[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Preparation and Chemical Composition of Difluoro-diphenyl-trichloroethane[1,2]

BY H. LEON BRADLOW AND CALVIN A. VANDERWERF

Although scattered reports have filtered out of Germany concerning DFDT,[3] which is claimed to be superior to DDT as an insecticide,[3a] nevertheless, no systematic study of the preparation and chemical composition of that product has been reported.[4] This fact has prompted the present investigation.

Various modifications of the general method for the preparation of DDT and its bromine analogs have been described.[5] Similar procedures were employed for the preparation of DFDT in the present study. All proved satisfactory, but the optimum yields of condensation products were obtained as follows: chloral was distilled directly into an excess of fluorobenzene. A 3:1 mixture of sulfuric acid and 20% oleum was added at 10–20° and the material stirred for twelve hours at 25–30°. Poorer yields resulted in runs made according to our interpretation[6] of the procedure described in the Department of Commerce Report No. 360.

Paralleling the results obtained in the case of DDT[7] and of its bromine analog,[5e] the principal product obtained in the condensation of chloral with fluorobenzene was the *p,p'*-compound, 1-trichloro-2,2-bis-(*p*-fluorophenyl)-ethane (hereinafter called *p,p'*-DFDT). Although isolable amounts of the *o,p'*-isomer, 1-trichloro-2-*o*-fluorophenyl-2-*p*-fluorophenylethane (hereinafter called *o,p'*-DFDT) were obtained, it is significant that the percentage of this isomer formed was in most cases considerably less than that of its chlorine analog found in DDT.[7] This fact is in line with previous observations[8] of predominantly *p*-orientation in fluorobenzene. No *o,o'*-isomer could be isolated from the reaction mixture. It is worthy of note in this connection that the yield of the *o,p'*-isomer was greatest in runs stirred for a short time and at low temperatures.

The structure of the *p,p'*- and *o,p'*-isomers was established in a manner similar to that employed for the analogous constituents of DDT.[7] The *p,p'*-DFDT was dehydrohalogenated to the corresponding olefin, which was then degraded to the known *p,p'*-difluorobenzophenone.[9] Attempted degradation of *p,p'*-DFDT to *p,p'*-difluorodiphenylmethane by the method of White and Sweeney[10] gave only a high boiling product which could not be oxidized to *p,p'*-difluorobenzophenone with chromic anhydride. It is worthy of note that the reduction of *p,p'*-difluorobenzophenone by the Clemmensen procedure led to excellent yields of the pinacolone, 1,1,1,2-*p*-fluorophenylethanone-1, instead of the expected diphenylmethane derivative.

The *o,p'*-isomer fraction was degraded to the corresponding difluorobenzophenone, the structure of the 2,4-dinitrophenylhydrazone of which was established by analysis and by comparison with that of the ketone prepared synthetically by two methods: (1) the Friedel–Crafts reaction between *o*-fluorobenzoyl chloride and fluorobenzene,[11] and (2) the Grignard reaction between *o*-fluorobenzoyl chloride and *p*-fluorophenylmagnesium bromide.

No fluorobenzenesulfonic acid could be found in the aqueous extract of the reaction mixture.

Experimental[12,13]

Preparation of DFDT. Procedure I.—To a mixture of 163.0 g. (1.1 mole) of chloral[14] and 192.0 g. (2.0 moles) of fluorobenzene,[15] 200 cc. of concentrated sulfuric acid was added at once, with vigorous stirring for one hour at 25°. Stirring was continued for an additional hour at room temperature. The mixture was then poured onto 400 g. of ice and the resulting oil taken up in 150 cc. of ether. The water layer was extracted with an additional 50-cc. portion of ether and the combined ether solutions washed with 5% sodium hydroxide solution until neutral, then with water, and finally dried over drierite. Following removal of the ether at the take-off, the residue was vacuum distilled to yield 7.3 g. of recovered chloral hydrate, 25.2 g. of a first fraction, b. p. 135–177° at 9 mm., and 76.7 g. of *p,p'*-DFDT, b. p. 177–178° at 9 mm. The

---

[1] The symbol DFDT will be employed throughout this article as a contraction for difluoro-diphenyl-trichloroethane, a generic name for the principal products resulting from the condensation of chloral with fluorobenzene in the presence of sulfuric acid.

