ally have a somewhat lower value than that appropriate to the actual dimerization reaction. By the same reasoning it appears that $K_{exp.}$ will always be less than K_2 but will approach K_2 as K_1 becomes very much larger than [Bz]. The influence of the dielectric constant of the medium represents an additional complicating factor in solution measurements but such factors are probably not first order if a substance of reasonably low dielectric constant, <3, is used as a medium. If the preceding discussion is correct one may expect different values of K and ΔH in media with the same dielectric constant but with different basicities such as say benzene and carbon tetrachloride.

Reactions of Polyfluoro Olefins. V.[1] Chemical Properties of Anionic Addition Products[2]

BY KARL E. RAPP, JOHN T. BARR, ROY L. PRUETT, CARL T. BAHNER, J. DONALD GIBSON AND ROBERT H. LAFFERTY, JR.

A variety of chemical reactions which normally involve the functional linkages of organic sulfides, ethers, and amines were investigated using the products of anionic addition of thiols, alcohols, and amines to polyfluoro olefins. The results of these reactions, in a number of cases negative results, established the strong influence exerted by fluorine upon neighboring functional groups of organic, fluorine-containing compounds. Thus the theory is supported that fluorine, in transmitting an extremely electronegative force through the C–F covalent bond, so distorts the electronic field of a neighboring functional group that chemical reaction involving the electrons of this group is virtually prevented except under the most rigorous conditions; and, conversely, the less electronegative nature the central atom of a functional group possesses the less resistance it offers to field distortion allowing the adjacent C–F bonds to become more polar, less covalent, and more susceptible to chemical attack.

Previous reports of this series have described the reactions of certain polyfluoro olefins with thiols,[3] alcohols[4] and amines.[5] The chemical properties of the products of these anionic addition reactions have been studied in an effort to elucidate the role played by fluorine in the chemistry of organic compounds of this type.

Sulfides

Attempts to form sulfoxides from polyfluoroalkyl sulfides, such as those obtained by the addition of thiols to chlorotrifluoroethylene and unsym-dichlorodifluoroethylene, by a standard procedure using hydrogen peroxide[6] were unsatisfactory. Experimental evidence indicated initial formation of a sulfoxide which decomposed during purification to revert to the original sulfide. Bromine also proved ineffective as a means of oxidation for subsequent hydrolysis to the sulfoxides. This is significant since the addition of bromine to form the dibromide has been reported to occur readily with organic sulfides.[7] Addition of methyl iodide[8] failed to take place to give the expected sulfonium salts. Although the reaction of alkyl sulfides in

adding heavy metal salts qualifies as a test for the C–S–C linkage,[9] its failure to occur in the case of polyfluoroalkyl sulfides has been reported.[3] These examples of the retiring nature assumed by the sulfur atom attest to the strong influence a pair of fluorine atoms bonded to the same carbon exerts upon the reactivity of the neighboring atoms. The strong electronegativity of the fluorine atoms, by drawing electrons from the carbon atom, causes the normal electronic fields of the neighboring atoms to become so distorted that these electrons are available for sharing or transfer only under much more strenuous conditions than are normally necessary. Since all reactions designed to attack these fluorinated molecules near the "fluorine center" would have involved sharing or transfer of electrons, a lack of reaction at this point should not be entirely unexpected.

By way of contrast, however, a more vigorous oxidation of these sulfides with potassium permanganate gave good yields of the corresponding sulfones.[3] The increases of molecular refraction produced by these oxidations (1.70–1.75) are greater by about one unit than that produced by oxidation of diethyl sulfide to diethyl sulfone.[10] According to the theory of Fajans,[11] this indicates that the electronic system undergoes more loosening, or less tightening, in the oxidation of the polyfluoroalkyl sulfides than in the oxidation of the unhalogenated sulfides.

Although sulfones are the normal products of a vigorous oxidation of organic sulfides, such treatment of bis-(alkyl- and arylthio)-tetrafluorocyclo-

(1) The previous paper in this series is: K. E. Rapp, THIS JOURNAL. 73, 5901 (1951).

(2) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company, a Division of Union Carbide and Carbon Corporation, at Oak Ridge, Tennessee.

(3) K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., THIS JOURNAL, 72, 3642 (1950).

(4) J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., ibid., 72, 4480 (1950).

(5) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., ibid., 72, 3646 (1950).

