carbazone, from methanol m.p. 201° (lit.,[10] 201°) and the 2,4-dinitrophenylhydrazone, from methanol, m.p. 172° (lit.,[10] 170–173°).

Isomerization of V. A mixture of 8 g. of V and 0.5 g. of palladium-charcoal was heated at 180–190° for 3 hr. The product was extracted with sodium hydroxide solution (10%), from which thymol (3.3 g.; 40%) was recovered by acidification, extraction with low-boiling petroleum ether, and distillation, b.p. 130° (35 mm.). When the material, insoluble in alkali, was subjected to the same treatment, some more (1 g., 12%) thymol was isolated. The phenol was characterized by its infrared spectrum (3350 cm.$^{-1}$ (OH), 815 cm.$^{-1}$ (trisubstituted benzene)) and through thymoxy-acetic acid, from water m.p. 146° (lit.,[11] 145°).

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A Rearrangement of Diaryltrichloromethylcarbinols

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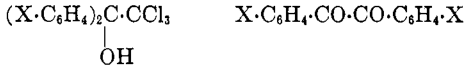
In view of the fact that diaryltrifluoromethylcarbinols rearrange in their halochromic solutions in concentrated sulfuric acid to yield fluorene derivatives,[1,2] it seemed of interest to study the behavior of the recently[3] described diaryltrichloromethylcarbinols (I) under similar conditions. When the solutions of these compounds in concentrated sulfuric acid are poured into water or alcohol, yellow crystalline compounds precipitate, which were identified as the corresponding benzils (II).



$$(X{\cdot}C_6H_4)_2\underset{OH}{C}{\cdot}CCl_3 \qquad X{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_4{\cdot}X$$

I II

X = H, F, Cl (*para*)

Rearrangement of asymmetric to symmetric diarylethanes and -ethylenes occurs in many cases; in particular one would recall the transformation of 1,1-diaryl-2,2-dichloro- or 1,2,2,2-tetrachloro-ethanes into chlorinated bibenzyls,[4–6] the preparation of α,α,β-trifluorobibenzyls from 1,1-diaryl-2,2,2-trichloroethanes under the influence of hydrogen fluoride and mercuric oxide,[7,8] and particularly the conversion of 1,1-di-(*p*-chlorophenyl) 2,2,2-trichloro- and 1,2,2,2-tetrachloroethane into 4,4′-dichlorobenzil under the influence of concentrated sulfuric acid.[9] The mechanism of the observed rearrangement can be formulated as follows in accordance with Barry and Boyer[9]:

$$Ar_2C(OH){\cdot}CCl_3 \xrightarrow{H_2SO_4} Ar_2\overset{+}{C}{\cdot}CCl_3 \qquad (1)$$

$$Ar_2\overset{+}{C}{\cdot}CCl_3 \longrightarrow (Ar)\,(Cl)\overset{+}{C}{\cdot}CCl_2Ar \qquad (2)$$

$$(Ar)(Cl)\overset{+}{C}{\cdot}CCl_2Ar \longrightarrow Ar{\cdot}\overset{+}{C}(OH)\,CCl_2Ar \qquad (3)$$

$$Ar{\cdot}\overset{+}{C}(OH){\cdot}CCl_2Ar \longrightarrow Ar{\cdot}CO{\cdot}CCl_2Ar + H^+ \qquad (4)$$

$$ArCO{\cdot}CCl_2Ar \longrightarrow ArCO{\cdot}COAr \qquad (5)$$

This mechanism is analogous to that accepted for the transformation of, *e.g.*, diphenylglycolaldehyde into benzoin.[10]

EXPERIMENTAL

The diaryl-trichloromethyl-carbinols (I) and their acetates were obtained as described earlier.[3] In the preparation of [I (X = H)], a yield of 84% (instead of the previously reported 56%) was obtained when the preparation was carried out on a larger scale. The acetates of I may be saponified directly (without prior isolation) by refluxing the filtered reaction mixture with dilute sulfuric acid for 1.5–2 hr.