[2] Presented before the Organic Division of the American Chemical Society at the Atlantic City Meeting in April, 1946.

[3] See for example: (a) Kuhn and others, *Chem. Eng. News*, **23**, 1516 (1945); (b) Kilgore, *Soap Sanit. Chemicals*, **21** [12], 137 (1945).

[4] A brief description [Kirkwood and Dacey, *Can. J. Research*, **24B**, 69 (1946)] of the preparation and isolation of 1-trichloro-2,2-bis-(*p*-fluorophenyl)-ethane has been kindly called to our attention by one of the referees.

[5] (a) Zeidler, *Ber.*, **7**, 1180 (1874); (b) U. S. Patent 2,329,074, Sept. 7, 1943; (c) Rueggeberg and Torrans, *Ind. Eng. Chem., Ind. Ed.*, **38**, 211 (1946); (d) Darling, *J. Chem. Ed.*, **22**, 170 (1945); (e) Cristol and Haller, THIS JOURNAL, **68**, 140 (1946).

[6] Directions for the condensation reported by Hall in the Department of Commerce Report No. 360, "Insecticides and Fungicides at the I. G. Farbenindustrie Plant, Hochst," call for the use of chloral acetal, but the reported yield, as well as the amount of fluorobenzene employed, obviously are based on chloral. The latter compound was probably the one actually used.

[7] Haller, Bartlett, Drake, Newman and others, THIS JOURNAL, **67**, 1591 (1945).

[8] (a) Lapworth and Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **72**, 43 (1927); (b) Schiemann and Pillarsky, *Ber.*, **64B**, 1340 (1931); (c) Fosdick and Campaigne, THIS JOURNAL, **63**, 974 (1941).

[9] Dunlop and Gardner, *ibid.*, **55**, 1665 (1933).

[10] White and Sweeney, *Public Health Reports*, **60**, 66 (1945).

[11] Dunlop and Gardner, ref. 9, reported only the *p,p'*-isomer as the product of the analogous reaction between *p*-fluorobenzoyl chloride and fluorobenzene.

[12] All melting points corrected.

[13] Boiling points uncorrected.

[14] Distilled in every case from a solution of chloral hydrate in concentrated sulfuric acid, directly into the fluorobenzene.

[15] Prepared according to the method of Flood in Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York. N. Y., 1943, pp. 295–298.

first fraction was fractionated under vacuum in a 30-cm. packed column to yield 3.1 g. of *o,p'*-DFDT, a colorless liquid, b. p. 135–136° at 9 mm.; 12.3 g. of *p,p'*-DFDT, b. p. 177–178° at 9 mm.; and 9.0 g. of an intermediate fraction. Upon standing, the two *p,p'*-DFDT fractions solidified to a crystalline mass, m. p. 41.9–43.0°, long colorless needles, m. p. 44.2–45.1°,[16] from alcohol–water.

Anal. Calcd. for $C_{14}H_9F_2Cl_3$: Cl, 33.1. Found: Cl, 33.1.

Procedure II.—This run was conducted as described above, excepting that the temperature was maintained at 0° with stirring for twelve hours. In addition to 38.0 g. of recovered fluorobenzene,[17] 5.4 g. of *o,p'*-DFDT, 158.2 g. of *p,p'*-DFDT, and 8.5 g. of an intermediate fraction were obtained.

Procedure III.—In this run, 120.0 g. of chloral and 192.0 g. of fluorobenzene were used, and a mixture of 150 cc. of concentrated sulfuric acid and 50 cc. of 20% fuming sulfuric acid was added dropwise with stirring at 10–15°. The mixture was stirred at 10–20° for two hours, and finally at 30° for ten hours. The resulting product was treated as before to yield 41.5 g. of recovered fluorobenzene,[17] 2.1 g. of *o,p'*-DFDT, 201.5 g. of *p,p'*-DFDT and 9.2 g. of an intermediate fraction. The total yield of products based on chloral was 81%.

Procedure IV. The German Process.[6]—To a cooled and stirred solution of 34.0 g. of chloral in 69.0 g. of fluorobenzene, 41.5 g. of chlorosulfonic acid was added. Stirring was continued overnight at room temperature. The yield of crude, washed and dried product, isolated as in the cases described above, was 56.1 g. (76%).

