

**2-Fluoro-4'-hydroxybiphenyl (III).**—The preparation of 2-fluorobiphenyl in 71% yield was carried out essentially as described by Schiemann and Roselius,<sup>7</sup> except that NaBF<sub>4</sub> was used as a source of the fluoborate ion instead of HBF<sub>4</sub>. Conversion of 7 g. of 2-fluoro-4'-biphenylamine<sup>8</sup> to 1 g. of pure III was carried out as described for compound I; colorless needles from ethanol, m. p. 131.5–133°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>9</sub>OF: F, 10.09. Found: F, 9.98, 10.19.

**4,4'-Difluoro-2-hydroxybiphenyl (IV).**—The diazonium sulfate prepared from 37 g. of 4,4'-difluoro-2-biphenylamine<sup>6</sup> was added slowly to a boiling mixture of 120 cc. of concentrated H<sub>2</sub>SO<sub>4</sub> and 90 cc. of water. Steam distillation produced 29 g. of faintly yellow IV. A second steam distillation gave 20 g. of pure IV; colorless needles from 70% ethanol, m. p. 93.5–94.5°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>F<sub>2</sub>: F, 18.43. Found: F, 18.41, 18.58.

**C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>F<sub>2</sub>, Probably 4,4'-Difluoro-2,3'-dihydroxybiphenyl (V).**—The dinitro-4,4'-difluorobiphenyl (m. p. 106–114°) was prepared following the directions of Shaw and Turner.<sup>3</sup> Recrystallization from various solvents and a second distillation did not change the melting point of the product, which Shaw and Turner found to consist of at least 75% 2,3'-dinitro-4,4'-difluorobiphenyl (m. p. 109–110°), the remainder being 2,2'-dinitro-4,4'-difluorobiphenyl (m. p. 163–165°).

Reduction of 10 g. of the dinitro compound was carried out in the usual way with tin and hydrochloric acid. The mixture was made basic with sodium hydroxide and extracted with ether. The ether solution was dried overnight with solid sodium hydroxide, the ether removed,

and the residue distilled under reduced pressure. A fraction of 7 g. of apparently pure material, b. p. 160–162° (3 mm.), was obtained; there was a slight forerun, and a residue of about 2 cc. remained in the flask. Standing at 0° for a week caused solidification to a light yellow mass, m. p. 54–72°. A second distillation and fractional precipitation from acid solution did not change the melting point appreciably.

Conversion of the diamine to V was carried out by adding the diazonium sulfate obtained from 6 g. of the amine to a boiling mixture of 25 cc. concentrated sulfuric acid and 19 cc. of water. The solution was steam distilled; very little product distilled. The solution was extracted with ether and the ethereal solution dried overnight with sodium sulfate; evaporation left 0.5 g. of a white solid which was recrystallized from 70% ethanol; fluffy white needles, m. p. 112.5–113°. This compound is presumably 4,4'-difluoro-2,3'-dihydroxybiphenyl (V).

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>F<sub>2</sub>: F, 17.10. Found: F, 17.39.

### Summary

Several new fluorohydroxybiphenyls have been prepared: 4-fluoro-4'-hydroxybiphenyl, 2-fluoro-2'-hydroxybiphenyl, 2-fluoro-4'-hydroxybiphenyl, 4,4'-difluoro-2-hydroxybiphenyl, and a compound whose probable structure is 4,4'-difluoro-2,3'-dihydroxybiphenyl.

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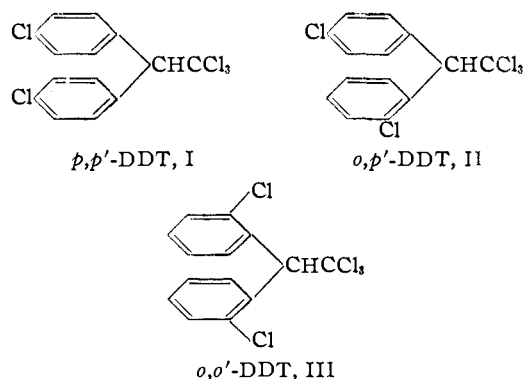
[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

## Isolation of the *o,o'*-DDT Isomer from Technical DDT<sup>1,2</sup>

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Previous fractionations<sup>3</sup> of various samples of technical DDT have shown that the two major products in the DDT condensation are *p,p'*-DDT (1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane, I) and *o,p'*-DDT (1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane, II). Small amounts of twelve other materials were found, but no other DDT isomer was isolated in that work, although substantial amounts of oily residues were isolated which were not well characterized and were suspected to contain other isomers of DDT. It is the purpose of this paper to describe the work resulting in the isolation of the *o,o'*-DDT isomer (1-trichloro-2,2-bis-(*o*-chlorophenyl)-ethane, III) from technical DDT and in its proof of structure. Isolation of this compound was of interest

in the course of a study of the effect of halogen position upon toxicity of DDT isomers.



(1) This work was conducted as part of a program supported by a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development and from the Office of the Quartermaster General to the Bureau of Entomology and Plant Quarantine. Not copyrighted.

