C, 67.94; H, 10.74. Found: C, 67.83; H, 10.98.

Both octadecenoic acids were subjected to catalytic hydrogenation using Adams catalyst[15]: 0.356 millimole of the 16,17-octadecenoic acid required 0.352 millimole of hydrogen for complete reduction, and 0.500 millimole of the 17,18-octadecenoic acid required 0.505 millimole of hydrogen. The stearic acid obtained from both reductions, after recrystallization from glacial acetic acid, melted at 69.5–70.2°; reported for stearic acid, 69–70.2°.[16]

Summary

8-Keto-16,17- and 8-keto-17,18-octadecenoic acids have been prepared by the acetoacetic ester synthesis. These acids have been reduced to the respective octadecenoic acids by the Wolff–Kishner method. Proof of structure of the octadecenoic acids rests on their reduction to stearic acid, on their oxidation to the expected dibasic acids, and on the method of synthesis.

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[15] "Organic Syntheses," Coll. Vol. I, 2d. ed., John Wiley and Sons, Inc., New York, N. Y., p. 463.

[16] Kass and Kayser, THIS JOURNAL, **62**, 230 (1940).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Fluorine Derivatives of Acetophenone and Ethylbenzene

BY J. H. SIMONS AND D. F. HERMAN

In a previous paper[1] the synthesis of 1,1,1,2,2-pentafluoro-2-phenylethane was suggested. This has now been accomplished and a number of fluorine derivatives of both acetophenone and ethylbenzene synthesized. In this work a variety of methods of fluorination were used. In some cases the replacement of chlorine with fluorine was accomplished by the use of antimony fluoride in the Swarts reaction. In other cases hydrogen fluoride was used following the method employed by Simons and Lewis[2] and Simons and Ramler.[1] A highly active silver fluoride made by the use of elementary fluorine and containing an excess of fluorine atoms over silver atoms was used for some of the more difficult replacements of chlorine. This was done in a liquid hydrogen fluoride solution. By using liquid anhydrous hydrogen fluoride as a solvent, a direct fluorination of acetophenone with elementary fluorine was accomplished.

Experimental

Preparation of ω,ω-Difluoroacetophenone from Dibromoacetophenone.—Into a 350-cc. steel bomb connected by a forged steel fitting to a steel water-cooled condenser fitted with an exhaust valve was placed 67 g. (0.24 mole) of ω,ω-dibromoacetophenone, 80 g. (0.63 mole) of silver fluoride and 100 g. (5 mole) of anhydrous hydrogen fluoride. The silver fluoride was prepared by passing elementary fluorine through a copper tube packed with silver which had been precipitated by the reduction of ammoniacal silver solution with hydroxylamine hydrochloride. The increase in weight of the silver is accounted for by the formula $AgF_{1.6}$. The formula $AgF_{1.8}$ has been reported.[3] The steel bomb was placed into a shaker and heated to 75° for twelve hours. The reaction products were poured over ice and extracted with ether. This extract was washed with water and then with several 50-cc. portions of 5% sodium bicarbonate solution. It was dried with anhydrous sodium sulfate. After the removal of the ether the products were fractionated in columns of 8 to 12 theoretical plates. There was obtained 15.2 g. (40% yield) of difluoroacetophenone b. p. 83–85° (29 mm.). There was no indication of the formation of the mixed fluorobromoacetophenone. Difluoroacetophenone readily yielded a 2,4-dinitrophenylhydrazone of m. p. 221–223°. *Anal.* Calcd. for $C_8H_6OF_2$; F, 24.36. Found: F, 24.5, 23.8.

