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# Dehydrochlorination of 1-Trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDT Isomer)[1]

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It has been shown[2] that the major product in technical DDT besides *p,p'*-DDT (1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane) is the *o,p'*-DDT isomer, 1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (I), and procedures for its synthesis or separation from technical DDT have been described. It has been also reported by the same workers that alcoholic potassium hydroxide converts I to the corresponding olefin, 1,1-dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethylene (II). In view of the importance of *p,p'*-DDT as an insecticidal agent, it was of interest to study some of the reactions of the *o,p'*-DDT isomer.

*o,p'*-DDT, when pure, is a reasonably stable compound. It does not eliminate hydrogen chloride upon heating at 115–120° for two hours. Decomposition of *o,p'*-DDT, like that of *p,p'*-DDT,[3] is catalyzed by traces of anhydrous ferric chloride; 1 mole of hydrogen chloride is eliminated and the olefin II results.[4]

One property of *p,p'*-DDT which has found use in methods of analysis[5,6] is the fact that a sample when treated with ethanolic potassium or sodium hydroxide will eliminate exactly 1 mole of hydrogen chloride. In the typical procedure the ethanolic solution of DDT and excess base is heated at reflux for a short period, cooled and acidified, and the solution is titrated for chloride ion by the Volhard procedure. When *o,p'*-DDT was first isolated from technical DDT in this laboratory, it was submitted to this procedure and it was noted that more than 1 mole of chloride ion was liberated, 1.1 to 1.2 moles usually being formed.

The product from these experiments was worked up in the usual fashion, the neutral fraction being the olefin II, and a small amount of alkali-soluble material was isolated. Larger quantities of this acidic material, *o,p'*-dichlorodiphenylacetic acid (III), were obtained by carrying out the hydrolysis with barium hydroxide in ethylene glycol at about 175°, following the method of White and Sweeney[7] for *p,p'*-DDT.

The mode of formation of III from *o,p'*-DDT was of some interest. It was noted at first that time of refluxing with alkali did not affect the amount of chloride produced, an indication that the olefin II was not an intermediate in the formation of acid. This was confirmed by an experiment in which it was found that the olefin was unaffected by refluxing ethanolic alkali, a discovery suggesting that olefin and acid are formed by independent reactions. With the idea that the reaction to form acid might be of the solvolytic type and therefore subject to catalysis by silver salts, *o,p'*-DDT was treated with silver carbonate in an acetone–water mixture. The *o,p'*-DDT was only slightly attacked and no acidic product was obtained. Boiling with ethanolic silver nitrate was also without effect. When *o,p'*-DDT was treated with ethanolic sodium hydroxide at room temperature, only 1.0 mole of chloride was liberated.[7a]

An independent synthesis of III was carried out by condensing *o*-chloromandelic acid with chlorobenzene in the presence of sulfuric acid. The acid was purified through the methyl ester, and identity with the product of hydrolysis was shown by mixed-melting-point determinations of the acid and ester.

When the hydrolysis with barium hydroxide in ethylene glycol was effected at above 190°, decarboxylation of the acid occurred and *o,p'*-dichlorodiphenylmethane (IV) was obtained. This was an oil, freezing in a refrigerator and melting at 15°. The position of the ring chlorine atoms in the whole series of compounds was shown by oxidation with chromic anhydride of IV to *o,p'*-dichlorobenzophenone.

## Experimental

**Dehydrochlorination of *o,p'*-DDT.**[8]—A typical quantitative experiment was as follows: 50 ml. of 0.0140 *M* *o,p'*-DDT (0.700 millimole) in 95% ethanol was mixed with 20 ml. of 0.35 *M* ethanolic sodium hydroxide and the resulting solution was heated at reflux for thirty minutes. The solution was cooled, 25 ml. of 1.5 *M* nitric acid was added, and the solution was titrated for chloride ion by the Volhard procedure requiring 0.802 milliequivalent of silver nitrate. This is equivalent to 1.15 moles of chloride ion per mole of *o,p'*-DDT. Similar experiments with amounts of *o,p'*-DDT up to 1.3 g. and with excess of base (either potassium or sodium hydroxide) ranging from 30 to 1,500% gave 1.1 to 1.2 moles of chloride ion per mole of *o,p'*-DDT, with no apparent consistency in results.[9] One experiment,

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[2] Haller, Bartlett, Drake, Newman and co-workers, THIS JOURNAL, **67**, 1591 (1945).

