

[FROM THE SCIENTIFIC DEPARTMENT, ISRAEL MINISTRY OF DEFENCE]

**Di(*p*-chlorophenyl)trichloromethylcarbinol and Related Compounds**

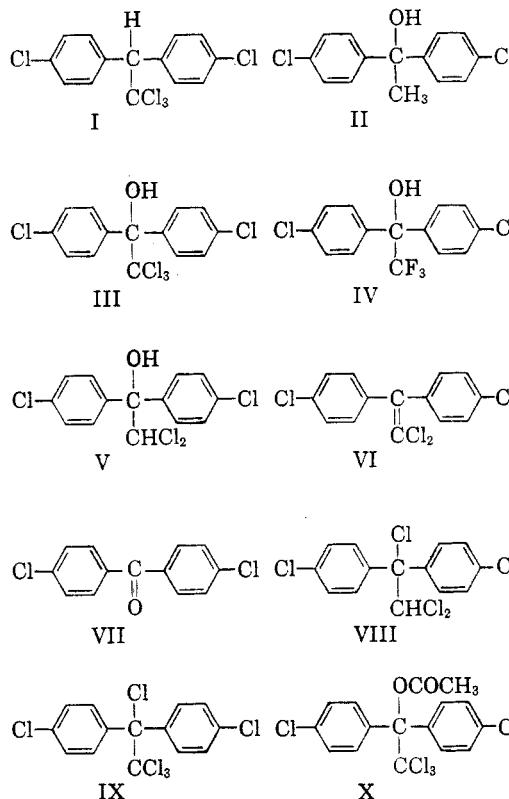
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Three diaryltrichloromethylcarbinols have been prepared by reaction of the corresponding 1,1-diaryl-1,2,2,2-tetrachloroethanes with silver acetate and subsequent acid hydrolysis. The high temperature (117°) chlorination of di(*p*-chlorophenyl)-methylcarbinol introduces, broadly speaking, only two chlorine atoms into the methyl group.

If the hypothesis<sup>1</sup> is correct that synergists for DDT (I) of the type of di(*p*-chlorophenyl)methylcarbinol (DMC) (II) are active because of their structural similarity to the insecticide, one would expect di(*p*-chlorophenyl)trichloromethylcarbinol (III) to be more active than II. An indication to this effect may be seen in the fact that di(*p*-chlorophenyl)trifluoromethylcarbinol (IV)<sup>2</sup> is, indeed, a more potent synergist for DDT than II. Curiously enough III has not been described in the scientific literature, although it is sold commercially as a powerful acaricide and its effects have been studied by various workers.<sup>3</sup> The reported method for its preparation is the high-temperature chlorination of II. When this reaction was carried out in glacial acetic acid under the conditions specified in the experimental part, three main constituents could be isolated from the product: di(*p*-chlorophenyl)-dichloromethylcarbinol (V), 1,1-di(*p*-chlorophenyl)-2,2-dichloroethylene (VI) and 4,4'-dichlorobenzophenone (VII).<sup>4</sup> In addition, an oil was formed, from which by dehydrohalogenation VI was obtained. It probably contains, therefore, 1,1-di(*p*-chlorophenyl)-1,2,2-trichloroethane (VIII),<sup>5</sup> which could owe its formation to the interaction of

V or VI with the gaseous hydrogen chloride. The compound III was present under these conditions only in minute amounts.<sup>6,7</sup> In this connection, it



(1) S. Tahori, *J. Econ. Entomol.*, **48**, 638 (1955). Cf. F. A. Gunther, R. C. Blinn, G. E. Carman, and R. L. Metcalf, *Arch. Biochem. Biophys.*, **50**, 504 (1954).

(2) (a) E. D. Bergmann, S. Tahori, A. Kaluszyner, and S. Reuter, *Nature*, **176**, 266 (1955). (b) A. Kaluszyner, S. Reuter, and E. D. Bergmann, *J. Am. Chem. Soc.*, **77**, 4164 (1955). (c) S. Reuter, S. Cohen, R. Mechoulam, A. Kaluszyner, and S. Tahori, *Riv. parassitol.*, **17**, 125 (1956). (d) S. Cohen and S. Tahori, *J. Agr. Food Chem.*, **5**, 519 (1957). See also S. Tahori, ref. 1.