This compound was shown to be the ω-difluoroacetophenone by the following experiment. One gram was warmed for forty-eight hours with 30 cc. of 5% sodium hydroxide solution. When this solution was acidified and ether extracted, mandelic acid was found: m. p. of recrystallized acid and mixed m. p. with an authentic sample was 117–118°.[4] Mandelic acid is similarly prepared from dichloroacetophenone.[4]

Dibromoacetophenone failed to react with antimony trifluoride in the presence of antimony pentachloride to give difluoroacetophenone. Also a reaction with anhydrous hydrogen fluoride using antimony pentachloride as a catalyst and a reaction with silver fluoride in a petroleum ether medium were unsuccessful.

Liquid Phase Fluorination of Acetophenone.—The fluorine used in this work was produced by fluorine generators similar to the one described by Simons.[5] The fluorine produced by each of two generators was passed through one-fourth inch copper tubing into a brass T-tube where it was diluted with five times its volume of nitrogen. It then passed through a copper surge chamber and into the reaction chamber. Two $^1/_8$" tube inlets were provided in the reaction chamber so that the fluorine from each generator entered at a different place. The generators were operated to yield approximately one-tenth mole of fluorine per hour. The nitrogen dilution was controlled by means of flowmeters. The copper reaction vessel was cylindrical, 5.8 cm. diameter and 26.2 cm. long. A copper condenser cooled with dry ice–acetone was provided. This condensed and returned most of the hydrogen fluoride carried out with the exit gases. From the top of the condenser the gases were led through a tube containing sodium fluoride and then through two traps cooled with liquid air.

The reaction vessel was charged with 60 g. (0.50 mole) of acetophenone, 2 g. of silver oxide and 200 g. of hydrogen fluoride. Approximately one mole of fluorine was passed in five hours. For the first two hours the reaction proceeded very smoothly at 0°. A slight odor of fluorine was then noticed in the exit gases. After five hours a large portion of the fluorine passed through unreacted. About 2 g. of carbon tetrafluoride contaminated with oxygen fluoride was found in the liquid air traps.

The contents of the reaction vessel were poured over ice,

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[1] J. H. Simons and E. O. Ramler, THIS JOURNAL, **65**, 389 (1943).

[2] J. H. Simons and C. J. Lewis, *ibid.*, **60**, 492 (1938).

[3] H. Jockusch, *Naturwissenschaften*, **22**, 561 (1934).

[4] J. Houben and W. Fischer, *Ber.*, **64B**, 2644 (1931); J. G. Aston, J. D. Newkirk, D. M. Jenkins and J. Dorsky, "Organic Syntheses," Vol. 23, John Wiley and Sons, Inc., New York, N. Y., 1943.

[5] J. H. Simons, THIS JOURNAL, **46**, 2175 (1924); "Inorganic Syntheses," McGraw-Hill Book Company, Inc., New York, N. Y., 1939, Vol. VI, p. 142.

and the organic layer was dissolved in ether. The dissolved hydrogen fluoride was removed with sodium fluoride, and the ether was dried with anhydrous magnesium sulfate. Fractionation of the product gave 2.1 g. of benzoyl fluoride, b. p. 74–79° (30 mm.). It tested for fluoride ion and (with aniline) formed benzanilide, m. p. and mixed m. p. with an authentic sample 162–163°. Difluoroacetophenone was obtained in 20.2% yield (15.7 g.). It was identified by its conversion to mandelic acid by treatment with 5% sodium hydroxide. Trifluoroacetophenone and monofluoroacetophenone were not found.

