Table I

Reduction of Halonitrobenzenes to Haloanilines

$XC_6H_4NO_2$				Sulfide catalyst		Temp, °C	Pressure, psig	Time, min	Yield, mole %[g]	
X	Registry no.	Wt, g	Moles	Type	Wt, g				Haloaniline	Aniline
p-Cl [a]	100-00-5	157.6	1.0	Pt[d]	1.6	130–175	500–800	45	98.5	0
[a]		157.6	1.0	Co[e]	[e]	110	500–800	400	97	0
[b]		17.0	0.108	Pt[d]	0.325	145	500–800	195	100	0
[b]		17.0	0.108	Pd[f]	0.325	145	500–800	150	100	0
o-Cl [a]	88-73-3	157.6	1.0	Pt[d]	1.6	150–175	500–800	40	94.5	0
[c]		78.3	0.50	Pt[d]	1.5	145	500–800	70	92.5	0
[c]		78.3	0.50	Rh[d]	1.5	100–145	500–800	15	95	0
[c]		78.3	0.50	Ru[d]	1.5	140–150	500–800	45	93.5	0
p-Br [c]	586-78-7	101	0.50	Pt[d]	1.5	100–130	500–800	60	99.5	0
						130		390		
[c]		101	0.50	Rh[d]	1.5	105	500–800	135	100	Trace
[c]		101	0.50	Co[e]	[e]	115	500–800	90	99	Trace
[b]		21.8	0.108	Pd[f]	0.325	140–150	500–800	45	36	64

[a] Experiment run in 600-ml Magne-Dash autoclave with 180 ml of methanol as solvent. [b] Experiment run in 170-ml Magne-Dash autoclave with 52 ml of methanol as solvent. [c] Experiment run in 600-ml Magne-Dash autoclave with 240 ml of methanol as solvent. [d] 5 wt % metal on carbon (Engelhard Industries). [e] Prepared *in situ* from 6.0 g of 50% Co on kieselguhr obtained from Chemetron Corp. (Girdler G-67RS) and H_2S in excess (50 psig at room temperature). [f] Bulk palladium sulfide prepared by passing H_2S into a solution of palladium chloride in aqueous hydrochloric acid. [g] Yields determined by quantitative glpc analyses. No nitro compound detected in any experiment. Failure of haloaniline and aniline yields to add up to 100% in some cases is probably due to mechanical losses.

cobalt; no detectable debromination occurred with platinum sulfide; trace debromination occurred with rhodium sulfide and cobalt sulfide; and appreciable debromination occurred with palladium sulfide.

Nickel[5] and palladium sulfide appear to be satisfactory for the reduction of chloronitro but not of bromonitro aromatic compounds. Platinum sulfide probably is the catalyst of choice in most cases because of its excellent selectivity and convenient commercial availability.

The selective hydrogenation of haloaryl nitro compounds also is applicable to polyhalo-substituted aromatics. For example, 2,5-dichloronitrobenzene was quantitatively hydrogenated with a platinum sulfide catalyst to 2,5-dichloroaniline.

The metal sulfide catalysts also are useful for the reductive alkylation[10–12] of haloaryl amines formed *in situ* by the reduction of halonitro compounds. For example, *p*-nitrochlorobenzene was quantitatively transformed to N-isopropyl-*p*-chloroaniline by reaction with hydrogen and acetone in the presence of a rhodium sulfide catalyst.

Experimental Section

A detailed description of two experiments is given to illustrate the procedure.

2,5-Dichloroaniline.—To a 600-ml stainless steel Magne-Dash autoclave were added 103.5 g (0.54 mole) of 2,5-dichloronitrobenzene (Eastman Kodak 187), 230 ml of methanol, and 3.0 g of 5% platinum sulfide on carbon (Engelhard Industries). The autoclave was sealed and purged first with nitrogen and then with hydrogen. Hydrogen was added to a pressure of 600 psig, and the reaction mixture then was heated for 1.3 hr at 85° (500–800 psig) at which point gas absorption stopped at approximately the theoretical usage of hydrogen. The autoclave was cooled and vented, and its contents were filtered to remove the catalyst. The filtrate was made strongly alkaline with dilute sodium hydroxide and the methanol solution was concentrated by distillation. Benzene was added and the remaining methanol was removed by distillation. The benzene solution was then cooled and washed with water. The combined aqueous solutions gave a negative silver nitrate test for chloride anion; thus there had been negligible dehalogenation. The benzene solution was distilled up to a pot temperature of 207° at atmospheric pressure. The residue consisted of 87 g (99.5% yield) of 2,5-dichloroaniline that melted at 48–49°; there was no depression on a mixture melting point with an authentic sample.

