Fluorination.—The passage from cyclo-$C_5F_6Cl_4O$ to cyclo-$C_5F_{10}O$ proved considerably more difficult than for the smaller ring. When the fluorination was vigorous, the ring broke; for less rigorous conditions, only part fluorination occurred. A two-step procedure finally succeeded. Cyclo-$C_5F_6Cl_4O$ (100 g. or 0.3 mole) was mixed with SbF_3Cl_2 (100 g. or 0.4 mole) and heated to 125° for seven hours in a 450-ml. steel bomb, with shaking. The pressure rose to 75 p.s.i. The temperature was raised to 160° for 16 hours, which brought the pressure up to 230 p.s.i. After cooling, a light fraction (41 g.), b.p. 52–95°, was collected by distillation, which was a mixture of cyclo-C_5F_9ClO and cyclo-$C_5F_8Cl_2O$. This mixture (78.5 g.) and SbF_3Cl_2 (46 g. or 0.184 mole) were shaken at 160° for five hours in a bomb. The pressure rose to 320 p.s.i. After cooling, repeated distillation of the crude gave about 3 g. of a material, b.p. 26°, which was regarded as the desired $\overline{CF_2CF_2\text{–}O\text{–}CF_2CF_2CF_2}$ on the basis of its boiling point and a carbon analysis, and about 10 g. of cyclo-C_5F_9ClO, b.p. 48–49°, which broke down when subjected to refluorination. Repetition of this last fluorination with antimony salts under a variety of conditions always led to extensive decomposition.

Solubilities.—The solubility tests confirm the expected lack of basic properties. They are listed in Table II. In doubtful cases, where the formation of a complex with ferric chloride could not be readily observed, calcium hydride was added[10] as this reagent evolves hydrogen and forms an easily detected complex.

(10) Reich and Serpek, *Helv. Chim. Acta*, **3**, 138 (1920).

COLUMBUS, OHIO

[CONTRIBUTION NO. 21 FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING & MANUFACTURING COMPANY]

The Chemistry of the Perfluoro Acids and Their Derivatives. III. The Perfluoro Aldehydes[1]

BY DONALD R. HUSTED AND ARTHUR H. AHLBRECHT

RECEIVED JUNE 4, 1952[2]

Perfluoro aldehydes and the corresponding aldehydrols have been prepared by a new synthetic method, namely, lithium aluminum hydride reduction of the perfluoro acid. The Rosenmund reaction has also been used to prepare perfluoro aldehydes from the corresponding perfluoro acid chlorides. The chemistry of the perfluoro aldehydes has been studied and 2,4-dinitrophenylhydrazones and diacyl derivatives prepared.

A number of fully fluorinated aldehydes have been prepared and this paper presents data on the first three members of the series: perfluoroacetaldehyde, perfluoropropionaldehyde and perfluorobutyraldehyde. These perfluoro aldehydes were obtained by the lithium aluminum hydride reduction of the corresponding perfluoro acids. The reduction product was a mixture composed mainly of the expected primary alcohol[3] and the aldehydrol from which the free aldehyde was obtained by dehydration. The alcohol (except in the case of 1,1-dihydroperfluorobutanol as noted below) was easily removed from the reaction product by distillation and the residue, consisting mainly of the aldehydrol, was treated with hot concentrated sulfuric acid or phosphorus pentoxide to liberate the aldehyde. The perfluoro aldehydes studied are low boiling liquids which distil readily from the reaction mixture.

Since the boiling points of 1,1-dihydroperfluorobutanol, $C_3F_7CH_2OH$, and the corresponding aldehydrol, $C_3F_7CH(OH)_2$, differ by only about one degree, the mixture of these two compounds was not conveniently separated by fractional distillation, but was treated directly with concentrated sulfuric acid. The perfluorobutyraldehyde distilled readily as the low boiling fraction and the 1,1-dihydroperfluorobutanol was recovered as the higher boiling fraction.

The perfluoroaldehydes react rapidly with water to form relatively stable solid hydrates, which may account for Swarts'[4] failure to obtain the aldehyde by dichromate oxidation of 1,1-dihydroperfluoroethanol in water solution. The aldehyde, if formed, would immediately react with water and the nonvolatile hydrate would be further oxidized to the corresponding perfluoro acid. The substitution of concentrated sulfuric acid for dilute sulfuric acid in the oxidation of 1,1-dihydroperfluorobutanol resulted in the formation of small amounts of perfluorobutyraldehyde.