Reaction of Trichloroacetophenone with Silver Fluoride in Anhydrous Hydrogen Fluoride.—In three similar experiments a total of 222 g. (1.74 moles) of silver fluoride in 300 g. of hydrogen fluoride was treated with 115 g. (0.51 mole) of trichloroacetophenone. The apparatus used consisted of a pure silver reaction vessel 4 cm. in diameter and 13 cm. high. A rubber stopper protected with copper foil carried an oil-sealed silver solder stirrer, a dropping funnel fitted with a copper delivery tube, and a copper delivery tube connected to a condenser set for distillation. The silver fluoride and hydrogen fluoride were put into the vessel; and the trichloroacetophenone was slowly added with stirring during the course of an hour and a half, while the vessel was cooled in a salt–ice bath. The reaction was vigorous. The stirring was continued for an hour. The ice-bath was then removed and the hydrogen fluoride distilled from the vessel. The product was extracted with ether and was washed with water and with sodium bicarbonate solution. It was dried with anhydrous sodium sulfate. Fractionation gave two new sweet smelling compounds, ω-chlorodifluoroacetophenone b. p. 84–85° (25 mm.) and ω-dichlorofluoroacetophenone b. p. 111–112° (24 mm.). The first was obtained in 8.5% yield and the second in 48.7% yield. Both compounds dissolved in warm 10% sodium hydroxide solution with the evolution of sweet smelling gases and the production of salts of benzoic acid in solution. A haloform split apparently occurred similar to that reported for trifluoroacetophenone.[1] The gases produced would be chlorodifluoromethane and dichlorofluoromethane. These mixed halogenated ketones failed to give 2,4-dinitrophenylhydrazones. *Anal.* Calcd. for $C_8H_5OF_2Cl$: F, 19.95; Cl, 18.61. Found: F, 21.2; Cl, 19.3. Calcd. for $C_8H_5OFCl_2$: F, 9.18; Cl, 34.27. Found: F, 8.75, 8.18; Cl, 35.5, 34.9.

A small amount of benzoyl fluoride was formed in the reaction. Attempts to prepare trifluoroacetophenone by treating either dichlorofluoroacetophenone or chlorodifluoroacetophenone with silver fluoride in hydrogen fluoride were unsuccessful.

Preparation of 1,1,1,2,2-Pentachloro-2-phenylethane.—Into a one-liter flask fitted with a condenser was placed one mole of trichloroacetophenone and 1.1 moles of phosphorus pentachloride. After heating for twelve hours at 220° the phosphorus oxychloride was removed by distillation. The product was washed with water and dilute sodium carbonate solution. After drying and fractionating a yield of 84% (208.5 g.) of 1,1,1,2,2-pentachloro-2-phenylethane, b. p. 155–156° (15 mm.), was obtained. This compound b. p. 178–179° (34 mm.) is reported to have been prepared by the action of chlorine on 1,1,2-trichloro-2-phenylethylene.[6]

Reaction of 1,1,1,2,2-Pentachloro-2-phenylethane with Hydrogen Fluoride.—Into the steel bomb previously described were placed 101 g. (0.36 mole) of pentachlorophenylethane and 190 g. (9.5 mole) of hydrogen fluoride. The bomb and condenser were placed in the shaker and heated to 145° while the pressure of the hydrogen chloride was kept below 300 lb./sq. in. by slow bleeding. The reaction was completed in six hours, and the reaction products were dissolved in ether. This solution was washed with water and with 5% sodium carbonate solution. It was dried with anhydrous sodium sulfate. Fractionation of the products gave 28.3 g. (29.8% yield) of trichlorodifluorophenylethane b. p. 100° (16 mm.) or 219° (731 mm.) and 45.4 g. (51.1% yield) of tetrachlorofluorophenylethane, b. p. 123–126° (14 mm.) or 246° (731 mm.). The fluorine atoms are presumedly in the α position.

Anal. Calcd. for $C_8H_5Cl_3F_2$: F, 15.48; Cl, 43.36. Found: F, 15.3, 14.3; Cl, 43.5, 44.2. Calcd. for $C_8H_5Cl_4F$: Cl, 54.17. Found: Cl, 53.6, 52.7.

A small amount of benzoyl fluoride was formed and there was an indication of a small amount of dichlorotrifluorophenylethane.