(2) This paper was presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 8–12, 1946.

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

The methods which had been used previously for separation included fractional crystallization and chromatographic adsorption techniques. In the previous work an oil (oil C, see Chart 1 of reference 3) had been isolated from technical DDT which represented 12.7% of the original technical DDT and from which over 90% of the *p,p'*-DDT and 70% of the *o,p'*-DDT known to be present in technical DDT had been removed. It had been

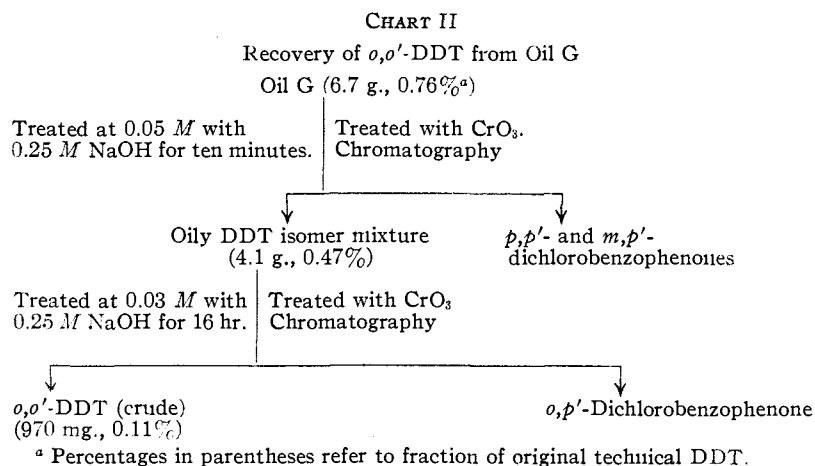
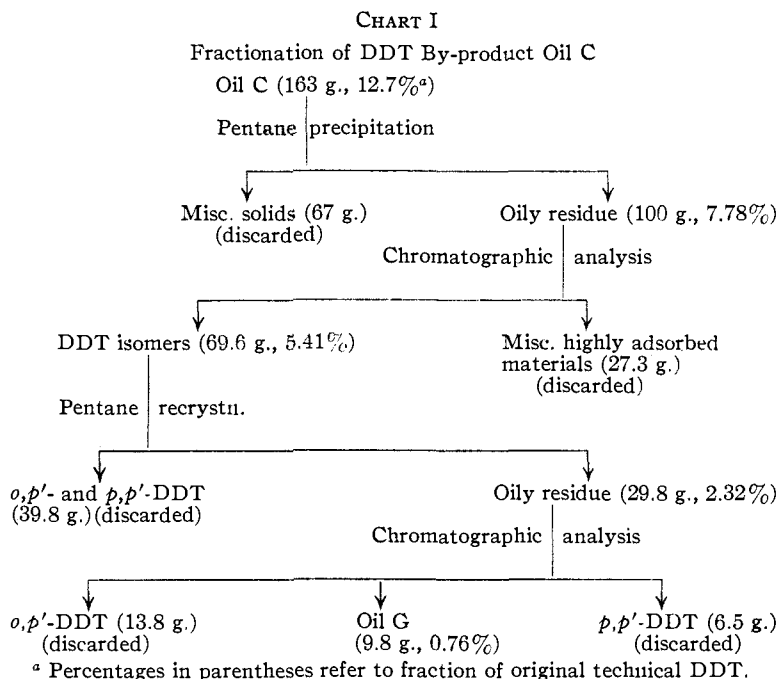
shown previously that this oil C was a mixture containing DDT isomers and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane, as well as various oxygen- and sulfur-containing materials present in technical DDT. In the previous work<sup>3</sup> emphasis was placed on the isolation of these by-product materials; in the present work interest lay only in the DDT isomers present in oil C.

The fractionation of this oil is summarized in Charts 1 and 2.

Separation of an *o,o'*-DDT-rich fraction (oil G) was effected by recrystallization and chromatographic techniques. Previous work<sup>4</sup> had shown that *o,p'*-DDT was dehydrochlorinated by ethanolic alkali at a rate one sixty-seventh that of *p,p'*-DDT, presumably due to the steric effect of the *ortho* chlorine atom. A "reaction-rate constant" determination on oil G was carried out as described for pure materials.<sup>4</sup> The extent of dehydrochlorination is plotted against time in Fig. 1, and the variation in "rate constant" with time and with fraction reacted are given in Table I. These values for the apparent reaction-rate "constants" when compared with values of 0.0248 liter/sec./mole for *p,p'*-DDT,<sup>4</sup> 0.028 for *m,p'*-DDT,<sup>5</sup> and 0.00037 for *o,p'*-DDT,<sup>4</sup> suggested that the oil contained about 20% of *o,o'*-DDT, which was predicted to have a very slow dehydrochlorination rate, with two *ortho* chlorine atoms providing considerable steric hindrance. The data also indicated the feasibility of use of this rate differential as a basis for effecting a separation of the material.

