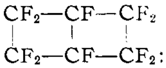
To this mixture was added 141.5 g. of $CF_2{=}CFCF_2CF_2$-$CF{=}CF_2$ (0.5 mole) during about one hour with the temperature kept below 20°.[20] Stirring was continued for an additional three hours until the evolution of carbon dioxide ceased. The oxidation mixture was worked up by reducing with $SO_2$ until there was no further lightening in color, filtering the slurry, acidifying the filtrate with 120 ml. of concd. $H_2SO_4$, and distilling out material up to the boiling point of water, mostly $CO_2$, $SO_2$ and acetone. The residue was extracted with diethyl ether in a continuous liquid-liquid extractor. The ether was then removed and the residue treated with 300 ml. of absolute ethyl alcohol. The excess alcohol was distilled off at atmospheric pressure, and the product fractionally distilled to give 75 g., 60% yield, of $C_2H_5OCOCF_2CF_2COOC_2H_5$ (XIVa), b.p. 96° (20 mm.). The physical properties of this material differed substantially from those reported by Henne and Zimmerschied[10]; see Table I, footnote *k*. For this reason, another sample of $C_2H_5OCOCF_2CF_2COOC_2H_5$ was prepared from $CF{=}CFCF_2CF_2$.[10]

**Oxidation of $CF{=}CFCF_2CF_2$.**—The oxidation of this compound, b.p. 0.2° (740 mm.), was carried out at atmospheric pressure, and the diethyl ester of perfluorosuccinic acid isolated by the technique described above for the oxidation of XII. The olefin, 81 g. (0.50 mole), was distilled into the reaction flask containing 137 g. of $KMnO_4$, 179 g. of $NaHCO_3$, 200 ml. of acetone and 800 ml. of water. No external cooling was required, since the refluxing olefin kept the mixture below 12°. Most of the olefin had reacted in 9 hours. From the resulting mixture was obtained 85 g., 70% yield, of $C_2H_5OCOCF_2CF_2COOC_2H_5$ (X), center cut (XIVb) b.p. 95° (20 mm.). The physical properties of XIVb were substantially identical with those of XIVa; see Table I.


$\begin{array}{ccccc} CF_2 & — & CF & — & CF_2 \\ | & & | & & | \\ CF_2 & — & CF & — & CF_2 \end{array}$: **Thermal Reaction of $CF_2{=}CFCF_2CF_2$-$CF{=}CF_2$.**—The diene XII was metered from a constant head dropping funnel into a copper coil vaporizer immersed in an oil-bath held at 100° and the vapor passed into a 45 cm. × 3.8 cm. i.d. electrically heated nickel reactor tube. A thermocouple well extended into the center of the reactor tube. The mixture of product and unreacted starting material was condensed by a water-cooled copper condenser with receiver connected to Dry Ice and liquid air-cooled traps. Before and after each run the system was swept out with dry nitrogen. The product, boiling 17° lower than the starting material, was separated readily by fractional distillation. In the first run, 0.84 mole of XII was passed through the tube at 350° with a contact time of two minutes to give less than 1% conversion to product; 97% of the starting material was recovered. In the second run, the temperature was raised to 450°; 0.62 mole of XII gave a 60% conversion to product and 37% of the starting material was recovered. In the third run, with the temperature at 450°, the contact time was increased to 6 minutes; 0.46 mole of XII gave a 70% conversion to product, and 27% of the starting material was recovered.

The product, compound XV, a solid melting at 41°, b.p. 42.6° (732 mm.), mol. wt. calcd. 262, found 262, was saturated to chlorine plus light and to $KMnO_4$ in acetone. It formed an azeotrope with $CCl_4$, b.p. 41.6° (737 mm.).

The structure proposed for this compound, perfluorobicyclo[2.2.0]hexane, is based on the following considerations. The formation of a single product from the diene XII with the same molecular weight and with more than 97% total weight recovery indicated that XV was formed from XII by thermal isomerization, a process which requires only an electronic rearrangement. The loss of two double bonds necessitates a bicyclo structure for XV. The relatively high freezing point and very small liquid range (about 3° at atmospheric pressure) suggest a high degree of symmetry. The marked ease of formation of four-membered rings by thermal reaction of a variety of olefins containing the terminal $CF_2{=}$ structure is well known. In addition, a compound analogous to XV, which contains three fused four membered rings, perfluorotricyclo[4.2.0.0$^{2,5}$]-octane, is known to be formed by thermal reaction of perfluoro-1,3-butadiene.[21]

An X-ray investigation of XV[22] failed to shed much light on the structure, because the material was found to show rotational disorder.

**$CF_2{=}CClCF_2I$ + Zn in Anhydrous Dioxane: $CF_2{=}CCl$-$CF_2CF_2CCl{=}CF_2$.**—To a well-stirred suspension of 100 g. of Zn dust in 400 ml. of anhydrous dioxane at reflux was added 169 g. of $CF_2{=}CClCF_2I$ (0.62 mole) over a half-hour period. There was no noticeable heat effect at any time; the mixture was held near reflux for 6 hours, and material was distilled out to the boiling point of dioxane, 100.7° (747 mm.). The distillate contained nothing boiling below room temperature. It contained a small amount of unidentified material boiling at 45°, having a very pungent odor, but was principally a dioxane azeotrope, b.p. 98.5° (747 mm.), $n^{20}_{D}$ 1.3989, *ca.* 54% dioxane by wt., which gave on drowning in water a 32% yield of $CF_2{=}CClCF_2CF_2CCl{=}CF_2$ (XVI), b.p. 112.8° (735 mm.). The structure proposed for this material is based on analogy with that demonstrated for XII.

