dichloroisobutane has shown it to contain an unsaturated impurity,[5] the aryloxy derivatives prepared by us probably contain some ethylenic admixture, as would be indicated by the molecular refractivities.

**1-Chloro-2-methyl-3-*o*-cresoxypropane.**—The procedure described above but with 108 g. of *o*-cresol in place of the phenol gave 117 g. (59%) of product of b. p. 112.8–114.5° at 6 mm.; $d^{20}{}_4$ 1.0898; $n^{20}{}_D$ 1.53377.

*Anal.* Calcd. for $C_{11}H_{15}OCl$: Cl, 17.86; *MR*D, 55.91. Found: Cl, 17.91; *MR*D, 56.53.

**1-Chloro-2-methyl-3-*p*-*t*-amylphenoxypropane.**—The use of 164 g. of *p*-*t*-amylphenol gave 81 g. of product of b. p. 135–147° at 3 mm.

*Anal.* Calcd. for $C_{15}H_{23}OCl$: Cl, 13.96. Found: Cl, 14.18.

**Action of Cuprous Cyanide on Eastman 1,3-Dichloroisobutane,**[1b,2]—A mixture of 90 g. (1 mole) of cuprous cyanide and 762 g. (6 moles) of Eastman practical 1,3-dichloroisobutane[5] was stirred and refluxed for twenty-four hours. During the course of the reaction a large lump of tarry material appeared in the flask and the liquid turned dark brown. The liquid was filtered into a distilling flask and the tar washed with a little dichloride. The mixed liquid was distilled at atmospheric pressure to about 140° and the residue fractionated under diminished pressure. In one run in which 2 g. each of the bromides of cobalt, copper and nickel were added, 25.5 g. of liquid 4-chloro-3-methyl-3-butenonitrile and 6.5 g. of solid nitrile (m. p. 51.5–52.5°) were obtained.

The liquid chloronitrile, b. p. 69–70° at 10 mm., has a somewhat ethereal odor and lachrymatory effect. In contact with the skin it gives a stinging burning sensation.

*Anal.* Calcd. for $C_5H_6NCl$: N, 12.12; Cl, 30.68. Found: N, 11.78, 11.07; Cl, 30.72, 29.79.

**Imido-ester.**—A mixture of 9.9 g. of chloronitrile and 5 g. of absolute ethanol was treated with dry hydrogen chloride and poured into 100 cc. of absolute ether. A yield of 13 g. (86.8%) of product was obtained. This was recrystallized by dissolving in anhydrous acetic acid and reprecipitated by the addition of anhydrous ether.

*Anal.* Calcd. for $C_7H_{13}NOCl_2$: N, 7.07. Found: N, 7.46, 7.28, 7.41.

Hartigan by a differential thermocouple method,[30] found that the compound melts at 102°, uncor., with decomposition to give an amide, a white crystalline solid of m. p. 156–157°, cor.

Unlike (IV) the new chloronitrile gave a black resinous mass with sodium amide in liquid ammonia and similar material with phenylmagnesium bromide.[2]

## Summary

1, β-Methyl-γ-chlorobutyronitrile and β-methylglutaronitrile may be prepared by the action of sodium cyanide on 1,3-dichloro-2-methylpropane.

2. 2-Methylcyclopropanecarbonitrile, whose structure has been established by its transformation into the corresponding amide, has been made in a 60% yield by the action of sodium amide on β-methyl-γ-chlorobutyronitrile in liquid ammonia solution.

3. β-Methyl-γ-aminobutyric acid and α-substituted-γ-methylpyrrolines may also be prepared from the β-methyl-γ-chlorobutyronitrile.

4. 2-Phenylpyrroline may be obtained in small yield by the action of phenylmagnesium bromide on γ-phenoxybutyronitrile. Similarly, 2,3-diphenylpyrroline is formed by the reaction of this Grignard reagent with α-phenyl-γ-ethoxybutyronitrile, which may be made from benzylcyanide, sodium amide and cellosolve bromide.

5. The 1,3-dichloro-2-methylpropane reacts with sodium aryloxides to give 1-chloro-2-methyl-3-aryloxypropanes.

6. An impurity in the 1,3-dichloro-2-methylpropane will react with cuprous cyanide to give a new chloronitrile and a solid dinitrile.

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(30) Hartigan and Cloke, THIS JOURNAL, **67**, 709 (1945).

TROY, N. Y. RECEIVED MAY 31, 1945

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[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE, AND THE DEPARTMENTS OF CHEMISTRY OF HARVARD UNIVERSITY, THE UNIVERSITY OF MARYLAND AND THE OHIO STATE UNIVERSITY]

# The Chemical Composition of Technical DDT[1]

BY H. L. HALLER,[2] PAUL D. BARTLETT,[3] NATHAN L. DRAKE,[4] MELVIN S. NEWMAN,[5] STANLEY J. CRISTOL,[2] CHARLES M. EAKER,[4] ROBERT A. HAYES,[2] GLEN W. KILMER,[4] BARNEY MAGERLEIN,[5] GEORGE P. MUELLER,[3] ABRAHAM SCHNEIDER,[3] AND WILLIAM WHEATLEY[5]

The recent discovery of the outstanding insecticidal properties of the product known as DDT and its successful application against the body louse and other disease-carrying insects have aroused considerable interest. Numerous articles praising its merits have appeared in scientific and trade magazines, as well as in newspapers and popular magazines. These usually include the history of its introduction into this country and, as might be expected, the stories are not always in agreement. Probably the most accurate account is given by Froelicher.[6] The studies leading to the discovery of DDT as an insecticide are presented by Läuger, Martin, and Müller.[7]

The symbol "DDT" is a contraction for di-

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[1] These researches were carried out under a transfer of funds to the Bureau of Entomology and Plant Quarantine from the Office of Scientific Research and Development, as recommended by the Committee on Medical Research, and under contracts between Harvard University, University of Maryland, and The Ohio State University, and the Office of Scientific Research and Development, as recommended by the National Defense Research Committee.

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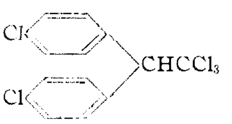
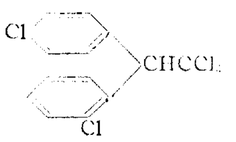
[6] Froelicher, *Soap and Sanit. Chem.*, **20** (7), 115 (1944).

[7] Läuger, Martin and Müller, *Helv. Chim. Acta*, **27**, 892 (1944).

chloro-diphenyl-trichloroethane, the generic name of the active insecticidal principle. Theoretically there are forty-five possible dichlorodiphenyltrichloroethanes. However, the term "DDT" is confined to the product obtained on condensation of chloral (or its alcoholate or hydrate) with chlorobenzene in the presence of sulfuric acid.

At the present time (spring 1945) three grades of DDT are recognized by the War Production Board and the armed forces of this country—technical DDT, purified or aerosol DDT, and pure DDT. As its name implies, technical DDT is a commercial grade complying with all the specifications outlined in the Joint Army-Navy Specifications (JAN-D-56A, Mar. 16, 1945). As will be shown in this report, it is a complex mixture containing upwards of 70% of 1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (hereinafter called *p,p'*-DDT) (I), the major impurity being the *o,p'*-DDT isomer, 1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (II).


I


II

Since technical DDT melts over a range, the setting point is used rather than melting point to give an indication of its purity.[8] Purified or aerosol DDT is a partially refined grade, containing greater amounts of *p,p'*-DDT than the technical grade and having a melting point of not less than 103°. Pure DDT is a highly purified grade of 1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane, m. p. 108.5–109.0° (cor.), and is intended as a standard of comparison for special physiological and pharmacological studies.

Insecticidal preparations containing DDT were first brought to the attention of the United States Department of Agriculture in October, 1942, by the Geigy Co., Inc., New York, N. Y. At that time concerted efforts were being made by the entomologists of the Bureau of Entomology and Plant Quarantine to find suitable substitutes for pyrethrum and derris, the imports of the former being insufficient to meet wartime demands and the supply of the latter having been completely curtailed since the fall of Singapore to the Japanese. The first entomological tests in this country were made in October, 1942, against a number of leaf-eating insects. In November tests were made against the body louse. Some of the early results were published in February, 1944 (Annand, *et al.*[9]). The results were so promising that DDT louse powder was adopted in May, 1943, and one company was requested to undertake the manufacture of DDT on a sizable scale. Pilot-plant production was begun in May, 1943, and by July a creditable showing was being made on a practical scale. Until early in 1944 this company was the sole producer of DDT in this country. By that time the demand had so increased that three other companies were asked to undertake its manufacture. To this group have since been added a number of other companies.

The rapid acceptance of DDT by the armed forces made it imperative to study the composition of the technical product in order that the nature and amount of the by-product materials might be determined and that these products might be compared insecticidally and pharmacologically with *p,p'*-DDT. Accordingly, in April, 1944 the studies on DDT under way in the Bureau of Entomology and Plant Quarantine were augmented by studies at Harvard University, the University of Maryland, and the Ohio State University under a program sponsored by the Office of Scientific Research and Development. Because of the complete coöperation among these groups, it was deemed advisable to present some of their findings in this joint report.

When the expanded program was initiated, only four companies were authorized by the War Production Board to produce DDT. For this reason the studies were limited to products obtained from them.

Of the four coöperating groups, three worked on different samples of technical DDT made from chloral and chlorobenzene, while the fourth worked on a sample of "by-product oil" from which much of the *p,p'*-DDT had been removed by refinement during isolation. In the latter case the process involved condensation of "chlorinated alcohol" and chlorobenzene. The method of attack varied somewhat in the different laboratories; fractional crystallization and chromatographic separations were employed rather generally by all, supplemented in one instance by cryoscopic analysis. Distillation in high vacuum was thoroughly explored as a means of separating the by-product oil into its components. In the experimental section the separation of one of the samples is described in detail; important deviations made in treatment of the other samples are also described.

Results obtained in the isolation of the components of technical DDT are indicated in Table I, as well as values for the *p,p'*-DDT content measured by recrystallization from 75% aqueous ethanol previously saturated with *p,p'*-DDT. This method is reported[10] to give results accurate to within 1%.

The occurrence of the fourteen compounds isolated may be explained from a consideration of the main and side reactions of chloral (and possible impurities in technical chloral) and chlorobenzene (and possible impurities in technical chlorobenzene) in the presence of sulfuric acid, followed by treatment of the product mixture with an alkaline

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(8) Fleck and Preston, *Soap and Sanit. Chem.*, **21**, [5], 111 (1945).

(9) Annand, *J. Econ. Entomol.*, **37**, 125 (1944).

