Chromous Chloride Reductions. V. Reaction of Endrin Ketone (II) with Chromous Chloride Solution

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Introduction

In the previous report (1), the isolation of a pentachloropentacyclic ketone from $CrCl_2$ reduction of endrin has been described. Based on IR spectroscopy, elemental analysis, mechanistic considerations and findings of Williamson et al (2), structure (III) was assigned to this compound. In view of the ease of acid-catalyzed isomerization of endrin (I) to the pentacyclic ketone (II), it was postulated that under acidic $CrCl_2$ solution (pH 3.9) the hexachloro-ketone (II) was the intermediate which was subsequently reduced to the pentachloro-ketone (III). We now wish to report our finding to substantiate this postulation.

Materials and Method

Reagents

1) Analytical grade hexane was redistilled as described previously (1).
2) Chromous chloride solution (Fisher Scientific Co.) was used without prior purification.
3) Endrin (99%) from City Chemical Corp., New York, U.S.A. was purified as described previously (1).

Instruments

IR spectra were taken on a Beckman IR-7 instrument in Nujol mulls or in chloroform solution.

Melting points were determined on a FISHER-JOHNS hot stage apparatus and were reported uncorrected.

Preparation of endrin ketone (II)

Using a pestle and mortar, grind 1.3 gm. of endrin with with 20 ml. of 90% aqueous H_2SO_4 solution which has been precooled for 15-20 min. in an ice-salt bath. After grinding for 5 min., allow the mixture to stand at room temperature for 1 hr. with occasional grinding. With caution, pour the contents into 200 ml. of ice-cold water. Extract the resulting mixture with 6x125 ml. portions of chloroform. Wash the combined chloroform extracts with 10% NaOH solution and twice with

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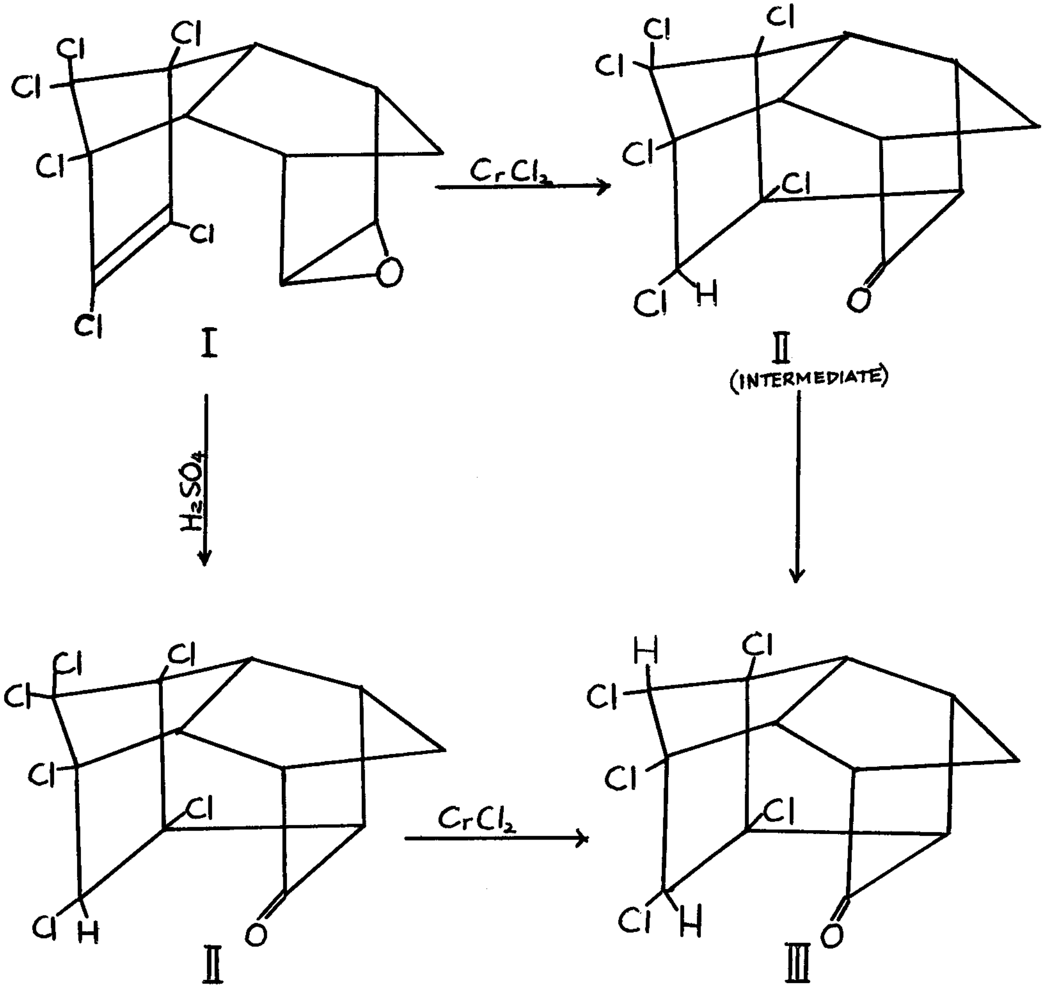
Bulletin of Environmental Contamination & Toxicology,
Vol. 6, No. 6, 1971, published by Springer-Verlag New York Inc.