Further evidence that anhydrous methods of reduction are to be preferred is the high yield obtained from the Rosenmund reduction of the perfluoro acid chloride with poisoned palladium catalyst.

The perfluoro aldehydes have also been obtained by the lithium aluminum hydride reduction of perfluoro acid amides. They were isolated in the form of the hydrate after the addition of water. A substantial amount of the 1,1-dihydroperfluoroamine was also formed in this reduction.[5]

The preparation of perfluoroacetaldehyde, recently reported by Henne[6] and by Shechter[7] has also been accomplished by reduction of the corresponding nitrile and by the oxidative nitration of 1,1,1-trifluoropropane.

The structure assignment of these compounds is based on a variety of chemical and physical evidence. The aldehydes give a positive test with Schiffs fuchsin aldehyde reagent. The aldehydrols

---

(1) Combination of two papers, one presented before the Fluorine Symposium at the 116th Meeting (Sept., 1949), Abstracts, p. 10K, paper #17, of the American Chemical Society, Atlantic City, New Jersey, and one before the 118th meeting at Chicago, Illinois. Paper I, "The Chemistry of Perfluorobutyric Acid" and II, "The Chemistry of Derivatives of Perfluorobutyric Acid" which were given at Atlantic City are in preparation for publication.

(2) Received originally October 20, 1950. The manuscript in its present form was received June 4, 1952.

(3) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

(4) F. Swarts, *Bull. soc. chim. Belg.*, **43**, 476 (1934).

(5) (a) A. Uffer and E. Schlitter, *Helv. Chim. Acta*, **31**, 1397 (1948); (b) L. Friedman, Atlantic City, N. J., A.C.S. Meeting, September 19, 1949, Organic Division, Section A, Paper No. 6, page 5M.

(6) A. L. Henne, R. L. Pelly and R. M. Alm, THIS JOURNAL, **72**, 3370 (1950).

(7) H. Shechter and F. Conrad, *ibid.*, **72**, 3371 (1950).