(6) M. Gazdar and S. Smiles, J. Chem. Soc., 93, 1833 (1908;) O. Hinsberg, Ber., 43, 289 (1910).

(7) J. R. Sampey, K. H. Slagle and E. E. Reid, THIS JOURNAL, 54, 3401 (1932).

(8) A. von Oefele, Ann., 132, 82 (1864); A. Cahours, ibid., 135, 352 (1865).

(9) R. Connor, "Organic Chemistry, An Advanced Treatise," H. Gilman, ed., 2nd ed., John Wiley and Sons, Inc., New York, N. Y., Vol. I. 1943, p. 858.

(10) W. Strecker and R. Spitaler, Ber., 59B, 1754 (1926).

(11) K. Fajans, "Physical Methods of Organic Chemistry," A. Weissberger, ed., 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1949, Vol. I, Part II, p. 1171.

butenes gave instead the dialkyl and diaryl esters of tetrafluorodithiolsuccinic acid, respectively. This evidence showed that the structures of the double sulfides formed by the addition of thiols to hexafluorocyclobutene in the presence of an alkaline catalyst[3] were unquestionably the 1,2-bis-(alkyl- and arylthio)-tetrafluorocyclobutenes. In the formation of these oxidation products, the influence of the fluorine apparently was negligble. Neither the sulfur atom nor the double bond was adjacent to a fluorine-bearing carbon and therefore reaction occurred normally at the more vulnerable double bond.

Subjecting the polyfluoroalkyl sulfides to the rather strenuous action of anhydrous aluminum chloride resulted in evident degradation to products with extremely obnoxious odors. These products were unreactive with water, amines, and alcohols in contrast to the initial product formed by the reaction of 2-chloro-1,1,2-trifluoroethyl methyl ether and aluminum chloride (q.v.). Long periods of exposure to chlorine in the presence of heat and ultraviolet light caused gradual darkening of the sulfide and the ultimate formation of products similar to those obtained with aluminum chloride. The presence of these olfactory "ruffians" is indicative of a successful attack made upon the C–S–C linkage.

Experimental

Reaction with Hydrogen Peroxide.—A solution of 2-chloro-1,1,2-trifluoroethyl ethyl sulfide (44.6 g.) and 30% hydrogen peroxide (28 ml.) in commercial acetone (250 ml.) was allowed to stand (48 hr.) at room temperature. The acetone was removed at room temperature under reduced pressure. The residue, consisting of two layers, was separated and the lower layer was dried over anhydrous calcium sulfate. After three days the dried liquid had n^{25}D 1.4113 and a continuous evolution of gas was noted. An attempt was made to distil a portion of this liquid. Distillation occurred at 42–44° and 40–43 mm. pressure but was accompanied by vigorous decomposition. The small amount of residue was a solid, m.p. 92–96°, which decomposed on standing. The remainder of the undistilled liquid after standing five days had n^{25}D 1.4067 as compared with 1.4079 for the original sulfide.

Oxidation of 1,2-Bis-(butylthio)-3,3,4,4-tetrafluorocyclobutene.—A solution of 1,2-bis-(butylthio)-3,3,4,4-tetrafluorocyclobutene (10 g.), n^{25}D 1.4791, in glacial acetic acid (100 ml.) was put into a three-neck flask equipped with a mechanical stirrer and a thermometer. Solid potassium permanganate (10 g.) was introduced in small portions while stirring vigorously and maintaining a reaction temperature of 12°. After this addition (1 hr.) water (20 ml.) was added and stirring was continued (3.5 hr.) while the mixture was allowed to warm to room temperature. The manganese dioxide formed during the reaction was destroyed with an aqueous solution of sodium bisulfite. A slightly yellow liquid separated as a lower layer. This was washed twice with water and dried over anhydrous sodium carbonate. The product was distilled in a Hickman alembic[12] molecular still (85–105° and <0.01 mm.) using Dry Ice in the condensing cone. Three one-gram fractions of dibutyl tetrafluorodithiolsuccinate were collected with constant n^{25}D 1.4719.

Anal. Calcd. for $C_{12}H_{18}F_4O_2S_2$: C, 43.10; H, 5.43; S, 19.18. Found: C, 43.32; H, 5.68; S, 19.10.