Cl
Cl
Cl
Cl
Cl
Cl
O
I
CrCl2
H2SO4
II
(INTERMEDIATE)
H
O
II
III
CrCl2

200 ml. of distilled water. Dry the extract by a rapid passage through 100 gm. of anhydrous Na_2SO_4 and then concentrate under vacuum to approximately 30-40 ml. Add an equal volume of benzene and then pass through a 50 gm. decolorizing charcoal column under suction. Wash the column with an additional 50 ml. of benzene. Combine the eluates and concentrate them to 10-15 ml. Allow the solution to stand at 10-15°C overnight to obtain large crystals (0.8 gm.). Recrystallization from boiling chloroform affords a pure sample, m.p. 280°C; identical to the product obtained from thermal isomerization of endrin (3).

$CrCl_2$ reduction of endrin ketone (II)

Dissolve 2.2 gm. of endrin ketone (II), prepared as above, in 230 ml. of boiled and cooled acetone. Place the solution in a magnetic stirrer, dropping funnel and a gas inlet. After flushing the flask with N_2 for 5-10 min., add 180 ml. of aqueous $CrCl_2$ solution through the dropping funnel. Connect one end of the rubber tubing to the mouth of the dropping funnel by means of a one-hole stopper fitted with a glass tube and immerse the other end in a large flask of water. Alternatively, a three-necked flask consisting of a gas inlet, outlet and a dropping funnel can be used. Stir the reaction mixture under nitrogen overnight at 60°C. Concentrate the reaction mixture under vacuum to approximately half the volume and transfer the resulting dark greenish solution, by rinsing with chloroform, to a 1 l. separatory funnel containing approximately 600 ml. of distilled water and extract five times with 150 ml. chloroform. Wash the combined chloroform extracts with 300 ml. of distilled water and dry the extracts by rapid passage under suction through 150 gm. of anhydrous sodium sulfate. Evaporate the extract to dryness under vacuum to give 1.7 gm. of solid. Recrystallize this three times from benzene-methanol mixture to give stout crystals, m.p. 202-203°C. An admixture with the pentachloro-ketone described previously (1) shows no depression in melting point. This product also has identical IR spectrum to that of the pantachloro-ketone.

Results and Discussion

Endrin is known to undergo isomerization to a pentacyclic ketone (II) thermally (3), photochemically (4), and chemically in the presence of boron trifluoride (5). It has also been shown (6) that many acids such as hydrochloric acid, hydrobromic acid, perchloric acid and sulfuric acid also induce such isomerization. Sulfuric acid is the preferred reagent because of fewer side reactions, higher yield and shorter reaction time for complete isomerization. We used 90% H_2SO_4 for the macro-scale preparation of this pentacyclic ketone (II) in order to decrease charring as in the case when concentrated sulfuric acid was used. On the other hand, diluted sulfuric acid resulted in a slightly lower yield of endrin ketone (II) and also a longer reaction time for complete isomerization.

Reaction of endrin ketone (II) with $CrCl_2$ yeilded a product identical in every aspect to the pentachloro-pentacyclic ketone (III) obtained by treatment of endrin with $CrCl_2$ directly (1). As expected, it required less time for the conversion to the pentachloro-ketone (III) from endrin than directly from endrin. In one experiment, endrin was reacted with $CrCl_2$ solution for 14-18 hrs. Both GLC and TLC analysis of the reaction extract indicated the presence of pentacyclic ketones (II) and (III); (III) being the major product. All these experiments showed that endrin ketone (II) was the intermediate during the reduction of endrin with $CrCl_2$.

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