(3) (a) D. Asquith, *J. Econ. Entomol.*, **48**, 329 (1955). (b) J. S. Barker and F. B. Maugham, *J. Econ. Entomol.*, **49**, 458 (1956). (c) F. A. Gunther, R. C. Blinn, and R. L. Metcalf, *J. Agr. Food Chem.*, **4**, 338 (1956). (d) R. D. Garmus and V. H. Unger, *Agr. Chem.*, **11**, No. 7, 41 (1956). (e) I. Rosenthal, G. J. Firson, and F. A. Gunther, *J. Agr. Food Chem.*, **5**, 514 (1957). (f) F. A. Gunther and R. C. Blinn, *J. Agr. Food Chem.*, **5**, 517 (1957). (g) L. R. Jeppson, H. S. Elmer, M. J. Jessor, and J. O. Complin, *J. Agr. Food Chem.*, **5**, 592 (1957). (h) F. A. Gunther, R. C. Blinn, L. R. Jeppson, J. H. Barkley, G. L. Frisone, and R. D. Garmus, *J. Agr. Food Chem.*, **5**, 597 (1957). (i) Two patents (U. S. 2,812,280 and 2,812,362) have recently been published which describe the preparation of III.

(4) It is possible that 4,4'-dichlorobenzophenone is formed by disproportionation of III, a reaction which occurs generally under the influence of alkali.

(5) S. Cohen, A. Kaluszyner, and R. Mechoulam, *J. Am. Chem. Soc.*, **79**, 5979 (1957).

may be recalled that also the reaction of ethyl trichloroacetate or 4,ω,ω-tetrachloroacetophenone with aromatic Grignard compounds did not lead to compound III.<sup>8,9</sup>

The method finally employed used as starting material the olefin (VI), which adds halogen to yield IX. The latter exchanges the chlorine in the 1-position for the acetoxy group, when it is treated

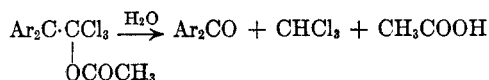
(6) According to a private communication from Dr. A. H. M. Kirby, East Malling Research Station (Maidstone, Kent), he has isolated small amounts of the carbinol (III) from a commercial product.

(7) The bromination of II gave exclusively 1,1-di(*p*-chlorophenyl)-2,2-dibromoethylene, the analog of (VI).

(8) A. Kaluszyner and S. Reuter, *J. Am. Chem. Soc.*, **75**, 5176 (1953). Cf. K. R. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956).

(9) J. M. Pepper and M. Kulka, *J. Am. Chem. Soc.*, **72**, 1417 (1950).

with silver acetate in boiling glacial acetic acid; potassium or lead acetate were without effect. Hydrolysis of the ester (X) so obtained in acidic medium (sulfuric acid in acetic acid) gave III. All attempts to carry out the conversion of IX to III in a single step failed. Furthermore, the alkaline hydrolysis of X only leads to decomposition to 4,4'-dichlorobenzophenone (VII) according to the scheme:



a reaction which is not without analogies.<sup>3e, 3f</sup>

In the same way, diphenyltrichloromethylcarbinol and di(*p*-fluoromethyl)trichloromethylcarbinol were obtained from 1,1-diphenyl- and 1,1-di(*p*-fluorophenyl)1,2,2,2-tetrachloroethane, respectively.

The reaction of IX with silver propionate gave in smooth reaction the propionate, corresponding to X.

The diaryltrichloromethylcarbinols give halochromic solutions in concentrated sulfuric acid; however, the color fades quickly. A similar observation has been made and the reaction occurring elucidated in the case of the di(*p*-halogenophenyl)-trifluoromethylcarbinols (such as IV).<sup>10</sup> The reaction taking place in the present case, will form the subject of a forthcoming publication.

The insecticidal activity, for resistant houseflies, of diphenyl-, di(*p*-chlorophenyl)-, and di(*p*-fluorophenyl)trichloromethylcarbinol is LD<sub>50</sub> 300, 33, and 12 $\gamma$  per fly, respectively. The acetates of these carbinols are inactive. At a ratio of DDT: synergist = 10:1, the synergistic effect of both III and di(*p*-fluorophenyl)trichloromethylcarbinol is 140, while that of the corresponding di(*p*-chlorophenyl)-trifluoromethylcarbinol (IV) is 30. Here, too, the acetates of the trichloromethylcarbinols had no effect.