Oxidation of 1,2-Bis-(2-naphthylthio)-3,3,4,4-tetrafluorocyclobutene.—A solution of 1,2-bis-(2-naphthylthio)-3,3,-4,4-tetrafluorocyclobutene (2.5 g.) in glacial acetic acid (75 ml.) was cooled to 20° and a solution of potassium permanganate (2.7 g.) in hot water (20 ml.) was added in small portions, keeping the temperature below 35°. After the addi-

tion of the permanganate, the mixture was stirred (1.5 hr.) and allowed to stand overnight. The manganese dioxide was destroyed with an aqueous solution of sodium bisulfite. Heating the resulting milky solution to 60° effected crystallization. After cooling, dl-2-naphthyl tetrafluorodithiolsuccinate (2.3 g.) was recovered. Repeated crystallization of the slightly yellow crystals gave a purified product, m.p. 130–131.5°.

Anal. Calcd. for $C_{24}H_{14}F_4O_2S_2$: C, 60.76; H, 2.97; S, 13.50. Found: C, 60.80; H, 3.14; S, 13.10.

Ethers

Polyfluoroalkyl ethers of the type formed by the addition of alcohols to chlorotrifluoroethylene are, in general, relatively stable compounds undergoing few of the reactions to which normal alkyl and chloroalkyl ethers are usually susceptible.

1-Chloroalkyl ethers when refluxed with sodium hydroxide, sodium alkoxide, or a tertiary amine are reported to lose hydrogen chloride readily to form a C=C bond.[13] A comparable reaction of 1,1-difluoroalkyl ethers, if occurring at all was extremely slow and by no means complete. Extended reflux with amine finally produced a small yield of black, tarry, nitrogenous material. Analysis of a water extract of this material indicated removal of equivalent amounts of chlorine and fluorine.

The ethers were unreactive toward Grignard reagents and could not be converted to Grignard reagents themselves, even in the presence of ethyl bromide, as evidenced by formation of only 3-methyl-3-pentanol when methyl ethyl ketone was added to the reagent mixture. For short periods of time these ethers were stable in the presence of molten sodium or reducing agents such as zinc dust in acetic acid and they exhibited no appreciable reaction with potassium permanganate in acetic acid solution.

At temperatures below 5° there was little reaction between anhydrous aluminum chloride and the polyfluoroalkyl ethers, but above this point a vigorous reaction took place resulting in extensive degradation to form a mixture of alkyl and acyl halides.

Chlorination of these ethers took place slowly in a stepwise manner at elevated temperatures and in the presence of ultraviolet light. In all cases the products obtained were chlorine-substituted upon the unfluorinated alkyl portion of the molecule. The first chlorine might have been expected to substitute on the carbon bearing one chlorine and one fluorine in accordance with the principle that oxidation tends to continue at the point of origin. However, the electronic field distortion mentioned earlier apparently caused the point of attack to be shifted to a more accessible supply of electrons for covalent bonding, the unflorinated alkyl group. This is in keeping with the directive influence of the difluoromethylene group reported by Henne[14] and McBee.[15]

The chlorinated polyfluoroalkyl ethers were fragrant liquids which proved to be very stable chemically and thermally. They were insoluble

(12) A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1938, p. 120.

(13) M. F. Shostakovskii and A. V. Bogdanova, *J. Gen. Chem.* (U. S. S. R.), 17, 565 (1947); C. A., 42, 4519 (1948).

(14) A. L. Henne and E. G. DeWitt, This Journal, 70, 1548 (1948).

(15) E. T. McBee and A. Truchan, *ibid.*, 70, 2910 (1948).

in concentrated sulfuric acid and hence could not be hydrolyzed to the corresponding esters by the method of Young and Tarrant.[16] Constant-boiling hydriodic acid had little effect upon these ethers when held at reflux temperature, but zinc chloride caused extensive degradation in a short time at 90–100°. Aluminum chloride was effective in splitting the chlorinated polyfluoroalkyl ethers but did so at a much slower rate than when used with the unchlorinated parent ethers. Proof of the shifted point of attack during chlorination was found in the cleavage products.

The particular ether formed by the addition of allyl alcohol to chlorotrifluoroethylene exhibited no unexpected chemical behavior. Although containing an alkenyl group, the compound was quite stable and showed little tendency to polymerize at atmospheric pressure even in the presence of a peroxide or fluoride catalyst. This is in agreement with the stability of the homologs of ethylene toward polymerization under similar conditions. As expected, halogen added readily to the double bond and further chlorination occurred slowly at elevated temperatures.