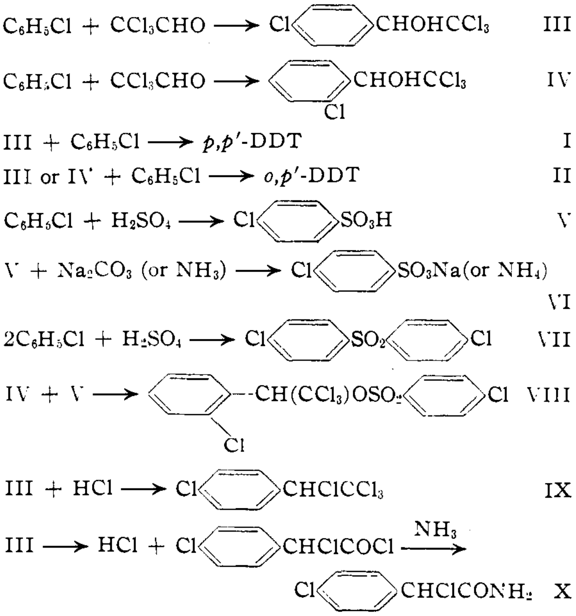
TABLE I

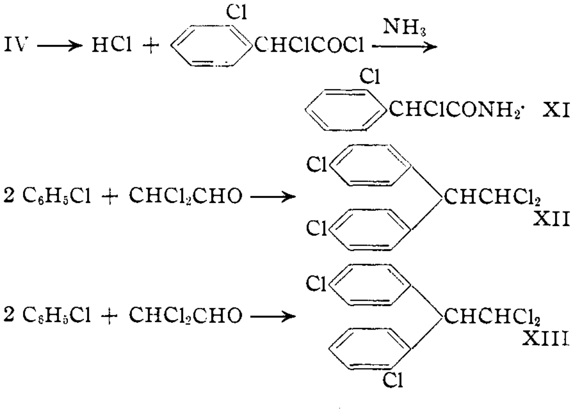
COMPOSITION OF TECHNICAL DDT

| Compound | Sample 1 (Setting point, 91.2°), % | Sample 2 (Setting point, 88.6°), % | Sample 3 (Setting point, 91.4°), % | Sample 4 (By-product oil), % |
|---|---|---|---|---|
| 1-Trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-DDT)[a] | (*a*) 66.7,<br>(*b*) 72.9 | (*b*) 70.5,<br>(*c*) 63.5,<br>(*d*) 64.5,<br>(*e*) 67.9 | (*a*) 72.7,<br>(*b*) 76.7 | ... |
| 1-Trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDT) | 19.0 | (*c*) 7.9,<br>(*d*) 15.3,<br>(*e*) 20.9 | 11.9[b] | 74.8[c] |
| 1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-DDD) | 0.3 | 4.0 | 0.17[d] | ... |
| 1,1-Dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDD) | ...... | ....... | 0.044 | ... |
| 2-Trichloro-1-*o*-chlorophenylethyl *p*-chlorobenzenesulfonate | 0.4 | 1.85 | 0.57 | 0.11 |
| 2-Trichloro-1-*p*-chlorophenylethanol | 0.2 | ....... | ....... | ... |
| Bis-(*p*-chlorophenyl)-sulfone | 0.6 | 0.1 | 0.034 | ... |
| α-Chloro-α-*p*-chlorophenylacetamide | ...... | 0.01 | 0.006 | ... |
| α-Chloro-α-*o*-chlorophenylacetamide | ...... | 0.007 | ....... | ... |
| Chlorobenzene | ...... | ....... | ....... | 2.44 |
| *p*-Dichlorobenzene | ...... | ....... | ....... | 0.73 |
| 1,1,1,2-Tetrachloro-2-*p*-chlorophenylethane | ...... | ....... | ....... | +[e] |
| Sodium *p*-chlorobenzene-sulfonate | 0.02 | ....... | ....... | ... |
| Ammonium *p*-chlorobenzene-sulfonate | ...... | ....... | 0.005 | ... |
| Inorganic | 0.1[f] | 0.04[g] | 0.01[h] | ... |
| Unidentified and losses | 6.5 | 5.1 | 10.6 | 19.4 |

[a] Letters in parentheses refer to analytical methods as follows: (*a*) Isolation from technical DDT, (*b*) recrystallization from 75% aqueous ethanol previously saturated with *p,p'*-DDT (Cristol, Hayes and Haller[10]), (*c*) fractional crystallization, (*d*) adsorption analysis and fractional crystallization, (*e*) isolation, supplemented by cryoscopic analysis on the residue. [b] This value does not represent all the *o,p'*-DDT present, as all oily fractions were not exhaustively studied. [c] Miscellaneous fractions containing *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDD. [d] Includes 0.06% of *p,p'*-DDD isolated as such and 0.11% of the corresponding olefin. [e] Isolated as nitro derivative from an oil mixture analyzing for a mixture of $C_8H_6Cl_4$ and $C_8H_5Cl_5$ and representing 2.54% of original material. [f] Qualitative tests for ferric, lead and magnesium carbonates were obtained. [g] Insoluble in boiling 95% ethanol. [h] Qualitative tests for ferric, ammonium, halide and sulfate ions were obtained.

wash material. These reactions may be summarized as follows





All the compounds isolated from technical DDT have been tested as insecticides, as have the uncrystallizable oils. Although some of the by-products are active insecticides, none of them are so toxic as *p,p'*-DDT.[11]

Of the fourteen compounds isolated from the various samples of technical DDT, seven have been described in the previous literature. These include chlorobenzene, *p*-dichlorobenzene, *p,p'*-DDT (I), 2-trichloro-*p*-chlorophenylethanol (III),

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(10) Cristol, Hayes and Haller, *Ind. Eng. Chem., Anal. Ed.*, **17**, 470 (1945).

(11) The entomological testing of these compounds has been carried out in several laboratories of the Bureau of Entomology and Plant Quarantine.

bis-(*p*-chlorophenyl)-sulfone (VII), and the sodium and ammonium salts of *p*-chlorobenzenesulfonic acid (VI). Chlorobenzene was identified by boiling point and conversion to *p*-nitrochlorobenzene. *p*-Dichlorobenzene was identified by its boiling point, melting point and mixed melting point. The structure of *p,p'*-DDT was established by degradation to *p,p'*-dichlorobenzophenone. The carbinol (III) was converted to its *p*-chlorobenzenesulfonate and this derivative was identical with the ester prepared from a known sample of carbinol.[12] The sulfone (VII) was identified by a mixed melting point with an authentic specimen and by conversion to its dinitro derivative.[13] The cations of the salts of *p*-chlorobenzenesulfonic acid were identified in the usual fashion; the organic portion was identified by conversion to *p*-chlorobenzenesulfonamide and the corresponding anilide.

The remaining compounds isolated apparently have not been described previously. The structure of each of these was established by elemental analysis and degradation to known materials and was confirmed by synthesis.

*o,p'*-DDT (II), 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (XII) and 1,1-dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (XIII) were degraded to the corresponding dichlorobenzophenones and were synthesized by the condensation of chlorobenzene with 2-trichloro-1-*o*-chlorophenylethanol,[14] 2,2-dichloro-1-*p*-chlorophenylethanol and 2,2-dichloro-1-*o*-chlorophenylethanol, respectively.

2-Trichloro-1-*o*-chlorophenylethyl *p*-chlorobenzenesulfonate was degraded to *o*-chlorobenzoic acid and to *p*-chlorobenzenesulfonic acid and its structure was established by synthesis from 2-trichloro-1-*o*-chlorophenylethanol[14] and *p*-chlorobenzenesulfonyl chloride.

α-Chloro-α-*p*-chlorophenylacetamide was degraded to *p*-chlorobenzoic acid and to ammonia and was synthesized by ammonolysis of its acid chloride which was in turn prepared by the reaction of phosphorus pentachloride on *p*-chloromandelic acid. The corresponding *o*-amide, which was not isolated in pure state, was synthesized from *o*-chloromandelic acid in a similar fashion.

1,1,1,2-Tetrachloro-2-*p*-chlorophenylethane was not isolated in pure state, but the nitro derivative of isolated material was shown to be identical with the nitro derivative of the synthetic material obtained by the action of phosphorus pentachloride on 2-trichloro-1-*p*-chlorophenylethanol.

The details of the isolation and synthesis of these compounds are given in the experimental section. Also included in the experimental section are descriptions of a number of compounds prepared either as derivatives or intermediates in the synthesis of the isolated compounds. These include the dinitro derivatives and the olefins obtained by dehydrochlorination of *o,p'*-DDT and *p,p'*-DDD, and α-chloro-α-*p*-chlorophenylacetic acid. 1-Trichloro-2-*m*-chlorophenyl-2-*p*-chlorophenylethane (*m,p'*-DDT) and its olefin and dinitro derivative are also described.

In the course of this work it was necessary to prepare all of the six isomeric dichlorobenzophenones with one chlorine atom on each ring. Of these, the *o,p'*- and *p,p'*-dichlorobenzophenones were already known. *m,p'*-Dichlorobenzophenone was prepared by degradation of *m,p'*-DDT. *o,m'*- and *m,m'*-dichlorobenzophenones were prepared by the addition of *m*-chlorophenylmagnesium bromide to the appropriate chlorobenzonitrile. *o,o'*-Dichlorobenzophenone was prepared by oxidation of *o,o'*-dichlorobenzilic acid or bis-(*o*-chlorophenyl)-carbinol. The acid was prepared by the reaction series, aldehyde, benzoin, benzil, benzilic acid, starting with *o*-chlorobenzaldehyde, and the carbinol was prepared by the addition of *o*-chlorophenylmagnesium bromide to *o*-chlorobenzaldehyde. The preparation and properties of the 2,4-dinitrophenylhydrazones of the six isomeric dichlorobenzophenones are also described.

The recovery of known compounds in the samples varied from 80.6 to 93.5%. It should be noted that the recovery of by-product materials, notably the *o,p'*-DDT isomer, was probably not complete in all cases as in some samples all of the by-product oils were not exhaustively studied. Of the material listed as unidentified, a large part consisted of an uncrystallizable oil which had total and hydrolyzable chlorine analyses equivalent to that of a DDT isomer or isomers. Degradation of two of these oils to olefin by dehydrochlorination and oxidation of the olefinic material with chromic anhydride did not lead to the formation of any solid dichlorobenzophenones other than *p,p'*- and *o,p'*-dichlorobenzophenone, nor did nitration lead to isolation of new solid nitro compounds. The evidence available suggests that these oils were mixtures of DDT isomers.

