Chromous Chloride Reductions. III.* Identification of Products Obtained from Prolonged Contact of Chlordene and Heptachlor with Chromous Chloride Solution.

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Introduction

Recently, a simple and sensitive confirmatory test for heptachlor pesticide residue was reported (1). It was based on the almost quantitative reductive dechlorination of heptachlor by Cr Cl_2 solution to chlordene. It was also found that p,p'-DDT(2), p,p'-DDD(2) and o,p'-DDT(3) also reacted with $CrCl_2$ solution; however, these compounds reacted at a much slower rate than that of heptachlor. Continued investigation on the reaction of $CrCl_2$ with other organochlorinated pesticides revealed that endrin was reduced to a pentachloro-pentacyclic ketone (4). In this communication, the author wishes to report his findings on the reactions of chlordene and heptachlor upon prolonged contact with $CrCl_2$.

Materials and Method

Materials

1) Petroleum ether (b.p.30-60°C), acetone and benzene were redistilled in an all glass system using a fractionation column (10 cm. x 2 1/2 cm. o.d.) packed with glass helices.

2) Aqueous chromous chloride solution (Fisher Scientific Company) was used without prior treatment.

3) Decolorizing charcoal (Fisher Scientific Company), nanograde hexane, analytical grade chloroform and methanol were used without prior treatment.

4) Thin layer chromatography: (a)TLC plates were coated with silica gel G to provide a layer thickness of 0.25 mm (for monitoring reaction mixtures) and 0.5 mm (for separation and purification). Plates were allowed to stand for half-hour and dried in an oven at 120°C for 3 hrs. prior to use; (b) developing solvents for 0.25 mm plates were 0.2ml acetone in 200 ml hexane; for 0.5 mm plates were 0.5 ml acetone in 200 ml hexane; (c) chromogenic solutions:

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*References (1) and (2) are considered as Part I and II of the series.

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Mitchell's (5) $AgNO_3$ spray and procedure were used to visualize developed 0.25 mm plates. To locate bands on preparative TLC plates (0.5 mm thick) water spray or U.V. light was used.

5) Pesticide standards: pure heptachlor and chlordene were obtained from Velsicol Chemical Corp., Chicago, U.S.A. Heptachlor was used without prior purification. Chlordene was passed through basic alumina (Woelm activity grade I), eluted with petroleum ether and recrystallized from the same solvent. These steps were necessary since 'aged' chlordene contained trace amount of chlordene epoxide resulting from partial oxidation particularly if not stored in the dark in a tightly capped bottle.