The one exception to the general rule of stability which was encountered was the t-butyl 2-chloro-1,1,2-trifluoroethyl ether. This particular ether, although stable when stored under an aqueous sodium carbonate solution, decomposed spontaneously at room temperature while being dried over anhydrous sodium carbonate. When decomposition was prevented at this stage of purification, it became quite vigorous soon after distillation was started even at reduced pressures and in the presence of anhydrous sodium carbonate. Because of this, purification was accomplished only by separation in a small column of silica gel. Even in this process, decomposition began and accelerated quite rapidly when approximately two-thirds of the charge had passed. Once isolated, the ether was relatively stable to aqueous mineral acids but was split as expected by concentrated sulfuric acid or anhydrous hydrogen chloride. All instances in which decomposition occurred under neutral or acidic conditions resulted in the formation of a liquid polymeric product containing no halogen. When precautions were taken to remove the hydrogen fluoride as it was formed, no polymerization took place and isobutylene escaped.

Monoalkoxy pentafluorocyclobutenes, such as those formed by the addition of alcohols to hexafluorocyclobutene and subsequent elimination of hydrogen fluoride, were quite stable to concentrated solutions of alkali hydroxides. As expected, however, the monoalkoxy pentafluorocyclobutenes reacted with sodium alkoxides in the appropriate alcohol to form the dialkoxy butenes which have been previously reported.[4,17]

Park, et al.,[17] have reported the oxidation of dialkoxy tetrafluorocyclobutenes with potassium permanganate to form dialkyl esters of tetrafluorosuccinic acid. The corresponding monoalkoxy pentafluorocyclobutenes followed a similar

(16) J. A. Young and P. Tarrant, THIS JOURNAL, 71, 2432 (1949).

(17) J. D. Park, M. L. Sharrah and J. R. Lacher, ibid., 71, 2337 (1949).

pattern of oxidation to give monoalkyl tetrafluorosuccinates since the single fluorine on the terminal carbon was attacked forming a free carboxyl group. These acidic monoalkyl esters displayed a tendency to undergo acid hydrolysis and decarboxylation. Monomethyl tetrafluorosuccinate proved to be so susceptible to acid hydrolysis that only tetrafluorosuccinic acid could be isolated. This free dibasic acid in dioxane readily formed a heat-stable association complex, $HOOC(CF_2)_2COOH \cdot C_4H_8O_2$, which could be sublimed without change.

Experimental

Reaction with Aluminum Chloride.—2-Chloro-1,1,2-trifluoroethyl methyl ether (136.3 g.) was placed in a three-neck flask fitted with a reflux condenser and thermometer. The upper end of the condenser was connected to a Dry Ice trap which was protected from atmospheric moisture by a drying tube. After the ether had been cooled to 1.5°, anhydrous aluminum chloride (3.5 g.) was added. No reaction took place until the mixture was allowed to warm to 5°. A vigorous reaction was then maintained (2 hr.) between 5° and 23° by the addition of small portions of additional aluminum chloride (18.5 g.). A rapid evolution of volatile products caused a drop in temperature after all additions except the last one which resulted in a sharp rise. The mixture was finally refluxed (0.5 hr.) while the temperature rose to 44°.

A low-temperature distillation of the cold trap material (45 g.) indicated that it was composed of HCl (1 part by volume), methyl fluoride (4 parts), and methyl chloride (8.5 parts). The liquid portion of the reaction mixture was decanted and distilled. Distillation occurred over a range of 36–65° with no constant-boiling flat, while the $n^{25}D$ rose from 1.3390 to 1.3510. The distillate fumed in moist air and was reactive with water, alcohols and amines. These properties were lost after standing two days, apparently due to polymerization of the distillate to high-boiling liquids. The distillate was probably a mixture of chlorofluoroacetyl fluoride and chloride, since treatment with aniline produced only N-phenyl-α-chloro-α-fluoroacetamide.