N-Isopropyl-*p*-chloroaniline.—To a 600-ml stainless steel Magne-Dash autoclave were added 31.5 g (0.20 mole) of *p*-nitrochlorobenzene (Eastman Kodak P-185), 158 g (2.73 moles) of acetone, and 2.5 g of 5% rhodium on carbon (Engelhard Industries). The autoclave was sealed and purged with nitrogen and then with hydrogen. Hydrogen sulfide was added to a pressure of 50 psig, followed by the addition of hydrogen to a pressure of 1300 psig. The reaction mixture then was heated with agitation for 4.4 hr at 180° (1200–1400 psig). The autoclave was cooled, vented, and the reaction product removed. The catalyst was removed by filtration and the filtrate topped to a pot temperature of 180° at atmospheric pressure. The residue was dissolved in benzene, and the benzene solution was washed twice with 5% aqueous sodium hydroxide, then twice with water. After removal of the benzene by distillation under reduced pressure, there was obtained a residue product that was shown by gas–liquid partition chromatographic analysis to contain 34 g (100% yield) of N-isopropyl-*p*-chloroaniline. Distillation of this residue gave a yellow oil (bp 100° (5 mm), mp 8–9°, $n^{32}{}_D$ 1.5470) that was soluble in hexane, benzene, methanol, and carbon tetrachloride, insoluble in cold water, and very slightly soluble in hot water. A portion was redistilled for analysis.

Anal. Calcd for $C_9H_{12}NCl$: C, 63.71; H, 7.13; N, 8.26; Cl, 20.90. Found: C, 64.20; H, 7.19; N, 8.15; Cl, 20.21.

The hydrochloride was prepared by saturation of an ether solution with gaseous hydrogen chloride and melted at 159.5–160.5° after two recrystallizations from benzene.

Anal. Calcd for $C_9H_{13}NCl_2$: C, 52.44; H, 6.36; N, 6.79; Cl, 34.40. Found: C, 52.99; H, 6.49; N, 6.79; Cl, 33.98.

Registry No.—2,5-Dichloronitrobenzene, 89-61-2; N-isopropyl-*p*-chloroaniline, 770-40-1; N-isopropyl-*p*-chloroaniline hydrochloride, 826-22-2.

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(11) W. S. Emerson, *Org. Reactions*, **4**, 174 (1948).

(12) F. S. Dovell and H. Greenfield, *J. Org. Chem.*, **29**, 1265 (1964).

Hydrogen Bonding in Fluoroaromatic Amines and Phenols

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Anomalous reactions of fluoroaromatic acids, amines, and phenols have been observed by us in solvents which act as hydrogen bond acceptors. The reasons

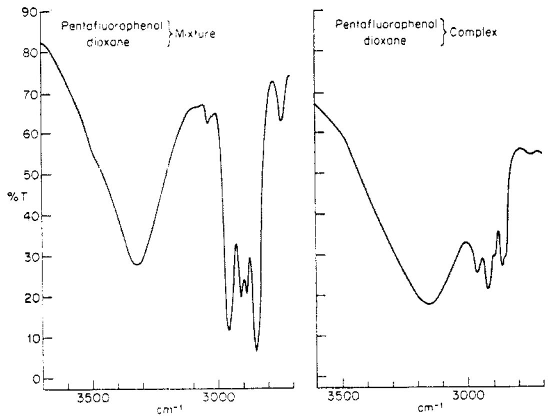
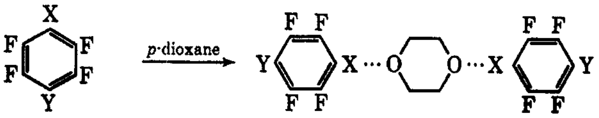


Figure 1.—Infrared spectra of mixture and complex.

for these difficulties have been clearly determined in the cases of fluoroaromatic amines and phenols, which have afforded stable complexes with *p*-dioxane.