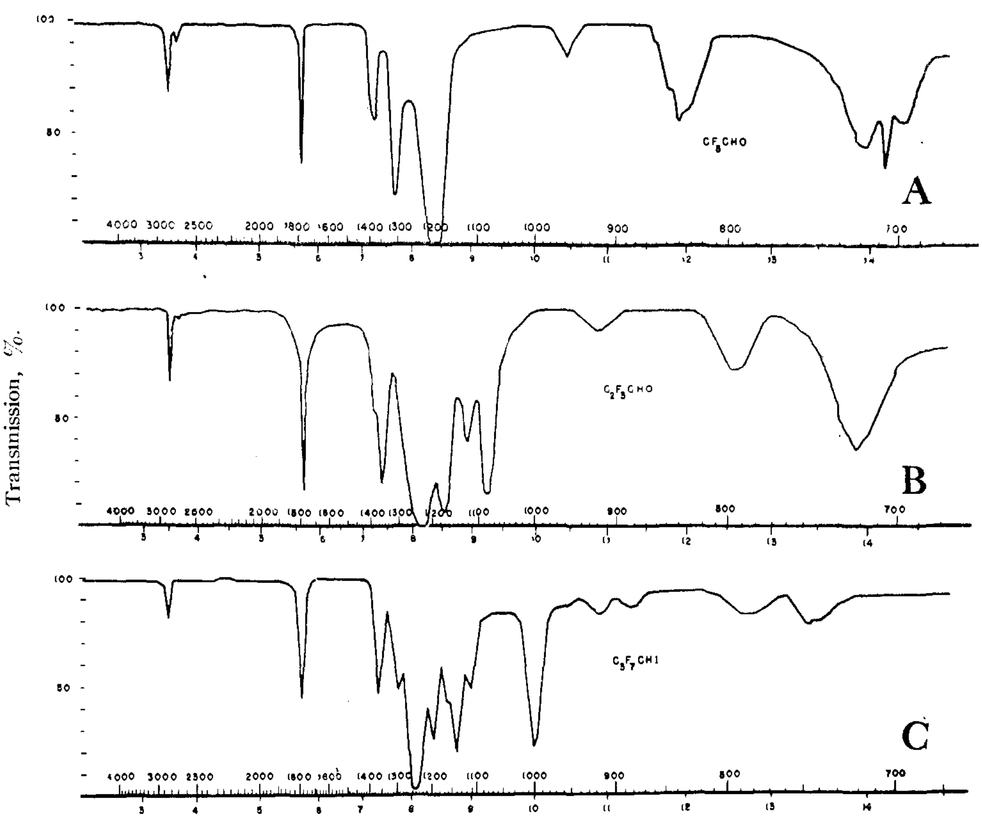


Fig. 1.—Infrared absorption spectral curves of three perfluoroalkyl aldehydes (vapor phase): abscissa, top scale, wave number in cm.$^{-1}$; bottom scale, wave length in microns; cell length, 25 mm.; pressure, 50 mm.: a, perfluoroacetaldehyde; b, perfluoropropionaldehyde; c, perfluorobutyraldehyde.

do not give a Schiff test but do give the original aldehyde on dehydration. Both the aldehyde and the aldehydrol give the parent acid on oxidation with potassium dichromate and sulfuric acid. Acid anhydrides react both with the aldehydes in the presence of sulfuric acid as a catalyst and with the aldehydrols in the presence of pyridine to give the same alkylidine diesters. These on hydrolysis consume three moles of base, two for the two acid groups and one for the aldehydrol, very similar to the behavior of related chloral derivatives.[8]

The aldehydrols react with a sulfuric acid solution of 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones.

Perfluorobutyraldehyde reacts normally with methyl Grignard reagent to form, after hydrolysis, the predicted secondary alcohol.[9]

The infrared absorption spectral curves of the perfluoroaldehydes exhibit the bands characteristic of the CF (1100–1400 cm.$^{-1}$), CH (2800 cm.$^{-1}$) and C=O (1780 cm.$^{-1}$) groupings but no bands characteristic of the –OH (3100–3300 cm.$^{-1}$) group (Fig. 1). The infrared absorption spectra of the aldehydrols contain absorption bands characteristic of the CF, CH and –OH groupings but no bands characteristic of the C=O group (Fig. 2).

The foregoing data along with the analytical data taken as a whole leave little reasonable doubt as to the correctness of the assigned structures.

These compounds exhibit certain peculiarities, a few of which have already been mentioned, such as the ease of hydration of the aldehyde and instability of the aldehydrol to alkali. The perfluoro aldehydes polymerize very easily to give viscous or solid polymers which are chemically and thermally quite stable, again showing marked difference from the unfluorinated aldehydes.

Perfluorobutyraldehyde, diethyl ether and hydrochloric acid in equimolar ratio form a constant boiling mixture or a loose molecular compound which distils at a higher temperature than any of the components and whose infrared absorption spectra show no evidence of the presence of the aldehyde group, but they do show the presence of C–OH group. The compound splits easily to give the aldehyde on the addition of a small amount of water. The infrared absorption curve of the vapor over the liquid exhibits the bands characteristic of the perfluorobutyraldehyde (Fig. 1) superimposed on those of ether.

Experimental

Preparation of Perfluorobutyraldehyde. Caution.—Lithium aluminum hydride should be ground only under an atmosphere of nitrogen and the powder added to the reaction flask with nitrogen flowing through the system. A minimum of 2 cu. ft./hr. is recommended. This is particularly important during the addition of water to decompose the excess lithium aluminum hydride. The water inlet tube should extend nearly to the surface of the ether solution so no water will strike the walls of the flask where a dried residue of lithium aluminum hydride is sometimes

---

[8] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 627.

[9] T. S. Reid (to be published). *Cf.* ref. 6 for the corresponding reaction with trifluoroacetaldehyde.

left by splashing of the ether solution and evaporation of the ether. Water striking such a residue causes flashes of flame. Oxygen must be absent to prevent explosions. Lithium aluminum hydride fires should be extinguished by the use of sodium chloride, sand, etc., never by carbon tetrachloride, water or carbon dioxide[10-12] extinguishers. The use of explosion shields and remote control during the addition of water is recommended strongly.