Oil G was first treated with ethanolic sodium hydroxide under conditions calculated<sup>6</sup> to effect dehydrochlorination of substantially all the *p,p'*- and *m,p'*-DDT present and leave unreacted the greater part of the *o,p'*- and *o,o'*-DDT. Treatment of the reaction products with chromic anhydride resulted in the oxidation of the olefins and did not affect the unreacted DDT isomers. Benzophenone and DDT fractions were separated. The ketone fractions contained *p,p'*- and *m,p'*-

dichlorobenzophenone. Isolation of *m,p'*-dichlorobenzophenone offered the first evidence we have



noted for the presence of *m,p'*-DDT in technical DDT.

TABLE I  
CALCULATED "RATE CONSTANTS" FOR THE ALKALINE DEHYDROCHLORINATION OF OIL G

Time interval, hours	Fraction reacted, %	Apparent "rate constant" liter/sec./mole
0.0-0.2	24	0.0085
0.2-0.6	33	.0019
0.6-3.4	41	.00031
3.4-7.8	48	.00023
7.8-32	70	.00015
32-96	78	.000036
96-144	80	.000014
Reflux	100	.....

(4) Cristol, THIS JOURNAL, 67, 1494 (1945).

(5) Cristol, unpublished work.

(6) The calculations were made by use of the second-order reaction-rate constants previously determined.

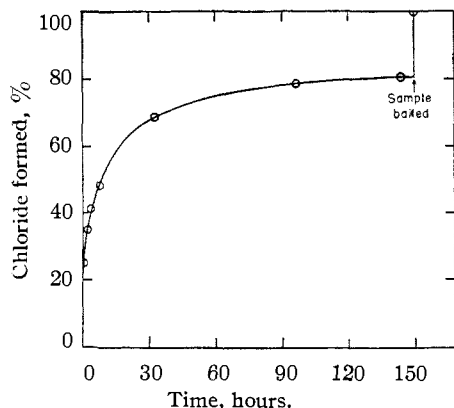
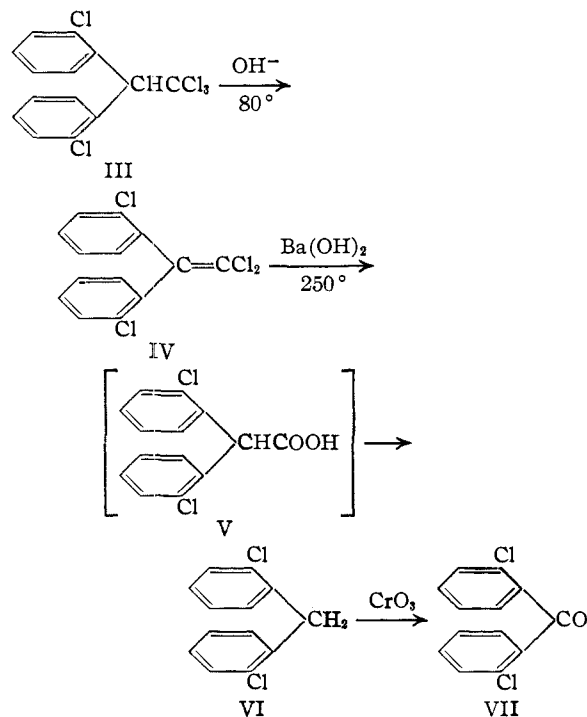


Fig. 1.—Quantitative dehydrochlorination of oil G: [DDT] = 0.01 M; [NaOH] = 0.05 M.

The oily DDT-isomer fraction was again treated with ethanolic alkali, this time under conditions calculated<sup>6</sup> to effect the preferential dehydrochlorination of the *o,p'*-DDT, and leave most of the *o,o'*-DDT unreacted, assuming a rate constant for *o,o'*-DDT of  $10^{-6}$  liter/sec./mole (cf. Table I). Oxidation and separation as above gave an oily DDT-isomer fraction, which, after crystallization and purification, was shown to be *o,o'*-DDT.

The proof of structure of *o,o'*-DDT was carried out by the following sequence of reactions



The round-about degradation of the olefin IV to the benzophenone VII was necessitated by the fact that IV was stable to chromic anhydride in refluxing glacial acetic acid in contrast to the correspondings olefins from *p,p'*- and *o,p'*-DDT,

which are rapidly oxidized. The olefin was also more stable to hydrolysis with barium hydroxide, a temperature of  $250^{\circ}$  being required, in contrast to a temperature around  $175^{\circ}$  for the other isomers.<sup>7,8</sup> The increased resistance of IV to oxidation or to hydrolysis is ascribed to the steric effect of the *ortho* chlorine atoms.

The benzophenone VII obtained from *o,o'*-DDT was shown to be identical with one obtained by degradation of an authentic sample of V, prepared by the reduction<sup>9</sup> with phosphorus and iodine of the corresponding benzilic acid.<sup>3</sup> Both samples of VII gave identical tetranitro derivatives.