[3] Fleck and Haller, *ibid.*, **66**, 2095 (1944).

[4] Fleck and Haller, unpublished work.

[5] Gunther, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 149 (1945).

[6] Neal and co-workers, *U. S. Pub. Health Serv.*, *Pub. Health Repts.*, Suppl. No. 177 (1944).

[7] White and Sweeney, *ibid.*, **60**, 66 (1945).

[7a] As noted by the Referee, the evidence suggests that the formation of olefin is a bimolecular elimination reaction involving attack of the base on the hydrogen atom attached to the phenylated carbon whereas the formation of acid is a hydrolysis initiated by the bimolecular attack of the hydroxyl ion upon the carbon of the trichloromethyl group.

[8] The authors are indebted to R. A. Hayes for aid in some of this work.

[9] Further data may be found in a paper by Soloway, Schechter and Jones, *Soap and Sanit. Chem.*, submitted for publication.

which could not be repeated, gave only 1.02 moles per mole. Increasing the length of time beyond fifteen minutes did not affect the amount of chloride ion formed. In an experiment at room temperature 1.009 moles of chloride ion were formed in two days under the conditions described above, and the reaction did not proceed further, the same value being observed on the third and fourth days. When the ethylene II was treated at reflux for two hours with ethanolic sodium hydroxide, less than 0.005 mole of chloride ion per mole of *o,p'*-DDT was formed.

Treatment of *o,p'*-DDT with a solution of ethanolic silver nitrate for two hours at reflux or for two days at 40°, did not result in the formation of any silver chloride. When a sample of *o,p'*-DDT (500 mg., 1.4 millimoles) was refluxed with silver carbonate (17 millimoles) in 67% acetone in water for five hours, only a small amount of silver chloride was formed, and no acidic product could be isolated. The neutral fraction (470 mg.) melted at 67.5–72.4°. It was slightly impure starting material, as one recrystallization from methanol raised the melting point to 73–74° (cor.) alone or when mixed with known *o,p'*-DDT.

A 2.52-g. sample of *o,p'*-DDT was dissolved in about 50 ml. of 95% ethanol, 10 ml. of 0.6 *N* potassium hydroxide was added, and the solution was heated at reflux for one hour. Back titration with standard acid indicated that 1.21 moles of base had been consumed. The neutral fraction, which consisted of the olefin II, weighed 2.12 g. (94%). The acid fraction weighed 81 mg. (4%), and was obtained as an oil, which crystallized slowly to a solid, melting after recrystallization from petroleum ether (b. p. 60–70°) at 105–107° (cor.). A mixed melting point with synthetic *o,p'*-dichlorodiphenylacetic acid was 106–107.5° (cor.).

***o,p'*-Dichlorodiphenylacetic Acid (III).**—This acid was made on a larger scale by treating 5.00 g. of *o,p'*-DDT with 12.5 g. of barium hydroxide octahydrate in 125 ml. of ethylene glycol. The mixture was heated to boiling, and solvent and water were removed slowly until the still temperature reached 175°. This is similar to the procedure of White and Sweeney[7] for *p,p'*-DDT. The mixture was held at this temperature for three hours, then cooled and diluted with about 200 ml. of water. The mixture was acidified with dilute hydrochloric acid and extracted with several portions of ether. The ethereal extracts were combined and extracted with two 20-ml. portions of 5% sodium hydroxide. The basic extracts were combined, washed with a little ether and acidified. The resulting oil was extracted with ether; the ethereal extract was dried over anhydrous sodium sulfate, and the ether was removed *in vacuo;* 0.50 g. (13%) of an oil was obtained, which solidified upon scratching, melting alone and when mixed with a synthetic sample of III at 107–108° (cor.).