The reduction of perfluorobutyric acid with lithium aluminum hydride was carried out in a manner similar to that described by Nystrom and Brown.[11] A 3-l. three-necked flask fitted with stirrer, dropping funnel, condenser and gas inlet tube was dried at 120° before use and assembled with a stream of nitrogen flowing through it. To a solution of 19 g. (0.5 mole) of lithium aluminum hydride in 1250 ml. of anhydrous ethyl ether was added dropwise a solution of 107 g. (0.5 mole) of perfluorobutyric acid in 1000 ml. of dry ether. The reaction flask was cooled in an ice-bath and the rate of addition of the acid was such as to maintain a gentle reflux of the ether. Upon completion of the addition of the acid, the mixture was stirred two hours at room temperature. At the end of this time the nitrogen flow rate was increased and the flask cooled with ice-salt mixture; then the excess lithium aluminum hydride was destroyed by the dropwise addition of water. Immediately after the addition of the water was completed, an ice-cold solution of 80 ml. (1.5 moles) of concentrated sulfuric acid in 200 ml. of ice-water was added with continued cooling of the flask. The two layers were separated, the water layer (usually the bottom layer) was extracted three times with ether, and the combined ether layers and ether extracts were distilled to remove the ether. The oily residue was dried with Drierite and distilled through a semi-micro fractionating column having 6 to 9 theoretical plates (5 mm. i.d., 25-cm. glass helices-packed column or 29-cm. stainless steel spiral column.[13] The fraction boiling at 85–95° (740 mm.) was removed and placed in a two-necked 200-ml. flask equipped with a dropping funnel and a semi-micro fractionating column having about 6 theoretical plates. Thirty-five milliliters of concentrated sulfuric acid was added slowly through the dropping funnel and the resulting mixture refluxed gently for approximately 5 minutes to cause decomposition of the aldehyde precursor. Care must be exercised in this distillation since continued heating of the sulfuric acid reaction mixture yields the 1,1-dihydroperfluorobutyl alcohol, as the high boiling constituent, b.p. 96° (740 mm.). The aldehyde was then distilled and collected in a cooled receiver. Redistillation resulted in a pure product, yield 33.6 g. (34%), b.p. 28.2–29° (740 mm.); d^{20}_4 1.505; n^4D 1.2730; Schiff fuchsin aldehyde test positive, infrared absorption curve (Fig. 1) shows presence of C=O, CH, CF, no C–OH groups. *Anal.* Calcd. for C_4HOF_7: mol. wt., 198; F, 67.2; C, 24.2. Found: mol. wt., 196; F, 66.8; C, 24.0.

Perfluorobutyraldehyde-2,4-dinitrophenylhydrazone.—This compound was purified by dissolving in ether and removing the insoluble unreacted 2,4-dinitrophenylhydrazine by filtration. The ether solution was evaporated and the residue recrystallized from ethyl alcohol–water mixture, followed by recrystallization from ether then from carbon tetrachloride; m.p. 107°. *Anal.* Calcd. for $C_{10}H_5O_4N_4F_7$: F, 35.2; H, 1.33; N, 14.8. Found: F, 35.1; H, 1.23; N, 14.71.

Perfluoroacetaldehyde.—The reaction was carried out in a manner similar to that described for the preparation of perfluorobutyraldehyde. The same safety precautions were observed.

To 19 g. (0.5 mole) of lithium aluminum hydride dissolved in 1250 ml. of dry ether was added 57 g. (0.5 mole) of perfluoroacetic acid in 1000 ml. of dry ether. After decomposition of excess reducing agent by addition of 36 ml. (2.00 moles) of water, 80 ml. of concentrated sulfuric acid in ice-water was added, the ether layer and ether extracts were combined and the ether removed by distillation. The 1,1-dihydroperfluoroethanol was removed by distillation and the oily residue, b.p. 103–105° (742 mm.) n^{20}D 1.3404, d^{20}_4 1.468, consisting mainly of the aldehydrol, was treated with concentrated sulfuric acid or phosphorus pentoxide. The reaction was sluggish and some refluxing was necessary, but prolonged heating was avoided because of the tendency of the aldehyde to polymerize. The aldehyde was distilled from the acid reaction mixture directly into a closed system and redistilled in a low temperature column, b.p. −19 to −18° (746 mm.); yield 12.7 g. (26%). *Anal.* Calcd. for C_2HOF_3: mol. wt., 98; F, 58.2; C, 24.5. Found: mol. wt., 106 (gas density balance); F, 58.4; C, 24.4. Infrared absorption curve showed the presence of CF, C=O, CH groups, but no C–OH group (Fig. 1).

Perfluoroacetaldehydrol was prepared by the addition of slightly less than the calculated amount of water to the pure perfluoroacetaldehyde and later evaporating off the excess perfluoroacetaldehyde, leaving behind the pure aldehydrol. Great care must be exercised because of the tendency of the material to retain traces of solvent (for example from recrystallization) or water and remain an oil, m.p. 68–70°.

