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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Dehalogenation in the Elbs Reaction

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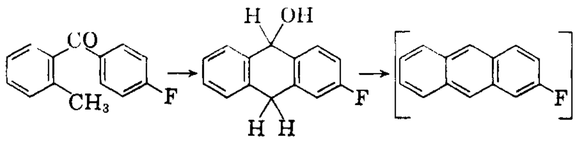
In the course of a study of fluoro-derivatives of carcinogenic polycyclic hydrocarbons[1], attempts were made to prepare 6-fluoro-20-methylcholanthrene (I) and 3-fluoro-1,2,5,6-dibenzanthracene (II) by pyrolysis (Elbs reaction) from 4-methyl-7-(4-fluoro-1-naphthoyl)hydrindene (III) and 4-fluoro - 2 - 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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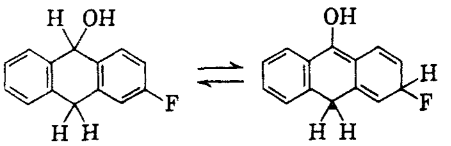
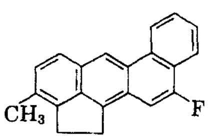
(1) E. D. Bergmann, J. Blum, S. Butanaro, and A. Heller, *Tetrahedron Letters*, No. 1, 15 (1959).

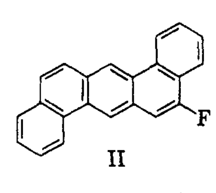


creating a nonaromatic fluorine atom and thus facilitating its elimination.[4] Similar schemes have been suggested in other abnormal reactions.[5]

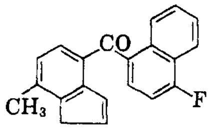
It is recalled that the synthesis of the chloro- and methoxy-analogs of I also resulted at least very largely in the elimination of the substituents,[6] while 2- and 3-methoxy-[6-8] and 3-chloro-20-methyl-cholanthrene[8] could be obtained without difficulties.



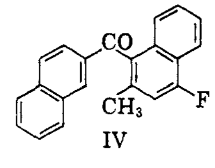
I



II



III



IV

EXPERIMENTAL

4-Methyl-7-(4-fluoro-1-naphthoyl)hydrindene (III). Following Fieser and Seligmann's work[9] for the synthesis of methylcholanthrene, 50 ml. of dry benzene and 17 g. of 4-methyl-7-cyanohydrindene[9] in 80 ml. of benzene were added to a Grignard solution prepared from 4 g. of magnesium and 27 g. of 4-fluoro-1-bromonaphthalene in 100 ml. of ether. The reaction mixture was refluxed and stirred for 12 hr. and decomposed with cold 18% hydrochloric acid. The organic solvents were then removed by steam distillation and the remaining imine hydrochloride of III was filtered and hydrolyzed by refluxing it for 3 hr. with a mixture of 100 ml. of hydrochloric acid, 200 ml. of water, 100 ml. of glacial acetic acid, and 120 ml. of toluene. The aqueous layer was extracted with toluene and the combined toluene solutions were treated with steam in the presence of 10% sodium hydroxide solution. A dark oil was obtained which was dissolved in benzene, dried, and distilled. The fraction boiling at 205° (0.5 mm.) was a viscous oil which crystallized quickly upon trituration with ether. From methanol, beautiful crystals of m.p. 123° were obtained. Yield, 22 g. (95%).

Anal. Calcd. for $C_{21}H_{17}FO$: C, 82.9; H, 5.6; F, 6.2. Found: C, 82.8; H, 5.7; F, 6.0.

Pyrolysis. The foregoing ketone (18 g.) was pyrolyzed for 40 min. at 410°. The product was dissolved in benzene and flash-distilled under 2 mm. pressure after drying. Thus, 1.3 g. of a product was obtained which upon addition of ether to its benzene solution deposited yellow crystals (0.85 g.) of m.p. 180–181° (lit.[9] m.p. 179.5–180°). The analysis and properties showed that 20-methylcholanthrene had been isolated; yield, 5%.

Anal. Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.6; H, 6.0.

By working at somewhat lower temperatures (365°) one can raise the yield to about 15%, but even under these conditions no fluorine-containing substance could be isolated.

1-Fluoro-3-methylnaphthalene. The diazotization of 9 g. of 1-amino-3-methylnaphthalene hydrochloride, prepared by the reduction of the nitro-compound,[10] was carried out with 15 ml. of concentrated hydrochloric acid, 20 ml. of water, and 3.5 g. of sodium nitrite at 0°. To the clear solution, 10 ml. of 56% fluoboric acid was added and the precipitate filtered after 30 min. Thermal decomposition of the salt gave a dark oil which was dissolved in benzene, washed with alkali, dried, and distilled. B.p. 123° (20 mm.); yield, 5 g. (62%).

Anal. Calcd. for $C_{11}H_9F$: C, 82.5; H, 5.6; F, 11.8. Found: C, 82.3; H, 5.7; F, 11.7.

4-Fluoro-2-methyl-1-(2-naphthoyl)-naphthalene (IV). To a mixture of 4.5 g. of 1-fluoro-3-methylnaphthalene, 4.5 g. of 2-naphthoyl chloride, and 50 ml. of carbon disulfide, 4.5 g. of aluminum chloride was added. The mixture was stirred at 0° for 5 hr. and decomposed by addition of 20 ml. of cold 18% hydrochloric acid. Upon distillation with steam, a brown oil remained which crystallized after trituration with petroleum ether. The solid was treated with hot 10% sodium carbonate solution, dried, and recrystallized successively from glacial acetic acid and ethanol. Thus 7.2 g. (91%) of almost colorless crystals of m.p. 136° was obtained.

Anal. Calcd. for $C_{22}H_{15}FO$: C, 84.1; H, 4.8; F, 6.0. Found: C, 83.8; H, 5.0; F, 6.5.

Pyrolysis. The pyrolysis of 4 g. of the foregoing ketone was carried out at 420° for 1 hr. and the product flash-distilled at 2 mm. pressure. The distillate was dissolved in hot benzene and separated upon cooling as glistening, yellowish platelets of m.p. 260–262°. They were identified by analysis as 1,2,5,6-dibenzanthracene (lit.[7], m.p. 266°). Yield, 0.35 g. (10%).

Anal. Calcd. for $C_{22}H_{14}$: C, 95.0; H, 5.0. Found: C, 94.7; H, 5.4.

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(4) For a review of the Elbs reaction, see L. F. Fieser, *Org. Reactions*, **III**, 129 (1942).

(5) *E.g.*, for the transformation of 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene into 2-chloro-9,10-diphenylanthracene. E. D. Bergmann and O. Blum-Bergmann, *J. Am. Chem. Soc.*, **59**, 1439 (1937). C. Dufraisse, A. Etienne and J. Salmon, *Bull. soc. chim. Belges*, **62**, 21 (1953).

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Preparation of L-Xylose

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L-Xylose has been prepared from D-glucose by Reichstein *et al.*[2] The preparation involved oxi-

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[1] Part of a thesis to be submitted to the Senate of the Hebrew University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.