#### EXPERIMENTAL

**1,1-Diphenyl-1,2,2,2-tetrachloroethane.** Thirty-nine g. of 1,1-diphenyl-2,2-dichloroethylene (m.p. 77–78°), prepared from 1,1-diphenyl-2,2,2-trichloroethane<sup>11</sup> and alcoholic potassium hydroxide solution, was added to a solution of 11.2 g. of chlorine in 200 ml. of glacial acetic acid and the mixture kept for 2 days in a closed flask. The solid was filtered and the mother liquid treated at 100° with a current of dry chlorine gas for 2 hr. Then the solvent was evaporated and the residue, together with the first crop, recrystallized from methanol. M.p. 87–88° (lit.<sup>12</sup>: 87–88°); yield, 41.1 g. (82%).

**1,1-Diphenyl-1-acetoxy-2,2,2-trichloroethane.** A mixture of 16.0 g. of the preceding compound, 8.4 g. of silver acetate, and 110 ml. of glacial acetic acid was refluxed for 90 min.,

cooled, and filtered, and the solution concentrated to half its volume and diluted with water. The oily product crystallized, when the excess of the acid was neutralized with sodium bicarbonate. Successive recrystallizations from methanol and petroleum ether (40–60°) gave 12.8 g. (74%) of m.p. 83–85°.  $\lambda_{\text{max}}^{\text{EtOH}}$  261 m $\mu$  (2.76); 266 m $\mu$  (2.81); 272 m $\mu$  (2.68).

*Anal.* Calcd. for C<sub>16</sub>H<sub>13</sub>Cl<sub>3</sub>O<sub>2</sub>: C, 55.9; H, 3.8. Found: C, 56.1; H, 4.1.

Ethanol potassium hydroxide (1.2 g.) transformed the compound (1.7 g.) (heating for 5 min.) into benzophenone (0.7 g.), which was characterized by its 2,4-dinitrophenylhydrazone, m.p. 238°.

**Diphenyltrichloromethylcarbinol.** A mixture of 3.4 g. of the foregoing ester, 20 ml. of glacial acetic acid, 15 ml. of water, and 2 ml. of concentrated sulfuric acid was refluxed for 90 min. and poured into ice. Upon addition of 25 g. of sodium hydroxide in 100 ml. of water, a solid separated which was dried and recrystallized from petroleum ether (60–90°). Crystals, of m.p. 67–68.5; yield, 1.7 g. (56%).  $\lambda_{\text{max}}^{\text{EtOH}}$  230 m $\mu$  (3.85); 250 m $\mu$  (3.00); 254 m $\mu$  (3.04); 258 m $\mu$  (3.04); 264 m $\mu$  (3.00); 270 m $\mu$  (2.85).

*Anal.* Calcd. for C<sub>14</sub>H<sub>11</sub>Cl<sub>3</sub>O: C, 55.8; H, 3.7. Found: C, 55.6; H, 3.6.

**1,1-Di(*p*-fluorophenyl)-1,2,2,2-tetrachloroethane.** A solution of 8.5 g. of chlorine and 35.7 g. of 1,1-di(*p*-fluorophenyl)-2,2-dichloroethylene<sup>13</sup> in 200 ml. of glacial acetic acid was exposed for 6 hr. to direct sunlight, a slightly exothermic reaction taking place. The solvent was removed *in vacuo* and the remaining oil distilled; b.p. 160–162° (2 mm.); yield, 28.3 g. (88%);  $n_D^{25}$  1.5855. Upon prolonged standing, the oil crystallized; m.p. 55–56°. The compound is mentioned briefly in the literature,<sup>14</sup> but without physical constants.

*Anal.* Calcd. for C<sub>14</sub>H<sub>8</sub>Cl<sub>4</sub>F<sub>2</sub>: C, 47.2; H, 2.3. Found: C, 47.4; H, 2.4.

**1,1-Di(*p*-fluorophenyl)-1-acetoxy-1,2,2-trichloroethane.** The reaction between 17.8 g. of the foregoing compound and 8.35 g. of silver acetate in 200 ml. of glacial acetic acid was carried out as above. From methanol, then from petroleum ether long rods of m.p. 135–136°; yield, 16.7 g. (88%).  $\lambda_{\text{max}}^{\text{EtOH}}$  266 m $\mu$  (2.81); 271 m $\mu$  (2.70).