2,4-Dinitrophenylhydrazone.—M.p. 149°, recorded value 149°.[5]

Diacetate.—B.p. 146–146.5° (743.2 mm.), n^{20}D 1.3530, d^{20}_4 1.291.

Anal. Calcd. for $C_6H_7O_4F_3$: F, 28.5; sapn. equiv., 66. Found: F, 28.3; sapn. equiv., 67 (12-hr. reflux, no fluorine was lost by hydrolysis).

Perfluoropropionaldehyde.—The reaction was carried out in a manner similar to that described for the preparation of heptafluorobutyraldehyde. The same safety precautions are observed.

To 38 g. (1 mole) of lithium aluminum hydride dissolved in 1000 ml. of dry ether was added 164 g. (1 mole) of perfluoropropionic acid dissolved in 1000 ml. of ether. After removal of excess reagent by addition of water (about 20 ml. was required), 80 ml. of concentrated sulfuric acid and 200 g. of ice (more may be required to keep temperature down) were added and the mixture treated as above. The ether layer and ether washes were combined after which the ether and the 1,1-dihydroperfluoropropanol, ($C_2F_5CH_2OH$), b.p. 80–81° (740 mm.), were removed by distillation. To the oily residue which consisted mainly of the aldehydrol was added concentrated sulfuric acid. The aldehyde was liberated by refluxing the reaction mixture for a few minutes then recovered as such by distillation. It is convenient to distil the aldehyde directly from the reaction flask into a low temperature distillation system; yield 29 g. (20%), b.p. 2° (746 mm.). *Anal.* Calcd. for C_3HOF_5: F, 64.2; C, 24.34; mol. wt., 148. Found: F, 64.4; C, 24.6; mol. wt., 148. Infrared absorption curve (Fig. 1) showed absorption bands characteristic of C–F, C=O and C–H groups.

Aldehydrol.—M.p. 52–53°, b.p. 92° (732 mm.) (micro). *Anal.* Calcd. for $C_3H_3O_2F_5$: F, 57.2; C, 21.7; sapn. equiv., 166. Found: F, 56.6; C, 21.4; sapn. equiv., 167.

Perfluorobutyraldehydrol from Perfluorobutyramide.—The reaction was carried out in a manner similar to that described for the preparation of perfluorobutyraldehyde from perfluorobutyric acid. To 44.6 g. (1.172 moles) of lithium aluminum hydride dissolved in 1250 ml. of dry ether was added 100 g. (0.469 mole) of perfluorobutyramide[1] dissolved in 500 ml. of dry ether. Immediately after decomposition of excess reducing agent by careful addition of about 96 ml. of water, an ice-cold solution of 260 ml. (4.9 moles) of concentrated sulfuric acid in 600 g. of ice was added. The 1,1-dihydrofluorobutylamine sulfate was precipitated as an insoluble solid. The ether (top) layer was removed, the 1,1-dihydroperfluorobutylamine sulfate removed by filtration, and the aqueous filtrate extracted three times with ether. The ether layer and ether washes were combined, dried with Drierite or by freezing and the ether removed by distillation. The residue, which contained a considerable proportion of perfluorobutyraldehydrol, was distilled through a semi-micro still having about 10 theoretical plates, and the fraction boiling 95–96° collected. This fraction was almost pure aldehydrol (n^{20}D 1.3255, infrared curve matched that shown in Fig. 2), from which the aldehyde may be recovered in the manner previously described, yield about 10–15%.

Diacetate of Perfluorobutyraldehyde.—In a flask fitted with a Dry Ice–acetone cooled reflux condenser was placed 10 g. of perfluorobutyraldehyde and 10.2 g. of acetic anhydride. One drop of concentrated sulfuric acid was added

---

(10) H. I. Schlesinger, THIS JOURNAL, **70**, 877 (1948).

(11) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

(12) Lithium Aluminum Hydride Brochure of Metal Hydrides, Inc., Beverly, Massachusetts.

(13) F. W. Mitchell, Jr., and J. M. O'Gorman, *Anal. Chem.*, **20**, 315 (1948).