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(21) M. Prober and W. T. Miller, Jr., THIS JOURNAL, **71**, 598 (1949). Evidence for the fused tricyclic structure consists of the isolation of the intermediate compound perfluoro-1,2-divinylcyclobutane and its conversion into the tricycloöctane under conditions similar to those utilized in the present work; R. T. Carroll and W. T. Miller, Jr., unpublished work.

(22) P. J. Shapiro and J. L. Hoard, THIS JOURNAL, **76**, 3347 (1954).

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[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY, THE LABORATORY OF APPLIED ORGANIC CHEMISTRY, RESEARCH COUNCIL OF ISRAEL, AND THE MEDICAL RESEARCH LABORATORIES, MEDICAL CORPS, ISRAEL DEFENCE FORCES]

# Methyl-fluorinated Methyldiarylcarbinols and Related Compounds

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Nine methyl-fluorinated derivatives of diphenylmethylcarbinol have been prepared by the Grignard reaction from suitable substitution products of ethyl fluoroacetate or acetophenone. The ultraviolet and infrared spectra of these carbinols are discussed. Some of the above acetophenones also have been reduced and the corresponding secondary alcohols condensed with chlorobenzene in the presence of fuming sulfuric acid. The chemical reactions of the new substances have been studied. Ethyl fluoroacetate is α-chlorinated by sulfuryl chloride in the presence of benzoyl peroxide.

The interesting biological properties[1-3] of the diaryl-(trifluoromethyl)-carbinols[4,5] made a study of

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(1) A. S. Tahori, *J. Econom. Entomol.*, **48**, 638 (1955).

(2) S. Reuter, S. Cohen, R. Mechoulam, A. Kaluszyner and A. S. Tahori, *Rivista di Parassitol.*, **17**, 125 (1956).

(3) K. R. S. Ascher, *Science*, **125**, in press (1957).

(4) E. D. Bergmann, A. S. Tahori, A. Kaluszyner and S. Reuter, *Nature*, **176**, 266 (1955).

(5) A. Kaluszyner, S. Reuter and E. D. Bergmann, THIS JOURNAL, **77**, 4164 (1955).

analogous methyl-fluorinated methyldiarylcarbinols appear worthwhile.

The purification of the products (I) from the Grignard reactions of arylmagnesium bromides (phenyl, *p*-chlorophenyl, *p*-bromophenyl and *p* methoxyphenyl) with ethyl *difluoroacetate* was made difficult by the presence of the biphenyl derivatives formed as by-products. Combination of distillation under reduced pressure and chromatography gave the pure carbinols, which were oils and showed ultraviolet and infrared spectra similar to those of the corresponding diaryl-(trifluoromethyl)-carbinols. In the infrared spectrum, the OH valency stretching frequency was observed at 3600 cm.$^{-1}$.

$(p\text{-XC}_6\text{H}_4)_2\text{(COH)CHF}_2$ I

$(p\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{C=CF}_2$ II

$(p\text{-ClC}_6\text{H}_4)_2\text{C(OH)CHFCl}$ III

$(p\text{-XC}_6\text{H}_4)_2\text{C(OH)CF}_2\text{Cl}$ IV

$(p\text{-XC}_6\text{H}_4)_2\text{C(OH)CFCl}_2$ V

The *p*-methoxyphenyl compound lost water spontaneously, even under mild conditions, and gave 1,1-di-(*p*-methoxyphenyl)-2,2-difluoroethylene (II), which has practically the same ultraviolet spectrum ($\lambda$ 241 m$\mu$, log $\epsilon$ 4.42) as 1,1-di-(*p*-chlorophenyl)-ethylene.[6] In the infrared, the hydroxyl frequency was absent; instead a band appeared at 1700 cm.$^{-1}$ which may be assigned to the $\text{C=CF}_2$ bond, conjugated with the *p*-methoxyphenyl groups.

The Grignard reaction between ethyl *chlorofluoroacetate* and *p*-chlorophenylmagnesium iodide gave the expected carbinol III, an oily liquid. In this connection it may be worthy of note that ethyl chlorofluoroacetate[7] can be prepared more easily (in 30% yield) by chlorination of ethyl fluoroacetate with sulfuryl chloride in the presence of benzoyl peroxide as catalyst than by the previously reported method.

The esters of *difluorochloro-* and *dichlorofluoro*-acetic acid reacted smoothly with phenylmagnesium bromide, giving the carbinols IV and V (X = H). Surprisingly, the reaction with *p*-chlorophenylmagnesium bromide was extremely sluggish, even under stringent conditions. The main reaction product was 4,4′-dichlorobiphenyl. These two esters, therefore, behave similarly to ethyl trichloroacetate.[8] A detour had to be employed for the preparation of the di-*p*-chloro-derivatives (X = Cl) of IV and V. The corresponding ketones VI and VII were prepared from difluorochloro- and dichlorofluoroacetic acid and an excess of *p*-chlorophenylmagnesium bromide according to the method of Sykes, Tatlow and Thomas.[9] These ketones gave the desired carbinols when treated for a considerable length of time with a twofold excess of *p*-chlorophenylmagnesium bromide.

