[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Isolation of 1,1-Dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane from Technical TDE[1]

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The recent discovery of the effectiveness of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (called *p,p'*-TDE or *p,p'*-DDD), as an anopheline larvicide made it desirable to have on hand a supply of its *o,p'* isomer, 1,1-dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane. This compound had been prepared previously by the condensation of chlorobenzene and 2,2-dichloro-1-*o*-chlorophenylethanol,[2] but the synthesis involved a difficultly available reactant, and optimum conditions had not been worked out. Separation of the isomers by fractional crystallization, an operation successful for *o,p'* and *p,p'*-DDT,[2] was also difficult, since both isomers crystallized in similar appearing crystals. The recent successful separation of *o,o'*-DDT from the *o,p'* and *p,p'* isomers,[3] by a procedure making use of the decrease in reactivity toward dehydrochlorination with ethanolic sodium hydroxide caused by the replacement of *para* by *ortho* chlorine atoms, suggested a parallel experiment for the separation of *o,p'*-TDE from *p,p'*-TDE.

A sample of technical TDE was recrystallized, giving pure *p,p'*-TDE. The oil recovered from the mother liquors was treated with ethanolic sodium hydroxide under conditions calculated[4] to effect the dehydrochlorination of substantially all the *p,p'* isomer and expected to leave unreacted most of the *o,p'* isomer. When this mixture of the unreacted *o,p'* isomer and the olefin related to the *p,p'* isomer was treated with chromic anhydride in glacial acetic acid, the olefin was oxidized to *p,p'*-dichlorobenzophenone but the saturated *o,p'*-TDE was not affected. The ketone–ethane mixture was separated by selective adsorption on and elution from activated alumina, the ketone being held more strongly on the column.

The recrystallized *o,p'*-TDE melted at 75.8–76.8°,[2] and was obtained in 7 to 8% yield from the original crude mixture of isomers. Mixed melting points with known samples[2] were not depressed.

Dinitro and tetranitro derivatives of *o,p'*-TDE, m. p. 134–135.5° and 183–185°, respectively, were prepared. Treatment of *o,p'*-TDE with ethanolic potassium hydroxide resulted in elimination of one mole of hydrogen chloride, but the resulting olefin, b. p. 160° (1 mm.), could not be made to crystallize.

The rate constant for the dehydrochlorination with sodium hydroxide of the *o,p'*-TDE was determined in 92.6% (by weight) ethanol at 20.11° (method used same as described earlier),[4] and a value of 0.000144 liter per second per mole (average of two determinations) was obtained. This compares with a value of 0.00567 for the *p,p'* isomer, and again indicates the importance of the steric and/or electrostatic effect of the *ortho* chlorine atom in hindering the elimination reaction.

Experimental

Separation of 1,1-Dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane from its *p,p'*-Isomer.—A two-hundred gram sample of technical TDE was recrystallized from 450 ml. of 95% ethanol. The solid (129 g.) was fairly pure *p,p'*-TDE and was discarded. The solvent was removed *in vacuo*, and the residual oil was taken up in 1200 ml. of 95% ethanol, brought to 20° in a constant-temperature bath, and treated with 800 ml. of 1 *M* ethanolic sodium hydroxide solution at 20° for exactly thirty minutes. The dehydrochlorination reaction was then stopped by the addition of 40 ml. of concentrated nitric acid in 500 ml. of water. Most of the ethanol was removed *in vacuo*, and the resulting mixture was extracted several times with ether. The ether extracts were washed with water, dilute aqueous sodium hydroxide, and saturated salt solution, and were then filtered. The ether was removed by distillation, leaving 60.4 g. of viscous oil.

This oil was taken up in 200 ml. of glacial acetic acid. To the refluxing solution was added 48 g. of solid chromium trioxide in small portions, violent oxidation occurring at each addition, over a period of one to two hours. Refluxing was continued for about fifteen minutes after the addition was complete. The mixture was cooled and poured onto ice. The presence of excess oxidant was shown by testing with potassium iodide–starch paper. The mixture was extracted twice with ether. The combined ether extracts were washed successively with water, dilute base until washings were basic, and saturated salt solution, and were then filtered. Evaporation of the ether left 49.1 g. of a brown solid mixture.

This solid was divided into two portions, and each portion was treated as follows: The solid was dissolved in 200 ml. of petroleum ether (b. p. 60–70°) and adsorbed on an activated alumina column 42 mm. in diameter and 200 mm. high, which had been washed with 200 ml. of petroleum ether. The column was then washed successively with five 200-ml. portions of petroleum ether, two 200-ml. portions of carbon tetrachloride, and two 200-ml. portions of 95% ethanol. The petroleum ether eluates consisted mostly of *o,p'*-TDE, while the later fractions were mostly *p,p'*-dichlorobenzophenone. The combined petroleum ether eluates from both runs weighed 25.0 g. After two recrystallizations from 95% ethanol, 14.8 g. of *o,p'*-TDE, m. p. 75.8–76.8°, was obtained. This is equivalent to 7.4% of the original technical TDE mixture. The melting point of this sample of *o,p'*-TDE was not depressed when mixed with material isolated from technical DDT[2] or obtained by synthesis.[2]

Dinitro-*o,p'*-TDE.[5]—This derivative was prepared by treatment of 500 mg. of *o,p'*-TDE with 5 ml. of fuming

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

(3) Cristol, Soloway and Haller, *ibid.*, **69**, 510 (1947).

(4) The calculations were made from the known reaction-rate constant previously determined for *p,p'*-TDE: see Cristol, THIS JOURNAL, **67**, 1494 (1945).