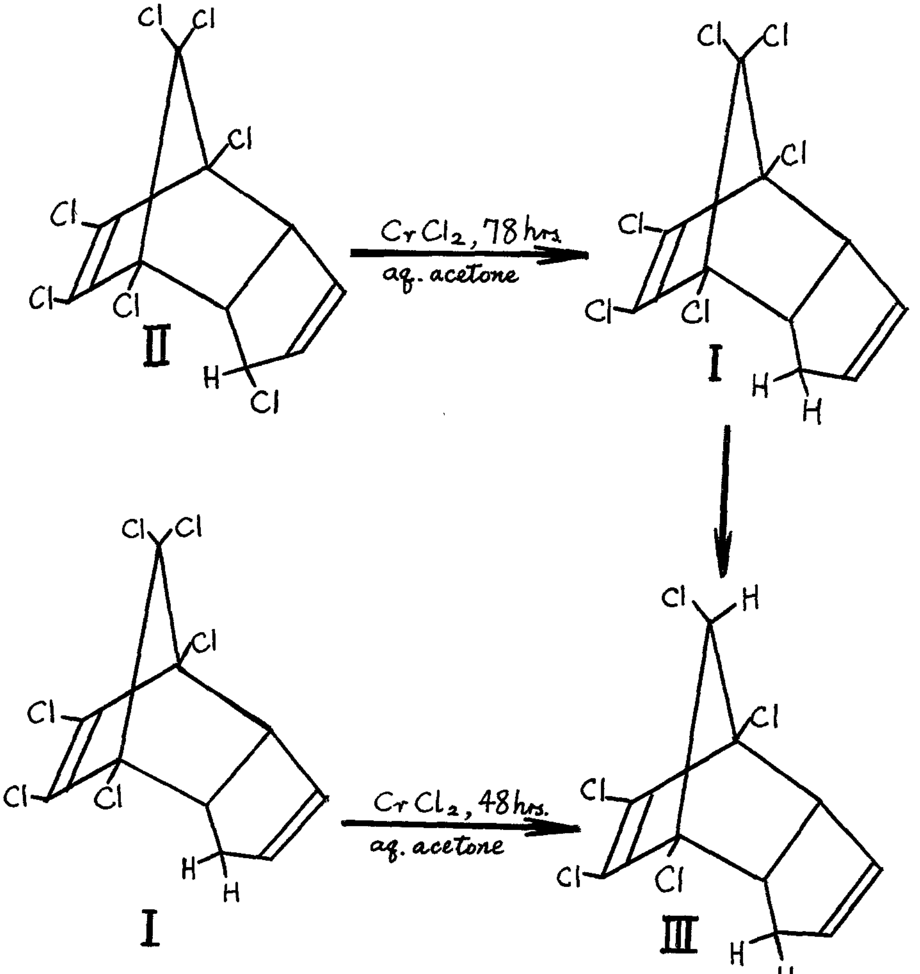
Instruments

IR spectra were recorded on a Beckman IR-7 in Nujol mulls. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. NMR spectra were determined at 60Mc/sec on a Varian 60Mc instrument; chemical shifts are given in τ units relative to tetramethylsilane as an internal standard. Sample concentrations were approximately 10% (W/V) in deuterochloroform as solvent.

$CrCl_2$ reduction of chlordene (I)

One gram of chlordene and approximately 190 ml of redistilled acetone were placed in a 250 ml two necked flask, equipped with a magnetic stirrer, dropping funnel and gas inlet. After the flask was flushed with N_2 for 5 to 10 minutes, approximately 130 ml $CrCl_2$ solution was added through the dropping funnel. The reaction mixture was refluxed under nitrogen and monitored by TLC (0.25 mm Silica gel G plates). After approximately 48 hrs., the reaction mixture was cooled, concentrated under vacuum to half of the original volume, diluted with 500 ml of distilled water and extracted with chloroform (4x75 ml). The dried (anhydrous Na_2SO_4) chloroform extracts were evaporated under vacuum. The resulting greenish oil was purified by rapid passage, under suction, through 20 gm of decolorizing charcoal. Elution with petroleum ether and subsequent evaporation gave a clear viscous oil which crystallized upon standing. Several recrystallization from ether-hexane (1:9) at 0°C afforded pure sample (0.74 gm), m.p. 102-103°C.

Calcd. for $C_{10}H_7CI_5$: C,39.5%;H,2.3°/o;
Cl,58.2%,
Found : C,39.55%;H,1.91%;
Cl,57.85%.


II
CrCl₂, 78 hrs.
aq. acetone
I
I
CrCl₂, 48 hrs.
aq. acetone
III

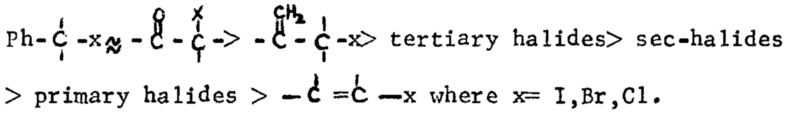
$CrCl_2$ reaction with heptachlor (II)

