Catalytic Dechlorination of Organochlorine Compounds. II. Heptachlor and Chlordane

W. H. Dennis, Jr. and W. J. Cooper

US Army Medical Bioengineering
Research and Development Laboratory
Fort Detrick, Frederick, Md. 21701

Nickel boride, produced *in-situ* by mixing a nickel chloride solution in methanol with aqueous sodium borohydride, was used to extensively dechlorinate DDT (DENNIS and COOPER, 1975). As part of a continuing study to develop methods for the chemical degradation of pesticides and pesticide formulations, this catalytic dechlorination system has now been applied to the pesticides heptachlor and chlordane. Both pesticides yield a common product mixture, the major component being a pentachloro derivative (Compound IV) shown in Figure 1.

METHODS AND MATERIALS

Heptachlor (I) was obtained from the Velsicol Chemical Corp. and was recrystallized twice from ethanol before use. Chlordane, (60% technical) was obtained from the City Chemical Co. and was used without purification. (Technical chlordane is a complex mixture of isomers and related materials produced by the chlorination of chlordene, $C_{10}H_6Cl_6$, MARTIN, 1972.)

Chloride determinations for the dechlorination of heptachlor were carried out potentiometrically. The chlorine determinations of the products obtained from the dechlorination of technical chlordane were made by elemental analysis of the isolated products.

Analyses of all reaction products were done using gas chromatography with an 8 foot, 10% OV-1 on 100-120 mesh GAS CHROM Q column. Structural identifications were made using a Dupont 490B Gas Chromatograph/Mass Spectrometer.

The procedure tested for the dechlorination of heptachlor required 1 mmol of pesticide dissolved in 30 ml of alcohol. To this solution was added 0.5 mmol of nickel chloride followed by dropwise addition of 1 to 6 ml of aqueous 5 M sodium borohydride. After 30 minutes, 200 ml of water was added and the organic product extracted with benzene/hexane (1:1). The organic phase was then analyzed using gas chromatography. The aqueous layer from heptachlor experiments was titrated for chloride content. Due to

Bulletin of Environmental Contamination & Toxicology,
Vol. 16, No. 4 © 1976 by Springer-Verlag New York Inc.

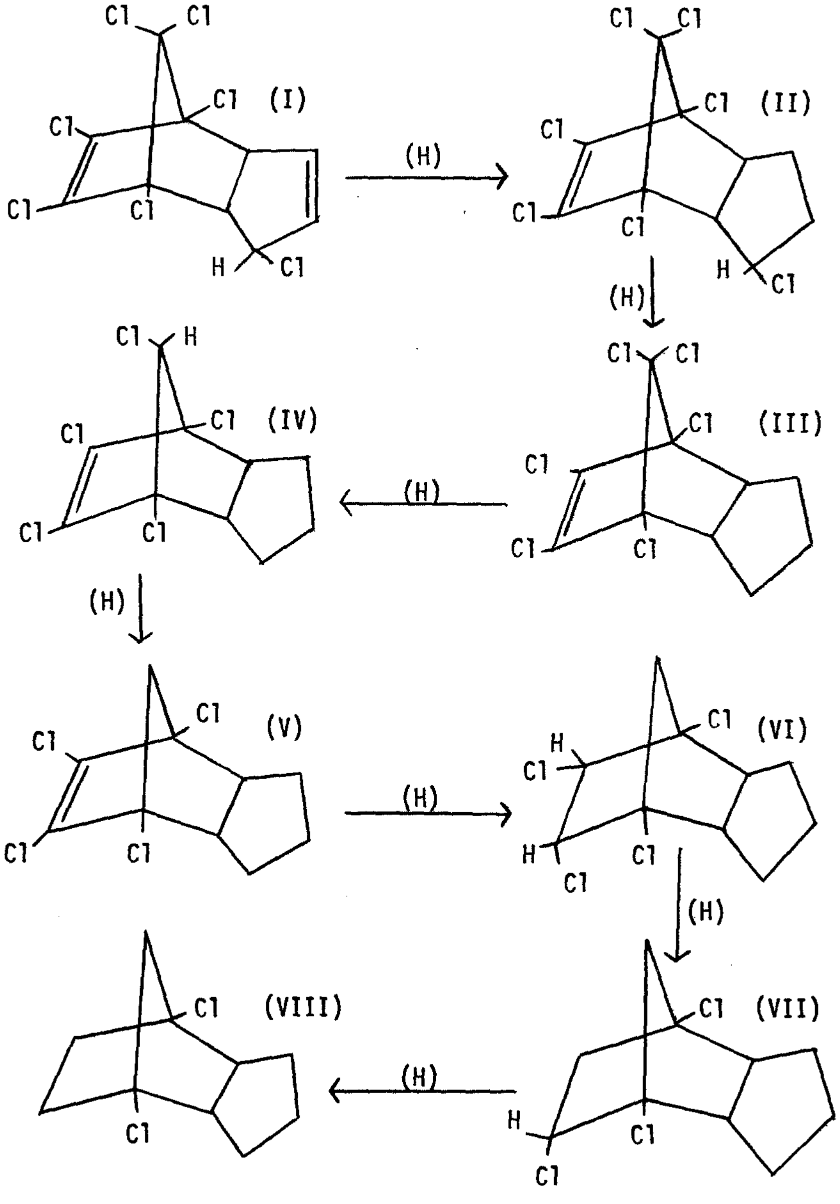

Figure 1. Reaction products and probable sequence for the dechlorination of heptachlor.

the uncertainty of the technical chlordane composition, the loss of organically-bound chlorine was determined by elemental analysis of the product rather than titration of the aqueous phase.