Pentafluoroaniline (**1**), pentafluorophenol (**2**), and 2,3,5,6-tetrafluorophenol (**3**) react exothermically with 1,4-dioxane to form crystalline 2:1 complexes.[1] These complexes are similar to the dioxane complexes reported[2] for fluoro alcohols, and to the well-known[3] molecular compounds of 1,4-dioxane.



1, X = NH$_2$; Y = F
2, X = OH; Y = F
3, X = OH; Y = F

These complexes are unstable toward mineral acids or heat above their melting points. Gas chromatography[4] of the dioxane–pentafluoroaniline complex in ether solution afforded two peaks, identical in retention time with samples of *p*-dioxane and pentafluoroaniline.

Ultraviolet spectra of the complexes in either *n*-hexane or carbon tetrachloride were identical with those obtained for the free fluoroaromatic compounds. However the formation of these complexes can be observed and studied by infrared and nuclear magnetic resonance spectroscopy.

Infrared Study.—A study of the pentafluorophenol–dioxane complex was performed in the infrared region 3500 to 2700 cm^{-1} by observing OH and CH stretching vibrations. Figure 1 shows the stretching bands for the mixture and for the complex compound in carbon tetrachloride. The spectrum of the mixture was equivalent to the sum of the spectra of 1,4-dioxane and pentafluorophenol. This spectrum was recorded before reaction took place and the concentration of the components was equivalent to their concentrations in the complex compound spectrum. The observed frequencies are shown in Table I.

TABLE I
OBSERVED OH AND CH STRETCHING FREQUENCIES OF PENTAFLUOROPHENOL

	1,4-Dioxane mixture, cm^{-1}	1,4-Dioxane complex, cm^{-1}
ν_{OH} (bonded)	3320	3160
ν_{CH}	2955	2970
	2910	2920
	2885	2895
	2850	2860
		2850

The band observed at 3320 cm^{-1} in the mixture is due to the intermolecularly bonded OH stretch of the pentafluorophenol dimer. The CH adsorption of the mixture can be attributed to the unreacted dioxane. The spectrum of the complex compound in solution shows that the OH stretching frequency has shifted to 3160 cm^{-1}. This frequency is attributed to the vibration of the pentafluorophenol OH bonded to the dioxane. The CH stretching vibrations now appear at higher frequencies than the corresponding mixture vibrations and the relative intensities have changed considerably.

The lower frequency observed for the OH stretching vibration in the complex can be attributed to the formation of a stronger bond between the pentafluorophenol hydrogen and the dioxane oxygen. This indicates that the dioxane oxygen is more basic than the oxygen in the pentafluorophenol leading to the formation of a stable complex.

An analogous study with pentafluoroaniline was more difficult to interpret due to the broad diffuse nature of the NH bonded stretching vibration; however, the study indicated that the dioxane oxygen was also more basic than the pentafluoroaniline nitrogen.

Nuclear Magnetic Resonance Study.—The concept of the formation of a complex with pentafluorophenol and dioxane is supported by ^{1}H and ^{19}F nmr data. The lower field position, 7.62 ppm, of the hydroxyl proton resonance for the pentafluorophenol and dioxane complex (22.8% by weight in CCl$_4$), as compared to the chemical shift, 5.45 ppm, for pentafluorophenol (20.8% by weight in CCl$_4$), indicates stronger bonding in the complex than in pentafluorophenol.

Fluorine nmr shows dramatic changes in the electron shielding of the *o*- and *m*-fluorines and in their spin–spin interactions. The ^{19}F nuclear magnetic spectrum of undiluted and uncomplexed pentafluorophenol has a typical A$_2$B$_2$X pattern, whereas the spectrum of the complex (22.8% by weight in CCl$_4$) is almost an A$_4$X pattern.

The pattern of the complex is equivalent to that observed for a 52.5% by weight solution of pentafluorophenol in CCl$_4$. Progressive dilution of pentafluorophenol with CCl$_4$ causes changes in intermolecular association resulting in shifts in electron density at the three types of fluorine environments.[5] *o*- and *m*-fluorine in pentafluorophenol become magnetically equivalent and show an A$_4$X pattern at a concentration of 20.8% by weight of pentafluorophenol in CCl$_4$.

Both ^{1}H and ^{19}F nmr data support the concept of greater basicity of the dioxane oxygen than that of the pentafluorophenol oxygen.