In the case of sample 2 (Table I) the amounts of *p,p'*DDT and *o,p'*-DDT in the oil and oily solid remaining from the fractional crystallization were estimated cryoscopically. A general method for determining the composition of a mixture is the determination of the freezing point depression produced by that mixture in a series of solvents known or suspected to be components of the mixture. If 1 g. of a mixture of A, B and C is dissolved in a known weight of the solvent X, which is not a component of the mixture, the freezing point depression gives directly $m$, the total number of moles in a gram of the mixture. On the other hand, if the same mixture is dissolved in pure A, the freezing point depression gives the total number of moles per gram which is *not* A, *i.e.*, $m - a$. The difference between these two figures is $a$, the number of moles of A in 1 g. of the

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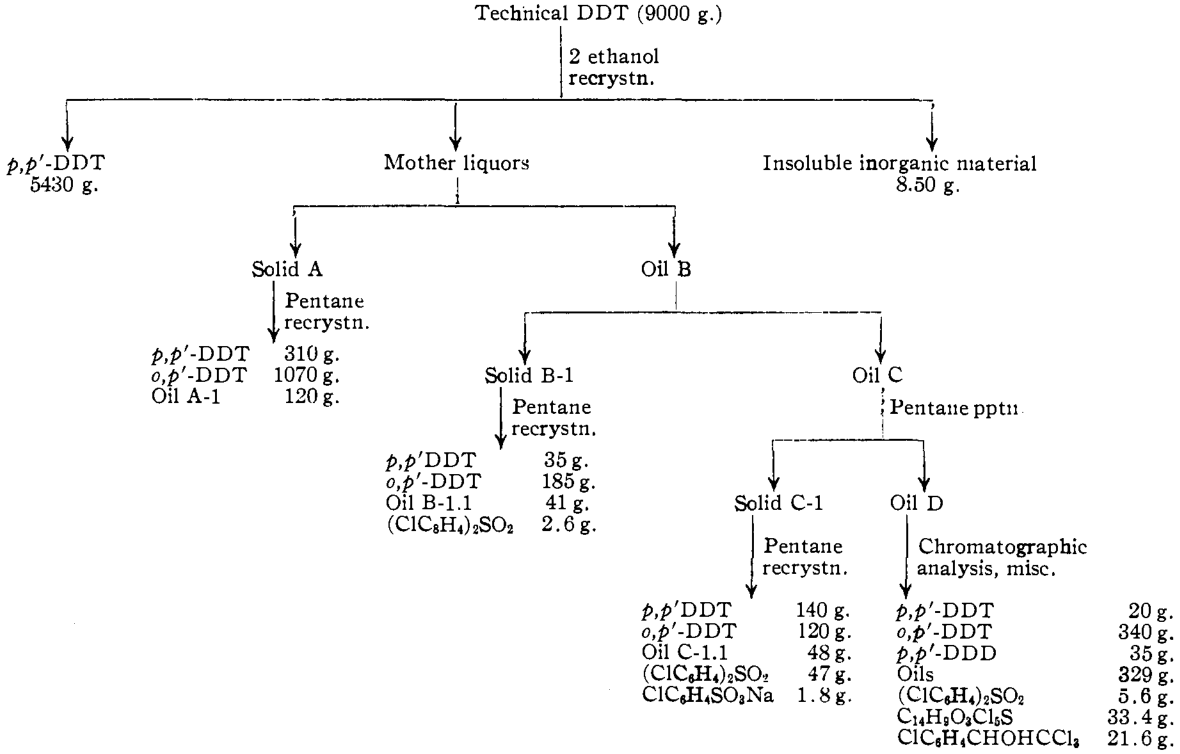
[12] Howard, THIS JOURNAL, **57**, 2317 (1935).

[13] Ullmann and Korselt, *Ber.*, **40**, 643 (1907).

[14] Howard and Castles, THIS JOURNAL, **57**, 376 (1935).

CHART 1

FRACTIONAL SEPARATION OF TECHNICAL DDT



mixture. In principle this method may be applied repeatedly for each component of the mixture, but a practical limit to its application is set by the difficulty of determining accurately a small difference between two large numbers. The method is therefore useful only for components present in substantial amounts. A recent precise application of this method is described by Streiff and Rossini.[15]

By application of this method an oil comprising 16.8% of sample 2 was found to contain 13% of $p,p'$-DDT and 43% of $o,p'$-DDT, and a crude, oily solid, representing 11.6% of sample 2, was found to contain 19% of $p,p'$-DDT and 49% of $o,p'$-DDT. This indicates 4.4% and 13.0%, respectively, of these two isomers in the original sample in addition to the amounts isolated directly by fractional crystallization. All except about 5% of sample 2 was thus accounted for.

## Experimental

### Separation of Technical DDT

The separation procedure described below is summarized in Chart 1. Nine kilograms of a sample of technical DDT was recrystallized twice from 95% ethanol (7.5 liters of solvent per kilogram of technical DDT). There was obtained directly 5.43 kg. of $p,p'$-DDT,[16] m. p. 107–108° (cor.). Further recrystallization from ethanol or ligroin gave a product melting at 108.5–109.0° (cor.).

The structure of $p,p'$-DDT was confirmed by dehydrochlorination with ethanolic potassium hydroxide to 1,1-dichloro-2,2-bis-($p$-chlorophenyl)-ethylene, m. p. 88–89° (cor.) and by oxidation of this compound with chromic anhydride in glacial acetic acid to $p,p'$-dichlorobenzophenone, which melted alone and when mixed with an authentic sample, at 146.5–147.5° (cor.).[17]

Concentration of the mother liquors gave about 1.5 kg. of a solid fraction (solid A on chart 1), which melted at 54–68°, and about 1.4 kg. of a red-brown oil, B. Fractional crystallization of solid A from $n$-pentane gave 310 g. of $p,p'$-DDT and 1070 g. of $o,p'$-DDT. The latter compound, 1-trichloro-2-$o$-chlorophenyl-2-$p$-chlorophenylethane, which has not been previously described, melted after recrystallization from methanol at 74.0–74.5° (cor.).

*Anal.* Calcd. for $C_{14}H_9Cl_5$: C, 47.43; H, 2.56; Cl, 50.01. Found: C, 47.35; H, 2.64; Cl, 49.84, 50.02.

The structure of this product was proved by dehydrochlorination to the corresponding 1,1-dichloro-2-$o$-chlorophenyl-2-$p$-chlorophenylethylene melting at 78.4–79.5° (cor.), and oxidation of this product with chromic anhydride to the known $o,p'$-dichlorobenzophenone, which melted, alone and when mixed with an authentic sample, at 64.2–65.2° (cor.). The melting point of the isolated $o,p'$-DDT was not depressed when a sample was mixed with a sample prepared by the condensation of 2-trichloro-1-$o$-chlorophenylethanol with chlorobenzene. Upon nitration with fuming nitric acid at 50°, $o,p'$-DDT gave a dinitro derivative which, after recrystallization from 95% ethanol, melted at 148–148.5° (cor.).

Separation of $p,p'$-DDT from $o,p'$-DDT in $n$-pentane was aided by the fact that $p,p'$-DDT crystallized in soft needles or clusters whereas $o,p'$-DDT crystallized in hard rhombs.

In addition to the solid fractions isolated in this frac-

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[15] Streiff and Rossini, *J. Research Natl. Bur. Standards*, **32**, 185 (1944).

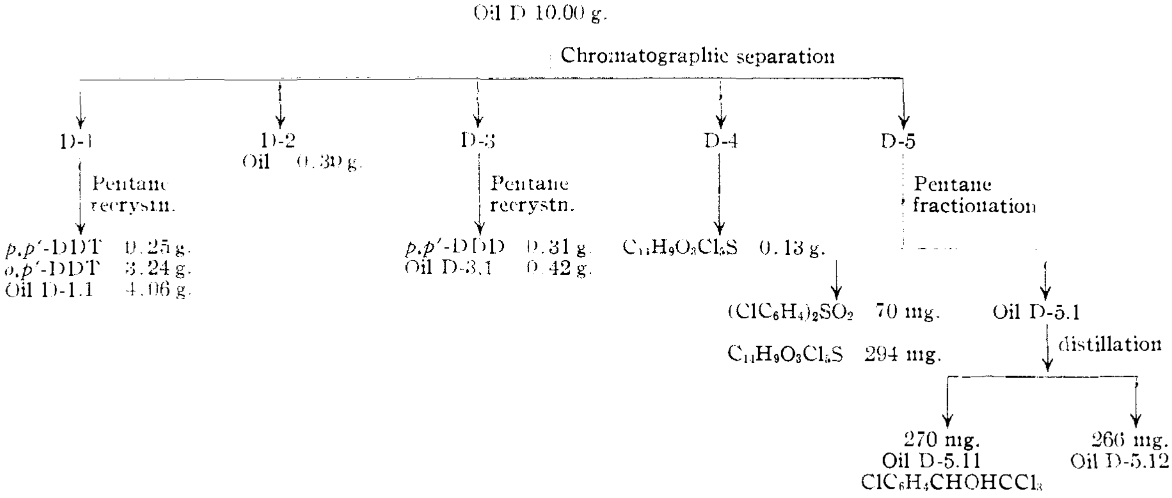
[16] Zeidler, *Ber.*, **7**, 1180 (1874).

[17] After this work had been completed and while this report was in preparation, proof of this structure was reported by Grummitt, Buck and Jenkins.[18]

[18] Grummitt, Buck and Jenkins, THIS JOURNAL, **67**, 155 (1945).

CHART 2

FRACTIONATION OF RESIDUAL OIL D



tionation, there was 120 g. of oil A-1 ($n^{25}$D 1.612). This oil, upon dehydrochlorination and oxidation, gave a benzophenone mixture from which 50% of $p,p'$-dichlorobenzophenone was separated, indicating that at least 60 g. of this oil was probably $p,p'$-DDT.

Oil B slowly deposited crystalline material. After standing for several weeks in a refrigerator, the mixture was filtered, and the separated solid was washed with cold $n$-pentane. This solid (B-1), m. p. 68–72°, represented 20% of oil B. Crystallization of this solid fraction from $n$-pentane gave 35 g. of $p,p'$-DDT, 185 g. of $o,p'$-DDT, 41 g. of oil B-1.1 ($n^{25}$D 1.612), and 2.6 g. of bis-($p$-chlorophenyl)-sulfone, m. p. and mixed m. p. 148–149° (cor.); dinitro derivative,[13] m. p. and mixed m. p. 201–202° (cor.).