Tetrachlorofluorophenylethane in the Swarts Reaction.—In a copper vessel 47.5 g. (0.18 mole) of tetrachlorofluorophenylethane, 96 g. (0.54 mole) of antimony trifluoride, and 10 g. (0.033 mole) of antimony pentachloride were mixed and heated for four hours at 170–180°. The reaction products were extracted with ether, and the extract was washed with 1:1 hydrochloric acid solution to remove antimony salts. Dissolved hydrogen fluoride was removed with sodium fluoride, benzoyl fluoride removed with aniline, the excess aniline removed with 1:1 hydrochloric acid solution, and the excess acid removed with a wash of sodium carbonate solution. It was dried with calcium chloride. Fractionation of the product gave 2.5 g. (6.7% yield) of dichlorotrifluorophenylethane b. p. 94–95° (42 mm.) or 177–178° (731 mm.), 19.8° g. (47.3% yield) of trichlorodifluorophenylethane b. p. 100–102° (15 mm.) and 9.9 g. (20.8% yield) of recovered tetrachlorofluorophenylethane. The dichlorotrifluoro compound is assumed to have two of the fluorine atoms in the α position.

Anal. Calcd. for $C_8H_5Cl_2F_3$: F, 24.91; Cl, 30.98. Found: F, 23.5, 24.0; Cl, 31.0, 31.4.

No appreciable amount of a compound containing more than three fluorine atoms was made by this method.

Preparation of Pentafluorophenylethane and Chlorotetrafluorophenylethane.—As the standard techniques were unsuccessful in replacing all five chlorine atoms of pentachlorophenylethane, use was made of active silver fluoride for the replacement of the last three. Even with this reagent repeated treatments were necessary. Trichlorodifluorophenylethane was added slowly to the silver fluoride in a copper vessel fitted with a copper condenser. A vigorous reaction took place at the start. When it subsided, the reaction mixture was heated to 180° for six hours. The product was ether extracted and treated with aniline. Fractionation followed. After five treatments with a total of 400 g. of silver fluoride, 51 g. (0.22 mole) of trichlorodifluorophenylethane yielded 22.8 g. of recovered halogenated ethylbenzenes. Fractionation gave 0.45 g. (1.3% yield) of 1,1,1,2,2-pentafluoro-2-phenylethane b. p. 128–129° (733 mm.) and 7.4 g. (19.9% yield) of chlorotetrafluorophenylethane, b. p. 152–153° (733 mm.). The chlorine atom is assumed to be on the β carbon atom. A 16.7% yield of dichlorotrifluorophenylethane was also obtained.

Anal. Calcd. for $C_8H_5F_5$: F, 48.46. Found: F, 49.3. Calcd. for $C_8H_5ClF_4$: F, 35.77; Cl, 16.69. Found: F, 37.5; Cl, 15.6.

Reaction of Anhydrous Hydrogen Fluoride with 1,1,1-Trifluoro-2,2-dichlorophenylethane.—The method of preparation of 1,1,1-trifluoro-2,2-dichlorophenylethane has been given by Simons and Ramler.[1] Into the steel bomb previously described was placed 6.9 g. (0.03 mole) of this compound, 50 g. of hydrogen fluoride, and 1 g. of antimony pentachloride. Heating was continued for five hours at 180°. The pressure was kept below 400 lb. per sq. in. by bleeding the gas slowly. After treating the product as previously described to remove impurities, it was fractionated. One gram of 1,1,1,2-tetrafluoro-2-chlorophenylethane (15% yield) b. p. 152 (731 mm.) was obtained. *Anal.* Calcd. for $C_8H_5ClF_4$: Cl, 16.69. Found: Cl, 17.4. A forecut b. p. 60–155° (734 mm.) was distilled through a micro distillation column and a small amount of a material was obtained which was shown by analysis to be a mixture of pentafluorophenylethane and the tetrafluorochlorophenylethane.

Anal. Calcd. for $C_8H_5F_5$: F, 48.46. Found: F 41.6.

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[6] H. Biltz, *Ann.*, **296**, 271 (1897).