Aniline (5 ml.) was added slowly to the above distillate (5 ml.). A vigorous reaction occurred with the evolution of heat which was removed by cooling in an ice-bath. The resulting mixture was poured into a cold, dilute solution of hydrochloric acid whereupon a precipitate immediately formed. After two recrystallizations from alcohol–water, the precipitate was shown to be identical in melting point, 80–81°, and mixed melting point with N-phenyl-α-chloro-α-fluoroacetamide formed by the hydrolysis of N,N'-diphenyl-α-chloro-α-fluoroacetamidine.[5]

Reaction with Chlorine.—Chlorine was passed through 2-chloro-1,1,2-trifluoroethyl methyl ether (100 g.) which was gently refluxing in the presence of ultraviolet light. During the chlorination the reflux temperature rose to approximately 100° when the gain in weight indicated that theoretical monochlorination had occurred. Distillation of the product gave 2-chloro-1,1,2-trifluoroethyl chloromethyl ether (70 g.), boiling at 112° and 745 mm., $n^{25}D$ 1.3745, d^{25}_{20} 1.530.

Anal. Calcd. for $C_3H_3Cl_2F_3O$: C, 19.69; H, 1.65. Found: C, 19.25; H, 1.52.

This chlorinated ether was insoluble in concentrated sulfuric acid, gave a precipitate with alcoholic silver nitrate, and was split by aluminum chloride to give chlorofluoroacetyl chloride from which the anilide, N-phenyl-α-chloro-α-fluoroacetamide was prepared.

A similar treatment of 2-chloro-1,1,2-trifluoroethyl ethyl ether (100 g.) until the reflux temperature reached 110° gave a mixture of 1- and 2-chloroethyl 2-chloro-1,1,2-trifluoroethyl ethers (82 g.) in a 4:1 ratio. The structure of the fraction, distilling at 120° and 750 mm., $n^{25}D$ 1.3742, d^{25}_{20} 1.3747, was shown to be 1-chloroethyl 2-chloro-1,1,2-trifluoroethyl ether by splitting with aluminum chloride to form chlorofluoroacetyl chloride, the formation of a precipitate with both alcoholic and aqueous silver nitrate, and analysis.

Anal. Calcd. for $C_4H_5Cl_2F_3O$: C, 24.39; H, 2.56; Cl, 36.00. Found: C, 24.27; H, 2.34; Cl, 36.15.

The structure of the fraction, distilling at 142–143° and

740 mm., n^{25}D 1.3920, d^{25}_{20} 1.4637, was shown to differ from the above fraction in that only a slight test was obtained with alcoholic silver nitrate and no test with aqueous silver nitrate. Analysis gave the same elemental composition, thereby indicating a 2-chloroethyl structure.

Anal. Found: C, 25.21; H, 2.92; Cl, 36.27.

Continued chlorination under the same conditions produced 1,2,2 - trichloroethyl 2 - chloro - 1,1,2 - trifluoroethyl ether, distilling at 85° and 23 mm., n^{25}D 1.4284, d^{25}_4 1.6330.

Anal. Calcd. for $C_4H_3Cl_4F_3O$: C, 18.07; H, 1.14. Found: C, 17.85; H, 1.33.

Although the ether gave a very slight test with alcoholic silver nitrate and no detectable test with aqueous silver nitrate, this assignment of structure is not inconsistent since the activity of 1-chloro ethers is materially reduced by the presence of additional chlorine.[18]

Halogenation of Allyl 2-Chloro-1,1,2-trifluoroethyl Ether. —Allyl 2-chloro-1,1,2-trifluoroethyl ether (25 g.) was cooled in an ice-bath while bromine (25 g.) was added slowly (1 hr.). A lower layer appeared but later redissolved. After standing at room temperature (2 hr.) the mixture was distilled to give 2,3-dibromopropyl 2-chloro-1,1,2-trifluoroethyl ether (43.8 g.) in 93% yield, b.p. 110–111° at 19 mm., n^{25}D 1.4675, d^{25}_{20} 1.956.

Anal. Calcd. for $C_5H_6Br_2ClF_3O$: C, 18.51; H, 1.86. Found: C, 18.10; H, 1.96.

Chlorine was bubbled slowly (2 hr.) through allyl 2-chloro-1,1,2-trifluoroethyl ether (24.9 g.) at room temperature until theoretical absorption (10 g.) was indicated by the weight gain. Distillation of the mixture gave 2-chloro-1,1,-2-trifluoroethyl 2,3-dichloropropyl ether (32.2 g.) in 92% yield, b.p. 86° at 17.5 mm., n^{25}D 1.4180, d^{25}_{20} 1.498.

Anal. Calcd. for $C_5H_6Cl_3F_3O$: C, 24.46; H, 2.46; Cl, 43.33. Found: C, 24.44; H, 2.46; Cl, 43.59.