$p\text{-ClC}_6\text{H}_4\text{COCF}_2\text{Cl}$ VI

$p\text{-ClC}_6\text{H}_4\text{COCFCl}_2$ VII

$(p\text{-ClC}_6\text{H}_4)_2\text{C(OH)CH}_2\text{F}$ VIII

$p\text{-ClC}_6\text{H}_4\text{COCH}_2\text{C}_6\text{H}_4\text{Cl-}p$ IX

Finally, ethyl *fluoroacetate* was converted, by reaction with *p*-chlorophenylmagnesium bromide, into 1,1-di-(*p*-chlorophenyl)-2-fluoroethanol (VIII). As a by-product, 4,4′-dichlorodesoxybenzoin (IX) was obtained, in analogy with the observations of Bergmann and Kalmus.[10] Dehydration of the carbinol VIII gave 1,1-di-(*p*-chlorophenyl)-2-fluoroethylene (X), whilst the chlorine-free parent compound of VIII gives a hydrindene derivative under these conditions.[10] The structure of X follows from the identity of its absorption spectrum ($\lambda$ 240 m$\mu$, log $\epsilon$ 4.22) with those of 1,1-di-(*p*-chlorophenyl)-ethylene[6] and II, and from its oxidation to *p,p*′-dichlorobenzophenone. Upon reduction with iodine and red phosphorus, the carbinol VIII was converted into 1,1-di-(*p*-chlorophenyl)-ethane.

When the ketones VI and VII and *p*-chloro-$\omega$-fluoroacetophenone[11] were reduced with lithium aluminum hydride, the corresponding secondary alcohols were obtained, without loss of the aliphatic halogen atoms. Condensation of the three alcohols with chlorobenzene in the presence of fuming sulfuric acid gave 1,1-di-(*p*-chlorophenyl)-2,2-difluoro-2-chloroethane (XI), -2,2-dichloro-2-fluoroethane (XII) and -2-fluoroethane (XIII).

$(p\text{-ClC}_6\text{H}_4)_2\text{C=CHF}$ X

$(p\text{-ClC}_6\text{H}_4)_2\text{CHCF}_2\text{Cl}$ XI

$(p\text{-ClC}_6\text{H}_4)_2\text{CHCFCl}_2$ XII

$(p\text{-ClC}_6\text{H}_4)_2\text{CHCH}_2\text{F}$ XIII

$(p\text{-ClC}_6\text{H}_4)_2\text{C=CF}_2$ XIV

$(p\text{-ClC}_6\text{H}_4)_2\text{C=CClF}$ XV

Compound XI melted at 54–55° and was obviously not identical with the product of m.p. 90° which has been obtained by Pouterman and Giraudet[12] by the treatment of DDT with antimony trifluoride and to which they assigned formula XI.

It appeared interesting to compare the behavior of the compounds XI and XII against alkali with that of the corresponding trifluoro compound. Whilst in the latter the $\text{CF}_3$ group is converted into a carboxyl or carbalkoxy group,[13] the former lose hydrogen chloride and give 1,1-di-(*p*-chlorophenyl)-2,2-difluoro- and -2-fluoro-2-chloroethylene (XIV, XV). Both olefins proved to be highly unstable; especially in contact with air they are converted quickly into brown polymers. The same behavior has been noted by Dittman and Wrightson[14] for the analogous 1,1-diphenyl-2,2-difluoroethylene. The fact that II is stable is undoubtedly due to the effect of the *p*-methoxy groups. This may be the same effect which makes 1,1-di-(*p*-methoxyphenyl)-ethylene stable to dimerization reactions.[15]

The **ultraviolet spectra** of the new carbinols show the longest wave length maximum at about

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(6) F. A. Gunther and R. C. Blinn, "Analysis of Insecticides and Acaricides," Interscience Publishers, New York, N. Y., 1955, p. 636.

(7) J. A. Young and P. Tarrant, THIS JOURNAL, **71**, 2432 (1949).

(8) A. Kaluszyner and S. Reuter, *ibid.*, **75**, 5126 (1953).

(9) A. Sykes, J. C. Tatlow and C. R. Thomas, *Chemistry & Industry*, 630 (1955); *J. Chem. Soc.*, 835 (1956); *cf.* R. C. Huston and D. L. Bailey, THIS JOURNAL, **68**, 1382 (1946).

(10) F. Bergmann and A. Kalmus, THIS JOURNAL, **76**, 4137 (1954).

(11) F. Bergmann, A. Kalmus and E. Breuer, *Bull. Res. Counc. Israel*, **A5**, 15 (1956).

(12) E. Pouterman and A. Giraudet, *Experientia*, **2**, 459 (1946).

(13) R. Mechoulam, S. Cohen and A. Kaluszyner, *J. Org. Chem.*, **21**, 801 (1956).

(14) A. L. Dittman and J. M. Wrightson, U. S. Patent 2,705,706 (*C. A.*, **49**, 13695 (1955)).

(15) O. Schmitz-Dumont, K. Thoemke and H. Diebold, *Ber.*, **70**, 175 (1937).

250–270 mμ; it is sometimes split into a doublet. Halogen in the *p*-positions has a distinct, though weak bathochromic affect, an observation which has also been made in the case of the diaryltrifluoromethylcarbinols.[5]

Also the **infrared spectra** of the tertiary carbinols described are fairly similar. The tertiary hydroxyl group absorbs at 3600 cm.$^{-1}$. In the acetyl derivatives, the carbonyl frequency at 1760 cm.$^{-1}$ is somewhat unusual; its shift from the expected frequency of about 1735 cm.$^{-1}$ may be due to the accumulation of negative substituents in the vicinity, in the same way as malonic esters absorb at 1761 cm.$^{-1}$ and ethyl trichloroacetate absorbs at 1768 cm.$^{-1}$.[16] As in the case of the diaryl-(trifluoromethyl)-carbinols,[5] there is no indication of internal hydrogen bonding. The biological properties of the substances described here will be reported elsewhere; the compounds have not shown any significant insecticidal properties.