The same acid was synthesized from *o*-chloromandelic acid and chlorobenzene. To a well-stirred mixture of 20.0 g. (0.107 mole) of *o*-chloromandelic acid[10] and 14.5 g. (0.129 mole) of chlorobenzene cooled in an ice-bath, 50 ml. of concentrated sulfuric acid was added dropwise over a period of twenty minutes. Stirring and cooling were continued for one hour and then the reaction mixture was allowed to come to room temperature; stirring was continued for three hours. The mixture was poured onto ice. The taffy-like organic fraction was extracted with ether and washed with water. The ethereal solution was extracted with dilute sodium hydroxide, and the basic extract was acidified with dilute hydrochloric acid and extracted with ether. As previous experience had shown that the product of this condensation was impure and that purification of the free acid was difficult, the dried ethereal extract was treated with diazomethane in ether. The excess diazomethane and ether were removed, and the mixture of methyl esters was distilled. The major fraction, b. p. 152–157° (2 mm.), weighed 17.0 g. (54%). A large amount of high-boiling material, b. p. 235–245° (2 mm.), was formed in the reaction. This material, a very viscous oil, was not further investigated. The main fraction of the distillation, methyl *o,p'*-dichlorodiphenylacetate, was recrystallized from methanol and melted after recrystallization at 70.5–71.2° (cor.).

*Anal.* Calcd. for $C_{15}H_{12}O_2Cl_2$: C, 61.03; H, 4.10; sapon. equiv., 293. Found: C, 60.78; H, 4.34; sapon. equiv., 288.

The melting point was not depressed when this ester was mixed with a sample prepared by the action of diazomethane on the acid prepared by hydrolysis of *o,p'*-DDT.

The methyl ester (4.00 g.) was refluxed with 2.0 g. of potassium hydroxide in 35 ml. of 95% ethanol for three hours. The acid was recovered in the usual manner (99% yield). After recrystallization from petroleum ether (b. p. 60–70°), it melted at 107.5–108.5° (cor.).

*Anal.* Calcd. for $C_{14}H_{10}O_2Cl_2$: C, 59.81; H, 3.59; equiv. wt., 281. Found: C, 60.17; H, 3.68; equiv. wt., 289.

***o,p'*-Dichlorodiphenylmethane (IV).**—The neutral fractions from three barium hydroxide dehydrochlorination reactions of 5-g. samples of *o,p'*-DDT at 175° were combined and retreated with barium hydroxide in ethylene glycol. Solvent and water were removed by slow distillation until the still temperature reached 195°. This temperature was maintained for four hours. The reaction mixture was cooled, diluted with water and acidified. The neutral fraction was isolated by extraction with ether, washing with dilute sodium hydroxide, drying with anhydrous sodium sulfate and removing the solvent. The residue was distilled twice in a Claisen flask, 4.3 g. of a center fraction boiling at 148–151° (3–4 mm.) being collected. Compound IV was an oil ($n^{25}$D 1.5972) at room temperature, but solidified when cooled and scratched. It melted at 15°.

*Anal.* Calcd. for $C_{13}H_{10}Cl_2$: C, 65.84; H, 4.25. Found: C, 65.74; H, 4.43.

A 250-mg. sample of IV was oxidized by treatment for two hours with 0.3 g. of chromic anhydride in 15 ml. of refluxing glacial acetic acid. The reaction mixture was cooled, poured onto ice and allowed to stand until crystallization was complete; 220 mg. of almost pure *o,p'*-dichlorobenzophenone, m. p. 63–65° (cor.), was obtained directly by filtration. The melting point of this material was not depressed by admixture with an authentic specimen.

## Summary

1 - Trichloro - 2 - *o* - chlorophenyl - 2 - *p* - chlorophenylethane (*o,p'*-DDT) has been shown to react with refluxing ethanolic alkali to give 1,1 - dichloro - 2 - *o* - chlorophenyl - 2 - *p* - chlorophenylethylene and *o,p'*-dichlorodiphenylacetic acid. Reaction with barium hydroxide in ethylene glycol at 175° gave larger amounts of the acid.

*o,p'*-Dichlorodiphenylacetic acid has been synthesized by the acid-catalyzed condensation of *o*-chloromandelic acid and chlorobenzene. The methyl ester and the decarboxylation product, *o,p'*-dichlorodiphenylmethane, have been prepared.

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[10] Jenkins, THIS JOURNAL, **53**, 2341 (1931).