Chlorination of the above product was continued (3.5 hr.) at 125° in the light of an E-H4 ultraviolet lamp, which resulted in a weight gain equivalent to $^2/_3$ theory for replacement of one hydrogen. Two distillations gave a small cut (6 g.), b.p. 77–78° at 7 mm., n^{25}D 1.4230, d^{25}_{20} 1.59.

Formation of 1,2-Diethoxytetrafluorocyclobutene.—A mixture of 1-ethoxypentafluorocyclobutene (23.5 g.) and sodium ethoxide (1.03 g.) in absolute ethanol (20 ml.) was refluxed (1 hr.), washed with water, and dried over calcium chloride. 1,2-Diethoxytetrafluorocyclobutene (2 g., 62% yield based upon sodium ethoxide), b.p. 62° at 12 mm., n^{25}D 1.3783, was separated from the excess monoethoxy compound by distillation.

Oxidation of 1-Ethoxypentafluorocyclobutene.—A solution of potassium permanganate (35 g.) in warm water was added slowly (2 hr.) with stirring to 1-ethoxypentafluorocyclobutene (20 g.) dissolved in acetone (100 ml.) and maintained at a temperature between 0–10°. After the addition, stirring was continued (2 hr.) at room temperature. The excess permanganate was reduced with sodium bisulfite and the manganese dioxide was removed by filtration. The filtrate was acidified with sulfuric acid and extracted with ether. After the extract had been dried and the ether was removed, distillation gave three cuts: I, 1-ethoxypentafluorocyclobutene (2.0 g.), b.p. 103° at 740 mm.; II, a neutral, water-insoluble, ester-like liquid (2.1 g.), boiling range 68–70° at 3.2 mm., n^{25}D 1.3663; and III, monoethyl tetrafluorosuccinate (10.5 g.), b.p. 92° at 1.5 mm., n^{25}D 1.3675.

Anal. Calcd. for $C_6H_8F_4O_4$: C, 33.04; H, 2.77; neut. equiv., 218; sapn. equiv., 109. Found: C, 33.26; H, 2.82; neut. equiv., 222; sapn. equiv., 112.

Cut II above was presumed to be ethyl tetrafluoropropionate formed by decarboxylation of compound III before the pressure was reduced during distillation. The pot residue was dissolved in dilute sodium hydroxide, the solution was acidified, and extracted with ether. Removal of the ether left tetrafluorosuccinic acid (2.0 g.), m.p. 85–86°. The reported m.p. is 87°.[17]

Oxidation of 1-Methoxypentafluorocyclobutene.—1-Methoxypentafluorocyclobutene (16 g.), when oxidized with potassium permanganate (23 g.) and extracted in the same manner as the corresponding ethoxy compound, gave a solid

residue upon removal of the ether. Recrystallization of the residue from dioxane gave a tetrafluorosuccinic acid–dioxane complex, $(CF_2COOH)_2 \cdot C_4H_8O_2$ (14 g.), m.p. 119°.
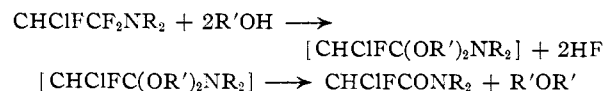
Anal. Calcd. for $C_8H_{10}F_4O_6$: C, 34.54; H, 3.62; neut. equiv., 139.1. Found: C, 33.68; H, 3.84; neut. equiv., 139.6.

This white, hygroscopic complex was soluble in water and dioxane, insoluble in benzene and carbon tetrachloride, and was unaffected by sublimation at 78° and 0.01 mm. It was esterified by warm alcohol and destroyed by concentrated hydriodic acid under reflux to give tetrafluorosuccinic acid, m.p. 87°.

Amines

The polyfluoroalkyl tertiary amines obtained by the addition of secondary aliphatic amines to chlorotrifluoroethylene are highly reactive in contrast to the corresponding ethers, sulfides and sulfones. The electronic field of nitrogen, being more labile than that of either oxygen or sulfur, is more available for sharing with the carbon and, because of this, the fluorine atoms which share electrons with a nitrogen-bonded carbon are able to drift further away with their "borrowed" electrons, whereupon the C-F bond becomes more polar, less covalent, and quite susceptible to attack. This theory of electronic behavior conforms qualitatively with those used in the derivation of individual bond energies[19] and in reconciling the difference between observed molecular refractions and those values calculated by strict addition of the increments contributed by the atoms and groups composing the molecules.[11]