## Experimental

**Difluoromethyl-diarylcarbinols (I).**—To the Grignard solution, prepared from 0.1 mole of the aryl bromide in 50 ml. of ether, a solution of ethyl difluoroacetate (0.05 mole) in ether (25 ml.) was added at 0° and with vigorous agitation. The reaction mixture was cooled in an ice–salt mixture and decomposed by the slow addition of a saturated aqueous solution of ammonium chloride. The clear supernatant layer was decanted from a little sludge and the latter treated with a small amount of dilute hydrochloric acid, which was then extracted with ether. The combined ethereal layers were washed with sodium bicarbonate solution and water and dried with sodium sulfate. After removal of the solvent, the product was fractionated under reduced pressure. The crude carbinol fraction was dissolved in light petroleum ether and chromatographed on activated alumina, an ether–petroleum ether mixture (1:4) serving as the eluent. The fraction containing the carbinol was redistilled under reduced pressure. The carbinols gave a strong red-violet color with concentrated sulfuric acid. Their properties are summarized in Table I.

TABLE I

(DIFLUOROMETHYL)-DIARYLCARBINOLS, $(p\text{-}XC_6H_4)_2C(OH)CHF_2$

| X | B.p. °C. | B.p. Mm. | $n^{15}_{\rm D}$ | Yield, % | Analysis Carbon, % Calcd. | Analysis Carbon, % Found | Analysis Hydrogen, % Calcd. | Analysis Hydrogen, % Found | U.v. spectrum, mμ (log ε) (in alcohol) |
|---|---|---|---|---|---|---|---|---|---|
| H | 120 | 0.16 | 1.5620 | 48 | 71.8 | 71.6 | 5.1 | 5.1 | 210 (4.10)<br>254 (2.70)<br>258 (2.74) |
| Cl[a] | 140 | 0.03 | 1.5783 | 27 | 55.5 | 55.6 | 3.3 | 3.5 | 225 (4.45)<br>260 (2.94)<br>265 (2.94) |
| Br[b] | 150 | 0.01 | 1.6030 | 25 | | | | | 230 (4.45)<br>250–260 (3.38) |

[a] Calcd.: Cl, 23.4. Found: Cl, 23.2. [b] Calcd.: F, 9.7. Found: F, 9.6.

**1,1-Di-(*p*-methoxyphenyl)-2,2-difluoroethylene (II).**—The reaction with *p*-methoxyphenylmagnesium bromide, carried out as above, gave—after distillation under reduced pressure (123–125° (0.001 mm.))—a solid product of m.p. 54.5–55.5°.

*Anal.* Calcd. for $C_{16}H_{14}F_2O_2$: C, 69.6; H, 5.1. Found: C, 69.5; H, 5.1.

**Ethyl chlorofluoroacetate** was obtained by the method of Young and Tarrant[7] or—in 30% yield—by the chlorination of ethyl fluoroacetate with sulfuryl chloride in the presence of benzoyl peroxide.

The mixture of 31.8 g. of ethyl fluoroacetate, 53.6 g. of sulfuryl chloride, 150 ml. of carbon tetrachloride and 0.1 g. of benzoyl peroxide was refluxed until the expected weight loss (30 g.) had taken place. The solution was distilled without further treatment and gave 13 g. (30%) of ethyl chlorofluoroacetate, b.p. 128–130°, $n^{20}_{\rm D}$ 1.3913.

**Fluorochloromethyl-di-(*p*-chlorophenyl)-carbinol (III).**—To the Grignard solution prepared from 2.4 g. of magnesium and 24 g. of *p*-chloroiodobenzene, an ethereal solution of 5.65 g. of ethyl chlorofluoroacetate was added at 0° within 2 hr. The mixture was kept at room temperature for 2 hr. and decomposed by addition of 10 g. of ammonium chloride in ice-water. The aqueous layer was extracted with ether, and the combined ethereal solutions were washed with sodium thiosulfate solution and water and dried. The carbinol boiled at 140–144° (0.15 mm.); it was a yellowish oil of $n^{21}_{\rm D}$ 1.4763; ultraviolet spectrum in alcohol (log ε): 226 mμ (4.27), 256–266 mμ (3.17).

*Anal.* Calcd. for $C_{14}H_{10}Cl_3FO$: Cl, 33.0; F, 5.9. Found: Cl, 33.3; F, 5.8.

**Ethyl Difluorochloroacetate.**[17]—A mixture of difluorochloroacetic acid (General Chemical Division, Allied Chemical and Dye Corp., Morristown, N. J.) (56 g.), absolute ethanol (46 ml.) and concd. sulfuric acid (25 ml.) was heated on the water-bath for 2 hr. The layers were separated and the organic layer was washed twice with water. The acid layer then was added to the aqueous washings, whereupon a further quantity of ester separated. The combined portions of the crude ester were dried over phosphorus pentoxide and distilled in a Vigreux column; b.p. 96–97.5°, yield 62 g. (78.5%), $n^{30}_{\rm D}$ 1.3525, $d^{30}_{30}$ 1.2471; *MR* calcd. 27.43, found 27.45.