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(1) The complex of pentafluoroaniline and 1,4-dioxane was erroneously reported as "2-(pentafluoroanilino)ethanol" by Holland, *et al.*, *J. Org. Chem.*, **29**, 1562 (1964).

(2) W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964).

(3) A. V. Dombrovskii, *Russ. Chem. Rev.*, **30**, 635 (1961).

(4) 20% Apiezon L on Chromasorb P column; 7.9°/min program from 80°; 280° injection port temperature.

(5) J. V. Pustinger, Jr. and J. E. Strobel, Monsanto Research Corp., Dayton Laboratories, unpublished work.

Experimental Section[6]

1,4-Dioxane–Pentafluoroaniline Complex.—To 27.5 g (0.15 mole) of pentafluoroaniline was slowly added 50 ml of 1,4-dioxane. The temperature of stirred reaction rose exothermically to 40° and was allowed to proceed for 15 min. The excess dioxane was stripped off at ambient temperature in a rotary vacuum evaporator. The white crystalline complex (28.3 g, 83%) was collected and sublimed twice at 40° (0.05 mm). The volatile crystalline complex, mp 55.5–56.5°, slowly turned blue on standing in an open container.

Anal. Calcd for $C_{16}H_{12}F_{10}N_2O_2$: C, 42.30; H, 2.66; F, 41.8; N, 6.17. Found: C, 42.09; H, 2.68; F, 42.1; N, 6.37.

The fluorine nmr spectrum in benzene (22.6% by weight) exhibits three multiplets at 86.2, 88.8, and 97.5 ppm from trifluoroacetic acid. Peak area ratios are 2:2:1, respectively.

Proton nmr spectra in benzene (22.6% by weight) and in carbon tetrachloride (19.2% by weight) show peaks at 3.40 and 3.03 ppm with area ratios of 4.0:1.6, and at 3.68 and 4.02 ppm with area ratios of 4.0:1.5, respectively.

1,4-Dioxane–Pentafluorophenol Complex.—Pentafluorophenol (0.15 mole) was treated with 1,4-dioxane, as above. The colorless crystalline complex, 28.0 g (82%) was sublimed twice at 55° (0.05 mm) affording the analytical sample, mp 50–51°.

Anal. Calcd for $C_{16}H_{10}F_{10}O_4$: C, 42.12; H, 2.21; F, 41.6. Found: C, 42.20; H, 2.18; F, 41.6.

The fluorine nmr spectrum in carbon tetrachloride (22.8% by weight) shows two multiplets at 86.0 and 91.6 ppm from trifluoroacetic acid. The peak area ratio is 4.0:1.0.

Proton nmr spectrum in carbon tetrachloride (22.8% by weight) has two peaks at 7.62 and 3.88 ppm with an area ratio of 1.0:4.0.

1,4-Dioxane–2,3,5,6-Tetrafluorophenol Complex.—2,3,5,6-Tetrafluorophenol (0.15 mole) was treated with 1,4-dioxane, as above. The colorless crystalline complex, 27.3 g (87%), was sublimed twice at 45° (0.1 mm) affording the analytical sample, mp 66–67°.

Anal. Calcd for $C_{16}H_{12}F_8O_4$: C, 45.72; H, 2.88; F, 36.2. Found: C, 45.54; H, 2.84; F, 35.6.

The fluorine nmr spectrum in carbon tetrachloride (16.0% by weight) exhibits two multiplets at 60.2 and 82.3 ppm, with a peak area ratio of 1.0:1.0.

Proton nmr spectrum in carbon tetrachloride (16.0% by weight) has peaks at 7.81, 6.60, and 3.85 ppm, with area ratios of 2.0:2.0:8.0.

Registry No.—1, 13811-14-8; 2, 13811-09-1; 3, 13811-10-4; pentafluorophenol, 771-61-9; 3,4-dioxane, 123-91-1.

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[6] Melting points are corrected.

