Chromous Chloride Reductions. IV. Reaction of Endrin with Chromous Chloride Solution.

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Introduction

Recently, during investigations on the applicability of chromous chloride as a reducing reagent for the confirmation of heptachlor residue (1) via reductive dechlorination, it was observed that p,p'-DDT(2), p,p'-DDD(2) and o,p'-DDT(3) also reacted with $CrCl_2$ although to a much slower rate than that observed for heptachlor. Chlordene and heptachlor, upon prolonged contact with $CrCl_2$, were converted to the same pentachloro derivative (4). Subsequent investigation indicated that other pesticide such as endrin, aldrin, heptachlor epoxide, dieldrin, cis- and trans-chlordane etc. were also reduced, to a more or less extent, upon prolonged contact with $CrCl_2$ reagent. In continuing the series of reports on the investigation of $CrCl_2$ reactions with other pesticides, the author wishes to report the reduction of endrin by $CrCl_2$ solution. Reduction of endrin by zinc and acetic acid is also discussed.

Materials and Methods

Reagents

1) Analytical grade hexane, petroleum ether (b.p. 30-60°C) and acetone were redistilled once using a fractionation column (12x2 1/2 cm. o.d.) lightly packed with glass helices.

2) Chromous chloride solution (Fisher Scientific Company), neutral alumina (Woelm, activity grade 1), glacial acetic acid and analytical grade chloroform were used without prior treatment.

3) Analytical grade zinc powder was prewashed in sequence with distilled water, redistilled acetone and ether and dried in an oven at 200°C overnight.

4) Endrin (99%) from City Chemical Corp., New York, U.S.A. was dissolved in benzene-hexane (3:7) and passed through charcoal column. The solid resulting from evaporation of solvent was recrystallized three or four times from hexane-ether (8:2) prior to use for the following experiments.

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Instruments

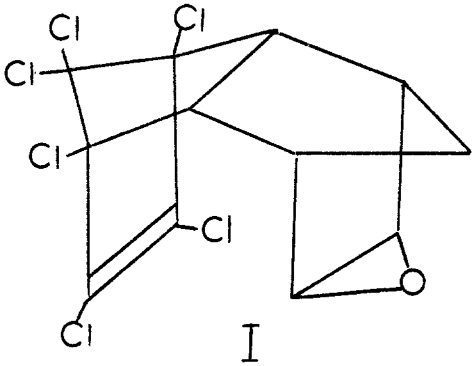
IR spectra were taken on a Beckman IR-7 instrument in Nujol mulls and in chloroform solution. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected.

Reaction of Endrin with $CrCl_2$

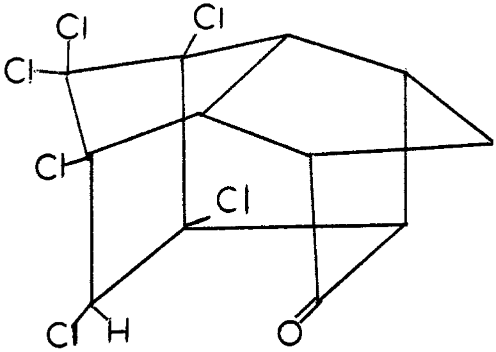
One gram of endrin in approximately 250 ml acetone were placed in a 500 ml two necked flask, equipped with a magnetic stirrer, dropping funnel and gas inlet. After the flask was flushed with N_2 for 5-10 min., 180-200 ml aqueous $CrCl_2$ solution was added through the dropping funnel. The reaction mixture was stirred at 60°C for 20-22 hrs. under nitrogen. The reaction mixture was then concentrated under vacuum to approximately half the volume. The resulting dark greenish solution was transferred, with chloroform rinsing, to a 1 l. separatory funnel containing approximately 500 ml distilled water and extracted with 6 x 125 ml chloroform. The combined chloroform extracts were washed with distilled water (2x250 ml), dried over anhydrous sodium sulfate and evaporated to give an oily gum. Tituration with ether immediately produced white crystals (0.85 gm). The crystals were washed several times with ether and recrystallized from benzene-methanol (6:4) to obtain big stout crystals. Two recrystallizations from chloroform at 5-10°C gave an analytical sample of (I), m.p. 202-203°C.