One gram of heptachlor was refluxed under N_2 with approximately 100 ml acetone and 130 ml aqueous $CrCl_2$ solution in the manner described previously. The reaction mixture was monitored by TLC as before. After approximately 20 hrs. all the heptachlor disappeared and two spots, one major and one minor appeared. The major spot had the same retention time and rf value as that of chlordene. TLC analysis of the mixture after further refluxing showed that the major spot decreased in intensity whereas the minor spot increased in intensity. After 78 hours, the reaction mixture was extracted and purified by passing through decolorizing charcoal as described above. The resulting yellow viscous oil resisted crystallization even after standing at 0°C for several days. Preparative TLC (0.5 mm thick) yielded two major bands. These were extracted with ether to give 0.31 and 0.52 gm solid respectively. The solid from the upper band was identical in every aspect with chlordene. (IR, TLC and mixed melting point). The crystals from the lower band were purified by preparative TLC and recrystallized from ether-hexane. Its IR spectrum was superimposable to that of the product, m.p. 103°C, obtained from $CrCl_2$ reduction of chlordene.

Results and Discussions

Under the conditions used for the confirmation of heptachlor by $CrCl_2$ reduction, i.e. 45 min. at 60°C, chlordene was not reduced. Significant reaction had not occurred even after several hours of contact with this reagent at 60°C. However, partial reduction was observed (by TLC analysis) when chlordene was in contact with $CrCl_2$ solution at 60°C overnight. After 3 or 4 days under the same conditions, chlordene was converted to a pentachloro compound (III), m.p. 103°C, with over 60% yield. At refluxing temperature, complete reduction was observed after 48 hours and a yield of over 85% for III was obtained. The same compound in lower yield was also obtained from Zn/HOAc reduction of chlordene or heptachlor. It is interesting to note that chlordene and the pentachloro compound (III) have the same retention time in gas chromatographs using either a 1:1 mixture of 4% DC-11 and 6% QF-1 on acid washed Chromosorb W as column packing materials. Differentiation between these two compounds can be obtained from TLC as described above and also from chemical confirmative tests to be reported later.

The reduction of heptachlor by $CrCl_2$ to III was a two stage process as demonstrated by its reduction first to chlordene and then to the pentachloro compound (III). As discussed elsewhere (4), the first stage of reduction to chlordene was much faster than the second stage due to the more labile allylic chloride as compared to the gem-dichloride. This is in accord with the reactivity series of various halides towards chromous ion as observed by Castro and Kray (6):



$$\text{Ph}-\overset{|}{\underset{|}{C}}-x \approx -\overset{O}{\overset{\|}{C}}-\overset{X}{\overset{|}{\underset{|}{C}}}-> -\overset{CH_2}{\overset{\|}{C}}-\overset{|}{\underset{|}{C}}-x> \text{tertiary halides}> \text{sec-halides}$$

$$> \text{primary halides} > -\overset{|}{C}=\overset{|}{C}-x$$

where x= I,Br,Cl.

The structure of the pentachloro compound followed in part from its mode of preparation and correct analysis. Corroborative evidence was provided by IR and NMR spectra. IR confirmed the presence of ClC=CCl moiety at 1600 cm^{-1}. NMR confirmed the presence of a chloromethylene moiety (a sharp singlet at 5.64τ). As expected, with the exception of this singlet, the NMR spectrum of III was identical to that of chlordene. The chemical shifts, in τ units, of protons in these two compounds are summarized below for comparison.

COMPDS	Olefinic protons	chloro-methylene proton	bridge-head protons	allylic protons
CHLORENE	4.3(m)	———	6.12(m) 6.51(m)	7.58(m)
III	4.2(m)	5.64(s)	6.35(m) 6.75(m)	7.50(m)

m = multiplet, s= singlet

The present spectroscopic data cannot differentiate whether the chlorine atom of the chloromethylene moiety in III is anti- or sym- to the chloro-olefin; however, based on the work of Williamson, Hsu and Young (7) on the reductive dechlorination of hexachloro-bicycloheptene derivatives, the present pentachloro compound was assigned to have the stereochemistry as depicted. This is also in line with mechanism of chromous ions reduction whereby the Cr^{++}ions, as a six ligand complex, attack preferably the less hindered anti-chlorine rather than the hindered sym-chlorine.

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