Nitration of diphenyl-trichloromethyl-carbinol (I, X = H). At −5 to −10°, a solution of 6.0 g. of diphenyl-trichloromethyl-carbinol in 15 ml. of chloroform was added dropwise, during 30 min., to a well stirred mixture of 20 ml. of nitric acid (d. 1.5) and 5 ml. of concentrated sulfuric acid. The stirring was continued for another half hour at −10° and for 4 hr. at room temperature, and the organic layer separated, washed with sodium bicarbonate solution and water and evaporated, yielding 8 g. of a yellow, very viscous product. As it could not be obtained in a crystalline state, it was acetylated by an excess of boiling acetic anhydride and 2 drops of concentrated sulfuric acid. The acetate so obtained melted at 115–130° and was a mixture of several isomers. By a number of tedious recrystallizations from acetic acid, toluene, and ethanol a small amount of colorless crystals of 154–156° was obtained. Their quantity did not suffice for the determination of the position of the two nitro groups.

Anal. Calcd. for $C_{16}H_{11}Cl_3N_2O_6$: C, 44.3; H, 2.6. Found: C, 44.3; H, 2.8.

Action of concentrated sulfuric acid on the carbinols (I). *4,4-Difluorobenzil* (II, X = F). To 2.3 g. of 1,1-di-(*p*-fluorophenyl)-1-acetoxy-2,2,2-trichloroethane, 25 ml. of concentrated sulfuric acid was added. The red color of the solution quickly turned greenish brown. The mixture was shaken for 2 hr. in a stoppered bottle and poured into cold water. The yellow 4,4′-difluorobenzil (0.6 g.; 40%), m.p. 114–120°, was recrystallized from petroleum ether (60–90°) and methanol and melted at 121.5–122.5° (lit.[6] 123–123.5°).

Anal. Calcd. for $C_{14}H_8F_2O_2$: C, 68.3; H, 3.3. Found: C, 68.1; H, 3.6.

Analogously, from the blue-violet solution of diphenyl-trichloromethyl-carbinol (I, X = H) or its acetate, *benzil,*

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m.p. and mixed m.p. 94–96° (yield, 48%), and from the red solution of di-(*p*-chlorophenyl)-trichloromethyl-carbinol (I, X = Cl), 4,4′-dichlorobenzil (yield, 36%), m.p. and mixed m.p. 200–201°,[6] was obtained. In these two cases, part of the starting material failed to dissolve in the acid and was recovered unchanged by filtration.

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Basic Alcoholysis of Diarylperfluoroalkylmethanes

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It has been reported[1] that diaryltrifluoromethylmethanes $Ar_2CH \cdot CF_3$ undergo facile alcoholysis in sodium alkoxide solution to yield the alkyl ester of the corresponding diarylacetic acid *via* the corresponding diarylketene dialkylacetal. It became of interest to investigate the behavior of diarylpentafluoroethylmethanes (I) and diarylheptafluoropropylmethanes (II) under similar conditions.

The reaction between I and sodium methoxide in anhydrous methanol, under mild conditions, caused dehydrofluorination of I and formation of the corresponding 1,1-diaryl-2,3,3,3-tetrafluoro-1-propene (III). However, when I (Ar = p-C_6H_4Cl) was refluxed with a five-fold excess of sodium methoxide and for an extended period of time, a compound (IV) different from (III) was isolated. IV was also obtained from III and boiling sodium methoxide solution. According to the analysis, one fluorine atom in (III) has been exchanged for a methoxyl group; the most likely formula for IV is, then, 1,1-di-(*p*-chlorophenyl)-2-methoxy-3,3,3-trifluoro-1-propene. Both III and IV were oxidized to 4,4′-dichlorobenzophenone by chromic acid; this lends support to the formula. The following reaction mechanism is suggested.

$$\underset{\text{I}}{Ar_2CH\cdot CF_2\cdot CF_3} + OCH_3^- \longrightarrow [Ar_2C\cdot CF_2\cdot CF_3]^- \xrightarrow{-F^-}$$

$$\underset{\text{III}}{Ar_2C{=}CF\cdot CF_3} \xrightarrow{+OCH_3^-} [Ar_2C\cdot CF(OCH)\cdot CF_3]^- \xrightarrow{-F^-}$$

$$\underset{\text{IV}}{Ar_2C{=}C(OCH)\cdot CF_3}$$

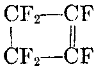
Di-(*p*-chlorophenyl)heptafluoropropylmethane (II) is even less reactive than the diarylpentafluoroethylmethanes (I); its reactivity amounts to about 60% of that of II in the reaction with boiling sodium methoxide solution, and only slowly V, the analog of IV, is formed.

