mm.), whose infrared spectrum had intense bands at 3400 (O—H) 1795 (C=O, intense), 1730 (C=O, weak), 1070 (Si—O—C), and 830 (Si-O—H) cm.$^{-1}$. From these data it appears that a mixture of triethylsilanol, triethylsilyl trifluoroacetate, and the trifluoroacetate ester of triethylsilylethylene glycol may be present. Examination of fraction 2 from the original distillation by careful fractional distillation and vapor phase chromatography revealed the presence of at least nine components. The infrared spectra of the resulting fractions were free of hydroxyl absorptions, but all possessed bands of varying intensities at 1795 (C=O), 1740 (C=O), 1390 and 1070 (Si—O—C) cm.$^{-1}$.

Epoxyethyltriphenylsilane.—To a stirred suspension of 13.2 ml. (0.50 mole) of 90% hydrogen peroxide in 250 ml. of methylene chloride cooled to 0° were added dropwise 121 g. (0.57 mole) of trifluoroacetic anhydride. The solution was then stirred at 0° for 15 min. The foregoing solution of peroxytrifluoroacetic acid was added dropwise to a well stirred mixture of 170 g. (1.60 moles) of anhydrous, granular sodium carbonate, 28.6 g. (0.10 mole) of triphenylvinylsilane, and 1500 ml. of methylene chloride. After being stirred for 4 hr. at room temperature, the system was filtered and the filtrate was freed of solvent. The crude epoxide was introduced onto a Florisil column with petroleum ether (b.p. 30-60°) and elution with ethyl ether yielded the epoxide, m.p. 82-85°, 25.3 g. (84%). Successive recrystallizations from methanol and cyclohexane provided an analytical sample, m.p. 85-86°. This product was shown to contain no triphenylvinylsilane by vapor phase chromatography on a 5% silicone gum rubber on firebrick column. Its infrared spectrum displayed the characteristic epoxide peak at 875 cm.$^{-1}$ but showed no hydroxyl or carbonyl absorptions.

Infrared Spectral Measurements.—Spectra of vinylsilanes and epoxyethylsilanes for characterization purposes were recorded on liquid film samples, where possible. Spectra of solids were obtained as mulls in Nujol oil.

For the comparative study of the infrared spectra of the vinylsilanes reported in Tables III and IV, the samples were recorded uniformly in solutions of reagent carbon disulfide (0.050 mole of vinylsilane in 100 ml. of solvent). By use of matched cells with sodium chloride optics, solvent-compensated spectra were obtained. Each recorded spectrum was calibrated by means of a polystyrene film, the known polystyrene band at 906 cm.$^{-1}$ in the region of interest serving as a standard. The instrument was linear with the frequency and the positions of the absorption bands were reproducible to within ±1 cm.$^{-1}$.

All the reported infrared spectra were measured on a Perkin-Elmer infrared spectrophotometer, Model 21 with a 927 slit program.

Acknowledgment.—The authors are indebted to Mr. Bruce Wenzel for his generous assistance in obtaining calibrated infrared spectra of the vinylsilanes.

Hydrogen Fluoride as a Condensing Agent. VI. Reactions of Fluoroölefins with Formaldehyde in Hydrogen Fluoride[1]

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Tetrafluoroethylene condenses with formaldehyde in liquid hydrogen fluoride to form 2,2,3,3,3-pentafluoro-1-propanol and fluoromethyl-2,2,3,3,3-pentafluoropropyl ether. 2,2,3,3-Tetrafluorooxetane, methyl-2,2,3,3,3-pentafluoropropyl ether, bis(2,2,3,3,3-pentafluoropropoxy)methane, and bis[(2,2,3,3,3-pentafluoropropoxy)-methyl] ether are formed as minor by-products. 2,3,3,3-Tetrafluoro-2-trifluoromethyl-1-propanol is obtained from hexafluoropropylene. 1,1-Difluoroethylene and fluoroethylene condense to give, respectively, bis(3,3,3-trifluoropropyl) ether and bis(3,3-difluoropropyl) ether. The formation of bis(fluoromethyl) ether from formaldehyde and hydrogen fluoride is postulated.