Oil C, the filtrate from solid B-1, was treated with twice its weight of $n$-pentane and placed in a refrigerator. After a week the precipitated solid was separated by filtration, yielding solid C-1. After removal of the solvent by distillation, oil D resulted.

Solid C-1 yielded 1.8 g. of an ether-insoluble, water-soluble solid. This solid gave a sodium flame test and left a basic ash upon ignition. A qualitative test (after sodium fusion) indicated the presence of organic chlorine and sulfur. Treatment of the solid with phosphorus pentachloride, followed by treatment with concentrated aqueous ammonia gave $p$-chlorobenzenesulfonamide, m. p. and mixed m. p. 144–145° (cor.). The anilide was also prepared in the usual fashion, m. p. 103–104°.[19] This solid was therefore sodium $p$-chlorobenzenesulfonate.

The remainder of C-1 upon recrystallization from $n$-pentane gave 47 g. of bis-($p$-chlorophenyl)-sulfone, 140 g. of $p,p'$-DDT, 120 g. of $o,p'$-DDT and 48 g. of oil C-1.1 ($n^{25}$D 1.612).

The fraction of oil D is outlined on chart 2.

As oil D did not deposit any solid upon standing with pentane in a refrigerator, an aliquot portion was submitted to adsorption analysis. A 10.00-g. sample (total material 765 g.) was dissolved in 25 ml. of carbon tetrachloride and subjected to adsorption on an activated alumina column 31 by 200 mm. and eluted as follows, 100 ml. of eluting solvent being used for each fraction:

| Fraction | Eluting solvent | Residue, g. |
|---|---|---|
| D-1 | Carbon tetrachloride | 7.52 |
| D-2 | Carbon tetrachloride | 0.30 |
| D-3 | Benzene | .73 |
| D-4 | Benzene and 5% ethanol | .12 |
| D-5 | Absolute ethanol | .90 |

Fraction D-1 upon recrystallization from pentane gave 0.25 g. of $p,p'$-DDT, 3.24 g. of $o,p'$-DDT, and 4.06 g. of oil D-1 ($n^{25}$D 1.613). Although no more solid could be isolated from oil D-1, nitration gave a mixture containing 23% of dinitro-$o,p'$-DDT, and oxidation of the dehydrochlorinated product gave a trace of $p,p'$-dichlorobenzophenone.

Fraction D-2 was an oil ($n^{25}$D 1.615) which could not be made to crystallize.

Fraction D-3, upon recrystallization from pentane, gave 0.31 g. of solid, m. p. after several recrystallizations from 95% ethanol 109.5–110° (cor.). The analysis indicated that this compound was a tetrachlorodiphenylethane.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$; Cl, 44.32. Found: Cl, 44.66.

Oxidation with chromic anhydride after dehydrochlorination gave $p,p'$-dichlorobenzophenone. These data suggested that this compound was 1,1-dichloro-2,2-bis-($p$-chlorophenyl)-ethane (hereinafter called $p,p'$-DDD), which might arise in technical DDT from an impurity of dichloroacetaldehyde in the starting chloral. The isolated compound did not depress the melting point of samples synthesized from dichloroacetaldehyde and chlorobenzene[20] or from 2,2-dichloro-1-$p$-chlorophenylethanol, as described in a later section.

Identical dinitro derivatives, m. p. and mixed m. p. 178–179° (cor.), were obtained from the isolated material and the synthetic material upon treatment with fuming nitric acid at 50° and recrystallization from 95% ethanol.

The residual portion from fraction D-3 was an oil, D-3.1 ($n^{25}$D 1.607), which did not crystallize and was not further investigated.

Fraction D-4 crystallized upon removal of the solvent and was recrystallized from 95% ethanol, m. p. 106.9–107.4° (cor.). The product depressed the melting points of $p,p'$-DDT and $p,p'$-DDD. It was soluble in ether and insoluble in water, dilute alkali or acid, and concentrated sulfuric acid; it was stable to boiling for fourteen hours with 10% aqueous potassium hydroxide; it did not distill at 250° (1 mm.). An elemental analysis indicated the formula $C_{14}H_9O_3Cl_5S$.

*Anal.* Calcd. for $C_{14}H_9O_3Cl_5S$: C, 38.69; H, 2.09; Cl, 40.80; S, 7.38. Found: C, 38.82, 38.91; H, 2.46, 2.48; Cl, 40.43, 40.65; S, 7.20.

Treatment of this material with ethanolic alkali gave a water-soluble acidic material, which was shown to be $p$-chlorobenzenesulfonic acid by conversion of its sodium salt through the acid chloride to $p$-chlorobenzenesulfon-

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[19] Wallach and Huth, *Ber.*, **9**, 420 (1876).

[20] This sample was kindly supplied by H. S. Mosher, of the Pennsylvania State College.

amide, m. p. and mixed m. p. with an authentic specimen 144–146°. The oil-soluble material separated from alkali treatment was oxidized with alkaline permanganate to a acidic material, which upon recrystallization from water gave long, white prisms, m. p. 130–139°. This behavior was suggestive of *o*-chlorobenzoic acid (m. p. 142°).

The isolation of these two materials indicated that the $C_{14}H_9O_3Cl_5S$ compound was the *p*-chlorobenzenesulfonate of 2-trichloro-1-*o*-chlorophenylethanol. This compound was shown to be identical with synthetic 2-trichloro-1-*o*-chlorophenylethyl *p*-chlorobenzenesulfonate.

Fraction D-5 was fractionally crystallized from ether-pentane solution, giving 70 mg. of bis-(*p*-chlorophenyl)-sulfone and 294 mg. of 2-trichloro-1-*o*-chlorophenylethyl *p*-chlorobenzenesulfonate. The residual oil was distilled at 1 mm. in a vacuum sublimation apparatus. The distillate, b. p. 140–170° (bath temperature), was a mobile oil ($n^{25}$D 1.580) weighing 270 mg. It gave a positive test for the $CCl_3CHO$-grouping with pyridine and concentrated sodium hydroxide solution,[21] and was shown to contain 2-trichloro-1-*p*-chlorophenylethanol,[12] the half-condensation product of *p,p'*-DDT, by subjecting the alcohol to a Schotten–Baumann reaction with *p*-chlorobenzenesulfonyl chloride, and the isolation of slightly impure sulfonate ester, m. p. 137–139° (cor.). This sulfonate ester was synthesized from known 2-trichloro-1-*p*-chlorophenylethanol, m. p. 141.3–142.0° (cor.), and a mixed melting point with the product from the isolated fraction was 137–141° (cor.). The residual oil from the distillation, oil D-5.12 ($n^{25}$D 1.589), weighed 266 mg.; it was not further investigated.

Results obtained from the chromatographic analysis of 10 g. of oil D have been recalculated on the basis of the total amount isolated, and are shown in Chart 1.

In the original ethanol recrystallizations 8.5 g. of inorganic materials insoluble in ethanol was recovered. Qualitative tests showed the presence of ferric, lead, magnesium and carbonate ions.

A study was made of some of the residual oils in order to determine whether other DDT isomers could be detected. Of special interest was oil D-1.1. This oil was nitrated with fuming nitric acid to give a mixture from which 23% of dinitro-*o,p'*-DDT could be isolated, but no other pure compound. Further nitration with concentrated sulfuric acid–fuming nitric acid (1:1 by volume) at 100° gave an intractable mixture.

Another sample (183 mg.) of this oil was treated with excess alcoholic potassium hydroxide at reflux for one hour. The aqueous extract was titrated for chloride ion and gave 9.5% of hydrolyzable chlorine (theoretical for DDT isomers 10.0%). The ether-soluble fraction was oxidized with chromic anhydride in glacial acetic acid; 75 mg. of base-insoluble product, m. p. 47–100°, was formed, from which a trace of *p,p'*-dichlorobenzophenone could be isolated. No other pure compound could be isolated. Only 1 mg. of base-soluble material was isolated from the oxidation.

Treatment of the other two samples of technical DDT followed fairly similar schemes. Certain other compounds were isolated from the oily fractions in addition to those obtained from sample 1. Instead of sodium *p*-chlorobenzenesulfonate, the ammonium salt was obtained in one of these samples. Both samples yielded small amounts of a solid, m. p. 134–135°, which was shown to be α-chloro-α-*p*-chlorophenylacetamide. This compound was isolated from oils similar to oil C (Chart 1) either by crystallization or by chromatographic adsorption. After repeated recrystallization from ethanol, white needles were obtained.

*Anal.* Calcd. for $C_8H_7Cl_2NO$: C, 47.08; H, 3.46; Cl, 34.75; N, 6.86 mol. wt., 204. Found: C, 47.29, 47.37; H, 3.69, 3.45; Cl, 34.43; N, 6.64; mol. wt., 210, 218.

A 60-mg. sample of this material was oxidized with alkaline permanganate in the usual manner to give 29.4 mg. (64%) of pure *p*-chlorobenzoic acid identified by melting point, mixed melting point, and neutral equivalent. Alkaline hydrolysis gave a steam-distillable base which was shown to be ammonia by the preparation of benzamide (identified by melting point and mixed melting point) from it by standard procedures.

The foregoing data suggested α-chloro-α-*p*-chlorophenylacetamide as the only reasonable structure for this compound. This was confirmed by synthesis of this compound by ammonolysis of the acid chloride prepared by the action of phosphorus pentachloride on *p*-chloromandelic acid. The melting point of the isolated material was not depressed by the synthetic material.

In connection with this compound, the corresponding acid, α-chloro-α-*p*-chlorophenylacetic acid, was synthesized by hydrolysis of the acid chloride. This acid melted at 75–76° and had the correct analysis for carbon, hydrogen, and chlorine. v. Walther and Raetze[22] have reported the synthesis of this substance by the action of boiling concentrated hydrochloric acid on *p*-chloromandelonitrile. Their product melted at 118°. It should be noted that this method is similar to that described for the synthesis of *p*-chloromandelic acid, which melts at about 120°.[23,24] It seems likely that v. Walther and Raetze may have had *p*-chloromandelic acid rather than α-chloro-α-*p*-chlorophenylacetic acid. Unfortunately, these authors did not report any derivatives of their product, nor was a chlorine analysis given.

In one case this material was accompanied by a small amount (0.007% of the original technical DDT) of a material, m. p. 87.8–90.5°, which gave analytical results for a dichlorophenylacetamide and which resisted further purification.

*Anal.* Calcd. for $C_8H_7ONCl_2$: C, 47.08; H, 3.46; N, 6.89; Cl, 34.75. Found: C, 46.97; H, 3.91; N, 6.78; Cl, 34.42.