An interesting parallel to these observations is the fact that perfluorocyclobutene (VI) is converted by methylalcoholic sodium hydroxide into 1,2 - dimethoxy - 3,3,4,4 - tetrafluorocyclobutene (VII).[2]

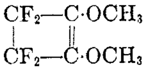
Examination of the infrared spectra of III and IV (Ar = p-C_6H_4Cl) shows that the 720–740 cm.$^{-1}$ frequency of the CF—CF_3 grouping in (III)[3] is absent in IV, while the latter possesses a band at 1000 cm.$^{-1}$

II $Ar_2CH\cdot CF_2\cdot CF_2\cdot CF_3$

V $Ar_2C{=}C(OCH_3)\cdot CF_2\cdot CF_3$



VI



VIII

EXPERIMENTAL

All m.p.'s were determined on a Kofler microstage; the b.p.'s are uncorrected.

β, β, γ, γ, γ-Pentafluoropropiophenone. To a Grignard solution prepared from 118 g. (0.75 mole) of bromobenzene and 18.2 g. of magnesium turnings in 250 ml. of ether, 41 g. (0.25 mole) of pentafluoropropionic acid in 70 ml. of ether was added at 5–10° over a period of 60 min. After decomposition with ice and sulfuric acid and distillation of the ether extract, 34.5 g. (61%) of pentafluoropropiophenone was obtained, b.p. 157–159° (lit.: 161–162°[4]; 158–161°[5]).

Phenylpentafluoroethylcarbinol. A quantity of 22.4 g. (0.1 mole) of the above ketone in 60 ml. of anhydrous ether was added with cooling and stirring to a suspension of 3 g. of lithium aluminum hydride in 100 ml. of ether. Ten min. later, 10 ml. of ethyl acetate was slowly added, followed by a cold solution of 100 ml. of 20% sulfuric acid. The ethereal layer was separated, dried and subjected to distillation. Yield, 15.0 g. (66%), b.p. 108–110° (42 mm.); 183–185° (760 mm.); n_D^{27} 1.4329; d_{27}^{27} 1.371; MR calcd., 42.96; MR found, 42.85.

Anal. Calcd. for $C_9H_7F_5O$: C, 47.8; H, 3.1. Found: C, 48.0; H, 3.0.

1,1-Diphenyl-2,2,3,3,3-pentafluoropropane (I, Ar = C_6H_5). When 8.2 g. (0.036 mole) of phenylpentafluoroethylcarbinol in 10 ml. of benzene was added, with stirring, to a mixture of 15 ml. of concentrated sulfuric acid and 1.5 ml. of 60% oleum within 15 min., the temperature rose from 25 to 50°. After 3 hr. of stirring at room temperature, the mixture was poured onto crushed ice and extracted with ether. Distillation gave 7.9 g. (76%) of the propane, b.p. 102–105° (2 mm.), which had been prepared previously by the reduction of diphenylpentafluoroethylcarbinol.[6]

1,1-Diphenyl-2,3,3,3-tetrafluoro-1-propene (III, Ar = C_6H_5). When 4.5 g. (0.015 mole) of I in 10 ml. of methanol was refluxed with 17.3 ml. (0.03 mole) of 1.65*N* sodium methoxide solution for 1.5 hr., some solid material precipitated which was removed by filtration. Most of the solvent was distilled off, and the resulting liquid filtered from white crystals of sodium fluoride (0.59 g.). The filtrate was then neutralized and extracted with petroleum ether (40–60°). Distillation yielded 2.4 g. (60%) of 1,1-diphenyl-2,3,3,3-

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