Degradation of *p,p'*-DFDT.—Exactly 50.4 g. of crude 1,1-dichloro-2,2-bis-(*p*-fluorophenyl)-ethylene, as colorless needles from alcohol–water, m. p. 42.0–42.5°, was obtained in the dehydrochlorination of 61.7 g. of *p,p'*-DFDT, by the same method used in the analogous case of *p,p'*-DDT.[7]

Anal. Calcd. for $C_{14}H_8F_2Cl_2$: Cl, 24.9. Found: Cl, 25.0.

To a solution of 10.0 g. of the olefin in 50 cc. of glacial acetic acid, 5.5 g. of chromic anhydride was added slowly. The mixture was refluxed for one and a quarter hours, then poured into ice water, and the oily layer extracted with benzene. The combined benzene extracts were washed with 10% sodium carbonate solution, then with water, and dried over drierite. The residue, following removal of the solvent at the take-off, was vacuum distilled to give 2.9 g. of recovered olefin and 4.0 g. of *p,p'*-difluorobenzophenone, b. p. 170–172° at 10 mm., colorless plates from Skellysolve, m. p. 106.8–107.5°. Neither the ketone nor its oxime, m. p. 131.8–132.5°, depressed the melting points of authentic samples prepared according to the methods of Dunlop and Gardner.[9]

1,1-Dichloro-2,2-bis-(*p*-fluorophenyl)-ethane.—Pressure reduction (30 lb.) of 9.0 g. of 1,1-dichloro-2,2-bis-(*p*-fluorophenyl)-ethylene dissolved in 50 cc. of methyl alcohol in the presence of 0.1 g. of Adams catalyst gave 8.5 g. (94%) of the corresponding ethane derivative, b. p. 135–140° at 4 mm., m. p. 44.2–45.4°.

Anal. Calcd. for $C_{14}H_{10}Cl_2F_2$: Cl, 24.7. Found: Cl, 25.0.

Attempted Degradation of *p,p'*-DFDT According to the General Method of White and Sweeney.[10]—A solution of 39.0 g. of potassium hydroxide and 19.0 g. of *p,p'*-DFDT in 1160 cc. of ethylene glycol was refluxed for twelve hours, then cooled, diluted with a liter of water, and extracted with benzene. Vacuum distillation of the residue following removal of the solvent, gave 9.1 g. of an oil, b. p. 165–230° at 3 mm. Oxidation of 5.0 g. of this oil with 2.5 g. of chromic anhydride in 25 cc. of glacial acetic acid gave only a black resinous material.

Reduction of *p,p'*-Difluorobenzophenone.—A mixture of 10.0 g. of the ketone, 12.0 g. of amalgamated zinc, 7.5 cc. of concentrated hydrochloric acid, 17.5 cc. of water, and 15 cc. of toluene was refluxed for thirty-two hours. Concentrated hydrochloric acid (5 cc.) was added every eight hours. The toluene layer was separated, the water layer extracted with benzene, and the combined benzene solutions washed and dried. Evaporation of the solvent gave 8.3 g. (83%) of the pinacolone, 1,1,2,2-*p*-fluorophenylethanone-1, m. p. 170.8–171.5° after recrystallization from alcohol or Skellysolve. The melting point was not depressed by mixing with an authentic sample of the pinacolone, prepared by treatment of the corresponding pinacol with iodine and acetic acid.[18]

Anal. Calcd. for $C_{26}H_{16}OF_4$: C, 74.3; H, 3.8. Found: C, 74.2, 74.3; H, 4.1, 4.2.

The pinacol was prepared by the photochemical reduction of *p,p'*-difluorobenzophenone according to the method for benzophenone described by Fieser.[19] After recrystallization from alcohol, it melted at 186.2–187.0°

Anal. Calcd. for $C_{26}H_{18}O_2F_4$: C, 71.2; H, 4.1. Found: C, 71.3, 71.4; H, 4.5, 4.4.

Degradation of *o,p'*-DFDT.—The *o,p'*-isomer was degraded to *o,p'*-difluorobenzophenone, b. p. 174–177° at 16 mm., by a similar method to that used for the *p,p'*-compound. Upon prolonged cooling in an ice-bath, the oily distillate crystallized in colorless prisms, m. p. 22.8–23.6°. The 2,4-dinitrophenylhydrazone, orange plates from alcohol, m. p. 166.0–168.3°,[20] did not depress the melting point of samples of the same derivative prepared from the ketone synthesized by the Grignard reaction and by the Friedel–Crafts reaction, as described below.