Hydrocarbons containing the ethylene linkage react with formaldehyde in the presence of acidic catalysts to form 1,3-glycols and formals.[2] Halogenated olefins react in much the same manner except that hydrolysis may occur in the presence of water leading to halohydracrylic acids.[3] Thus tetrafluoroethylene condenses with formaldehyde in sulfuric acid to give α,α-difluorohydracrylic acid.[4] Quite different results are obtained when fluoroölefins react with solutions of formaldehyde in hydrogen fluoride.

The reaction of aromatic compounds with formaldehyde in hydrogen fluoride, leading to diarylmethanes, has been reported[5] and has led these authors to postulate the initial formation of fluoromethanol, FCH_2OH. Our nuclear magnetic resonance investigation of a solution of paraformaldehyde in hydrogen fluoride confirmed the existence of the FCH_2— group. We have further determined that paraformaldehyde dissolves in hydrogen fluoride with the formation of water. Based on this analysis it is likely that we are dealing with a solution in which an equilibrium exists of fluoromethanol (about 25–30%) and bis(fluoromethyl) ether FCH_2OCH_2F (about 70–75%). The formation of the products obtained when fluoroölefins react with a solution of paraformaldehyde in hydrogen fluoride can be visualized as involving reaction with this hypothetical bis(fluoromethyl) ether.

One mole of tetrafluoroethylene reacts with one mole of bis(fluoromethyl) ether to give fluoromethyl-2,2,3,3,3-pentafluoropropyl ether, $CF_3CF_2CH_2OCH_2F$, b.p. 60°. 2,2,3,3,3-Pentafluoro-1-propanol, b.p. 81°, is formed simultaneously due to hydrolysis from the water formed in the formation of the bis(fluoromethyl) ether. At a low reaction temperature (20°) the fluoromethyl 2,2,3,3,3-pentafluoropropyl ether is the predominant product; at a higher reaction temperature (50–100°) the 2,2,3,3,3-pentafluoro-1-propanol forms the principal product. Small quantities of 2,2,3,3,3-tetrafluorooxetane, $\underbrace{CF_2CF_2CH_2O}$, b.p. 28°, methyl-2,2,3,3,3-pentafluoropropyl ether, $CF_3CF_2CH_2OCH_3$, b.p. 46°, bis(2,2,3,3,3-pentafluoropropoxy)methane, $(CF_3CF_2CH_2O)_2CH_2$, b.p. 125° and bis[(2,2,3,3,3-pentafluoropropoxy)methyl] ether $(CF_3CF_2CH_2OCH_2)_2O$, b.p. 69°/15 mm., are also formed.

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[1] For paper V see V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

[2] J. F. Walker, American Chemical Society Monograph, "Formaldehyde," 2nd ed., pp. 326–335.

[3] H. J. Prins, *Rec. trav. chim.*, **51**, 469 (1932).

[4] D. D. Coffman, M. S. Raasch, G. W. Rigby, P. L. Barrick, and W. E. Hanford, *J. Org. Chem.*, **14**, 747 (1949).

[5] G. Olah and A. Palath, *Acta Chim. Acad. Sci. Hung.*, **3**, 425 (1953); *Chem. Abstr.*, **49**, 2384 (1956).

Hexafluoropropylene reacts with paraformaldehyde in hydrogen fluoride only above 100° and 2,3,3,3-tetrafluoro-2-trifluoromethyl-1-propanol $CF_3CF(CF_3)CH_2OH$, b.p. 93°, is the sole reaction product that can be isolated. The off gases from the reaction contain small amounts of carbon monoxide and hydrogen.

In contrast to the relatively unreactive tetrafluoroethylene, 1,1-difluoroethylene reacts with bis(fluoromethyl) ether even below 0° and at atmospheric pressure. Two moles of 1,1-difluoroethylene condense with one mole of bis(fluoromethyl) ether to give bis(3,3,3-trifluoropropyl) ether $(CF_3CH_2CH_2)_2O$, b.p. 114°. Although 1,1-difluoroethylene adds hydrogen fluoride readily to give 1,1,1-trifluoroethane, this addition does not occur as long as bis(fluoromethyl) ether is present. A fluoromethyl ether analogous to that obtained with tetrafluoroethylene cannot be isolated because, assuming it is being formed, it reacts at once with a second mole of 1,1-difluoroethylene and for the same reason a 3,3,3-trifluoro-1-propanol is not detectable in the reaction mass.