*Anal.* Calcd. for C<sub>16</sub>H<sub>11</sub>Cl<sub>3</sub>FO<sub>2</sub>: C, 50.6; H, 2.8. Found: C, 51.1; H, 3.0.

**Di(*p*-fluorophenyl)trichloromethylcarbinol.** In the manner described before 7.6 g. of the foregoing ester, 80 ml. of glacial acetic acid, 25 ml. of water, and 5 ml. of concentrated sulfuric acid, gave 4.7 g. (70%) of the desired compound; after recrystallization from petroleum ether (60–90°) it melted at 78.5–80°.  $\lambda_{\text{max}}^{\text{EtOH}}$  230 m $\mu$  (3.76) (inflection); 258 m $\mu$  (2.93); 265 m $\mu$  (3.00); 271 m $\mu$  (3.00).

*Anal.* Calcd. for C<sub>14</sub>H<sub>9</sub>Cl<sub>3</sub>F<sub>2</sub>O: C, 49.8; H, 2.7. Found: C, 50.3; H, 3.0.

**1,1-Di(*p*-chlorophenyl)-1-acetoxy-2,2,2-trichloroethane (X).** From 29.2 g. of 1,1-di(*p*-chlorophenyl)-1,2,2,2-tetrachloroethane (IX)<sup>15</sup> and 13.7 g. of silver acetate in 300 ml. of boiling glacial acetic acid (90 min.), 22.1 g. (71%) of the desired product, m.p. 127.5–128.5° was obtained after recrystallization from methanol and petroleum ether (40–60°).  $\lambda_{\text{max}}^{\text{EtOH}}$  230 m $\mu$  (4.48); 255 m $\mu$  (2.70); 266 m $\mu$  (2.76).

*Anal.* Calcd. for C<sub>16</sub>H<sub>11</sub>Cl<sub>5</sub>O<sub>2</sub>: C, 46.6; H, 2.7. Found: C, 46.9; H, 2.9.

**1,1-Di(*p*-chlorophenyl)-1-propionyloxy-2,2,2-trichloromethane.** A mixture of 7.8 g. of (IX), 2.3 g. of silver oxide, and 100 ml. of propionic acid was refluxed for 90 min., filtered, poured into water, and almost completely neutralized by addition of sodium hydroxide solution. The precipitate was filtered, dried, and recrystallized first from methanol, then from low-

(10) S. Cohen and A. Kaluszyner, *Experientia*, **13**, 236 (1957). S. Cohen, *J. Am. Chem. Soc.*, **79**, 1499 (1957).

(11) A. v. Baeyer, *Ber.*, **5**, 1094 (1872).

(12) O. G. Backeberg and J. L. Marais, *J. Chem. Soc.*, 803 (1945). For another method, see H. Bader, W. A. Edmiston, and H. H. Rosen, *J. Am. Chem. Soc.*, **78**, 2590 (1956).

(13) H. L. Bradlow and C. A. Vander Werf, *J. Am. Chem. Soc.*, **69**, 662 (1947).

(14) W. Voegtli and P. Laeuger, *Helv. Chim. Acta*, **38**, 46 (1955).

(15) O. Grummit, A. Buck, and A. Jenkins, *J. Am. Chem. Soc.*, **67**, 155 (1945).

boiling (40–60°) petroleum ether. M.p. 86.5–87°; yield, 3.9 g. (46%).

Anal. Calcd. for  $C_{17}H_{13}Cl_5O_2$ : C, 47.9; H, 3.1. Found: C, 47.6; H, 3.1.

*Di(p-chlorophenyl)trichloromethylcarbinol* (III). The hydrolysis of the ester (X) (12.4 g.) with concentrated sulfuric acid (5 ml.) and 75% acetic acid (160 ml.) was carried out as described above. The oily product was dissolved in chloroform, washed with sodium bicarbonate solution, and recovered by evaporation of the solvent. From petroleum ether (40–60°), m.p. 77–78°.  $\lambda_{max}^{EtOH}$  226 m $\mu$  (4.43); 258 m $\mu$  (2.82), 266 m $\mu$  (2.85), 276 m $\mu$  (2.60).