**Ethyl dichlorofluoroacetate**[17a] was prepared by the same procedure from dichlorofluoroacetic acid (General Chemical Division, Allied Chemical and Dye Corp., Morristown, N. J.) (74 g.); b.p. 130–132°, yield 76 g. (86%), $n^{30}_{\rm D}$ 1.4002, $d^{30}_{30}$ 1.307; *MR* calcd. 32.02, found 32.46.

**Difluorochloromethyldiphenylcarbinol (IV, X = H).**—To a boiling Grignard solution, prepared from magnesium (6 g.) and bromobenzene (39.2 g.) in ether (200 ml.), a solution of ethyl difluorochloroacetate (15.9 g.) in ether (60 ml.) was added, dropwise and with stirring, within 20 minutes. The heating was continued for another 10 minutes and the solution decomposed with ice and hydrochloric acid. The carbinol (IV) distilled at 130–160° (8 mm.), solidified and was recrystallized from petroleum ether; yield 15 g. (56%), m.p. 78–79°. Ultraviolet spectrum in alcohol: (log ε): 259 mμ (2.58), 263 mμ (2.52).

*Anal.* Calcd. for $C_{14}H_{11}F_2ClO$: C, 62.7; H, 4.1. Found: C, 62.3; H, 4.2.

**The acetate** was prepared by heating the carbinol (1 g.) with acetic anhydride (5 ml.) and sulfuric acid (2 drops) for 4 hr. at 100°. After hydrolysis of the excess of acetic anhydride with water, extraction with ether, evaporation of the solvent and recrystallization from methanol, the acetate was obtained as colorless prisms, m.p. 82–83°, yield 0.7 g. (61%); ultraviolet spectrum 264 mμ (log ε 2.64).

*Anal.* Calcd. for $C_{16}H_{13}ClF_2O_2$: C, 61.9; H, 4.2. Found: C, 61.7; H, 4.5.

**Dichlorofluoromethyldiphenylcarbinol (V, X = H).**—The carbinol V was obtained analogously from ethyl dichlorofluoroacetate (17.5 g.), magnesium (6 g.) and bromobenzene (39.2 g.). It distilled as a heavy yellowish oil at

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[16] E. J. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

[17] *Cf.* F. Swarts, *Chem. Centr.*, **67**, I, 1237 (1906); **68**, II, 581 (1907).

[17a] F. Swarts, *Bull. Soc. chim. France*, [3], **13**, 992 (1898).

140–145° (2 mm.) and could not be induced to crystallize; yield 15 g. (52%), $n^{30}$D 1.5821, $d^{30}{}_{30}$ 1.342; *MR* calcd. 71.06, found 70.78; ultraviolet spectrum in alcohol (log ε): 254 mμ (3.12).

*Anal.* Calcd. for $C_{14}H_{11}Cl_2FO$: Cl, 25.0. Found: Cl, 24.6.

The acetate was obtained as described above, m.p. 78–79°, yield 65%; ultraviolet spectrum 257 mμ (log ε 2.53).

*Anal.* Calcd. for $C_{16}H_{13}Cl_2FO_2$: C, 58.7; H, 4.0. Found: C, 58.2; H, 4.1.

**Reaction of *p*-Chlorophenylmagnesium Bromide and Ethyl Difluorochloroacetate.**—To the solution prepared from magnesium (5.3 g.) and *p*-chlorobromobenzene (42.2 g.) in ether (200 ml.), toluene (100 ml.) was added and the ether distilled off at 90–100°. The ester (15.85 g.) in toluene (60 ml.) was then added to the hot mixture, dropwise and with stirring, within 15 minutes, and the heating continued for another 15 minutes. After decomposition of the mixture with ice and hydrochloric acid, removal of the solvents and distillation *in vacuo*, the main product proved to be 4,4′-dichlorobiphenyl; the desired carbinol could not be separated in pure form, though the crude reaction product gave the typical color reaction with concentrated sulfuric acid.

**ω,ω-Difluoro-ω,*p*-dichloroacetophenone (VI).**—A solution of difluorochloroacetic acid (32.6 g.) in ether (70 ml.) was added at 10–15° to a Grignard solution, prepared from *p*-chlorobromobenzene (144 g.) and magnesium (18 g.) in ether (300 ml.), during 90 minutes. After decomposition with ice and hydrochloric acid and removal of the solvent, the reaction product was fractionally distilled *in vacuo;* the ketone VI distilled at 110–125° (25 mm.) and upon redistillation at 211–213° (760 mm.); yield 35 g. (63%), $n^{30}$D 1.5241, $d^{30}{}_{30}$ 1.445; *MR* calcd. 45.37, found 47.60; ultraviolet spectrum in ethanol (log ε): 222 mμ (4.00) 1263 mμ (3.03); infrared spectrum: $\nu_{C=O}$ 1710 cm.$^{-1}$.

*Anal.* Calcd. for $C_8H_4Cl_2F_2O$: C, 42.7; H, 1.8. Found: C, 42.5; H, 2.0.

It is well known[18] that the halogen in α-halogenoketones raises the frequency of the carbonyl group (for liquid acetophenone, $\nu_{C=O}$ is 1682 cm.$^{-1}$). Neither in this case nor in those of VII or of *p*-chloro-ω-fluoroacetophenone have we observed doublets (at about 1700 and 1682 cm.$^{-1}$) as reported, *e.g.*, for ω-chloro- and ω,ω-dichloroacetophenone by Bellamy, Thomas and Williams[19] and ascribed to rotational isomers of the compounds. On the other hand, the observation[19,20] has been confirmed that in such α-halogenations only the first halogen has a major effect on the location of the carbonyl frequency.