Tetrafluoroethylene reacts with fluoromethyl 2,2,-3,3,3-pentafluoropropyl ether in hydrogen fluoride only under pressure and at elevated temperatures to give bis(2,2,3,3,3-pentafluoropropyl) ether, $(CF_3CF_2CH_2)_2O$, b.p. 92°.

In contrast 1,1-difluoroethylene reacts in hydrogen fluoride already at 0° and atmospheric pressure to give 2,2,3,3,3-pentafluoropropyl-3,3,3-trifluoropropyl ether, $CF_3CF_2CH_2OCH_2CH_2CF_3$, b.p. 107–109°.

Fluoroethylene reacts with bis(fluoromethyl) ether to give bis(3,3-difluoropropyl) ether, b.p. 147°.

Experimental

Analysis of Solutions of Paraformaldehyde in Hydrogen Fluoride.—Paraformaldehyde (10 g., containing 0.06 g. of water) was put into a stainless steel cylinder and hydrogen fluoride (48 g., containing 0.003 g. of water as determined by a conductivity method) was added. The solution stood at room temperature (20–30°) for several days and was then analyzed for water by the Karl Fischer[6] method. Based on the following equation 3.00 g. of water could have been formed.

$$2CH_2O + 2HF \xrightarrow[HF]{} CH_2FOCH_2F + H_2O$$

Water found: 2.52 g., 2.62 g., 2.62 g. Correction needed due to the error introduced in manipulating the sample: 0.36 g., 0.33 g., 0.38 g. water. Water formed in the reaction: 2.10 g., 2.23 g., 2.18 g., equal to 70.1, 74.4, 72.7% of theory.

Determination of the Nuclear Magnetic Resonance Spectrum of a Solution of Paraformaldehyde in Hydrogen Fluoride.—A solution of paraformaldehyde (3 g.) in hydrogen fluoride was prepared as described above. Nuclear magnetic resonance 5-mm. glass tubes were drawn out to a capillary end, evacuated and heat-sealed. The tube was cooled in ice and the capillary was broken under the surface of the formaldehyde solution. A control sample containing only hydrogen fluoride was prepared similarly.

The nuclear magnetic resonance spectrum was measured at approximately −5° using a thermostated probe. The spectra were observed at 40 Mc. No precise measurements of chemical shifts or coupling constants were made.

The fluorine spectrum consisted of a broad singlet with a chemical shift comparable to that of a sample of pure liquid hydrogen fluoride and a smaller, sharper triplet with a coupling constant of about 50 c.p.s., corresponding to a $—CFH_2$ group. The proton spectrum consisted of a very large singlet corresponding to the proton spectrum of liquid hydrogen fluoride and an irregular group of three peaks which were not well resolved. It is believed that the outer two are the doublet arising from the $—CFH_2$ group, because their separation was about 50 c.p.s.

Reaction of Tetrafluoroethylene with Formaldehyde.—Paraformaldehyde (180 g., 6 moles) and Terpene B (3 g.) were put into a stainless steel autoclave (operating volume 1400 cc.). The autoclave was swept with nitrogen, evacuated, and technical hydrogen fluoride (600 g.) was added. A tetrafluoroethylene pressure of about 20 atm. was maintained on the charge while it was agitated at 50° for 24 hr. The charge was cooled to 0° and blown on 2500 g. of ice. Three moles of tetrafluoroethylene had reacted. The dilution mass was made slightly alkaline with gaseous ammonia at 25–30° (Dry Ice and acetone cooling). After an exhaustive steam distillation 583 g. of a water immiscible oil was obtained. Upon fractionation fluoromethyl 2,2,3,3,3-pentafluoropropyl ether (61 g.) was obtained distilling at 60°. The structure of this product and that of all other products reported in this paper was established by infrared and nuclear magnetic resonance analysis.

