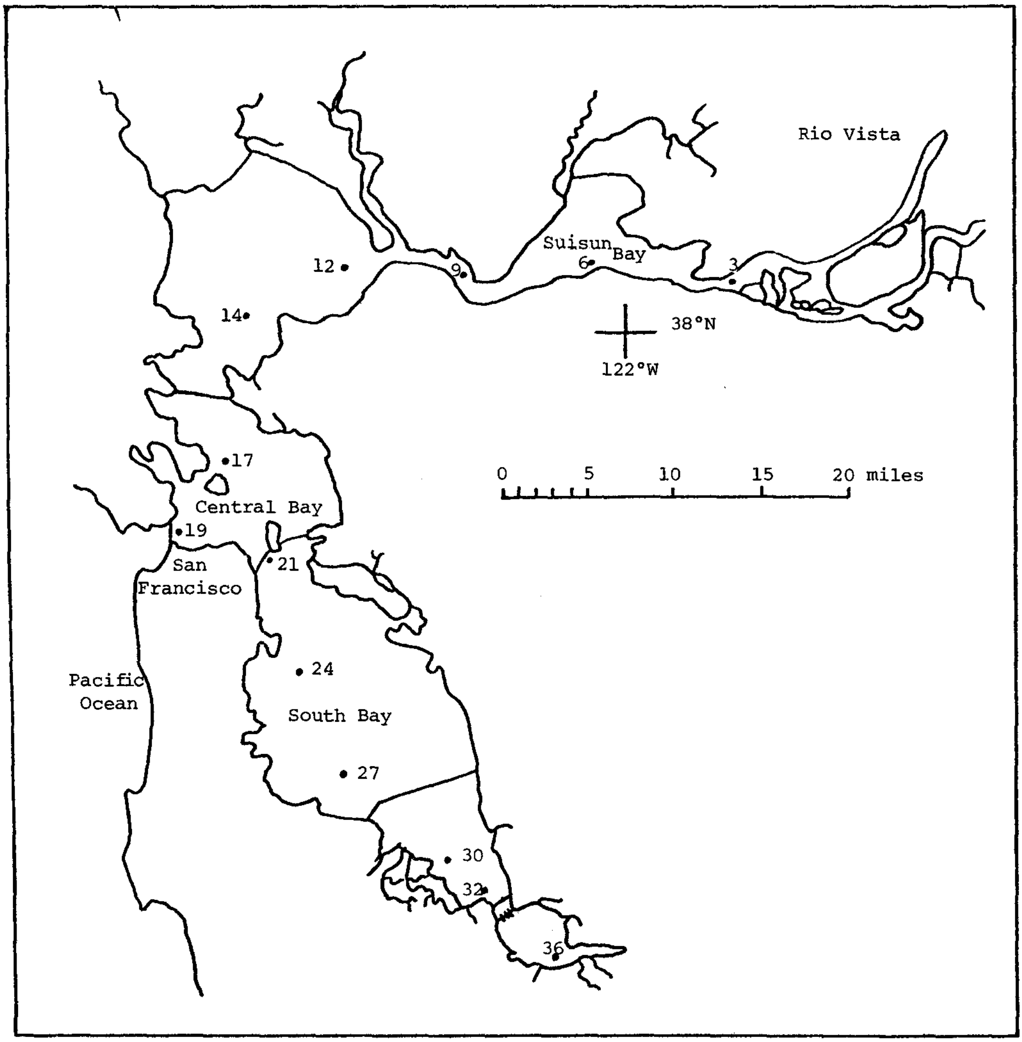

FIGURE 1

Index map of the San Francisco Bay estuary showing the location of seston sampling stations, which conform with the vertical profile stations of the U.S. Geological Survey.