(5) The structure of this compound has not been proved but it is presumably 1,1-dichloro-2-(2-chloro-5-nitrophenyl)-2-(4-chloro-3-nitrophenyl)-ethane.

nitric acid for one-half hour at 50°. The reaction mixture was cooled and poured onto ice. The resulting solid was recrystallized from 95% ethanol to constant m. p., 134–135.5°.

Anal. Calcd. for $C_{14}H_8Cl_4N_2O_4$: N, 6.83. Found: N, 7.02.[6]

Tetranitro-*o,p'*-TDE.[7]—A mixture of 500 mg. of *o,p'*-TDE, 2.5 ml. of concentrated sulfuric acid, and 2.5 ml. of fuming nitric acid was heated on a steam-bath for one hour. The reaction mixture was cooled and poured onto ice. The resulting solid was recrystallized from acetone–ethanol to constant m. p., 183–185°.

Anal. Calcd. for $C_{14}H_6Cl_4N_4O_8$: N, 11.21. Found: N, 11.14.[6]

***o,p'*-TDE Olefin.**—A solution of 500 mg. of *o,p'*-TDE and 0.4 g. of potassium hydroxide in 20 ml. of ethanol was heated at reflux for three hours. The resulting mixture was poured into water. The mixture was extracted with ether, and the ether extract was washed with water and saturated salt solution and filtered. The ether was evaporated off, leaving a viscous oil. This oil, b. p. 160° (1 mm.), was distilled in a vacuum sublimation apparatus. The product remained as an oil after standing at room temperature for over a year.

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Summary

1,1-Dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-TDE) has been separated from a mixture with its *p,p'* isomer by a procedure making use of the lowered reactivity with ethanolic sodium hydroxide of the *o,p'* isomer compared with the *p,p'* isomer.

Nitration and dehydrochlorination products of *o,p'*-TDE have been described. The rate constant for the reaction of *o,p'*-TDE with ethanolic sodium hydroxide has been determined.

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[6] The authors are indebted to Mr. Harlan L. Goering for the nitrogen analyses.

[7] The structure of this compound has not been proved, but it is presumably 1,1-dichloro-2-(2-chloro-3,5-dinitrophenyl)-2-(4-chloro-3,5-dinitrophenyl)-ethane.

[CONTRIBUTION FROM PULP MILLS RESEARCH PROJECT, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Lignin. I. Purification of Lignin Sulfonic Acids by Continuous Dialysis

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Introduction

Lignin sulfonic acids[1] have several times been separated from sulfite waste liquor and purified by metal or amine salt precipitations.[2] Although dialysis has been employed as a step in some of these procedures, and has been practically considered by Ogland,[3] no detailed study appears to have been made of the degree of purity and extent of recovery of the lignin sulfonic acids attainable by direct continuous dialysis of sulfite waste liquor. This easily conducted procedure was thought worthy of investigation both as a method for laboratory preparation of purified lignin sulfonic acids for research purposes and as a means of characterization of sulfite waste liquor components.

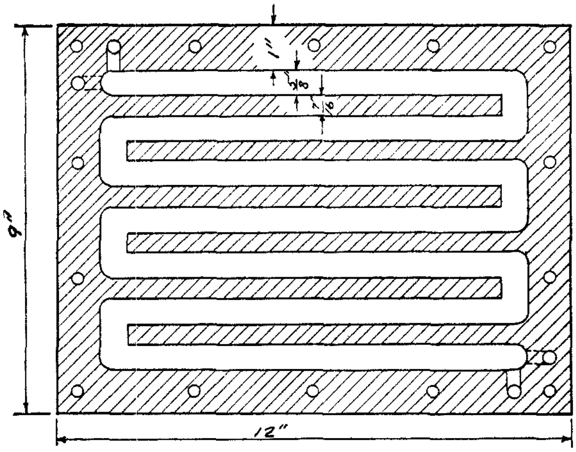

Fig. 1.—Dialyzer plate detail.

Experimental Part

Dialysis Apparatus.—To obtain a high ratio of membrane area to liquor volume and a close approach to true counter-current operation, a multicellular apparatus was constructed from $^1/_8''$ × 9″ × 12″ plates of "Plexiglas." This material was chosen for its resistance to chemical attack, dimensional stability in water, workability, and transparency. The last quality is desirable since it aids detection of air blocks or other obstructions to flow. The cells consisted of zig-zag channels $^5/_8''$ wide sawn in the "Plexiglas" plates. Both liquor and water plates were identical except for interplate connections. The design details are indicated in Fig. 1. Fifteen pairs of such plates were used, each pair being isolated by separator plates of $^1/_{16}''$ "Plexiglas." Connections between cells were by means of ports grooved about half through the plates at the ends of the channels. The ports fed into holes which led through membrane and separator to the next appropriate cell. The entire assembly was held between $^1/_4''$ stainless steel plates by means of 14 stainless steel machine bolts.

The total volume of the apparatus amounted to 2780 ml., and the total membrane area to 0.435 square meter. With no bulging of the membrane, the volumes in liquor and water channels were equal.

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[1] Hagglund, "Holzchemie," Akademische Verlagsgesellschaft. m. b. h., Leipzig, 1939, 2nd. ed., Lithoprinted 1944 by Edwards Bros., Ann Arbor, Michigan.

[2] (a) E. G. King, F. Brauns and H. Hibbert, *Can. J. Res.* (B) **13**, 88 (1935); (b) G. H. Tomlinson and H. Hibbert, THIS JOURNAL, **58**, 340 (1936); (c) H. Erdtman, *Svensk. Papperstidn.*, **45**, 315–323 (1942); (d) W. Lautsch and Piazolo, *Cellulose chemie*, **22**, 48–54 (1944).

[3] N. J. Ogland, *Svensk. Papperstidn.*, **47**, 288–291 (1944).