Anal. Calcd. for $C_4H_4F_6O$: C, 26.35; H, 2.2; F, 62.6; mol. wt., 182. Found: C, 26.3; H, 2.25; F, 62.0; mol. wt. 187.

The next product was 2,2,3,3,3-pentafluoro-1-propanol (429 g.) which distilled at 78–80° as an azeotrope with 5% water.

Anal. Calcd. for $C_3F_5H_3O$: F, 63.4. Found: water, 5.0; F, 60.2.

Upon further distillation bis(2,2,3,3,3-pentafluoropropoxy)-methane (5 g.), b.p. 125°, and bis[(2,2,3,3,3-pentafluoropropyl)-methyl] ether (5 g.), b.p. 69°/15 mm., were separated.

Anal. Calcd. for $C_7H_6F_{10}O_2$: C, 26.42; H, 2.08; F, 60.9; mol. wt., 312. Found: C, 27.00; H, 2.10; F, 60.8; mol. wt., 310.

Anal. Calcd. for $C_8H_8F_{10}O_3$: C, 28.05; H, 2.34; F, 55.5; mol. wt., 342. Found: C, 28.00; H, 2.4; F, 55.2; mol. wt., 347.

In a similar charge maintained at 20° for 24 hr. 78% of the steam distilled reaction product was fluoromethyl 2,2,3,3,3-pentafluoropropyl ether and 22% was 2,2,3,3,3-pentafluoro-1-propanol.

The fluoromethyl 2,2,3,3,3-pentafluoropropyl ether was apparently quite stable in dilute hydrofluoric acid and dilute ammonia (which were the isolation conditions). Upon warming with 96% sulfuric acid hydrogen fluoride and formaldehyde were evolved and anhydrous 2,2,3,3,3-pentafluoro-1-propanol and a small amount of bis(2,2,3,3,3-pentafluoropropoxy)methane were formed.

Anhydrous 2,2,3,3,3-pentafluoro-1-propanol, b.p. 81°, was readily obtained in a 92% yield when the 95% propanol (1134 g.) was added to 96% sulfuric acid (350 g.) and distilled directly from the reaction mass.

2,2,3,3-Tetrafluoroöxetane and Methyl-2,2,3,3,3-pentafluoropropyl Ether.—Nine condensations made as described above were combined and extra care was taken to keep the dilution and neutralization temperature below 10° because it had been observed that small amounts of products distilling below 50° were present. From these experiments 445 g. of material distilling below 55° was separated. Upon careful fractionation 300 g. of 2,2,3,3-tetrafluoroöxetane, b.p. 28°, and 80 g. of methyl-2,2,3,3,3-pentafluoropropyl ether, b.p. 46°, were obtained.

Anal. Calcd. for 2,2,3,3-tetrafluoroöxetane, $C_3H_2F_4O$: C, 27.68; F, 58.45; mol. wt., 130. Found: C, 27.40; F, 58.10; mol. wt., 134.

Infrared analysis was in agreement with the structure of an oxetane.

Anal. Calcd. for methyl-2,2,3,3,3-pentafluoropropyl ether, $C_4H_5F_5O$: C, 29.26; H, 3.05; F, 57.95; mol. wt., 164. Found: C, 29.30; H, 3.10; F, 58.00; mol. wt., 168.

The infrared analysis was in agreement with the structure.

The n.m.r. spectra of these two compounds were run on a Varian high-resolution n.m.r. spectrometer operated at 40 Mc. Chemical shifts were measured by the common side band technique using an audio oscillator. The proton chemical shifts have tetramethylsilane as a reference, while the fluorine chemical shifts are compared to trifluoroacetic acid. The numbers increase algebraically with increasing field.

The fluorine spectrum of the 2,2,3,3-tetrafluoroöxetane consists of two peaks of equal area. One is a singlet and has a chemical shift of 3.35 p.p.m. consistent with an $O—CF_2$ group. The other is a triplet with a chemical shift of 43.3 p.p.m. The triplet arises from coupling with the adjacent CH_2 group and the coupling constant is 10 c.p.s. The coupling between the two CF_2 groups was very small and not measured. The proton spectrum consists of a triplet with a splitting of 10 c.p.s. and a chemical shift of

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[6] John Mitchel, Jr. and Donald Milton Smith, "Aquametry, Application of the Karl Fischer Reagent to Quantitative Analyses Involving Water," Interscience Publishers, Inc.," New York, N. Y., 1948, p. 243.