The fact that N-(2-chloro-1,1,2-trifluoroethyl)-diethylamine and 1-(2-chloro-1,1,2-trifluoroethyl)-piperidine react quantitatively with water almost immediately to form hydrogen fluoride and the corresponding amide has been noted[5] and may account for the Rigby and Schroeder process of preparing fluoroacetamides.[20] These polyfluoroalkyl tertiary amines also react with anhydrous alcohols to form amides, hydrogen fluoride, and ethers. A suggested mechanism for this reaction is

$$CHClFCF_2NR_2 + 2R'OH \longrightarrow$$
$$[CHClFC(OR')_2NR_2] + 2HF$$
$$[CHClFC(OR')_2NR_2] \longrightarrow CHClFCONR_2 + R'OR'$$

The decomposition of the hypothetical intermediate is analogous to the formation of ethyl acetate and diethyl ether upon heating ethyl orthoacetate.[21]

These active amines reacted so vigorously with thiols that black tars were produced unless cooling was provided to maintain the reaction mixture near room temperature. A limited investigation of the light yellow liquid products obtained from controlled-temperature reactions showed them to be highly complex mixtures. The high boiling points and instability of these compounds combined to prevent sufficient purification for the identification of most of them. The absence of dialkyl sulfides among the products indicated that the reaction with thiols was not completely analogous to that

(18) M. F. Shostakovskii, Yu. B. Kagan and F. P. Sidel'kovskaya, *J. Gen. Chem. (U. S. S. R.)*, **17**, 957 (1947); *C. A.*, **42**, 4520 (1948).

(19) J. R. Johnson, "Organic Chemistry, An Advanced Treatise," H. Gilman, ed., 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, Vol. II, p. 1853.

(20) G. W. Rigby and H. E. Schroeder, U. S. Patent 2,409,315 (1946).

(21) H. Staudinger and G. Rathsam, *Helv. Chim. Acta.*, **5** 645 (1922).

with alcohols. Regardless of the complete mechanism, however, the difluoromethylene group was again indicated as the primary point of attack.

Experimental

Reaction of Polyfluoroalkyl Tertiary Amines with Alcohols.—1-(2-Chloro-1,1,2-trifluoroethyl)-piperidine (59.0 g.) was added in small portions to 98% isopropyl alcohol (41.6 g.) in a polyethylene bottle. The mixture was shaken after each addition and cooled in a water-bath during the entire time (45 min.). After standing overnight, the mixture was heated at 95° while a stream of dry nitrogen was bubbled through under anhydrous conditions. The effluent gases were passed through a sodium hydroxide solution to remove hydrogen fluoride and thence to a trap chilled in Dry Ice–acetone slush. A portion of the isopropyl ether collected in the trap was lost through accident, but a small amount (6 ml.) was retained. Additional ether (11 ml.) was obtained by distillation of the mixture remaining in the bottle. The main fraction (39.0 g.) distilled at 74° and 0.5 mm. This corresponds to 74% theoretical yield of 1-(chlorofluoroacetyl)-piperidine, which melted at 34–35° after recrystallization from acetone.

Anal. Calcd. for $C_7H_{11}ClFNO$: C, 46.80; H, 6.17; N, 7.80. Found: C, 46.79; H, 6.52; N, 6.99.

N-(2-Chloro-1,1,2-trifluoroethyl)-diethylamine (118.7 g.) was added in small portions to absolute ethanol (53 g.) with agitation and cooling as in the previous reaction. Distillation of the reaction mixture gave low-boiling fractions containing hydrogen fluoride, diethyl ether, and ethanol. A larger fraction (66.2 g.), distilling at 47° and 0.7 mm., was later identified as N,N-diethyl-α-chloro-α-fluoroacetamide. This is equivalent to a 63% theoretical yield.

Reaction of Polyfluoroalkyl Tertiary Amines with Thiols.—1-(2-Chloro-1,1,2-trifluoroethyl)-piperidine (27.8 g.) reacted smoothly with ethane thiol (18.5 g.) when the mixture was held at about 30°. The two liquid layers formed (after 2 hr.) were both heavier than water. After washing the lower layer with water, distillation gave a small amount of ethyl chlorofluorothiolacetate (2.6 g.), b.p. 38° at 2 mm., $n^{25}D$ 1.4680, d^{25}_4 1.2587.