*o,o'*-DDT was found to be relatively ineffective as an insecticide. Experimental results on the *o,o'*, *o,p'* and *p,p'* isomers have recently been published.<sup>10</sup>

After the other work reported in this paper was completed, a slightly larger sample of *o,o'*-DDT became available by a similar treatment of a by-product oil from the synthesis of *o,p'*-DDT.<sup>3</sup> A rate constant of the dehydrochlorination reaction was determined at  $20.1^{\circ}$  by the method described previously,<sup>4</sup> and was found to be 0.0000108 liter/sec./mole, a value in excellent agreement with the value predicted from the data of Table I.

## Experimental

**Fractionation of By-product Oil.**—In the previous work<sup>3</sup> a large amount of oil, representing 12.7% of the technical DDT, had been isolated, and a partial separation of this oil into its components had been made. This oil was labeled "oil C" in the previous work.

A solution of 163 g. of oil C in about 400 ml. of *n*-pentane was allowed to stand in a refrigerator for several days; the precipitated solids were removed by filtration, and a portion of the solvent was removed by distillation and the solution replaced in the refrigerator. This was repeated several times; 67 g. of solids and 100 g. of oil were obtained. The solids were found to comprise essentially a mixture of *p,p'*-DDT (I) and *o,p'*-DDT (II).

The oil (oil C-1) was dissolved in 200 ml. of Skellysolve B (petroleum ether, b. p.  $60-70^{\circ}$ ) and chromatographed in two portions on activated alumina columns ( $48 \times 420$  mm.). Elutions were carried out as shown in Table II.

TABLE II  
CHROMATOGRAPHIC ANALYSIS OF OIL C-1 (50 G.)

Fraction	Eluting solvent	Volume of each fraction, ml.	Wt., g.	Remarks
1	Skellysolve B	200	4.2	M. p. $55-71^{\circ}$
2	Skellysolve B	400	18.9	M. p. $50-67^{\circ}$
3-6	Skellysolve B	400	11.9	Oily solids
7	Skellysolve B	400	0.7	M. p. $65-89^{\circ}$
8	Skellysolve B	400	.5	M. p. $70-91^{\circ}$
9, 10	10% CCl <sub>4</sub> in Skellysolve B	400	.8	.....
11	CCl <sub>4</sub>	400	1.3	.....
12	95% EtOH	800	11.8	.....

(7) White and Sweeney, *U. S. Public Health Serv., Pub. Health Repts.*, **60**, 66 (1945).

(8) Cristol and Haller, *THIS JOURNAL*, **67**, 2222 (1945).

(9) Bartlett, Mueller and Schneider, unpublished work.

(10) Cristol, Haller and Lindquist, *Science*, **104**, 343 (1946).

Fractions 7 and 8 were mainly *p,p'*-DDT, and the later fractions were by-product materials described previously.<sup>8</sup> After removal of solvent, fractions 1 to 6 were recrystallized separately from pentane. Fraction 1 gave 3.1 g. of *o,p'*-DDT; fraction 2 gave 11.4 g. of *o,p'*-DDT and 1.5 g. of a mixture of *o,p'*-DDT and *p,p'*-DDT; fractions 3 to 6 gave 5.0 g. of mixtures of *o,p'*- and *p,p'*-DDT. The mother liquors from the recrystallization of these fractions of both portions of oil were combined. The solvent was removed, leaving 29.5 g. of oil.

This oil was rechromatographed on an activated alumina column as above. Four liters of Skellysolve B was used as eluting solvent, followed by 400 ml. of carbon tetrachloride and 800 ml. of 95% ethanol. After removal of solvent, the first three and last two 400-ml. Skellysolve fractions solidified upon scratching; the former contained *o,p'*-DDT and the later *p,p'*-DDT. The center five fractions did not crystallize when seeded with either *o,p'*- or *p,p'*-DDT. These oils were combined; 9.8 g. (representing 0.76% of technical DDT) of a pale-yellow oil was obtained. Analysis of this oil, designated oil G, indicated a mixture of DDT isomers.

*Anal.* Calcd. for  $C_{14}H_9Cl_5$ : Cl, 50.0. Found: Cl, 49.6.

**Isolation of *o,o'*-DDT from Oil G.**—To a solution of 6.73 g. (0.019 mole) of oil G in 200 ml. of 95% ethanol was added 200 ml. of 0.50 *M* ethanolic sodium hydroxide. The dehydrochlorination was conducted at 20°. After ten minutes, excess 1.2 *N* hydrochloric acid was added to stop the reaction. Most of the ethanol was removed by distillation of the mixture *in vacuo*. This was necessary for satisfactory extraction of the mixture with ether. The ethereal extract was washed with water, dried, filtered and the ether removed.