The melting point of this product was raised to 94–100° by admixture with synthetic α-chloro-α-*o*-chlorophenylacetamide, m. p. 104–105°. It was probably a mixture of the *o*- and *p*- isomers.

The oily fractions from sample 3 gave, as fractions in the chromatographic separation, small amounts of two materials not isolated in the other samples. One of these was the olefin related to *p,p'*-DDD, 2-chloro-1,1-bis-(*p*-chlorophenyl)-ethylene, m. p. after recrystallization from petroleum ether and absolute ethanol 64–65°.

*Anal.* Calcd. for $C_{14}H_9Cl_3$: C, 59.29; H, 3.20; Cl, 37.51. Found: C, 59.40, 59.53; H, 3.55, 3.51; Cl, 37.33.

This compound, which represented 0.11% of the original technical DDT, did not depress the melting point of a sample prepared by the dehydrochlorination of *p,p'*-DDD with ethanolic alkali. Data are not at hand on which to determine whether or not this olefin was present as such in the technical DDT sample or was formed by the degradation of *p,p'*-DDD in the isolation procedure. We have noted that some batches of alumina cause the formation of olefin from *p,p'*- and *o,p'*-DDT, and such may be the case here.

The other material was isolated from an eluate fraction, and after recrystallization from petroleum ether and from methanol was obtained as fine white elongated prisms, m. p. 74.5–75.5°. The material depressed the melting points of both *o,p'*-DDT and its corresponding olefin. The analytical data suggested that it was a DDD isomer.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.32. Found: C, 52.55, 52.41; H, 3.33, 3.35; Cl, 44.19.

*o,p'*-DDD was prepared synthetically from chlorobenzene and 2,2-dichloro-1-*o*-chlorophenylethanol. The melting point of this synthetic material was not depressed when mixed with the isolated sample.

Sample 4, which was a by-product oil, was treated by a different scheme from the other samples.

A solution of 2176 g. of the oil in 28.8 liters of petroleum ether (Skellysolve F, b. p. 35–52°) was cooled to −60° until crystallization was essentially complete (six hours).

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(21) Snell and Snell, "Colorimetric Methods of Analysis," Vol. 2, Van Nostrand Co., New York, N. Y., 1937, p. 560.

(22) v. Walther and Raetze, *J. prakt. Chem.*, [2] **65**, 266 (1902).

(23) Straus, *Ann.*, **393**, 320 (1912).

(24) Jenkins, THIS JOURNAL, **53**, 2341 (1931).

The mother liquor was removed by suction using a porcelain filter-plate piece which resembled a Büchner funnel with the vertical sides removed. The solid melted at 52–88° and weighed 1372 g. (63.1%). This solid gave no test for sulfur or nitrogen and, on the basis of experience with similar crystalline material, was assumed to be a mixture of *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDD.

The material remaining in the mother liquor, oil E, was distilled *in vacuo* after removal of solvent. The results are given in Table II.

TABLE II

FRACTIONATION OF OIL E

| Fraction | Boiling pt. °C. | Press., mm. | $n^{20}D$ | Wt., g. | Proportion of oil E, % |
|---|---|---|---|---|---|
| E-1 | [a] | 1 | 1.5690 | 93 | 4.27 |
| E-2[b] | To 155° | 1 | 1.5688 | 120 | 5.52 |
| E-3[c] | To 165°[d] | $10^{-2}$ | 1.5948 | 27 | 1.24 |
| E-4[c] | 165–170°[d] | $10^{-2}$ | 1.6028 | 221 | 10.15 |
| E-5[c] | 170–180°[d] | $10^{-2}$ | 1.6090 | 254 | 11.80 |
| E-6 | Residue | .. | .... | 44 | 2.02 |
| Mixt. of solids obtained by crystallization | | | | | 63.1 |
| | | | | Recovered | 98.1 |

[a] Caught in cold trap, cooled in solid carbon dioxide. [b] This fraction was removed in an ordinary modified all-glass Claisen flask. [c] These fractions were removed in a special distillation flask which had a stirrer designed in accordance with suggestions given by K. M. Hickman. The general principle is described in "Synthetic Organic Chemicals," Vol. 13, No. 5, Eastman Kodak Co., Rochester, N. Y., 1941. [d] Bath temperature.

Fraction E-1 was distilled at atmospheric pressure through a helices-packed (55 cm.) column equipped with a total condensation partial take-off head. Two main fractions, b. p. 129.5° and 167–172°, were obtained. The former fraction, which was shown to be chlorobenzene by nitration to *p*-nitrochlorobenzene, which melted at 82.5–83.2° alone and when mixed with an authentic specimen, represented 2.44% of the original by-product oil. The latter fraction, a solid which upon recrystallization melted at 52.6–53.7°, was identified as *p*-dichlorobenzene by a mixed melting point determination. This fraction represented 0.51% of the starting material.

Fraction E-2 was fractionally distilled at 1.5 mm. through a column (40 cm.) packed with 0.25-inch Berl ceramic saddles and equipped with a total-reflux, partial take-off head. Two main fractions were obtained. The first, b. p. 33–35°, which represented 0.22% of original material, was identified as *p*-dichlorobenzene as above. The second fraction, b. p. 111–113.5°, representing 2.54% of the by-product oil, $n^{20}D$ 1.5702, proved to be a mixture of compounds having the empirical formulas $C_8H_5Cl_5$ and $C_8H_6Cl_4$ by elemental analysis and quantitative dehydrochlorination.

*Anal.* Calcd. for $C_8H_5Cl_5$: C, 34.6; H, 1.8; Cl, 63.7. Calcd. for $C_8H_6Cl_4$: C, 39.3; H, 2.4; Cl, 58.4. Found: C, 36.1; H, 2.4; Cl, 61.4.

On the assumption of 1 molecule of hydrogen chloride to be removed by ethanolic alkali, the molecular weight of this fraction was found to be 230; molecular weight calcd. for $C_8H_5Cl_5$ was 278, for $C_8H_6Cl_4$ was 244.

On nitration of this mixture with fuming nitric acid, a small amount of a crystalline nitro compound, m. p. 71.3–72.9°, was obtained. The melting point was not depressed when mixed with the nitro compound obtained from pure synthetic 1,1,1,2-tetrachloro-2-*p*-chlorophenylethane, indicating the presence of this material in the mixture.

Fraction E-3 was not examined.

Since preliminary work indicated that fractions E-4 and E-5 were similar, further work was carried out only with E-5. This fraction was investigated by chromatographic adsorption. A typical experiment was as follows:

A column 5 cm. in diameter was packed with <80-mesh, grade A chromatographic alumina to a height of 12 cm. with use of suction. Two-hundred milliliters of Skellysolve F was poured in, followed by the sample, 15.298 g., dissolved in 400 ml. of Skellysolve F. Following this various solvents were used for elution. No suction was needed. The results are given in Table III.

The identity of these major components was established by mixed melting points after recrystallization from Skellysolve F. The sulfur compound was identified as 2-trichloro-1-*o*-chlorophenylethyl *p*-chlorobenzenesulfonate. When the oily materials of fraction E-5.3 were combined and rechromatographed, further small amounts of solid were obtained. Of the original 15.3-g. sample, there was isolated 55.5% of various known crystalline materials and 9.7% of oils from fractions E-5.4 and E-5.5 (not further investigated); 35.2% was left as noncrystallizable oils. Several batches of these oils were combined and distilled *in vacuo*. This material gave the following analysis for chlorine: Found: 49.9; calcd. for $C_{14}H_9Cl_5$: 50.0. A summary of the work described above is given in Table I.

In each of the investigations of the technical DDT materials, after all the material that could be induced to crystallize had been separated, there always remained a small amount (from 4 to 8%) of residual oily fractions which resisted crystallization, but which had analytical properties and boiling ranges similar to those of a DDT isomer or isomers. Work on such an oil (oil D-1.1) has been described above.

Another such oil was obtained from the work on the by-product oil described above. A sample (5.0 g.) of thrice chromatographed oil (F), with separation and rejection of crystalline material after each chromatograph, was dehydrochlorinated with ethanolic potassium hydroxide, and 4.5 g. of the resulting oily olefin, F-1, was oxidized by refluxing for two hours with a solution of 7.3 g. of chromic anhydride and 8 ml. of concentrated sulfuric acid in 75 ml. of glacial acetic acid. The neutral fraction of the reaction products (there was no acidic fraction) was distilled *in vacuo* to yield 3.33 g. (91%) of "ketonic" material, F-2. From this a total of 0.26 g. (7.1%) of *p,p'*-dichlorobenzophenone was separated by crystallization. The remaining oil was chromatographed on alumina. The only crystalline fraction thus obtained was *p,p'*-dichlorobenzophenone, 0.62 g., or 20.2%, making 27.3% of the "ketonic" material. The remaining fractions were treated with 2,4-

TABLE III

CHROMATOGRAPHIC ANALYSIS OF OIL E-5

| Fraction | Solvent | Solvent, ml. | Wt., g. | Proportion of oil E-5, % | Major component |
|---|---|---|---|---|---|
| E-5.1[a] | Skellysolve F | 600 | 5.337 | 34.9 | *o,p'*-DDT |
| E-5.2 | Petroleum ether (65–110°) | 700 | 5.406 | 35.3 | *p,p'*-DDT |
| E-5.3[a] | Petroleum ether (65–110°) | 800 | 1.542 | 10.1 | *p,p'*-DDT |
| E-5.4[a] | Carbon tetrachloride | 400 | 1.767 | 11.6 | *p,p'*-DDD |
| E-5.5 | Absolute ether | 500 | 1.133 | 7.4 | *p,p'*-DDD, sulfur compound |
| E-5.6 | Methanol | 600 | 0.587 | 3.8 | NaCl |
| | | | | 103.1 | |

[a] Crystallized upon standing.

dinitrophenylhydrazine, but no crystalline products were obtained. In another similar run 15.2% of *p,p'*-dichlorobenzophenone was isolated directly. The residual fractions from the chromatograph, upon treatment with 2,4-dinitrophenylhydrazine, gave two crystalline products—the 2,4-dinitrophenylhydrazone of *p,p'*-dichlorobenzophenone (1.6%), m. p. and mixed m. p. with authentic material 238–240° (cor.); and the 2,4-dinitrophenylhydrazone of *o,p'*-dichlorobenzophenone (2.1%), m. p. and mixed m. p. with authentic material 230–231° (cor.)—as well as an additional 2.1% of a mixture of these two compounds. No other crystalline fraction was obtained.