−4.33 p.p.m. The individual members of the triplet showed some fine structure.

The fluorine spectrum of the methyl-2,2,3,3,3-pentafluoropropyl ether consists of a CF_3 peak with a chemical shift of 7.6 p.p.m. and a triplet from the CF_2 group with a chemical shift of 47.2 p.p.m. The triplet arises due to the coupling with the adjacent CH_2 group. The coupling constant is 13 c.p.s. The coupling between the CF_3 group and the CF_2 group was not measured. The proton spectrum consists of a triplet from the CH_2 group with a chemical shift of −3.55 p.p.m. and a singlet from the OCH_3 group with a chemical shift of −3.15 p.p.m.

2,2,3,3,3-Pentafluoropropoxy Acetic Acid.—2,2,3,3,3-Pentafluoro-1-propanol (100 g.) containing 5% water, and chloroacetic acid (70 g.) were heated to 90° and 40% aqueous sodium hydroxide (250 cc.) was added in 2 hr. The charge was heated to 110° for 7 hr. and then acidified with 36% hydrochloric acid (110 cc.). The oil which precipitated was dissolved in aqueous ammonia and reprecipitated (65 g., containing 27.8% F and 0.4% Cl). The distillation was of interest because 20 g. of water distilled first from this water-immiscible oil before the 2,2,3,3,3-pentafluoropropoxyacetic acid (35 g.) distilled at 93°/9 mm.

Anal. Calcd. for $C_5H_5F_5O_3$: C, 28.8; H, 2.4; F, 45.6. Found: C, 29.0; H, 2.35; F, 45.0.

Condensation of Tetrafluoroethylene with Fluoromethyl 2,2,-3,3,3-Pentafluoropropyl Ether.—A charge of fluoromethyl 2,2,3,-3,3-pentafluoropropyl ether (60 g.), hydrogen fluoride (120 g.), and tetrafluoroethylene (50 g.) was heated to 50° for 12 hr.

The reaction mass was poured on ice, the oil which separated (37 g.) was washed acid free, dried, and distilled. Bis(2,2,3,3,3-pentafluoropropyl) ether (10 g.) was obtained, distilling at 92°.

Anal. Calcd. for $C_6H_4F_{10}O$: C, 25.5; H, 1.4; F, 67.4; mol. wt., 282. Found: C, 25.7; H, 1.6; F, 66.9; mol. wt., 292.

Condensation of 1,1-Difluoroethylene with Fluoromethyl 2,2,-3,3,3-Pentafluoropropyl Ether.—Fluoromethyl 2,2,3,3,3-pentafluoropropyl ether (206 g.) was dropped into well agitated hydrogen fluoride over a period of 90 min. at 4–7° and 1,1-difluoroethylene (90 g.) was bubbled through the reaction mass during that time. A colorless oil (165 g.) was obtained when the reaction mass was poured on ice and steam distilled. Upon fractionation of 130 g. of this product, fluoromethyl 2,2,3,3,3-pentafluoropropyl ether (16 g.), b.p. 60°, and 2,2,3,3,3-pentafluoropropanol (9 g.), b.p. 78–80°, were obtained first. The product distilling from 107–109° (22 g.) consisted (based on a nuclear magnetic resonance analysis) of 75% of 2,2,3,3,3-pentafluoropropyl 3,3,3-trifluoropropyl ether and 25% bis(3,3,3-trifluoropropyl) ether.

Anal. Calcd. for $C_6H_6F_8O$: C, 29.8; H, 2.44; F, 61.8; mol. wt., 246. Found: C, 30.4; H, 2.90; F, 60.8; mol. wt., 238.

Bis(3,3,3-trifluoropropyl) ether (13 g.) distilling at 114° was the final fraction. The distillation residue (14 g.) was not investigated.