Anal.[21] Calcd. for $C_{19}H_{12}O_4N_4F_2$: N, 14.1. Found: N, 14.0, 13.9.

Synthesis of *o,p'*-Difluorobenzophenone. Friedel–Crafts Method.—Exactly 13.0 g. of *o*-fluorobenzoyl chloride[22] was condensed with fluorobenzene after the method of Dunlop and Gardner[9] to yield 9.6 g. of a colorless oil, b. p. 176–178° at 16 mm. The 2,4-dinitrophenylhydrazone, prepared by the method of Haller, *et al.*,[7] crystallized from alcohol as orange prisms, m. p. 168.7–169.8°.

Grignard Method.—A solution of *p*-fluorophenylmagnesium bromide,[8c] from 25.0 g. of *p*-fluorobromobenzene,[8b] in 80 cc. of ether, was added dropwise to a solution of 22.0 g. of *o*-fluorobenzoyl chloride in 50 cc. of dry ether. After three hours of stirring, the complex was decomposed with 100 cc. of hydrochloric acid (2:1). The ether layer was washed with 5% sodium hydroxide solution, then with water, and finally dried over drierite. Vacuum distillation of the residue, after the removal of solvent, gave 6.0 g. of a colorless oil, b. p. 140–145° at 6 mm., m. p. of 2,4-dinitrophenylhydrazone, 167.8–169.1°. Considerable amounts of *o*-fluorobenzoic acid, b. p. 163–165° at 6 mm., were recovered.[23]

Summary

1. Studies have been made of the preparation and composition of DFDT. Only two compounds were obtained, 1-trichloro-2,2-bis-(*p*-fluorophenyl)-ethane, the major product, together with small amounts of 1-trichloro-2-*o*-fluorophenyl-2-*p*-fluorophenylethane.
2. Work on the proof of structure, including synthesis of the degradation products, is described.
3. The reduction of *p,p'*-difluorobenzophe-

---

[16] Cristol, THIS JOURNAL, **67**, 1494 (1945), reported 42–45°.

[17] It is believed that some fluorobenzene was lost by codistillation with ether.

[18] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[19] Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, pp. 202–204.

[20] The low value was probably due to traces of the *p,p'*-isomer.

[21] Analysis by Arlington Laboratories, Fairfax, Virginia.

[22] Prepared by the procedure of Bergmann and Bondi, *Ber.*, **64**, 1455 (1931).

[23] Essentially the same results were obtained when the corresponding cadmium compound was used in place of the Grignard reagent.

none by the Clemmensen procedure was found to give the pinacolone, 1,2,2,2-tetra-*p*-fluorophenylethanone-1.

LAWRENCE, KANSAS RECEIVED JULY 31, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Recovery of Sucrose from Cane Blackstrap and Beet Molasses

BY W. W. BINKLEY[1] AND M. L. WOLFROM

The crystallization of sucrose from the juices of the two main plant sources, the sugar cane and the sugar beet, constitutes a major industry. After all of the sucrose has been removed by crystallization procedures to the extent that is feasible, there remains a mother liquor which is known as molasses. That from the sugar cane, commonly known as blackstrap, is used mainly as a source of alcohol. Various attempts have been made to recover further amounts of sucrose from blackstrap molasses after prior removal of the reducing sugars with invertase-free yeasts (Olivarius process[2]), lime (Battelle process[3]) or barium hydroxide (Holven process[4]). None of these methods have proved commercially successful. The molasses from the sugar beet, however, is processed in various ways to recover further sucrose. The methods employed rest upon the separation of sucrose as a chemical derivative, generally a metallic saccharate, from which the sucrose is regenerated.

In the work herein recorded, we wish to report the application of chromatographic procedures to the recovery of sucrose from cane or beet molasses. To this end, the molasses was adsorbed on a native clay and the chromatogram was developed with dilute ethanol. From the effluent (Table I) the sucrose was readily crystallized as a colorless, high purity product. From the cane blackstrap molasses, there was recovered 74% of the sucrose present; from the beet molasses, the recovery was 93%. The nature of the effluent was further investigated by collecting it in the series of fractions shown in the table. Fractions 2, 3 and 4 (Table I) of the effluent from the cane molasses possessed a strong, pleasant and rum-like odor. The residual sirups from the sucrose crystallizations with the cane molasses were highly palatable.