Zn/HOAc reaction with endrin

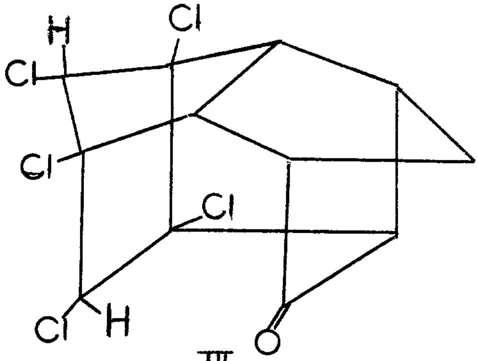
In a 50 ml round bottom flask, 1 gm. of endrin was dissolved in 25 ml of hot glacial acetic acid. After dissolution, approximately 1 gm. of Zn powder was added and the mixture was refluxed. GLC analysis of the reaction mixture indicated the reaction took place in the first 10 minutes and after 20 minutes only a small amount of starting material was left (based on peak height). The reaction mixture was allowed to cool slowly to room temperature. The solution was then filtered and the residue washed with 3 x 20 ml hot chloroform. The combined filtrate and chloroform washings were transferred to a 1 l. separatory funnel containing ca. 500 ml distilled water and the mixture extracted with chloroform (4 x 100 ml). The combined chloroform extracts were washed with 100 ml 5% NaOH solution followed by 3 x 250 ml water. Evaporation



I



II



III

of the dried chloroform extract gave a yellowish gum which, after being dissolved in a minimum volume of benzene, was passed through 30 gm. decolorizing charcoal. Elution with a 150 ml benzene-hexane (8:2) mixture gave,after evaporation of solvent, a light yellowish oil. This oil was chromatographed over an alumina (40gm) column. Petroleum-ether elution gave 0.12 gm. of a clear oil which crystallized upon standing. IR and GLC analysis indicated it was the starting material. Benzene-petroleum ether (9:1) mixture eluted a gummy solid (0.54 gm). Two recrystallizations from chloroform-methanol (7:3) at 0°C gave stout crystals, m.p. 202-203°C, identical in every aspect with the product obtained above from $CrCl_2$ reduction. Benzene and benzene-chloroform (1:1) eluted yellow oil. Separation by preparative TLC (silica gel) gave 0.12 gm of white solid. Recrystallization from hot acetone gave stout crystals, m.p. 280°C.-282°C. Its IR spectrum was identical to the pentacyclic ketone (II) obtained from thermal (5) isomerization of endrin.

Results and Discussions

Reaction of endrin with $CrCl_2$ afforded a pentachloro-pentacyclic ketone (I) in high yield (80-90%). Based on IR spectrum, elemental analysis and mechanistic consideration, its structure is tentatively assigned as I. IR spectrum confirmed the absence of the ClC=CCl moiety indicating that transannular reaction had occurred to form the half-cage compound. The presence of a pentacyclic ketone is suggested by the absorption at 1749 cm^{-1}. The inertness of I towards hydroxylamine hydrochloride, semicarbazide, 2, 4-dinitrophenylhydrazine and sodium bisulfite could be explained by the steric congestion around the carbonyl group, a situation reminiscent of the behaviour of ketone II towards these reagents. Elemental analysis, which agreed with the formulation $C_{12}H_9Cl_5O$, indicates that the compound contains 5 chlorine atoms. The stability of the bridgehead chlorines and chloro-olefin moiety renders the dechlorination at these positions in the molecule unlikely. The comparatively more reactive gem-dichloride suggests that it is the site for monodechlorination by either $CrCl_2$ or Zn/HOAc. Based on the finding of Williamson et al. (6) on the Cr^{++} ion reduction of hexachlorobicyclohexanes, the present pentachloro ketone I was assigned with the anti-chloro stereochemistry.

In view of the ease of acid-catalyzed isomerization of endrin (7) to the pentacyclic ketone (II), it is tempting to postulate that under the acidic $CrCl_2$ solution

(PH 3.9), the hexachloroketone (II) was the intermediate which was subsequently reduced to the pentachloroketone (I). The route to this pentachloro compound and the application of the $CrCl_2$ reaction to the confirmation of endrin at pesticide residue level in various agricultural sample extracts will be the subject of future communications.

Acknowledgment

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