ISOLATION OF MAJOR PRODUCT

The major product obtained in the dechlorination of both heptachlor and chlordane by the $Ni_2B/NaBH_4$ system was compound IV shown in Figure 1. This was isolated by passing the crude product mixture (from the benzene/hexane extract) through a 30 cm x 1 cm column of Woelm acidic alumina. Ether was used to elute the components from the column. The fractions collected were analyzed by gas chromatography and those containing the major component pooled. The compound melted at 84°C and was shown by GC to be >98% pure. The analytical data in Table 1 support structure IV.

TABLE 1

Analytical Data Compiled on Isolated Product
from the Dechlorination of
Heptachlor and Chlordane

Analysis	Comments
NMR Spectrum	Singlet 5.67 τ (1H) Multiplet 6.90 τ (2H) Multiplet 8.30 τ (6H)
Infrared Spectrum	1610 cm^{-1} Double bond in strained ring. 1445 cm^{-1} $-CH_2-$ cyclopentane ring
Elemental Analysis	Found: C, 39.4%; H, 2.8%; Cl, 58.0% Theoretical: C, 39.19%; H, 2.95%; Cl, 57.85%
Mass Spectrum	Molecular Ion *m/e* = 304

The mass spectrum showed a molecular ion at *m/e* 304. The base peak at *m/e* 236 ($C_5HCl_5^{\dot{+}}$) and the peak at *m/e* 68 ($C_5H_8^{\dot{+}}$) presumably arise from retro-Diels-Alder processes (DAMICO, 1972). The two other major ions in the spectrum result from the loss of one chlorine from the molecular ion (*m/e* 269, $C_{10}H_9Cl_4^+$) and the major retro-Diels-Alder product (*m/e* 201, $C_5HCl_4^+$), respectively.

The orientation of the chlorine and hydrogen atoms at the methylene bridge was determined by NMR spectroscopy. The proton on the methylene bridge yields a singlet, which undergoes an up-field solvent-induced shift of 0.68 τ when the solvent was changed from deuterochloroform to deuterobenzene. This indicated that the methylene proton was anti to the dechloro olefin moeity of the molecule. An up-field shift is indicative of the anti position (CHAU, 1974).

RESULTS AND DISCUSSION

The amount of chloride ion produced in the dechlorination of heptachlor is a function of the solvent and the amount of sodium borohydride added. Table 1 shows the data obtained from chloride titrations of the reactions with heptachlor where these parameters were varied.

TABLE 1

Chloride Produced in the Dechlorination of 1 mmol of Heptachlor in the Presence of 0.5 mmol $NiCl_2$ as a Function of Solvent and $NaBH_4$ Added

Solvent (30 ml)	$NaBH_4$ (mmol)	Chloride Produced (mmol)
Methanol	5	2.02
	10	2.31
	15	2.39
	30	2.35
Ethanol	5	1.67
	10	1.94
	15	2.03
	30	2.18
2-Propanol	5	1.37
	10	1.88
	15	2.06
	30	2.23
Methanol*	15	0.33*

*Control to measure the extent of dechlorination in the absence of Ni_2B.

The maximum dechlorination is obtained in methanol with a molar ratio of heptachlor:$NaBH_4$:Ni(II) = 1:15:0.5. No totally dechlorinated heptachlor, tricyclo [5.2.1.0^{2,6}] decane, was found in the product mixture. The major product, as mentioned earlier, was the anti isomer of the pentachloro compound (IV) with lesser amounts of the syn isomer of IV and the tetrachloro compoumd V. Trace amounts of compounds VI, VII and VIII were observed. No unreacted heptachlor remained after 30 minutes reaction time.

The dechlorination of chlordane yields a product distribution which is similar to that for heptachlor. The effect of varying the concentration of $NaBH_4$ was studied by holding the concentration of Ni(II) constant and using only methanol. The chlorine content of the extracted product was compared with that of the unreacted technical chlordane. Table 2 presents these data.

TABLE 2

Percentage of Chlorine in Products of the Dechlorination of Technical Chlordane as a Function of Sodium Borohydride Added[1]

$NaBH_4$ (mmol)	Chlorine Content of Product (% Cl)	Average Number of Cl Atoms/Molecule
0	65.4	7.16
5	58.1	5.25
10	49.9	4.00
15	46.4	3.45
20	43.2	3.06

[1] 0.82 g of technical chlordane were dissolved in 30 ml of methanol containing 0.5 mmol $NiCl_2$

The rate of addition of the sodium borohydride to the methanol solutions of chlordane and nickel chloride was not a factor in the efficiency of the reaction. The catalyst concentration was also found to have little effect on the extent of dechlorination as seen in Table 3.

TABLE 3

Percentage of Chlorine in the Product as a Function of the Chlordane/$NiCl_2$ Ratio[1]

Chlordane/$NiCl_2$	Chlorine in Product (%)
2/1	54.8
20/1	53.5
80/1	58.1

[1] 0.82 g of technical chlordane were dissolved in 30 ml of methanol and 10 mmol of $NaBH_4$ was added.

In order to use the $Ni_2B/NaBH_4$ system as a possible disposal technique the toxicity and biodegradibility of the reaction product mixtures should be determined. In addition the applicability of the catalytic dechlorination system to heptachlor and chlordane formulations require testing.

REFERENCES

CHAU, A.S.Y., A. DEMAYO, J. APSIMON, J. BUCCINI and A. FRUCHIER: J.A.O.A.C., 57, 205 (1974).

DENNIS, W.H. AND W.J. COOPER: Bull. Environ. Contam. Toxicol., to be published.

DAMICO, J.N. "Pesticides" in Biochemical Applications of Mass Spectrometry ed. G.W. Waller, Wiley-Interscience N.Y., N.Y. p. 623-654 (1972)

MARTIN, H. ed., Pesticide Manual, 3 ed., British Crop Protection Council, 1972.