The procedure employed in this work is an adaptation to the materials in hand of the general chromatographic procedures developed in this Laboratory[5] and especially those[5b] employing clay as an adsorbent. Further work is in progress to determine the non-sucrose constituents of the fractions herein separated.

Experimental

Cane Blackstrap Molasses.—The cane blackstrap molasses was produced in Cuba by the Cunagua Central of the American Sugar Refining Co., New York, N. Y.[6] It was stored at 8–10°. This molasses was obtained from a mixture of 75–80% Javan varieties POJ 2714 and POJ 2878 and 20–25% Cuban stock termed Crystalina.

Anal. (% original molasses) Solids, 82.3; ash, 5.5; sucrose,[7] 32; reducing sugars (as invert sugar),[8] 15; *d*, 1.468 g. per ml. at 25°; color, nearly black; taste, burnt sweet.

Adsorption of Cane Blackstrap Molasses on Clay.—An amount of 50 g. of the above cane blackstrap molasses was diluted with 25 ml. of distilled water. A smooth paste was prepared by the addition of 25 g. of a mixture of 5 parts (by wt.) of clay[9] and 1 part of "Celite"[10] to the diluted molasses. This paste was suspended, employing good agitation, in 500 ml. of absolute ethanol.

Sucrose Separation from Cane Blackstrap Molasses.—The molasses-clay-"Celite"-ethanol suspension was added at the top of a 7–9 by 11–12 cm. column[11] of a mixture (250 g.) of 5/1: clay/"Celite" in a 2-liter percolator arranged to permit the collection of the effluent without interfering with the operation of the column. The chromatogram was developed with three liters of 95% ethanol (the azeotrope). A total of 11.87 g. of sucrose (74.2% of that present) of excellent purity was obtained on concentration of the effluent. The residual sirup obtained on solvent removal was sweet and highly palatable. The nature of the effluent was investigated by collection in nine fractions, data on which are given in Table I. Fraction 2 was light green in color; fractions 3 to 8 were a golden color; fractions 8 and 9 were nearly colorless. Fractions 2, 3 and 4 had strong, pleasant, rum-like odors and it was obvious that the characteristic flavoring substances were concentrated therein. The other fractions had virtually no odor. The residual sirups obtained on solvent removal were sweet and highly palatable.

Beet Molasses.—The beet molasses was produced by the Michigan Sugar Co., Saginaw, Michigan.[12] It was stored at 8–10°.

Anal. (% original molasses) Solids, 81.2; ash, 2.0; sucrose,[7] 46.6; raffinose,[7] 2.2; reducing sugars, absent; *d*, 1.416 g. per ml. at 25°; color, brown.

Adsorption of Beet Molasses on Clay.—An amount of 50 g. of the above beet molasses was adsorbed on 30 g. of clay as described above for cane molasses.

Sucrose Separation from Beet Molasses.—The chromatogram was developed as described above for cane black-

---

[1] Sugar Research Foundation Associate of The Ohio State University Research Foundation (Project 190).

[2] H. DeF. Olivarius, U. S. Patents 1,730,473 (1929), 1,788,628 (1931).

[3] E. E. Battelle, U. S. Patents 1,044,003 (1913), 1,044,004 (1913).

[4] A. L. Holven, U. S. Patents 1,878,144 (1933), 1,878,145 (1933).

[5a] W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945); (b) B. W. Lew, M. L. Wolfrom and R. M. Goepp, Jr., *ibid.*, **67**, 1865 (1945); **68**, 1449 (1946); (c) L. W. Georges, R. S. Bower and M. L. Wolfrom, *ibid.*, **68**, 2169 (1946).

[6] We are indebted to Mr. Louis A. Wills of the above company for this material.

[7] Modified Clerget method.

[8] Munson-Walker method.

[9] Florex XXX, manufactured by the Floridin Co., Warren, Pennsylvania.

[10] No. 535, manufactured by Johns-Manville Co., New York, N. Y.

[11] Column dimensions refer to the adsorbent.

[12] We are indebted to Mr. Geoffrey S. Childs of the above company for this material.