The residual oil, which weighed 6.1 g., was dissolved in 100 ml. of Skellysolve B and chromatographed as above. It was hoped that separation of the less strongly adsorbed olefins from the DDT isomers could be effected in this manner. Some separation was noted, but quantitative separation did not obtain. The alumina column was prewashed with 200 ml. of Skellysolve B, the solution was then added, followed by 5300 ml. of Skellysolve B, 800 ml. of carbon tetrachloride, and 800 ml. of 95% ethanol. Eighteen 400-ml. fractions were taken; the first five contained only negligible quantities of material and were discarded. Fractions 6 to 9 (weighing 2.8 g.) contained substantial quantities of olefin, as shown by their chlorine analyses, whereas fractions 10 to 16 (weighing 3.1 g.) were mixtures of DDT isomers. The ethanol eluates were negligible and were discarded. In repeating this work, it would seem preferable to eliminate this chromatographic step and proceed directly to the oxidation described below with the whole of the oil.

Fractions 6 to 9 were combined and dissolved in 50 ml. of glacial acetic acid. The solution was heated to reflux, and 1.5 g. of chromic anhydride was added in portions. After a ninety-minute reflux the mixture was cooled and poured onto ice. The solution contained excess oxidant, as shown with potassium iodide-starch test paper. The reaction product was extracted with ether, washed with water, dilute sodium hydroxide until washings were basic, and saturated salt solution. After filtration of the solution, the ether was removed by distillation. The residue was dissolved in 100 ml. of Skellysolve B and chromatographed on an activated-alumina column 31 × 160 mm. which had been prewashed with 100 ml. of Skellysolve B. Elution was carried out with 300 ml. of Skellysolve B, 200 ml. of 10% carbon tetrachloride in Skellysolve B, 200 ml. of carbon tetrachloride, and 250 ml. of 95% ethanol. The petroleum ether and carbon tetrachloride eluates contained DDT isomers (weight, 1.11 g.), which were combined with fractions 10 to 16 of the previous chromatograph and treated as described below.

The ethanol eluate was isolated by evaporation of the solvent, leaving 1.116 g. of a tan solid, m. p. 90–120°. This was a particularly intractable mixture; however, small amounts of *p,p'*- and *m,p'*-dichlorobenzophenones were isolated by fractional crystallization from Skellysolve

B. The initial fractions, upon recrystallization from aqueous ethanol, gave about 20 mg. of *p,p'*-dichlorobenzophenone, m. p. and mixed m. p. with an authentic specimen, 145–146.5° (cor.). The later fractions, upon recrystallization from 95% ethanol, gave about 20 mg. of *m,p'*-dichlorobenzophenone, m. p. and mixed m. p. with an authentic specimen<sup>9</sup> 112–113° (cor.). Only small amounts of the pure ketones were obtained in the fractionation, as it was extremely difficult to free the individual components from the eutectic mixture of the isomers, which melted in the range 90–93°.

The combined DDT-isomer fractions (4.1 g., 0.012 mole) were dissolved in 200 ml. of 95% ethanol and treated with 200 ml. of 0.5 *M* ethanolic sodium hydroxide at 20.1° for sixteen hours. The reaction was then stopped by the addition of 400 ml. of water and 10 ml. of concentrated nitric acid. Most of the ethanol was removed by partial distillation *in vacuo*, and the residue was cooled and extracted with ether. The ethereal extract was washed with water, dilute sodium carbonate, water and saturated salt solution. The ether was evaporated off, leaving 3.98 g. of brown oil.

This oil was dissolved in 50 ml. of Skellysolve B and chromatographed on a 45 × 270 mm. column of activated alumina, which had been prewashed with 400 ml. of Skellysolve B, and eluted successively with Skellysolve B, 10% carbon tetrachloride in Skellysolve B, carbon tetrachloride, and 95% ethanol as described in Table III.

TABLE III

CHROMATOGRAPHIC ANALYSIS OF PARTIALLY DEHYDROCHLORINATED OIL

Fraction	Eluting solvent <sup>a</sup>	Total wt. of fractions, g.	Remarks, major components
1–5	Skellysolve B	0.100	Oils, discarded
6–9	Skellysolve B	2.076	Solid, olefin fractions
11–13	Skellysolve B	1.061	Mixed fractions
14–17	Skellysolve B	0.356	Solid, <i>o,o'</i> -DDT
18	10% $CCl_4$ in Skellysolve B	.065	Solid, <i>o,o'</i> -DDT
19	$CCl_4$	.186	Solid, <i>o,o'</i> -DDT
20–21	$CCl_4$	.040	Oil, discarded
22–23	95% EtOH	.056	Oil, discarded

<sup>a</sup> 400 ml. of solvent used in each fraction.

The solvents were removed from all the fractions, and the resulting oils were scratched to induce crystallization. Fraction 18 crystallized spontaneously, and fractions 14 to 19 crystallized partially or completely when seeded with fraction 18. Fractions 14 to 19 were combined and recrystallized twice from methanol to give a crystalline solid, m. p. 78–80° (cor.). Recrystallization of this material from methanol containing a little water caused a change in crystal form to give *o,o'*-DDT melting at 92–93° (cor.). After the higher melting form had been obtained, it was not possible to obtain more of the lower melting form. These fractions gave directly 290 mg. of pure *o,o'*-DDT.