After all the crystalline benzophenones and their 2,4-dinitrophenylhydrazones had been separated from the F-2 fractions, the remainder was distilled and the clear and the almost colorless oily distillate of each of the runs was analyzed. *Anal.* Calcd. for $C_{14}H_8Cl_4$: C, 52.7; H, 2.8; Cl, 44.4. Found: first sample; C, 52.5; H, 2.7; Cl, 42.4 (total 97.6%); second sample; C, 53.3; H, 2.8; Cl, 44.2 (total 100.3%).

This indicates that there are present in fractions F not only materials which on dehydrochlorination and oxidation yield *o,p'*- and *p,p'*-dichlorobenzophenones, but also materials of formula $C_{14}H_8Cl_4$ which are resistant to oxidation with chromic acid. It is possible that these materials may contain the *o,o'* isomer of DDT.

### Cryoscopic Analysis

For the melting point determinations about 20 g. of the sample was placed in a 25 by 300 mm. test-tube within a 30 by 300 mm. test-tube. The tube was provided with a manually operated glass stirrer and a Beckmann thermometer. Probably the accuracy of the results could be improved somewhat by the use of a thermocouple instead. The whole was immersed in an electrically controlled oil-bath, and the slow rise in temperature of the sample was plotted. The straight portions of the curve below and above the bend were projected to obtain the melting point, taken as their point of intersection. As a solvent not represented in the mixture, triphenylmethane was at first chosen because of its convenient melting point (93.4°) and cryoscopic constant ($K_f$ 12.45). However, it was found that the freezing point of a solution of DDT in triphenylmethane changed with time, and benzil (m. p. 95°, $K_f$ 10.50) was later adopted as a more suitable solvent. Two determinations of the cryoscopic constant of *p,p'*-DDT using *o,p'*-DDT as solute gave 14.92 and 15.38°, or an average of 15.15° per mole per 1000 g. of *p,p'*-DDT. The cryoscopic constant of *o,p'*-DDT was found to be 14.70° per mole per 1000 g. With these data determinations were made of the *p,p'*- and *o,p'*-DDT contents of two materials—the solid-free residual oil from the recrystallization of sample 2 of Table I, representing 16.8% of the technical DDT, and the crude solids obtained in the crystallization, comprising 11.6% of sample 2.

**Cryoscopic Analysis of the Oil.**—Addition of 0.7817 g. of the oil to 20.06 g. of *o,p'*-DDT caused a depression of 0.823° in the melting point. Substitution in the formula

$$M = \frac{W\Delta t}{1000wK_f}$$

where $M$ = moles of material other than solvent in 1 g. of solute, $W$ = weight of solvent in grams, $w$ = weight of solute in grams, $\Delta t$ = freezing-point depression, and $K_f$ = cryoscopic constant of solvent, yields $M$ = 0.001437. By a determination in benzil the total number of moles in 1 g. of the oil was found to be 0.00268. Therefore the number of moles of *o,p'*-DDT in 1 g. of the oil is 0.00268 − 0.001437 = 0.00124. This is a weight of 0.00124 × 354.5 = 0.439 g., or 43.9% of the sample. By adding this 0.439 g., as a correction to the weight of solvent taken in the original calculation, a revised figure of 43.2% of *o,p'*-DDT in the oil is obtained.

The melting point of 18.54 g. of *p,p'*-DDT was depressed 1.704° by 0.9127 g. of the oil. This corresponds to 0.0229 mole per gram not *p,p'*-DDT, or 0.00039 (0.00268 − 0.00229) mole per gram of *p,p'*-DDT. The weight per cent. is accordingly 13.8% (354.5 × 0.00039). The corrected values are 0.00231 mole per gram not *p,p'*-DDT and 0.00037 mole, or 13.1% of *p,p'*-DDT. These results account for 0.563 g. and 0.00159 mole out of every gram of oil. The remaining 43.7% therefore has an average molecular weight of 401 (0.437/0.00109). This is still near enough to the molecular weight of DDT (354.5) to suggest the presence of one or more as yet unidentified isomers of DDT in the oil.

**Cryoscopic Analysis of Intermediate Solids in Crystallization of Crude DDT.**—The material was melted and heated at 100° under 0.8 mm. pressure for three hours to ensure removal of solvent. In 20.11 g. of benzil 0.9203 g. of the solid produced a depression of 1.261° in the freezing point. This corresponds to 0.00262 mole per gram. In 20.19 g. of *p,p'*-DDT 0.9164 g. gave a depression of 1.424°. This corresponds to 0.00207 mole per gram not *p,p'*-DDT, and 0.00055 mole per gram which is *p,p'*-DDT. The uncorrected and corrected contents of *p,p'*-DDT are hence 19.5 and 18.8%, respectively. In *o,p'*-DDT (20.51 g.) a depression of 0.780° was produced by a sample of 0.8987 g. This indicates 0.00141 mole uncorrected and 0.00138 mole corrected of *o,p'*-DDT in the mixture. The corrected percentage is 48.9%. The unidentified material here has an average molecular weight of 455.

### Synthesis and Reactions of Technical DDT Components

**Degradation of *o,p'*- and *p,p'*-DDT.**—*o,p'*-DDT was heated under reflux for three hours with half its weight of potassium hydroxide in 95% ethanol. The reaction mixture was diluted with water and extracted with ether; the ethereal extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed, giving the corresponding olefin, 1,1-dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethylene, in 97% yield. After several recrystallizations from methanol or 95% ethanol, it was obtained in large rectangular plates, m. p. 78.4–79.5° (cor.).

*Anal.* Calcd. for $C_{14}H_8Cl_4$: C, 52.87; H, 2.53; Cl, 44.60. Found: C, 52.68; H, 2.75; Cl, 44.40.

In the same way 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene,[16] m. p. 88–89° (cor.), was obtained by the elimination of hydrogen chloride from *p,p'*-DDT.

Each of the olefins was converted to the corresponding dichlorobenzophenone by the cautious addition of about 1 part of chromic anhydride to a refluxing solution of 2 parts of the olefin in 10 parts of glacial acetic acid. After one hour under reflux the reaction mixture was cooled and poured into ice water. The precipitated material was separated, dried, and recrystallized from aqueous ethanol. The *o,p'*-dichlorobenzophenone, m. p. 64.2–65.2° (cor.), did not depress the melting point of an authentic specimen. The *p,p'*-dichlorobenzophenone, m. p. 146.5–147.5° (cor.), did not depress the melting point of an authentic specimen.

**Synthesis of 1-Trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDT).**—A solution of 37 g. (0.25 mole) of freshly distilled chloral in 130 ml. of dry ether was added, at 0° over a period of three hours, to 65 ml. of 1.52 *N* *o*-chlorophenylmagnesium bromide (0.25 mole) prepared by the reaction of 288 g. (1.5 mole) of *o*-chlorobromobenzene[25] in 700 ml. of dry ether with 39 g. (1.6 mole) of magnesium turnings. The reaction mixture was decomposed with dilute hydrochloric acid and worked up in the usual manner. Distillation at 1 mm. yielded 33 g. (50%) of 2-trichloro-1-*o*-chlorophenylethanol, b. p. 108–112°. This carbinol was also prepared by the base-catalyzed condensation of *o*-chlorobenzaldehyde and chloroform.[14]

The carbinol (312 g., 1.20 moles) was added dropwise during one hour to a well-stirred emulsion of 260 g. of chlorobenzene (2.33 mole) in concentrated sulfuric acid (160 ml. of 25% oleum and 480 ml. of 96% acid) with the temperature at 60°. After six hours of stirring the organic layer was separated and washed with water. The ma-

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(25) Hartwell, "Organic Syntheses," **24**, 22 (1944).

terial crystallized on standing and was recrystallized twice from ethanol–acetone solution. It melted at 73–74° and weighed 271 g. (64% yield).

**Nitration of *o,p'*-DDT.**—A dinitro derivative was obtained by the treatment of 1 part of the compound with 10 volumes of fuming nitric acid at 50° for one-half hour. The product mixture was cooled and poured onto ice. The separated solid was removed by filtration (yield, *ca.* 90%) and recrystallized from 95% ethanol, m. p. 148–148.5° (cor.).

*Anal.* Calcd. for $C_{14}H_7O_4N_2Cl_5$: C, 37.8; H, 1.6; N, 6.3; Cl, 39.9. Found: C, 37.9; H, 1.6; N, 6.4; Cl, 39.9.

The melting point of this compound was depressed upon admixture with the dinitro compound from *p,p'*-DDT, m. p. 148–148.3°, prepared in like manner [16]

**2,2-Dichloro-1-*p*-chlorophenylethanol.**—A solution of 1 mole of aluminum isopropoxide in 500 ml. of isopropyl alcohol was heated under reflux with 0.5 mole of *p*,$\alpha$,$\alpha$-trichloroacetophenone (112 g.)[26] for eight hours with partial take-off to remove acetone. Excess solvent was removed, the product treated with concentrated hydrochloric acid, and the carbinol washed, dried, and distilled. A yield of 75 g. (67%) was obtained, b. p. 140–145° (2 mm.).

**1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-DDD).**—Into a well-stirred mixture of 40 g. of chlorobenzene, 40 ml. of 25% oleum and 120 ml. of 96% sulfuric acid, 40 g. of 2,2-dichloro-1-*p*-chlorophenylethanol was added dropwise. After twenty minutes a solid began to form. After four hours at 60° the mixture was filtered and the solid recrystallized twice from 95% ethanol to give 36.1 g. (63%) of long, thick prisms, m. p. 108.5–110°. This melting point was not depressed when the compound was mixed with an analyzed sample isolated from technical DDT.

**Degradation of *p,p'*-DDD.**—*p,p'*-DDD was converted to 2-chloro-1,1-bis-(*p*-chlorophenyl)-ethylene with ethanolic alkali as described above for *o,p'*-DDT. A 215-mg. sample gave 147 mg. (77%) of thrice recrystallized (from ligroin) product, m. p. 64–65°. This compound did not depress the melting point of an analyzed sample isolated from technical DDT.

Another sample (0.5 g.) was subjected to elimination of hydrogen chloride, and the resulting compound was oxidized with chromic anhydride. There resulted, after one recrystallization, an 84% yield of *p,p'*-dichlorobenzophenone, m. p. 145°.

**Nitration of *p,p'*-DDD.**—Nitration as described for *o,p'*-DDT gave a dinitro compound, pale-yellow prismatic needles, m. p. after recrystallization from ethanol 178–179°, in about 90% yield.

*Anal.* Calcd. for $C_{14}H_8O_4N_2Cl_4$: Cl, 34.59. Found: Cl, 34.72.

