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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Received December 8, 1958

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′-dichlorobenzophenenone by chromic acid; this lends support to the formula. The following reaction mechanism is suggested.

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

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

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

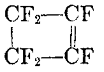
Di-(p-chlorophenyl)heptafluoropropylmethane (II) is even less reactive than the diarylpentafluoroethylmethanes (I); its reactivity amounts to about 60% of that of II in the reaction with boiling sodium methoxide solution, and only slowly V, the analog of IV, is formed.

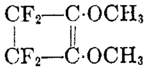
An interesting parallel to these observations is the fact that perfluorocyclobutene (VI) is converted by methylalcoholic sodium hydroxide into 1,2 - dimethoxy - 3,3,4,4 - tetrafluorocyclobutene (VII).[2]

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 1.65N 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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tetrafluoro-1-propene (III, Ar = C_6H_5), b.p. 147–149° (30 mm.). n_D^{30} 1.5180; d_{30}^{30} 1.235; MR calcd., 65.10; MR found, 65.30.

Anal. Calcd. for $C_{15}H_{10}F_4$: C, 67.7; H, 3.8. Found: C, 67.5; H, 4.2.

Oxidation of III (Ar = C_6H_5) with chromic anhydride in boiling acetic acid gave benzophenone (identified as its dinitrophenylhydrazone, m.p. 236–238°).

p-Chlorophenyl pentafluoroethyl ketone. This ketone was prepared by the above described procedure using 288 g. of *p*-chlorobromobenzene, 36.4 g. of magnesium and 82 g. of pentafluoropropionic acid. Yield, 54.9 g. (42%), b.p. 186–188°.

Anal. Calcd. for $C_9H_4ClF_5O$: C, 41.8; H, 1.6. Found: C, 41.6; H, 1.7. The *dinitrophenylhydrazone* melts at 180–182° (from methanol).

Anal. Calcd. for $C_{15}H_8ClF_5N_4O_4$: C, 41.1; H, 1.8. Found: C, 41.0; H, 2.1.

(p-Chlorophenyl)pentafluoroethyl-carbinol. Reduction of the foregoing ketone (25.9 g.) with lithium aluminum hydride (3.0 g.) as described above, afforded 20.3 g. (78%) of the carbinol, b.p. 115–125° (30 mm.). It solidified and was recrystallized from petroleum ether (40–60°); m.p. 41–42°.

Anal. Calcd. for $C_9H_6ClF_5O$: C, 41.5; H, 2.3. Found: C, 40.8; H, 2.6.

1,1-Di(p-chlorophenyl)-2,2,3,3,3-pentafluoropropane (I, Ar = *p*-C_6H_4Cl). A solution of 19.7 g. (0.075 mole) of (*p*-chlorophenyl)pentafluoroethylcarbinol and 5 ml. of chlorobenzene was added to a mixture of 11 ml. of chlorobenzene, 37 ml. of 95% sulfuric acid and 3.7 ml. of 60% oleum, in the manner described before. After the usual procedure, 22 g. (83%) of the propane was obtained, b.p. 148–152° (5–6 mm.), m.p. 46–50° (from methanol). An analytical sample was obtained by recrystallization from petroleum ether (40–60°), b.p. 52–53°.

Anal. Calcd. for $C_{15}H_9Cl_2F_5$: C, 50.7; H, 2.5. Found: C, 51.0; H, 2.8.

The same compound was obtained in 48% yield by refluxing for 250 hr. 7.4 g. of di-(*p*-chlorophenyl)pentafluoroethylcarbinol[6] with 2 g. of red phosphorus and 0.8 g. of iodine in 20 ml. of glacial acetic acid and 0.5 ml. of water.

Alkaline alcoholysis of 1,1-di-(p-chlorophenyl)-2,2,3,3,3-pentafluoropropane (I, Ar = *p*-C_6H_4Cl). (a). A mixture of 14.2 g. (0.04 mole) of I (Ar = *p*-C_6H_4Cl) and 24.2 ml. of 1.65*M* sodium methoxide was refluxed for 2 hr., cooled, and filtered. The white precipitate of sodium fluoride weighed 1.55 g. Titration of the filtrate showed that 4% of the sodium methoxide had not reacted. After removal of the solvent, the residue was distilled under reduced pressure to yield 10.2 g. (76%) of 1,1-di-(*p*-chlorophenyl)-2,3,3,3-tetrafluoro-1-propene (III, Ar = *p*-C_6H_4Cl), b.p. 130–132° (4 mm.). It solidified slowly and was recrystallized from methanol or petroleum ether; m.p. 40–41°.