**ω-Fluoro-ω,ω,*p*-trichloroacetophenone (VII).**—The ketone VII was prepared from dichlorofluoroacetic acid (37 g.), *p*-chlorobromobenzene (144 g.) and magnesium (18 g.). It distilled at 110–130° (9 mm.) and upon redistillation, at 245–250° (760 mm.); yield 24 g. (38%), $n^{30}$D 1.5522, $d^{30}{}_{30}$ 1.450; *MR* calcd. 50.21, found 52.96; ultraviolet spectrum (log ε): 221 mμ (4.04), 257 mμ (2.32); infrared spectrum: $\nu_{C=O}$ 1700 cm.$^{-1}$.

*Anal.* Calcd. for $C_8H_4Cl_3FO$: Cl, 44.0; Found: Cl, 43.8.

**Difluorochloromethyl-di-(*p*-chlorophenyl)-carbinol (IV, X = Cl).**—A solution of VI (16 g.) in ether (50 ml.) was added, dropwise and with stirring, to a boiling Grignard solution prepared from *p*-chlorobromobenzene (15.5 g.) and magnesium (1.9 g.) in ether (100 ml.), over a period of 15 minutes. The heating was continued for 10 minutesand the mixture decomposed with ice and hydrochloric acid. Part of the ketone (2.5 g.) was recovered unchanged; the desired carbinol (IV, X = Cl) distilled at 175–178° (2 mm.) as a colorless oil, yield 7.5 g. (24%), $n^{22}$D 1.5750; $d^{22}{}_{22}$ 1.548; *MR* calcd. 76.41, found 76.53; ultraviolet spectrum in alcohol (log ε): 226 mμ (4.20); 266 mμ (2.88).

*Anal.* Calcd. for $C_{14}H_9Cl_3F_2O$: C, 49.8; H, 2.7. Found: C, 50.3; H, 3.1.

**The acetate,** prepared as described above, had m.p. 78–79°, yield 72%; ultraviolet spectrum: 227 mμ (4.23), 264 mμ (2.66).

*Anal.* Calcd. for $C_{16}H_{11}Cl_3F_2O_2$: C, 50.6; H, 2.9. Found: C, 50.7; H, 3.1.

**Dichlorofluoromethyl-di-(*p*-chlorophenyl)-carbinol (V, X = Cl)** was prepared from a solution of VII (10 g.) in ether (50 ml.) and a Grignard solution, prepared from *p*-chlorobromobenzene (15.5 g.) and magnesium (1.9 g.) in ether (150 ml.). It distilled at 190–195° (2 mm.) and solidified spontaneously. By recrystallization from petroleum ether, waxy prisms of m.p. 79–80° were obtained, yield 9.5 g. (60%); ultraviolet spectrum in alcohol (log ε): 230 mμ (4.14), 260 mμ (2.84), 265 mμ (2.86).

*Anal.* Calcd. for $C_{14}H_9Cl_4FO$: C, 47.5; H, 2.6. Found: C, 47.7; H, 2.7.

**The acetate** melted at 100.5–101.5°, yield 72%. *Anal.* Calcd. for $C_{16}H_{11}Cl_4FO_2$: C, 48.5; H, 2.8. Found: C, 48.6; H, 3.0.

**1,1-Di-(*p*-chlorophenyl)-2-fluoroethanol (VIII).**—To an ice-cold Grignard solution, prepared from magnesium (6.9 g.) and *p*-chlorobromobenzene (57.5 g.) in ether (150 ml.), a solution of ethyl fluoroacetate (17. g.) in ether (150 ml.) was added within 20 minutes. This was followed immediately by a cold saturated solution of ammonium chloride in water. The organic layer was separated, washed and filtered with the help of filter-aid and evaporated. The solid residue was recrystallized from methanol. Thus 4,4′-dichlorodesoxybenzoin (IX) (4 g.), m.p. 113–114°, was obtained; it was identified by its mixed m.p. with an authentic sample. The methanolic mother liquor was evaporated and the residue distilled *in vacuo*. 1,1-Di-(*p*-chlorophenyl)-2-fluoroethanol (VIII) boiled at 173–176° (2 mm.). It solidified and was recrystallized from petroleum ether; m.p. 75–76°, yield 24.6 g. (58%); ultraviolet spectrum in alcohol (log ε): 226 mμ (4.24), 266 mμ (2.60), 275 mμ (2.44).

*Anal.* Calcd. for $C_{14}H_{11}Cl_2FO$: C, 59.0; H, 3.9. Found: C, 59.5; H, 4.0.

**1,1-Di-(*p*-chlorophenyl)-2-fluoroethylene (X).**—The mixture of VIII (1 g.) and concentrated sulfuric acid (20 g.) was kept for 12 hr. at room temperature. By addition of ice, extraction with ether, evaporation of the solvent and recrystallization of the solid residue from methanol, 0.5 g. (53%) of X was obtained, m.p. 79–80°; ultraviolet spectrum: 240 mμ (log ε 4.22); infrared spectrum (KBr pellet): 3500, 3000, 1640, 1500, 1400, 1178, 1088, 1070, 1015, 925, 840, 830, 822, 765, 705 cm.$^{-1}$.