**2,2-Dichloro-1-*o*-chlorophenylethanol.**—To the Grignard reagent prepared from 25 g. (0.13 mole) of *o*-bromochlorobenzene,[26] 3.02 g. (0.124 mole) of magnesium and 200 ml. of ether was added, with mechanical stirring, 13.25 g. (0.117 mole) of dichloroacetaldehyde in 80 ml. of ether. The ether soon began to boil vigorously, and an ice bath was applied. The aldehyde was added dropwise over a period of forty-five minutes. The addition compound was decomposed with 6 *N* sulfuric acid, and the product was extracted with ether; the ethereal solution was dried, and the solvent was removed by flask distillation. The residue was distilled *in vacuo*, yielding 3 g. of forerun and 3.25 g. of fluid material, b. p. 112–125° (2–3 mm.). The remainder of the material was a very viscous, high-boiling tar. The 112–125° fraction was redistilled to give 1.6 g. (6%) of product boiling at 126–129° and 3 mm.

**1,1-Dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDD).**—A mixture of 2,2-dichloro-1-*o*-chlorophenylethanol (1.51 g., 0.0067 mole) and chlorobenzene (0.685 g., 0.0061 mole) was kept at 30° while 50 drops of *ca.* 100% sulfuric acid were added dropwise with stirring. The darkened mixture was then stirred in a bath at 60° for about one hour. The mixture was cooled and extracted with pentane; the pentane layer was washed with water and with dilute ammonia. Evaporation of the pentane gave an oil which soon partially crystallized. Repeated crystallization from pentane and from methanol gave white crystals, m. p. 76–78°; yield 763 mg. (39%). No depression in melting point was noted when this compound was mixed with an analyzed sample isolated from technical DDT.

**Degradation of *o,p'*-DDD.**—A sample (42.6 mg.) of mixed synthetic and isolated *o,p'*-DDD was dehydrochlorinated and oxidized in the usual manner. Addition of the oxidation mixture to ice water produced a milky emulsion, which crystallized on standing. The crystalline material was filtered, washed with water, and dried in air. The unrecrystallized product melted at 63.2–64.2° (cor.) and weighed 12.5 mg. (41%). The melting point was not depressed when this sample was mixed with an authentic specimen of *o,p'*-dichlorobenzophenone.

**Synthesis of 1-Trichloro-2-*m*-chlorophenyl-2-*p*-chlorophenylethane (*m,p'*-DDT).**—2-Trichloro-1-*m*-chlorophenylethanol was prepared from chloral and *m*-chlorophenylmagnesium bromide in 70% yield as described above for the *o*-isomer. The carbinol was condensed with chlorobenzene by stirring a mixture of the carbinol with 50% excess chlorobenzene and oleum (amount such that the final acid concentration was 100%) at room temperature for six hours. The organic fraction was worked up to give 48% of an oily fraction, boiling at 180–195° (1 mm.). Redistillation gave a colorless oil, b. p. 181–185° (1 mm.), $n^{20}D$ 1.6146.

*Anal.* Calcd. for $C_{14}H_9Cl_5$: C, 47.4; H, 2.6; Cl, 50.0. Found: C, 47.2, 47.0; H, 2.7, 2.7; Cl, 49.6, 49.5.

The product did not yield to crystallization attempts.

**Degradation of *m,p'*-DDT.**—*m,p'*-DDT was dehydrochlorinated with ethanolic alkali to give the corresponding ethylene, an oil which distilled at 158–162° (1 mm.), in 80% yield. Oxidation of this oil with chromic anhydride gave the corresponding *m,p'*-dichlorobenzophenone, which melted at 112.6–113.4° after recrystallization from aqueous ethanol. This new ketone was obtained in 41% yield.

*Anal.* Calcd. for $C_{13}H_8OCl_2$: C, 62.2; H, 3.2; Cl, 28.2. Found: C, 62.4; H, 3.4; Cl, 28.2.

**Nitration of *m,p'*-DDT.**—Fuming nitric acid (10 g.) was added to 10 g. of *m,p'*-DDT; the hot solution was allowed to come to room temperature and was poured onto ice. The precipitated solid melted at 118.8–120.1° after recrystallization. The yield of dinitro-*m,p'*-DDT was 90%.

*Anal.* Calcd. for $C_{14}H_7O_4N_2Cl_5$: C, 37.8; H, 1.6; Cl, 39.9; N, 6.3. Found: C, 37.8; H, 1.6; Cl, 39.8; N, 6.6.

**Degradation of Isolated 2-Trichloro-1-*o*-chlorophenylethyl *p*-Chlorobenzenesulfonate.**—A sample (64 mg.) of this material was heated at reflux for one hour with 0.57 millimole of 0.5 *N* ethanolic sodium hydroxide. The organic material was extracted. Removal of the solvent left 25 mg. of oily material. This oil was oxidized with alkaline permanganate to give 5–10 mg. of an acidic material; this was recrystallized once from water to give long white prisms, m. p. 130–139°. Such behavior was suggestive of impure *o*-chlorobenzoic acid (m. p. 142°). Another sample (190 mg.) was heated at reflux for three and a half hours with 5.0 millimoles of ethanolic sodium hydroxide. After extraction of the alkaline solution to remove neutral material and extraction of the acidified solution to remove benzene-soluble acidic material, the aqueous phase was again made alkaline and evaporated to dryness. Extraction of this residue with hot absolute ethanol gave 189 mg. of impure material, which gave a qualitative test for sulfur. On the assumption that a sodium sulfonate was present, the crude material was treated with excess phosphorus pentachloride (500 mg.); the benzene extract of this reaction mixture was treated with an excess of ammonia. After repeated crystallization of the material obtained by benzene extraction of this product, 8.6 mg. of fine white needles, m. p. 144–146°, was obtained. This material did not depress the melting point of authentic *p*-chlorobenzenesulfonamide.

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[26] Gautier, *Ann. chim.*, [6] **14**, 402 (1888).

**Synthesis of 2-Trichloro-1-*o*-chlorophenylethyl *p*-Chlorobenzenesulfonate.**—When 25 g. (0.096 mole) of 2-trichloro-1-*o*-chlorophenylethanol was mixed with 25 g. of *p*-chlorobenzenesulfonyl chloride in 50 ml. of dry pyridine, considerable heat was generated. Pouring the mixture into water gave a product which melted at 105.5–106.5° after recrystallization from methanol and weighed 29.8 g. (72% yield).

This compound was also prepared by allowing a mixture of 500 mg. of the alcohol, 1.5 g. of the acid chloride, and 10 ml. of 30% potassium hydroxide to stand for two days. The compound was isolated in the same manner as above; yield, 630 mg. (75%). A sample was prepared for analysis by repeated recrystallization from 95% ethanol, m. p. 106.9–107.4° (cor.).

*Anal.* Calcd. for $C_{14}H_9O_3Cl_5S$: Cl, 40.78; S, 7.38. Found: Cl, 40.02; S, 7.24.

**2-Trichloro-1-*p*-chlorophenylethyl *p*-Chlorobenzenesulfonate.**—This compound was prepared by the Schotten-Baumann procedure with potassium hydroxide, as described above, using 2-trichloro-1-*p*-chlorophenylethanol,[12] except that the mixture was allowed to stand only two hours. The yield was 660 mg. (78%). An analytical sample was prepared by several recrystallizations from 95% ethanol, m. p. 141.3–142.0°.

*Anal.* Calcd. for $C_{14}H_9O_3Cl_5S$: Cl, 40.78; S, 7.38. Found: Cl, 40.26, 40.66; S, 7.20.

**$\alpha$-Chloro-$\alpha$-*p*-chlorophenylacetamide.**—After 3.7 g. of *p*-chloromandelic acid,[27] had been heated with 8.3 g. of phosphorus pentachloride for one hour at 120° and one hour at 150°, the product was cooled and poured into concentrated aqueous ammonia. Three recrystallizations from benzene gave 3.2 g. (79%) of fine needles, m. p. 133–134° alone or when mixed with an analyzed sample isolated from technical DDT.

**$\alpha$-Chloro-$\alpha$-*p*-chlorophenylacetic acid.**—This compound was prepared by warming the corresponding acid chloride with water for two hours. Crystallization occurred on long standing in petroleum ether. After two recrystallizations from petroleum ether the product melted at 75–76°. The acid gave a strong silver nitrate test on warming.

*Anal.* Calcd. for $C_8H_6O_2Cl_2$: C, 46.86; H, 2.95; Cl, 34.59. Found: C, 47.02; H, 3.14; Cl, 34.77.

**$\alpha$-Chloro-$\alpha$,*o*-chlorophenylacetamide.**—This compound was prepared as described above for the *p*-isomer, starting with *o*-chloromandelic acid.[24] The amide was recrystallized from petroleum ether and melted at 103–105°.

*Anal.* Calcd. for $C_8H_7OCl_2N$: C, 47.08; H, 3.46; N, 6.89; Cl, 34.75. Found: C, 47.20; H, 3.53; N, 6.81; Cl, 34.82.

**Synthesis of 1,1,1,2-Tetrachloro-2-*p*-chlorophenylethane.**—A solution of 258 g. (1.75 mole) of freshly distilled chloral in 400 ml. of dry ether was added over a period of three and a half hours, at 5–10°, to approximately 830 ml. of 2.23 *N* *p*-chlorophenylmagnesium bromide (1.75 mole) prepared by the reaction of 335 g. (1.75 mole) of *p*-chlorobromobenzene in 750 ml. of dry ether with 44 g. (1.80 mole) of magnesium turnings. The reaction mixture was decomposed with dilute hydrochloric acid. Distillation at 1 mm. yielded 282 g. (62%) of 2-trichloro-1-*p*-chlorophenylethanol, boiling at 123–125°.

A solution of 26.0 g. (0.1 mole) of 2-trichloro-1-*p*-chlorophenylethanol in 50 ml. of dry benzene was slowly added to a suspension of 20.8 g. (0.1 mole) of phosphorus pentachloride in 20 ml. of dry benzene. The reaction mixture was warmed for fifteen minutes at 50° following the initial reaction. The benzene and phosphorus oxychloride were removed under vacuum. The 1,1,1,2-tetrachloro-2-*p*-chlorophenylethane distilled at 112–117° (1 mm.); it weighed 24.0 g. (86%).

**Nitro Derivative of 1,1,1,2-Tetrachloro-2-*p*-chlorophenylethane.**—To 5 g. of 1,1,1,2-tetrachloro-2-*p*-chlorophenylethane was added 10 ml. of fuming nitric acid. The reaction was exothermic, and the hot solution was allowed to cool to room temperature and then poured onto ice. The product, when recrystallized from Skellysolve F and benzene, melted at 71.9–73.0°.