Anal. Calcd. for $C_{15}H_8Cl_2F_4$: C, 53.8; H, 2.4. Found: C, 53.9; H, 2.2.

Oxidation with chromic anhydride in hot acetic acid yielded 4,4'-dichlorobenzophenone, m.p. and mixed m.p. with an authentic sample 146–147°.

(b) The same operation was repeated, using a five-fold excess of sodium methoxide solution and a reflux period of 4 hr. Thus, 6.9 g. (50%) of the well crystallized 1.1-di-(*p*-chlorophenyl)-2-methoxy-3,3,3-trifluoro-1-propene (IV, Ar = *p*-C_6H_4Cl) was obtained; m.p. 58–59° (from petroleum ether).

Anal. Calcd. for $C_{16}H_{11}Cl_2F_3O$: C, 55.3; H, 3.2; F, 16.4; OCH_3, 8.9. Found: C, 55.3; H, 2.9; F, 16.8; OCH_3, 9.0.

(c) A mixture of 6.7 g. (0.02 mole) of di-(*p*-chlorophenyl)-2,3,3,3-tetrafluoro-1-propene (III, Ar = *p*-C_6H_4Cl) and 30.4 ml. of 1.65*N* sodium methoxide solution was refluxed for 2 hr. After cooling, the solution was filtered from sodium fluoride (0.80 g.); titration of the filtrate showed that 38% of the sodium methoxide employed had reacted. Upon dilution with water, 1,1-di-(*p*-chlorophenyl)-2-methoxy-3,3,3-trifluoro-1-propene (IV, Ar = *p*-C_6H_4Cl) precipitated; it solidified quickly and was recrystallized from methanol. Yield, 5.9 g. (85%), m.p. 56–58°.

Oxidation of IV (Ar = *p*-C_6H_4Cl) by chromic anhydride in hot acetic acid yielded 4,4'-dichlorobenzophenone. It may be noted that I (Ar = *p*-C_6H_4Cl) is refractory to this treatment and is recovered unchanged.

1,1-Di(p-chlorophenyl)-2,2,3,3,4,4,4-heptafluorobutane (II). A quantity of 10.5 g. (0.025 mole) of di-(*p*-chlorophenyl)-heptafluoropropylcarbinol[6] was reduced with red phosphorus and iodine in aqueous acetic acid as described above. Thus, 6.6 g. (65%) of II was obtained; b.p. 155–160° (4 mm.). The distillate solidified on standing and was recrystallized from methanol; m.p. 58–59°.

Anal. Calcd. for $C_{16}H_9Cl_2F_7$: C, 47.4; H, 2.2. Found: C, 47.0; H, 2.5.

Alkaline alcoholysis of II. When 2.1 g. of II was refluxed for 2 hr. with 3 ml. of 1.65*N* sodium methoxide solution, 0.12 g. (58% of theory) of sodium fluoride was obtained and 33% of the methoxide had not reacted. The oily product which was precipitated by addition of water, was refluxed again for 4 hr. with 10 ml. of 1.65*N* sodium methoxide solution; the solvent was evaporated after neutralization and the residue extracted with ether and fractionated. The fraction (0.7 g.), boiling at 172–175° (5 mm.), n_D^{30} 1.5312, was mainly the methoxy olefin V.

Anal. Calcd. for $C_{17}H_{10}Cl_2F_6O$: C, 51.5; H, 2.5; F, 24.0. Found: C, 51.2; H, 2.6; F, 25.8.

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Pteridines. XXI. A One-Step Synthesis of 4-Aminopteridines[1,2]

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Received December 8, 1958

A facile synthesis of 2-substituted adenines has recently been described[3] which involves the isomerization of an amidine salt of isonitrosomalononitrile (I) in an appropriate basic solvent to a 2-substituted 4,6-diamino-5-nitrosopyrimidine (II), followed by reduction to III, formylation to IV and dehydration to V in a single operation by treatment with a mixture of formamide, formic acid, and sodium hydrosulfite. The conversion of I to V may be carried out in one step by employing formamide as the solvent for the initial isomerization of I to II. Since 4,5-diaminopyrimidines (III) may be converted to pteridines by reaction with α-diketones,[4] it was apparent that the above reaction sequence leading to purines might be adapted to the synthesis of pteridines by employing a solvent for the isomerization which could not react

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[1] This investigation was supported by a research grant (C-2551) to Princeton University from the National Cancer Institute of the National Institutes of Health, Public Health Service.

[2] For the previous paper in this series, see E. C. Taylor, O. Vogl and P. K. Loeffler, *J. Am. Chem. Soc.*, **81**, 2479 (1959).

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