*Anal.* Calcd. for $C_{14}H_9Cl_2F$: C, 63.0; H, 3.4; Cl, 26.6. Found: C, 63.4; H, 3.2; Cl, 26.0.

When the carbinol VIII (2 g.) was refluxed with acetic anhydride (10 ml.) and concentrated sulfuric acid (2 drops) for 3 hr., the ethylene X was obtained in 80% yield.

**Oxidation.**—The ethylene X (1 g.) was refluxed with chromic acid (2 g.) in glacial acetic acid (10 ml.) for 30 minutes. By addition of water, extraction with ether, evaporation of the solvent and recrystallization of the residue from ethanol, 4,4′-dichlorobenzophenone (0.5 g.) was obtained. It was identified by its melting point and by a mixed melting point with an authentic sample.

**1,1′-Di(*p*-chlorophenyl)-ethane.**—The carbinol VIII (1.5 g.) was refluxed in glacial acetic acid (10 ml.) with red phosphorus (0.6 g.) and iodine (0.25 g.) for 30 minutes. Water (0.1 ml.) was added and the heating continued for 48 hr. The product was diluted with water, extracted with ether and the extract washed with a solution of sodium thiosulfate and water. Evaporation of the solvent and recrystallization of the residue from methanol gave 1,1-di-(*p*-chlorophenyl)-ethane (0.7 g., 54%), identified by its melting point (54–55°) and by the mixed melting point with an authentic sample.

***p*-Chloro-ω-fluoroacetophenone.**—Finely divided aluminum chloride (250 g.) and subsequently a solution of fluoroacetyl chloride (80 g.) in ethylene dichloride (300 ml.) was added to 1 l. of ethylene dichloride with vigorous agitation which was continued for 30 minutes. The dark solution was decanted into a three-necked flask, cooled at 0° and a mixture of chlorobenzene (90 g.) and ethylene dichloride (75 ml.) added dropwise, with stirring, within 20 minutes; stirring was continued for 15 minutes and the mixture poured onto ice and hydrochloric acid. The

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(18) R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1916, p. 474.

(19) L. J. Bellamy, L. C. Thomas and R. L. Williams, *J. Chem. Soc.*, 3704 (1956).

(20) R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

organic layer was separated, washed with water and sodium bicarbonate solution and dried. *p*-Chloro-ω-fluoroacetophenone distilled at 115–119° (8 mm.) and crystallized immediately as plates, m.p. 54–55° (from aqueous ethanol), yield 72 g. (52%). This ketone also has been described by Bergmann, Kalmus and Breuer,[11] who also have carried out the reduction with lithium aluminum hydride, described below; ultraviolet spectrum: 255 mμ (log ε 4.25); infrared spectrum (KBr pellet): $\nu_{C=O}$ 1700 cm.$^{-1}$.

*Anal.* Calcd. for $C_8H_6ClFO$: C, 55.8; H, 3.5. Found: C, 55.7; H, 4.5.

**1-(*p*-Chlorophenyl)-2-fluoroethanol.**—To an ice-cold solution of lithium aluminum hydride (1.5 g.) in anhydrous ether (80 ml.), a solution of *p*-chloro-ω-fluoroacetophenone (12 g.) in ether (50 ml.) was added during 90 minutes. After 10 minutes, the mixture was decomposed with a solution of sulfuric acid (1 ml.) in 30 ml. of ice-water, and the ethereal layer separated, washed and dried. 1-(*p*-Chlorophenyl)-2-fluoroethanol distilled at 124–134° (8 mm.) as a colorless oil; yield 11 g. (90%), $n^{29}$D 1.5398; infrared spectrum: 3400, 1500, 1100, 1010, 900, 830 and 750 cm.$^{-1}$.

*Anal.* Calcd. for $C_8H_8OClF$: C, 55.2; H, 4.6. Found: C, 55.5; H, 4.7.

**1,1-Di-(*p*-chlorophenyl)-2-fluoroethane (XIII).**—To an ice-cold mixture of 1-(*p*-chlorophenyl)-2-fluoroethanol (2 g.) and chlorobenzene (5 g.), a mixture of concentrated sulfuric acid (20 ml.) and fuming sulfuric acid (4 ml.) was added dropwise. The reaction mixture was shaken mechanically for 2 hr., then poured onto ice and extracted with ether. The ethereal solution was washed, dried, evaporated and the product distilled *in vacuo*. It boiled at 155–165° (2 mm.) and solidified spontaneously; from methanol, m.p. 54–55°, yield 1 g. (32%).

*Anal.* Calcd. for $C_{14}H_{11}Cl_2F$: Cl, 26.3. Found: Cl, 26.0.

**Reaction with Alkali.**—The compound XIII (0.3 g.) was refluxed with 1 *N* methanolic potassium hydroxide solution (5 ml.) for 1 hr., hydrochloric acid (2 ml.) and water (30 ml.) added and the product extracted with ether. The ether residue was recrystallized from methanol (0.2 g.) and melted at 84–85°. It was identified as 1,1-di-(*p*-chlorophenyl)-ethylene by comparison with an authentic sample; infrared spectrum: 3400, 1600, 1500, 1420, 1190, 1120, 1085, 1018, 970, 855, 825, 790, 725 cm.$^{-1}$.