*Anal.* Calcd. for $C_8H_4O_2Cl_5N$: C, 29.7; H, 1.2; Cl, 54.8; N, 4.3. Found: C, 29.8; H, 1.4; Cl, 54.8; N, 4.7.

**Synthesis of Dichlorobenzophenones.**—Of the six possible isomeric dichlorobenzophenones with one chlorine in each benzene ring, only two, the *p,p'* and *o,p'* isomers, have been described in the literature. In the course of this work it was desired to prepare the remaining four. Of these the preparation of *m,p'*-dichlorobenzophenone has been described above. The *m,o'* and *m,m'* isomers were prepared by the addition of *m*-chlorophenylmagnesium bromide to the proper chlorobenzonitrile and heating under reflux in benzene for two hours. The *m,o'*-dichlorobenzophenone was an oil, b. p. 140–142° (1 mm.), and was obtained in 73% yield.

*Anal.* Calcd. for $C_{13}H_8OCl_2$: C, 62.2; H, 3.2; Cl, 28.2. Found: C, 62.5; H, 3.5; Cl, 28.3.

The *m,m'*-dichlorobenzophenone, which was obtained in 77% yield, distilled at 160–166° (2 mm.) and melted at 123.8–124.9°.

*Anal.* Calcd. for $C_{13}H_8OCl_2$: C, 62.2; H, 3.2; Cl, 28.2. Found: C, 62.2; H, 3.3; Cl, 28.2.

*o,o'*-Dichlorobenzophenone was prepared by oxidation of *o,o'*-dichlorobenzilic acid, which was obtained by the series of reactions *o*-chlorobenzaldehyde, *o,o'*-dichlorobenzoin, *o,o'*-dichlorobenzil, *o,o'*-dichlorobenzilic acid.

***o,o'*-Dichlorobenzoin.**—*o*-Chlorobenzaldehyde (technical grade) was redistilled, and 98.5 g. (0.7 mole) of this was heated at reflux for half an hour with 95 ml. of ethanol, 75 ml. of water and 10 g. of potassium cyanide. The orange oil which separated upon cooling did not crystallize. It was washed by swirling with cold water and used in the following preparation.

***o,o'*-Dichlorobenzil.**[28]—The crude *o,o'*-dichlorobenzoin was placed in a 1-liter flask and 250 ml. of concentrated nitric acid added through the condenser. An immediate and vigorous reaction ensued. When the reaction had quieted, the mixture was warmed on a steam-bath for five hours and then poured into 2 liters of cold water. The yellow product was collected and recrystallized from 1300 ml. of ethanol. Concentration of the mother liquors gave additional material. It formed light yellow prisms, m. p. 133–135°. The total yield was 85 g., or 91%, on the basis of the *o*-chlorobenzaldehyde used.

***o,o'*-Dichlorobenzilic Acid.**—The benzil, 75 g. (0.268 mole), was heated at reflux on a steam-bath for ten minutes in a mixture of 50 g. of potassium hydroxide, 100 ml. of water, and 100 g. of ethanol. The mixture was evaporated in a dish until only a dark-brown oil remained; it was then dissolved in 2 liters of water and the benzilic acid precipitated by the slow addition of dilute hydrochloric acid. The acid was collected, dried, and recrystallized from benzene, m. p. 162–163°. The yield was 72 g. (90%).

*Anal.* Calcd. for $C_{14}H_{10}O_3Cl_2$: C, 56.59; H, 3.39. Found: C, 56.92; H, 3.41.

**Bis-(*o*-chlorophenyl)-carbinol.**—To a solution of 27.0 g. (0.192 mole) of *o*-chlorobenzaldehyde in 100 ml. of dry ether 160 ml. of a 1.2 *N* (0.192 mole) solution of *o*-chlorophenylmagnesium bromide was added with stirring. The reaction mixture was heated at reflux for one hour and was then hydrolyzed with dilute hydrochloric acid. Distillation of the ethereal solution gave 24.0 g. (49%) of oil, b. p. 155–165° (1.5–2 mm.). The acetate of this alcohol melted at 137–138°.

***o,o'*-Dichlorobenzophenone.**—An acetic acid solution of chromic anhydride (3 g. in 20 ml. of acetic acid) was mixed with 3 g. of *o,o'*-dichlorobenzilic acid. A vigorous evolution of gas occurred. After further warming, a solid was obtained by pouring into dilute alkali. Three crystallizations from ethanol, sublimation and a further crystallization gave 1.19 g. of large, octahedral crystals melting at 45–46°.

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[27] Collet, *Bull. soc. chim.*, [3] **21**, 70 (1899).

[28] Hodgson and Rosenberg, *J. Chem. Soc.*, 14 (1930).

*Anal.* Calcd. for $C_{13}H_8Cl_2O$: C, 62.18; H, 3.21; Cl, 28.24. Found: C, 62.41; H, 3.62; Cl, 28.35.

The same ketone was prepared by heating at reflux a mixture of bis-(*o*-chlorophenyl)-carbinol and sodium dichromate in sulfuric acid and acetic acid for three hours. The neutral fraction gave upon distillation a nearly quantitative yield of oil, b. p. 127–135° (1 mm.), which upon crystallization from ethanol, melted at 45.4–46.6 (cor.).

**2,4-Dinitrophenylhydrazones of the Isomeric Dichlorobenzophenones.**—To 1.0 g. (0.0073 mole) of 2,4-dinitrophenylhydrazine dissolved in 2 ml. of concentrated sulfuric acid 15 ml. of 95% ethanol was added; this solution was then mixed with a solution of 1.25 g. (0.005 mole) of the ketone dissolved in 25 ml. of 95% ethanol. In most cases crystallization was complete in one to two hours; the *o*,*o*′-dichlorobenzophenone was allowed to stand overnight as crystallization was very slow. Yields were not calculated, but were high. The crude 2,4-dinitrophenylhydrazones were dissolved in hot pyridine and recrystallized by the addition of warm 95% ethanol. This is similar to the method of Brady.[29] The properties of the dinitrophenylhydrazones are given in Table IV.

TABLE IV

2,4-DINITROPHENYLHYDRAZONES OF ISOMERIC DICHLOROBENZOPHENONES

| Isomer | M. p. of derivative | | Analyses,[a] % | | |
|---|---|---|---|---|---|
| | Crude, °C. | Pure, °C. | C | H | Cl |
| *o*,*o*′ | 200–205 | 206–208 | 53.3 | 2.8 | 13.2 |
| *o*,*p*′ | 225–228 | 230–231 | 52.8 | 2.8 | 13.1 |
| *o*,*m*′ | 253–257 | 255–257 | 52.8 | 3.0 | 12.9 |
| *m*,*m*′ | 234–238 | 235–238 | 53.2 | 2.8 | 12.9 |
| *m*,*p*′ | 253–256 | 258–260 | 52.9 | 2.8 | 12.8 |
| *p*,*p*′ | 195–203 | 238–240 | 53.3 | 2.8 | 13.2 |

[a] Calcd. for $C_{19}H_{12}O_4N_4Cl_2$: C, 52.9; H, 2.8; N, 13.0.

## Summary

Studies have been made of the composition of several samples of technical DDT and a sample of "by-product oil" recovered from a process of refinement of crude DDT prepared from "chlorinated alcohol" and chlorobenzene. Technical DDT has been found to contain upwards of 70% of 1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p*,*p*′-DDT), the most active insecticidal ingredient. The major impurity is 1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o*,*p*′-DDT).

Lesser amounts of twelve other organic impurities have been found, the presence of which may be explained on the basis of side reactions involving chloral, chlorobenzene, sulfuric acid, and impurities in the starting materials.

Work on the proof of structure, including synthesis, of the by-product materials, is described.

The *o*,*p*′- and the *m*,*p*′-isomers of *p*,*p*′-DDT and various derivatives of these compounds are described.

The synthesis of all the isomeric dichlorobenzophenones with one chlorine atom on each ring and of the 2,4-dinitrophenylhydrazones of these ketones is described.

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(29) Brady, *J. Chem. Soc.*, 756 (1931).

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# The Reactions of Antisera Homologous to Various Azophenylarsonic Acid Groups and the *p*-Azophenylmethylarsinic Acid Group with Some Heterologous Haptens[*]

BY DAVID PRESSMAN, ARTHUR B. PARDEE AND LINUS PAULING

Recently we have made quantitative studies of the combining powers of substituted phenylarsonic acids and of naphthylarsonic acids with antisera homologous to the *o*-, *m*-, and *p*-azophenylarsonic acid groups[1,2,3] (anti-$R_o$, -$R_m$, and -$R_p$ sera, respectively) and to the *p*-(*p*-azophenylazo)-phenylarsonic acid group[2,4] (anti-$R'_p$ serum). The quantitative studies of these antisera have now been extended to include their reactions with substances related to phenylarsonic acid but in which the aromatic nucleus attached to the arsenic atom of the arsonic acid group is replaced by an aliphatic or alkaryl residue, or one of the hydroxy groups of the arsonic acid is replaced by a second organic residue to form an arsinic acid, or the arsonic acid group is altered to form the dimethylarsine dihydroxide or the arsine oxide group, or the arsenic atom is replaced by another atom (phosphorus, antimony, or sulfur). We have studied also the reactions of antiserum homologous to the *p*-azophenylmethylarsinic acid group (anti-$R_{CH_3}$ serum) with several heterologous substances.

Some similar reactions of antisera with heterologous substances have been studied qualitatively by other investigators. Erlenmeyer and Berger[5] found that an antiserum to horse serum coupled with diazotized *p*-aminophenylarsonic acid formed precipitates with ovalbumin coupled with diazotized *p*-aminophenylphosphonic acid as well as with the antigen from diazotized *p*-aminophenylarsonic acid, but not with the antigen from diazotized *p*-aminophenylstibonic acid. Haurowitz

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[*] The Serological Properties of Simple Substances. XI. For No. X of this series see THIS JOURNAL, **67**, 1219 (1945).

(1) D. Pressman, D. H. Brown, and L. Pauling, *ibid.*, **64**, 3015 (1942).

(2) L. Pauling, D. Pressman, and A. L. Grossberg, *ibid.*, **66**, 784 (1944).

(3) L. Pauling and D. Pressman, *ibid.*, **67**, 1003 (1945).

(4) D. Pressman, J. T. Maynard, A. L. Grossberg, and L. Pauling, *ibid.*, **65**, 728 (1943).

(5) H. Erlenmeyer and E. Berger, *Biochem. Z.*, **255**, 429 (1932).