gave 1,1-dichloroacetone in low yield resulting from dehydrochlorination rather than dehydration.

EXPERIMENTAL

Preparation of 1,1,1-trichloro-2-propanol. Methylmagnesium bromide (2*M* solution in ether) was added to a cold ethereal solution of chloral. The hydrolyzed mixture was dried and distilled, b.p. 69–71°/25 mm., m.p. (from ligroin) 46–48°. The average yield of several preparations was 75%. The structure of this material was confirmed by nuclear magnetic resonance spectroscopy.

A. *Reaction with alumina.* The alcohol was heated and swept by means of a stream of nitrogen into a one-inch diameter glass tube packed with 8 mesh alumina. The tube was heated over the length of its packing by a tube furnace, one foot in length. The temperature of the reacting surfaces was maintained between 200–250°. The exit end of the tube was connected to a Dry Ice-cooled trap. At the conclusion of the reaction, the product in the trap was washed with water, dried, and distilled. The product thus obtained had the properties: b.p. 115°, n_D^{25} 1.4440. It was shown by infrared analysis to contain a carbonyl group, and a qualitative test for chloride ion following sodium fusion was positive.

Anal. Calcd. for $C_4H_4Cl_2O$: Cl, 55.8; C, 28.3. Found: Cl, 55.8; C, 28.8.

The 2,4-dinitrophenylhydrazone was prepared; m.p. (from ethanol) 110–112°.

Anal. Calcd. for $C_9H_8Cl_2N_4O_4$: N, 18.2. Found: N, 17.9.

The semicarbazone was prepared, and found to behave as follows on heating: sintering at 163°, melting with decomposition between 173–175°.

Anal. Calcd. for $C_4H_7Cl_2N_3O$: Cl, 36.5. Found: Cl, 35.8.

The yield of 1,1-dichloroacetone was poor, only 18 g. (0.14 mole, 28%) being obtained from 79 g. of the alcohol.

B. *Reaction with zinc chloride–hydrochloric acid.* A solution of zinc chloride (136 g., 1 mole) in concentrated hydrochloric acid (100 ml.) was prepared and a few grams of the alcohol was added. The mixture was heated to reflux and the remainder of the alcohol (82 g., 0.5 mole) was added slowly. After 5 hr. the mixture was distilled with steam. The organic layer was separated, dried, and distilled to yield 13.5 g. (21% yield) of 1,1-dichloroacetone, b.p. 115°, n_D^{25} 1.4440. The infrared spectrum of this material was superimposable on that obtained from the material from A above; a mixture of semicarbazone derivative with that from A melted without depression.

C. *Reaction with phosphorus pentoxide.* An intimate mixture of the alcohol (92 g., 0.56 mole) with excess phosphorus pentoxide was heated until no more distillation occurred. The resulting distillate was redistilled from phosphorus pentoxide then fractionally distilled. Three fractions were obtained: Fraction A (17 g.), b.p. 105–112°; Fraction B (13 g.), b.p. 112–115°; and Fraction C (34 g.), b.p. 115–116°, n_D^{25} 1.4790.

Fraction C was identified as 1,1,2-trichloro-1-propene by its physical properties and by comparison of its infrared spectrum with that from an authentic sample of 1,1,2-trichloro-1-propene.[6]

Fractions A and B were shown to contain, respectively, 69% and 80% 1,1,2-trichloro-1-propene by infrared analysis. The remainder of the material appeared to be a mixture of an acid chloride and anhydride.

The yield of 1,1,2-trichloro-1-propene was 69% based on the pure material in all fractions and 41% based on Fraction C alone.

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Cyclic Analogs of DDT-like Compounds

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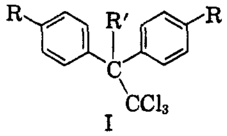
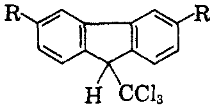
Received July 16, 1959

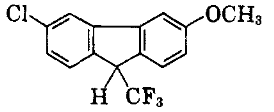
In view of the current theories on the correlation between geometrical structure and biological activity of the insecticides of the DDT group,[1] it seemed of interest to compare the insecticidal properties of 1,1-diaryl-2,2,2-trichloroethanes (I) and of the corresponding fluorenes (II). Unlike I, compounds of type II have a completely rigid molecular structure.