*Anal.* Calcd. for  $C_{14}H_9Cl_5$ : C, 47.43; H, 2.56; Cl, 50.01. Found: C, 47.52; H, 2.79; Cl,<sup>11</sup> 49.58, 49.63.

The residues from the mother liquors from this recrystallization and fractions 11 to 13 of the previous chromatograph (Table III) were treated with excess chromic anhydride in refluxing glacial acetic acid, and the product was separated by chromatographic analysis in the usual manner to give 682 mg. of crude *o,o'*-DDT fractions and 395 mg. of crude *o,p'*-dichlorobenzophenone fractions. Recrystallization of the *o,o'*-DDT fractions from aqueous methanol gave 472 mg. of pure material.

The rather cumbersome separation procedure described herein might be shortened by elimination of the chromatographic separation described in Table III and by treatment

(11) Chlorine analysis by Miss E. Werble, University of Maryland.

of the unfractionated oil with oxidant, followed by chromatographic separation of the products.

**1,1-Dichloro-2,2-bis-(*o*-chlorophenyl)-ethylene, IV.**—Fractions 6 to 9 of the chromatograph (Table III) were combined, oxidized with excess chromic anhydride, and the product separated as usual by chromatographic analysis. The benzophenone fractions (essentially *o,p'*-dichlorobenzophenone) weighed 1.055 g. The "DDT isomer" fractions (wt. 415 mg.) melted over a wide range and was suspected to comprise a mixture of *o,o'*-DDT with its olefin. The mixture was therefore treated with refluxing ethanolic sodium hydroxide to convert all the DDT to its olefin, which was then worked up to give 380 mg. of crude product. Four recrystallizations from aqueous ethanol gave 182 mg. of 1,1-dichloro-2,2-bis-(*o*-chlorophenyl)-ethylene, m. p. 147.3–147.9° (cor.). A mixed melting point with a sample prepared directly from *o,o'*-DDT was not depressed.

*Anal.* Calcd. for  $C_{14}H_9Cl_2$ : C, 52.87; H, 2.53; Cl, 44.60. Found: C, 52.87; H, 2.61; Cl,<sup>11</sup> 44.66, 44.73.

A small sample of *o,o'*-DDT was treated with excess ethanolic 0.17 *M* sodium hydroxide at reflux for four hours. This treatment resulted in the elimination of 1.3 moles of chloride ion per mole of *o,o'*-DDT, rather than the expected 1 mole. This excess is probably due to the formation of a small amount of bis-(*o*-chlorophenyl)-acetic acid (V), similar to that noted in the case of the *o,p'*-isomer.<sup>3</sup> The neutral product (IV) was isolated and was comparable in properties to that isolated as described above.

Compound IV is stable to three-hour treatment with chromic anhydride in refluxing glacial acetic acid.

**Degradation of *o,o'*-DDT.**—A mixture of 0.40 g. (1.3 millimole) of barium hydroxide octahydrate, 142 mg. (0.4 millimole) of *o,o'*-DDT and 15 ml. of ethylene glycol was heated under reflux for four hours. The still temperature of the mixture varied from 173–180° when the bath temperature was varied from 186–205°. The reaction mixture was separated into acidic and neutral fractions by usual procedures. Only a trace of acidic material was found, and the neutral material was the olefin IV, indicating that only 1 mole of hydrogen chloride had been removed. This material was then added to a mixture of 0.40 g. of barium hydroxide octahydrate and 25 ml. of ethylene glycol, from which the water had been removed by the distillation of ca. 8 ml. of the solvent. The reaction mixture was heated at reflux (still temperature 197°, bath temperature 220°) for five hours. The product was worked up as above, and again only a trace of acidic material was obtained, and 124 mg. of olefin IV was recovered.

This substance was added to a mixture of 1.0 g. of barium hydroxide octahydrate and 25 ml. of diethylene glycol, from which the water had been removed by distillation of the solvent until the b. p. (245°) of diethylene glycol had been reached. The mixture was held at reflux (bath temperature 255°) for five hours. The product was worked up as above, and no acid fraction was obtained. The neutral fraction was a brown oil (wt. 131 mg.) with  $n_D^{26}$  1.550. The refractive index of this product was considerably below that of the expected product VI, presumably owing to the presence of decomposition products of the solvent. Sublimation of the product did not result in much improvement. As we had prepared VI previously and knew that it was a very low melting solid and consequently difficult to purify, we decided to convert the product directly to the benzophenone VII, as it seemed likely that the impurities would be readily oxidizable to low molecular weight substances.

The sublimate containing VI was dissolved in 10 ml. of glacial acetic acid and heated at reflux while 500 mg. of chromium trioxide was added slowly. Refluxing was continued for five hours. The reaction mixture was cooled, poured into water, and extracted with ether. After washing with water and dilute alkali and drying, the solution was filtered and the ether evaporated off. The neutral residue (wt. 66 mg.) solidified upon seeding with *o,o'*-dichlorobenzophenone (VII) and melted at 40–44°. The

product was recrystallized from aqueous ethanol to give 54 mg. of reasonably pure *o,o'*-dichlorobenzophenone, m. p. 43.5–45.5° (cor.). The melting point was 43.7–45.6° (cor.) when this sample was mixed with an authentic specimen<sup>3</sup> of m. p. 45.5–46.1° (cor.).