**Difluorochloromethyl-*p*-chlorophenylcarbinol.**—A solution of the ketone VI (11.3 g.) in ether (30 ml.) was added, dropwise, to a well-stirred ice-cold suspension of lithium aluminum hydride (1.5 g.) in ether (50 ml.). An ice-cold mixture of sulfuric acid (10 ml.) and water (50 ml.) was added cautiously, the ethereal layer separated, washed with water and concentrated and the residue distilled *in vacuo;* b.p. 115–120° (10 mm.), colorless liquid, $n^{28}$D 1.5144, yield 9 g. (80%).

*Anal.* Calcd. for $C_8H_6Cl_2F_2O$: C, 42.3; H, 2.7. Found: C, 42.4; H, 2.8.

**Dichlorofluoromethyl-*p*-chlorophenylcarbinol.**—The ketone VII (4 g.) in ether (15 ml.) was reduced with lithium aluminum hydride (0.5 g.) in ether (20 ml.). The product distilled at 120–125° (2 mm.) as a colorless liquid, $n^{30}$D 1.543, yield 3.5 g. (87%); infrared spectrum: 3500, 1600, 1400, 1200, 1085, 1010, 950, 870–880, 820, 795, 771, 715 cm.$^{-1}$.

*Anal.* Calcd. for $C_8H_6Cl_3FO$: Cl, 43.7. Found: Cl, 43.4.

**1,1-Di-(*p*-chlorophenyl)-2,2-difluoro-2-chloroethane (XI).**—To a well-stirred mixture of chlorobenzene (4.5 g.), concentrated sulfuric acid (10 ml.) and 20% fuming sulfuric acid (3 ml.), was added, slowly and with cooling, *p*-chlorophenyldifluorochloromethylcarbinol (5 g.). The mixture was then shaken for 5 hr., added to crushed ice and extracted with ether. After removal of the ether and excess chlorobenzene by distillation, the ethane XI distilled at 160–165° (2 mm.), yield 6 g. (85%). The product solidified; after recrystallization from methanol, it melted at 54–55°; ultraviolet spectrum: 228 mμ (4.20); 260 mμ (2.60); 267 mμ (2.62); infrared spectrum (KBr pellet): 1500, 1400, 1210, 1170, 1090, 1015, 962, 765 cm.$^{-1}$.

*Anal.* Calcd. for $C_{14}H_9Cl_3F_2$: C, 52.3; H, 2.8. Found: C, 52.1; H, 2.9.

**Reaction with Alkali.**—The compound XI (1 g.) was refluxed for 1 hr. with 1 *N* methanolic potassium hydroxide (20 ml.). Water was added and the mixture extracted with ether. After removal of the solvent, **1,1-di-(*p*-chlorophenyl)-2,2-difluoroethylene (XIV)** distilled at 165–169° (2 mm.), yield 0.7 g. (79%), $n^{30}$D 1.5732. The substance was so unstable that only approximate analyses could be obtained. However, the spectrum indicated (see above) that the compound had structure XIV; ultraviolet spectrum (isoöctane): 228 mμ (4.46); 255 mμ (4.06).

**1,1-Di-(*p*-chlorophenyl)-2,2-dichloro-2-fluoroethane (XII).**—Condensation of *p*-chlorophenyldichlorofluoromethylcarbinol (2.5 g.) and chlorobenzene (2 g.) in the presence of concentrated sulfuric acid (5 ml.) and 20% fuming sulfuric acid (1.5 ml.) gave XII (2 g., 57%); b.p. 180–185° (2 mm.), m.p. after recrystallization from methanol 78–79°; ultraviolet spectrum (log ε): 232 mμ (4.26), 260 mμ (2.74), 267 mμ (2.76); infrared spectrum (KBr pellet): 1500, 1400, 1120, 1090, 1015, 940, 810, 780 cm.$^{-1}$.

*Anal.* Calcd. for $C_{14}H_9Cl_4F$: C, 49.8; H, 2.7. Found: C, 50.4; H, 2.8.

**Reaction with Alkali.**—Upon alkaline hydrolysis of the ethane XII (0.75 g.) as described above, **1,1-di-(*p*-chlorophenyl)-2-chloro-2-fluoroethylene (XV)** (0.55 g., 85%) was very probably obtained. It distilled at 165–166° (3 mm.) as a colorless but unstable oil, of $n^{28}$D 1.6059.

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[Contribution from the Department of Pharmacology of the Hebrew University-Hadassah Medical School]

# ω-Fluoroacetophenone. III. Reaction of Fluoroacetyl Chloride with Halobenzenes. On the Mechanism of Side-chain Chlorination by Sulfuryl Chloride

By Felix Bergmann, Abraham Kalmus and Eli Breuer[1]

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The synthesis of ω-fluoroacetophenone has been extended to halobenzenes. The mechanism of side-chain chlorination of these ketones by sulfuryl chloride has been studied and a reaction scheme proposed.

The synthesis of ω-fluoroacetophenone (I), which was described previously,[2] was based on the observation that prolonged contact of I with aluminum chloride is responsible for halogen exchange, producing ω-chloroacetophenone (II). Short reaction periods are required to secure sizable yields of I. It remained undecided, however, whether the same type of exchange proceeds with fluoroacetyl chloride, prior to condensation. This possibility was tested by treating the latter with the Friedel–Crafts catalyst in methylene chloride at room tem-

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[1] Part of a M.Sc. thesis, submitted to the Faculty of Science, The Hebrew University, Jerusalem, 1957.

[2] F. Bergmann and A. Kalmus, This Journal, 76, 4137 (1954).