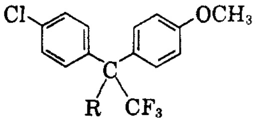
I



II



III



IV

Attempts to prepare 9-trichloromethylfluorene (II, R = H) by chlorination of 9-methylfluorene, by addition of hydrogen chloride to 9-dichloromethylenefluorene or by reaction between 9-fluorenyl sodium and carbon tetrachloride, failed.[2] Another route we explored and which is analogous to the well known conversion of benzilic acid into 9-fluorene-carboxylic acid under the influence of aluminum chloride, is the reaction of the recently[3] described diphenyltrichloromethylcarbinol (I, R = H; R′ = OH) with aluminum chloride. While in benzene mainly tarry material was formed, the reaction in carbon disulfide as solvent gave, in addition to much polymeric material, a compound of m.p. 164–166°, which was identified as $\alpha,\alpha,\alpha',\alpha'$-tetrachlorobibenzyl. Analogous rearrangements are known.[4]

Eventually, 3-chloro-6-methoxy-9-trifluoromethylfluorene (III) and 1-(*p*-chlorophenyl)-1-(*p*-methoxyphenyl)-2,2,2-trifluoroethane (IV, X = H) were used for the comparative experiments. The choice of (III) and (IV, R = H) seemed reasonable since replacement of the *para*-chlorine atoms in DDT by methoxyl groups does not destroy the insecticidal activity.[5]

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(1) R. Riemschneider in *Advances in Pest Control Research* (Interscience Publishers Inc., New York 1958), Vol. 2, p. 307.

(2) E. J. Greenhow, A. S. Harris, and E. N. White, *J. Chem. Soc.*, 3116 (1954).

(3) E. D. Bergmann and A. Kaluszyner, *J. Org. Chem.*, **23**, 1306 (1958).

(4) W. L. Walton, *J. Am. Chem. Soc.*, **69**, 1544 (1947).

(5) E. A. Prill, A. Hartzell, and J. M. Arthur, *Science*, **101**, 464 (1945).

Compound (III) has been prepared before;[6,7] compound IV, R = H was obtained by the reduction of 1-(*p*-chlorophenyl)-1-(*p*-methoxyphenyl) 2,2,2-trifluoroethanol (IV, R = OH), which in turn was synthesized by the reaction between *p*-chloro-ω,ω,ω-trifluoroacetophenone and *p*-methoxyphenylmagnesium bromide.

Attempts to prepare (IV. R = H) by the reaction between 1 - (*p* - methoxyphenyl) - 2,2,2 - trifluoroethanol and chlorobenzene or between 1-(*p*-chlorophenyl)-2,2,2-trifluoroethanol and anisole in the presence of concentrated sulphuric acid, failed.

The biological tests carried out by Dr. A. S. Tahori (Israel Institute of Biological Research) showed that for a housefly strain of moderate resistance to DDT, compound IV was six to seven times more active (LD_{50} = 10–12γ per fly) than compound III (LD_{50} = 75γ per fly). Cyclization and the ensuing greater rigidity of the molecule thus reduce the insecticidal activity.

EXPERIMENTAL

Reaction of diphenyltrichloromethylcarbinol and aluminum chloride. To diphenyltrichloromethylcarbinol[8] (7.6 g.; 0.025 mol.) in carbon disulphide (90 ml.), anhydrous aluminum chloride (10 g.; 0.075 mol.) was added with stirring. The mixture was refluxed for 3 hr., cooled, and decomposed with ice, followed by cold water (100 ml.) and concentrated hydrochloric acid (50 ml.). The organic solution yielded on evaporation a brown solid (1.2 g.), which was treated with ethyl acetate, leaving 0.25 g. undissolved. The insoluble material did not melt at 300° and was not further investigated. The ethyl acetate solution was concentrated and the residue purified by sublimation. Colorless crystals melting at 164–166° were obtained; the compound was identified as α,α,α′,α′-tetrachlorobibenzyl[8] by mixed melting point.

p-Chloro-ω,ω,ω-trifluoroacetophenone. To the Grignard reagent prepared from *p*-bromochlorobenzene (144 g.; 0.75 mol.) and magnesium turnings (18.2 g.; 0.75 mol.) in ether (300 ml.), trifluoroacetic acid (28.5 g.; 0.25 mol.) in ether (70 ml.) was added at 5–10°. After decomposition with 5% hydrochloric acid, separation of the organic layer and distillation in a Todd column, the desired *ketone* (30.5 g.; 58%) was obtained, b.p. 182–184° (lit.[9]: b.p. 180–183°).