Tetranitration of 47 mg. of this substance by the procedure described below gave 57 mg. of crude product, which after several recrystallizations from acetone-ethanol melted at 192–194° (cor.). A mixed melting point with an analyzed authentic sample was not depressed.

**bis-(*o*-Chlorophenyl)-acetic Acid (V).**—This material was prepared by the reduction of the corresponding benzoic acid<sup>3</sup> with phosphorus and iodine according to the directions of Bartlett, Mueller and Schneider.<sup>9</sup> It melted at 168.5–169° (cor.).

*Anal.* Calcd. for  $C_{14}H_{10}O_2Cl_2$ : C, 59.81; H, 3.59. Found: C, 59.79; H, 3.63.

**bis-(*o*-Chlorophenyl)-methane (VI).**—A mixture of 43.5 g. (0.155 mole) of V, 54 g. (0.17 mole) of barium hydroxide octahydrate, and 200 ml. of ethylene glycol was distilled slowly until the water present was removed and the still temperature reached 197°. After three hours at this temperature, the reaction mixture was cooled, decomposed with 250 ml. of 3 *N* hydrochloric acid, and extracted with ether. The ethereal extract was washed with water, dilute sodium hydroxide, and water again. The solution was dried over anhydrous sodium sulfate and the ether removed. The product was distilled, and the fraction distilling at 141.5–142.5° (3 mm.) was collected. The yield was 33.0 g. (90%). bis-(*o*-Chlorophenyl)-methane was an oil at room temperature with  $n_D^{20}$  1.596. It froze when cooled and melted at 23°.

*Anal.* Calcd. for  $C_{13}H_{10}Cl_2$ : C, 65.84; H, 4.25. Found: C, 65.76; H, 4.17.

Compound VI did not produce tractable solid nitration products when treated with fuming nitric acid or with a mixture of nitric acid and sulfuric acid on the steam-bath.

The methane was slowly oxidized by chromic anhydride in refluxing glacial acetic acid to the benzophenone VII. Treatment with excess chromic anhydride for ten minutes resulted in the oxidation of less than half of the methane, but treatment for three hours gave total conversion.

**Tetranitro-*o,o'*-dichlorobenzophenone.**—To 233 mg. of VII was added 6 ml. of an ice-cold 1:1 mixture of fuming nitric acid and concentrated sulfuric acid. The mixture was allowed to come to room temperature slowly and was then heated on a steam-bath for two hours. The reaction mixture was cooled and poured onto ice. The resulting precipitate was filtered and washed with water, 5% sodium bicarbonate, and water again. After several recrystallizations from acetone-ethanol, 137 mg. of product melting at 192–194° was obtained.

*Anal.* Calcd. for  $C_{13}H_4O_8N_4Cl_2$ : C, 36.22; H, 0.94. Found: C, 36.28; H, 1.16.

**Tetranitro-*o,o'*-DDT.**—Treatment of 52 mg. of *o,o'*-DDT with fuming nitric acid and concentrated sulfuric acid according to the procedure for the other DDT isomers,<sup>12,13</sup> followed by recrystallization of the product from acetone-ethanol, gave 50 mg. of the tetranitro derivative, m. p. 241–243°.

*Anal.* Calcd. for  $C_{14}H_5O_8N_4Cl_2$ : C, 31.46; H, 0.94; N, 10.46. Found: C, 32.05, 32.09; H, 1.03, 1.09; N, 10.38, 10.67.

Treatment of a benzene solution of tetranitro-*o,o'*-DDT with methanolic sodium methoxide according to the procedure of the Schechter-Haller color test for DDT<sup>12,13</sup> resulted in the formation of a peach color with adsorption maxima at 496 and 370  $m\mu$  and corresponding molar extinction coefficients of 20,200 and 15,800 and with a minimum at a wave length of about 415  $m\mu$  and an extinction coefficient of 3300.

(12) Schechter and Haller, *THIS JOURNAL*, **66**, 2129 (1944).

(13) Schechter, Soloway, Hayes and Haller, *Ind. Eng. Chem., Anal. Ed.*, **17**, 704 (1945).

## Summary

A procedure is reported leading to the isolation of *o,o'*-DDT from technical DDT in amounts of about 0.1% of the original product. The method involved isolation of the DDT-isomer fractions by crystallization and chromatographic analysis and preferential dehydrochlorination of the more reactive DDT isomers, followed by oxidation of

these products, leaving the unreactive *o,o'*-DDT. The structure of *o,o'*-DDT has been proved by degradation.

A number of derivatives and compounds related to *o,o'*-DDT have been described.