Anal. Calcd. for C_4H_6ClFOS: C, 30.70; H, 3.83. Found: C, 30.75; H, 4.03.

A limited examination of both layers failed to establish the presence of diethyl sulfide as might have been expected by analogy to the reaction with alcohols.

1-(2-Chloro-1,1,2-trifluoroethyl)-piperidine (80.8 g.) and butane thiol (72.0 g.) reacted under the same conditions as when ethane thiol was used. Distillation of the washed lower layer gave butyl chlorofluorothiolacetate (7.0 g.), b.p. 43° at 0.3 mm., $n^{25}D$ 1.4668, d^{25}_4 1.175. Heating this compound with aniline formed butane thiol and the solid derivative, N-phenyl-α-chloro-α-fluoroacetamide, m.p. 81–82°.

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Synthesis of Phosphanilic Acid and Related Compounds[1]

BY G. O. DOAK AND LEON D. FREEDMAN

The m- and p-isomers of both nitrobenzenephosphonic acid and bis-(nitrophenyl)-phosphinic acid are readily reduced to the corresponding amino derivatives by means of Raney nickel and hydrogen at 40 lb. pressure. The corresponding hydroxy derivatives, none of which have been previously described, are obtained from the amino compounds by diazotization with ethyl nitrite and subsequent decomposition of the diazonium salts. o-Aminobenzene-phosphonic acid was prepared by the action of aqueous ammonia on o-bromobenzenephosphonic acid in the presence of cuprous oxide.

There is evidence that phosphanilic acid and certain of its derivatives have considerable bactericidal activity.[2] Research on these compounds has been hindered by a lack of convenient synthetic methods. With none of the procedures has it been found possible to prepare a wide variety of phosphonic acids.

A recent communication[3] from this Laboratory has described a new synthesis of arylphosphonic and diarylphosphinic acids by the reaction between diazonium fluoborates and phosphorus trichloride in organic solvents. This method makes readily available a wide variety of organophosphorus compounds which hitherto have been difficult if not impossible to prepare.

The present paper describes the preparation of several amino and hydroxy substituted arylphosphonic and phosphinic acids. The amino acids were readily prepared, following the procedure of Arnold and Hamilton,[4] by catalytic reduction of the corresponding nitro acids. We have been unable to obtain o-nitrobenzenephosphonic acid by our general procedure. Accordingly, the desired o-amino compound was prepared from o-bromobenzenephosphonic acid by the procedure described by Limaye and Bhide[5] for the corresponding para isomer. Because of the properties of the ortho compound it was found necessary to modify the isolation procedure. The hydroxy acids were obtained from the corresponding amino acids by diazotization with ethyl nitrite and subsequent decomposition of the resulting diazonium salts. The compounds prepared together with their analyses, yields and m.p.'s are listed in Table I.

Experimental

p-Aminobenzenephosphonic Acid (Phosphanilic Acid).—Either p-nitrobenzenephosphonic acid or the corresponding hemi-potassium salt[6] was suspended in water and sufficient 10% potassium hydroxide added to give a clear solution. The pH of this solution should be approximately 6.7; if the pH was above 8, the reduction was slow and incomplete. Raney nickel was added and the compound reduced at 40 pounds pressure. The addition of a few drops of 10% chloroplatinic acid materially increased the rate of reduction of all nitro phosphonic and phosphinic acids. The catalyst was removed and the solution acidified with acetic acid whereupon crystalline phosphanilic acid separated from

(1) Presented before the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(2) H. Bauer and S. M. Rosenthal, *U. S. Public Health Rep.*, **54**, 2093 (1939); M. I. Smith, E. W. Emmart and B. B. Westfall, *J. Pharmacol. Exp. Therap.*, **74**, 163 (1942); U. K. Kanitkar and B. V. Bhide, *Current Sci.*, *(India)*, **16**, 223 (1947); G. S. Pendse and B. V. Bhide, *ibid.*, **17**, 125 (1948).

(3) G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5658 (1951).

(4) G. B. Arnold and C. S. Hamilton, *ibid.*, **63**, 2637 (1941).

(5) M. S. Limaye and B. V. Bhide, *J. Indian Chem. Soc.*, **25**, 251 (1948).

(6) This salt, admixed with potassium chloride, is obtained in the procedure for isolating the free acid, as previously described.[5] The use of this salt for reduction avoids the isolation of the soluble acid.