1-(p-Chlorophenyl)-1-(p-methoxyphenyl)-2,2,2-trifluoroethanol (IV, R = OH). To a solution of *p*-methoxyphenylmagnesium bromide, prepared from *p*-bromoanisole (28 g.; 0.15 mol.) in ether (70 ml.), toluene (35 ml.) was added, the ether removed and a solution of *p*-chloro-ω,ω,ω-trifluoroacetophenone (15.6 g.; 0.075 mol.) in toluene (35 ml.) added slowly. After the usual treatment, the *carbinol* (IV. R = OH) (15.6 g.; 66%) boiled at 170–173° (4 mm). The product was purified by chromatography on alumina (solvent: petroleum ether; eluent: ether–petroleum ether) and distilled again.

Anal. Calcd. for $C_{15}H_{12}ClF_3O_2$: C, 57.0; H, 3.8. Found: C, 56.9; H, 4.0.

1-(p-Chlorophenyl)-1-(p-methoxyphenyl)-2,2,2-trifluoroethane (IV, R = H). (a) A mixture of the *foregoing compound,* (IV, R = OH) (9.5 g.), glacial acetic acid (20 ml.), water (0.3 ml.), red phosphorus (3.0) and iodine (1.3 g.) was refluxed for 250 hr. The mixture was cooled, filtered, poured into water, neutralized with sodium bicarbonate solution, extracted with ether, and distilled. A slightly yellowish viscous oil (6.9 g.; 77%), b.p. 150–155° (2 mm.), was obtained. n_D^{25} 1.5440, d_{25}^{25} 1.324; MR, calcd. 71.87; MR, found, 71.64. The compound slowly crystallized from petroleum ether and melted at 50–51°.

Anal. Calcd. for $C_{15}H_{12}ClF_3O$: C, 60.0; H, 4.0. Found: C, 59.6; H, 3.9.

(b) *p*-Methoxy-ω,ω,ω-trifluoroacetophenone was prepared in 70% yield by the same procedure as the *p*-chloro compound; b.p. 115–120° (25 mm.) (lit.[10]): 70–70.5° (2 mm.)). Reduction of this compound with lithium aluminum hydride in ether gave a 79% yield of 1-(*p*-methoxyphenyl)-2,2,-2-trifluoroethanol, b.p. 102–103° (3 mm.); n_D^{30} 1.4740; (lit.[10]: b.p. 87–88° (1 mm.); n_D^{30} 1.4743). From the reaction of this product (5.2 g.) with concentrated sulfuric acid (50 ml.) and chlorobenzene (8 ml.), no defined products could be isolated.

(c) In the analogous condensation of 1-(*p*-chlorophenyl)-2,2,2-trifluoroethanol[9] with anisole (with or without acetic acid as diluent), only the starting materials were recovered.

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(6) S. Cohen, *J. Am. Chem. Soc.*, **79**, 1499 (1957).

(7) S. Cohen and A. Kaluszyner, *Experientia*, **13**, 236 (1957).

(8) L. V. Johnson, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 4710 (1952).

(9) A. Kaluszyner, S. Reuter, and E. D. Bergmann, *J. Am. Chem. Soc.*, **77**, 4164 (1955).

(10) R. Fuchs and G. J. Park, *J. Org. Chem.*, 22, 993 (1957).

Dehalogenation in the Elbs Reaction

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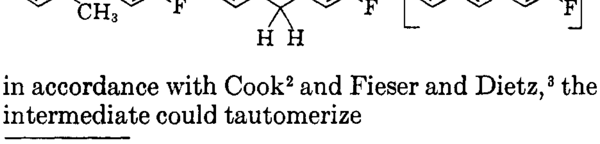
Received August 13, 1959

In the course of a study of fluoro-derivatives of carcinogenic polycyclic hydrocarbons[1], attempts were made to prepare 6-fluoro-20-methylcholanthrene (I) and 3-fluoro-1,2,5,6-dibenzanthracene (II) by pyrolysis (Elbs reaction) from 4-methyl-7-(4-fluoro-1-naphthoyl)hydrindene (III) and 4-fluoro - 2 - methyl - 1 - (2 - naphthoyl)naphthalene (IV), respectively. The only defined products which could be isolated (in 5 and 10%, respectively) were 20 - methylcholanthrene and 1,2,5,6-dibenzanthracene, the fluorine-free parent compounds of the desired substances. It appears difficult to rationalize the hydrogenolysis of the C—F bonds in these reactions. It is significant, however, that in both III and IV the fluorine atom is in the *para*-position to the carbonyl group. If one assumes in the Elbs reaction an intermediate as follows:



in accordance with Cook[2] and Fieser and Dietz,[3] the intermediate could tautomerize

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(1) E. D. Bergmann, J. Blum, S. Butanaro, and A. Heller, *Tetrahedron Letters*, No. 1, 15 (1959).