The isolation of a degradation product, *m,p'*-dichlorobenzophenone, indicates the presence of *m,p'*-DDT in technical DDT.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE NAVAL RESEARCH LABORATORY]

Organic Fungicides. I. The Preparation of Some  $\alpha$ -Bromoacetamides

BY W. E. WEAVER AND W. M. WHALEY

The synthesis of N-alkyl- $\alpha$ -bromoacetamides was undertaken because certain  $\alpha$ -bromoacetanilides prepared in this Laboratory were found to be very fungicidal. It has been noted also that haloacylamides are claimed as seed disinfectants.<sup>1</sup> Since the unhalogenated amides and monohalogenated paraffins investigated were non-toxic, the fungicidal activity of  $\alpha$ -bromo amides may be attributed to the position of the halogen, which is particularly reactive.

There is a surprising lack of information in the literature concerning these compounds. N-Ethyl- $\alpha$ -bromoacetamide has been reported as a product of hydrolysis from the corresponding imide chloride.<sup>2</sup> The N,N-diethyl compound has been prepared in 20% yield from diethylamine and bromoacetyl bromide.<sup>3</sup> The N-allyl derivative has been prepared in 85% yield by Bergmann, Dreyer and Radt<sup>4</sup> according to the method used by Harries<sup>5</sup> for the corresponding chloro compound. The rest of the compounds reported here are new.

Analytical results and physical properties of all the compounds prepared are given in Table I. All the monosubstituted amides were low-melting solids, while the disubstituted compounds were liquids as anticipated from well-known theories of association.<sup>6</sup> The properties of the bromoacetamides do not render them unsuitable for many fungicidal purposes. The lower liquid amides were sternutatory and lachrymatory, though not as markedly as the corresponding  $\alpha$ -bromo esters. The other members exhibited these properties upon heating. It was not necessary to work in hoods and the compounds were only mildly irritating to the skin. The di-*i*-propyl and the di-*n*-butyl compounds were yellow liquids. The other compounds were white and have remained so for several months. The analytical data illustrate that several products were difficult to purify de-

spite repeated distillations and alternate methods of preparation.

The standard practice of conducting acylations with acid halides in ether<sup>7</sup> has been discarded in favor of ethylene dichloride, which can be used without drying, is easily removed at reduced pressure without foaming, can be recovered for re-use, is inexpensive and apparently affords excellent yields. It is relatively non-inflammable and does not form explosive peroxides. This superiority of ethylene dichloride was pointed out by Wacker<sup>8</sup> and Seymour.<sup>9</sup>

## Experimental

**Reagents.**—The bromoacetyl bromide, diethylamine, di-*n*-butylamine, allylamine and the amine hydrochlorides were obtained from Eastman Kodak Company, the *i*-propylamine and di-*i*-propylamine from Commercial Solvents Corporation, and the ethylene dichloride from Carbide and Carbon Chemicals Corporation. The other amines used were generously supplied by Sharples Chemicals, Inc. None of the reagents was purified before use.

**Method Ia.**—In a 500-cc., three-necked, round-bottomed flask equipped with a pentane thermometer, a dropping funnel and a mechanical stirrer were placed 150 cc. of ethylene dichloride and 0.2 mole of the amine. This solution was cooled to and maintained at  $-10^\circ$  by a Dry Ice-ethanol bath while 0.1 mole of bromoacetyl bromide in 25 cc. of ethylene dichloride was added during a period of five to ten minutes. After stirring for five minutes longer, the mixture was filtered with suction to remove the crystallized amine hydrobromide. The filtrate was washed with several 25-cc. portions of very dilute hydrochloric acid and dried over anhydrous magnesium sulfate. After removal of the solvent by vacuum distillation (water-pump), the product was distilled at pressures obtainable with a mechanical pump.

**Method Ib.**—This method was the same as the first except that the filtrate was not washed due to the solubility of the lower members in water.

**Method Ic.**—This method was identical with Method Ia except that absolute ether was substituted for the ethylene dichloride. Commercial ether, when used as a solvent, contained sufficient ethanol to yield appreciable quantities of ethyl  $\alpha$ -bromoacetate.

**Method Id.**—A solution of 0.2 mole of amine in 100 cc. of benzene was shaken in an ice-bath while 0.1 mole of

(1) Maier-Bode, German Patent 695,907.

(2) von Braun, Jostes and Munch, *Ann.*, **453**, 113 (1927).

(3) Miller and Johnson, *J. Org. Chem.*, **1**, 135 (1936).

(4) Bergmann, Dreyer and Radt, *Ber.*, **54B**, 2139 (1921).

(5) Harries, *ibid.*, **43**, 634 (1910).

(6) Hantzsch, *ibid.*, **64**, 661 (1931); Buswell, Rodebush and Roy, *THIS JOURNAL*, **60**, 2444 (1938).

(7) Jacobs, Heidelberger and Rolf, *ibid.*, **41**, 458 (1919); Dehn, *ibid.*, **34**, 1399 (1912).

(8) Wacker, *Chem. Ztg.*, **45**, 266 (1920).

(9) Seymour, *J. Chem. Ed.*, **16**, 285 (1939).