Anal. Calcd. for  $C_{14}H_9Cl_3O$ : C, 45.4, H, 2.5. Found: C, 45.6; H, 2.7.

*Chlorination of di(p-chlorophenyl)methylcarbinol* [DMC (II)]. A current of chlorine was passed through a solution of 26.7 g. of (II) in 250 ml. of glacial acetic acid. The initial reaction was fairly exothermic. When it had somewhat subsided, chlorination was continued for 2.5 hr. at 65–75° and for 8 hr. at the boiling temperature of the solvent. About 200 ml. of glacial acetic acid was then distilled off and the residue diluted with water and cautiously neutralized with sodium bicarbonate. The product was dissolved in ether, dried, concentrated, and taken up in 20 ml. of petroleum ether (60–90°). Thus, 3.2 g. of a crystalline product was obtained; two recrystallizations from methanol gave 1 g. of 4,4'-dichlorobenzophenone, m.p. and mixed m.p. with an authentic specimen, m.p. 146–147°.

The petroleum ether solution was distilled under 2-mm. pressure, two fractions being secured:

(a) 150–180°, 8.6 g., and (b) 180–205°, 12.0 g.

*Fraction (a)*. From the solution in 15 ml. of petroleum ether (40–60°) there crystallized first 0.8 g. of 4,4'-dichlorobenzophenone, then 2.1 g., which crystallized from methanol, had m.p. 84–86° and were identified as 1,1-di(p-chlorophenyl)-2,2-dichloroethylene (VI), and 2.0 g. of unsharp m.p. 78–84° which were not identical with (VI), but were not further investigated. *Fraction (b)*. From the solution

(16) The compound showed no depression of the melting point upon admixture of a sample kindly supplied by Dr. Kirby, see ref. 5.

in 20 ml. of petroleum ether (40–60°), there crystallized upon cooling 4.8 g. of m.p. 95–104° and, after recrystallization from petroleum ether (70–90°), 107–109°. This is di(p-chlorophenyl)dichloromethylcarbinol (V), for which the literature gives m.p. 108–109°;<sup>9</sup> b.p. 200–210° (1 mm.), and m.p. 105–106°.<sup>17,18</sup>

Anal. Calcd. for  $C_{14}H_{10}Cl_4O$ : C, 50.0; H, 3.0. Found: C, 49.0; H, 2.9. Ultraviolet spectrum (in ethanol): 231 m $\mu$  (4.45); 260 m $\mu$  (2.87); 266 m $\mu$  (2.85). Infrared spectrum (KBr disk):  $\nu(OH)$  3570  $cm^{-1}$ ;  $\nu(CCl_2)$  770–780  $cm^{-1}$ .

No further crystalline material could be obtained upon concentration of the petroleum ether solution of fraction (b). Treatment of the remaining oil with alcoholic potassium hydroxide gave only (VI).

*Bromination of di(p-chlorophenyl)methylcarbinol* (II). To a solution of 13.4 g. of II in 100 ml. of glacial acetic acid, 24 g. of bromine in 50 ml. of the same solvent was added with stirring. When the color of the bromine had disappeared, the solution was diluted with water and the solid filtered and recrystallized from ethanol. Thus 12.3 g. (41%) of 1,1-di(p-chlorophenyl)-2,2-dibromoethylene was obtained, m.p. 102–104° (lit.,<sup>19</sup> 104–105°).

Anal. Calcd. for  $C_{14}H_8Cl_2Br_2$ : C, 41.3; H, 2.0. Found: 41.1; H, 2.4.

*Acknowledgment*. Thanks are due to Mr. Sasson Cohen for his advice in this investigation, and to Dr. S. Tahori for the biological evaluation of the compounds.

TEL-AVIV, ISRAEL

(17) Cf. W. E. Craig, E. Y. Shropshire, and H. F. Wilson, U. S. Patent 2,720,548 (*Chem. Abstr.*, **50**, 8735 (1956)). In this patent, V was formed by hydrolysis of VIII, which in turn was obtained from 1,1-di(p-chlorophenyl)-2-chloroethylene.

(18) The solution in concentrated sulfuric acid is reddish, but the color fades quickly, due to formation of VI.

(19) S. J. Cristol and H. L. Haller, *J. Am. Chem. Soc.*, **68**, 140 (1946).