Discussion

ω-Difluoroacetophenone can be prepared in two ways. One of these is the replacement of bromine in ω-dibromoacetophenone with active silver fluoride, and the other is the direct fluorination of acetophenone with elementary fluorine. Liquid anhydrous hydrogen fluoride is used for a solvent in both methods. The first method is of interest as this replacement reaction is not accomplished by the more usual reagents; and the use of the solvent avoids the usual difficulties of heterogeneous reactions, *i. e.*, surface coating by products, etc. Silver fluoride has been used infrequently in the past[7] and never in connection with hydrogen fluoride as a solvent. The silver fluoride used in the present work had the empirical formula of $AgF_{1.6}$.

The direct fluorination in the liquid phase of acetophenone to form ω-difluoroacetophenone is also of interest as liquid phase reactions of elementary fluorine do not usually produce single isolatable products in good yields. Rupture of carbon to carbon bonds is usually obtained with the formation of fission products such as carbon tetrafluoride. The utility of hydrogen fluoride as the liquid medium is demonstrated. The fact that the reaction stopped at the difluoro compound can be compared to the chlorination of acetophenone[8] which stops at the dichloro compound in an acid medium and goes to the trichloro compound only when the solution is buffered. It is an interesting fact that difluoroacetophenone resists the action of elementary fluorine at 0°. This demonstrates the extreme resistance to oxidation imparted to the organic molecule by the fluorine atoms. A similar fact is the resistance to replacement of the third chlorine atom of trichloroacetophenone even with very active silver fluoride.

The resistance to replacement of the chlorine atoms in the progressive replacement of the chlorine in pentachlorophenylethane increases as the amount of chlorine remaining becomes smaller. The last atom on the terminal carbon atom is extremely difficult to replace. Starting with the terminal carbon completely fluorinated in ω-trifluoroacetophenone and replacing the oxygen with chlorine places the chlorine on the α carbon atom adjacent to the benzene ring. It is much easier to replace in this position, even hydrogen fluoride assisted with antimony compounds will do it. In this compound the effect of the fluorine atoms on the next carbon atom is to increase the difficulty of replacement, and these chlorine atoms are more difficult to replace than those in benzotrichloride. These latter are replaced readily by hydrogen fluoride[2] alone at 0°. These facts in regard to the case of replacement, when considered in connection with all the compounds, has led to the assumptions of the structures as given. It is thus reasonably assumed that the chlorine atoms adjacent to the benzene ring are the first ones to be replaced in pentachlorophenylethane, hydrogen fluoride being sufficiently powerful to do this. The more resistant compounds appear in the final states of the progressive replacement of the chlorine atoms in this compound. These contain one or two chlorine atoms and can be safely assumed to be those with the chlorine on the terminal carbon atom.

Summary

Two new modifications of techniques of fluorination are reported. One is the use of active silver fluoride in an anhydrous hydrogen fluoride solvent as the reagent in a replacement reaction on an aliphatic chloride. The other is the direct replacement by elementary fluorine of hydrogen atoms of the organic compound dissolved in liquid hydrogen fluoride.

The following new compounds have been prepared: ω-difluoroacetophenone, ω-dichlorofluoroacetophenone, ω-chlorodifluoroacetophenone, 1,1,-1,2-tetrachloro-2-fluoro-2-phenylethane, 1,1,1-trichloro-2,2-difluoro-2-phenylethane, 1,1-dichloro-1,2,2-trifluoro-2-phenylethane, 1-chloro-1,1,2,2-tetrafluoro-2-phenylethane, 2-chloro-1,1,1,2-tetrafluoro-2-phenylethane, 1,1,1,2,2-pentafluoro-2-phenylethane.

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[7] Swarts, *Bull. soc. chim.*, [3] **15**, 1134 (1896).

[8] J. G. Aston, J. D. Newkirk, J. Dorsky and D. M. Jenkins, This Journal, **64**, 1413 (1942).