Reaction of Hexafluoropropylene with Formaldehyde.—Paraformaldehyde (30 g.), hydrogen fluoride (200 g.), and hexafluoropropylene (160 g.) were heated to 160° for 8 hr. (maximum pressure 140 atm.). After dilution on ice, steam distillation and fractionation 2,3,3,3-tetrafluoro-2-trifluoromethyl-1-propanol (28 g.) was obtained as the anhydrous product, b.p. 94.5°. Its identity was established by infrared and nuclear magnetic resonance analysis. The unchanged hexafluoropropylene contained carbon monoxide and hydrogen.

Reaction of 1,1-Difluoroethylene with Formaldehyde.—Paraformaldehyde (120 g., 4 moles) was dissolved in hydrogen fluoride (560 g.) and 1,1-difluoroethylene was passed into the solution at 0–10°. It was completely absorbed for 45 min. and gas (1,1,1-trifluoroethane) started to pass through the reaction when 271 g. of 1,1-difluoroethylene (4.2 moles) had been used. The reaction mass was poured on ice (3000 g.), and the oil which precipitated was steam distilled, dried over sodium sulfate and fractionated. Bis(3,3,3-trifluoropropyl) ether (200 g.), b.p. 114°, was obtained. A distillation residue (63 g.) could not be distilled without decomposition.

Anal. Calcd. for $C_6H_8F_6O$: C, 34.28; H, 3.81; F, 54.3; mol. wt., 210. Found: C, 34.1; H, 3.9; F, 54.2; mol. wt., 212.

A vapor phase chromatographic analysis showed the absence of impurities.

Reaction of Fluoroethylene with Formaldehyde.—Fluoroethylene (160 g.) was added to a Dry Ice and acetone-cooled solution of paraformaldehyde (30 g.) in hydrogen fluoride (200 g.). Because of a valve failure the addition took place in less than 1 min., causing the temperature to rise to 100°. Upon dilution on ice, steam distillation, and fractionation bis(3,3-difluoropropyl) ether (37 g.), b.p. 147°, was obtained.

Anal. Calcd. for $C_6H_{10}F_4O$: C, 41.3; H, 5.74; F, 43.7. Found: C, 41.6; H, 5.8; F, 43.0.

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The Addition of Fluorine to Halogenated Olefins by Means of Metal Fluorides

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The selective addition of fluorine to the double bond of olefins by means of vapor phase reaction with cobalt trifluoride at 20–125° has been found to be quite general for stable halogenated olefins. Chloroethylene, *cis*-1,2-dichloroethylene, trichloroethylene, 1,1-difluoroethylene, 2-bromo-1,1,1-trifluoropropene, and 2-fluoropropene produced the respective vicinal difluoro derivatives in fair yields. In addition, compounds produced by the displacement of hydrogen or halogen by fluorine were obtained in lesser amounts, dependent upon the temperature of the reaction. The presence of an inert gas diluent and contact time were also important variables in the process. Silver difluoride, cerium tetrafluoride, and manganese trifluoride also added fluorine selectively to 1,1-difluoroethylene and *trans*-1,2-dichloroethylene.

The ability of some of the high valence metallic fluorides, notably cobaltic fluoride, silver difluoride, manganese trifluoride, cerium tetrafluoride, and lead tetrafluoride to fluorinate organic compounds is well known and has been extensively utilized to synthesize perfluorinated compounds. The various reactions of this class of fluorides has been excellently reviewed by Stacey and Tatlow.[1]

In general, these high valence metallic fluorides undergo three types of reaction.

(1) Replacement of hydrogen

$$-\overset{|}{\underset{|}{C}}H + 2MF_x \longrightarrow -\overset{|}{\underset{|}{C}}F + HF + 2MF_{x-1}$$

(2) Replacement of halogen

$$2-\overset{|}{\underset{|}{C}}X + 2MF_x \longrightarrow 2-\overset{|}{\underset{|}{C}}F + X_2 + 2MF_{x-1}$$

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[1] M. Stacey and J. C. Tatlow, "Advances in Fluorine Chemistry," Vol. 1, M. Stacey, J. C. Tatlow, and A. G. Sharpe, ed., Academic Press, Inc., New York, N. Y., 1960, p. 166.