The Synthesis of Monobromoperfluoroalkanecarboxylic Acids and Derivatives

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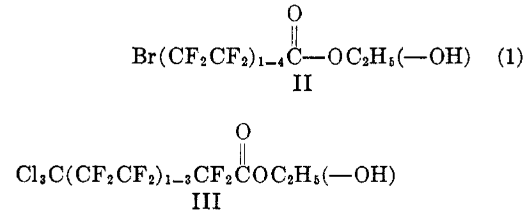
As a part of our program directed toward the synthesis of new versatile fluoroorganic intermediates, it was of interest to prepare the perfluorinated alkanecarboxylic acids and their derivatives containing a reactive substituent at the end of the chain.[1] Although perfluoroalkanecarboxylic acids and their derivatives containing a reactive substituent at the end of the chain are potentially useful organic intermediates, very little synthetic work in this area has been reported in the literature.[2]

In the present paper, a convenient method for the synthesis of a series of heretofore unreported ω-bromoperfluoroalkanecarboxylic acids and their derivatives is described. The synthesis is illustrated in eq 1.



$$\underset{\text{I}}{Cl_3C(CF_2CF_2)_{1-4}Br} \xrightarrow[\text{2. } C_2H_5OH \text{ or } H_2O]{\text{1. } H_2SO_4\text{–}SO_3} \underset{\text{II}}{Br(CF_2CF_2)_{1-4}\overset{\overset{\Large O}{\|}}{C}\text{—}OC_2H_5(\text{—}OH)} \quad (1)$$

$$\underset{\text{III}}{Cl_3C(CF_2CF_2)_{1-3}CF_2\overset{\overset{\Large O}{\|}}{C}OC_2H_5(\text{—}OH)}$$

The free radical catalyzed telomerization of tetrafluoroethylene with bromotrichloromethane provided the required starting material, I.[3] The conversion of I to ω-bromoperfluoroalkanecarboxylic acid or to ester II was successfully effected by treatment with 30% oleum in the presence of a small amount of a mixture of mercuric sulfate and mercurous sulfate followed by hydrolysis or alcoholysis of the resulting mixture, respectively.[4] In no case was ω-trichloromethylperfluoroalkanecarboxylic acid or ester III detected. Under the conditions of the reaction employed, the exclusive product obtained was II in high yield.[5]

Assignment of the structure II rather than III was made on the basis of elemental analysis, infrared, and F^{19} resonance spectral properties. Also the treatment of the ester II (n = 2) with zinc dust in ethanol yielded the known ethyl ω-hydroperfluoropentanoate. The ester II could easily be converted to the corresponding amide which, in turn, gives rise to the corresponding nitrile upon dehydration with phosphorus pentoxide.

In the absence of the mercury salts, the rate of the reaction was found to be slow. This conclusion was based on the observation that under the identical reaction conditions, the presence of the salts led to the complete reaction of I (n = 1) while the absence of the salts gave only about 50% conversion of I (n = 1). The rate of the reaction also decreases with increasing the value of n in I. For example, a reaction temperature of 100–105° and a reaction time of about 45 hr are sufficient for the complete reaction of I (n = 1), whereas a reaction temperature of 115–120° and a reaction time of about 70 hr are required for I (n = 2).

Under conditions identical with those described above, a compound, arising from the free radical catalyzed addition of bromotrichloromethane to perfluoropropene, gave 3-bromoperfluorobutanoic ester (V) (see eq 2). The formation of V confirms that the com-

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[1] In general, compounds of the type R_fH and R_fCl (where R_f is a polyfluoro group) are chemically extremely inert and have not been reported to be useful for further synthetic work. For example, the free radical catalyzed addition of ethylene to R_fCl has not been reported, whereas R_fBr reacts with ethylene in the presence of free radical generating catalysts to yield $R_f(CH_2CH_2)_nBr$; K. C. Smeltz, U. S. Patent 3,055,953 (1962). For the information as to the relative reactivity of compounds of the type R_fX (X = H, Cl, Br, or I), see W. C. Francis and R. N. Haszeldine, *J. Chem. Soc.*, 2151 (1955).

[2] For a brief review of method of synthesis of polyfluorinated acids, see Chapter VII, A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, and Chapter 3, R. E. Banks, "Fluorocarbons and Their Derivatives," Oldbourne Press, London, 1964.

[3] A. Sieglitz, *et al.*, German Patent 949,822 (1956).

[4] For the convenience of handling, all products were isolated as an ester rather than a free acid.

[5] In the acid hydrolysis using oleum of $Cl_3C(CF_2CFCl)_nBr$, it has been reported that -CFClBr group undergoes hydrolysis faster than the -CCl_3 group; W. S. Barnhart and R. H. Wade, U. S. Patent 2,806,865 (1957).