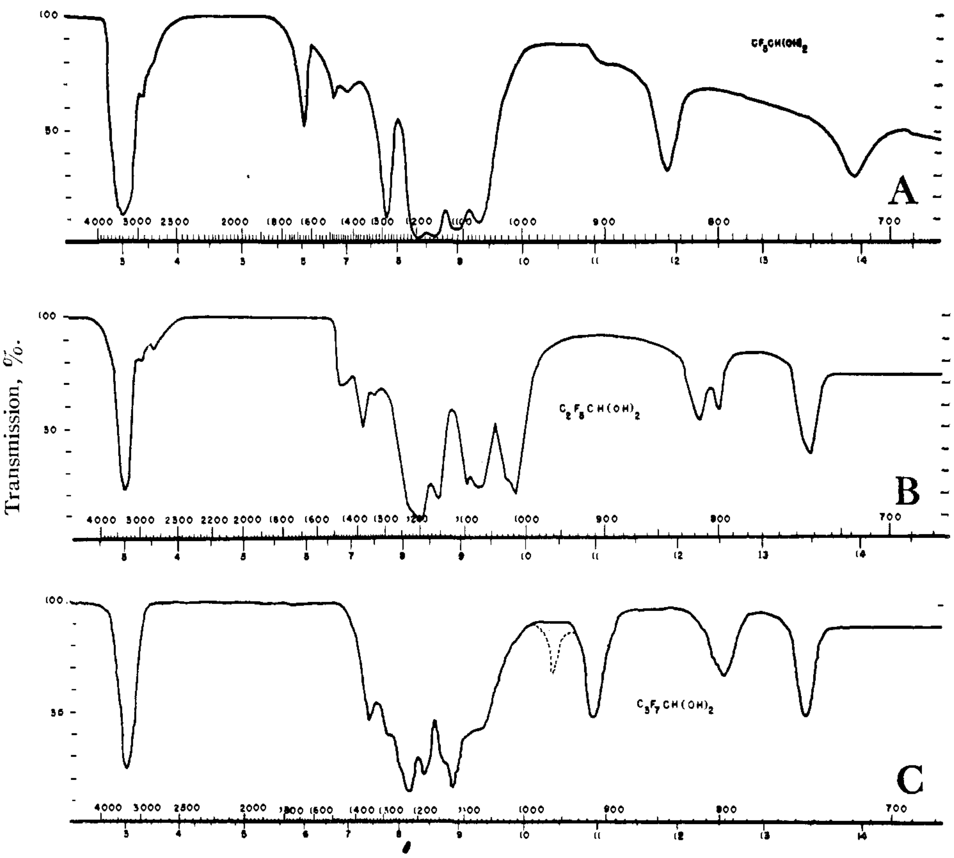


Fig. 2.—Infrared absorption spectral curves of three perfluoroalkylhydrols: abscissa, top scale, wave number in cm.$^{-1}$; bottom scale, wave length in microns. Perfluoroacetaldehydrol (a) and perfluorobutyraldehydrol (c) were mulled in Nujol. Perfluoropropionaldehydrol (b) was melted and pressed out between two rock salt plates. The band shown by the dotted line at 963 cm.$^{-1}$ in the curve for perfluorobutyraldehydrol appeared in all samples but in varying intensity. It appears to be characteristic but the reason for the variation is unknown.

as a catalyst. The reaction was very rapid. The product was recovered by washing with water, drying with Drierite, and distilling; yield 11.5 g. (75%), b.p. 165° (743 mm.), n^{20}_{D} 1.3378, d^{20}_{4} 1.431. *Anal.* Calcd. for $C_8H_7O_4F_7$: F, 44.3; sapn. equiv., 100. Found: F, 44.3; sapn. equiv., 101.5.

The alkylidene diesters of the other aldehydes were prepared in a similar manner.

Dibutyrate of Perfluorobutyraldehyde.—B.p. 112–114° (24 mm.), n^{20}_{D} 1.3626, d^{20}_{4} 1.269. *Anal.* Calcd. for $C_{12}H_{15}O_4F_7$: F, 37.3; sapn. equiv., 118.6. Found: F, 37.3; sapn. equiv., 119.

Diacrylate of Perfluorobutyraldehyde.—B.p. 89.5–90° (15 mm.), n^{25}_{D} 1.3652, d^{20}_{4} 1.399. *Anal.* Calcd. for $C_{10}H_7O_4F_7$: C, 37.0; F, 41; sapn. equiv., 108. Found: C, 36.9; F, 40.9; sapn. equiv., 109.

Perfluorobutyraldehyde Diacetate from the Aldehydrol–Alcohol Mixture.—To a dry 100-ml. one-necked flask equipped with a reflux condenser were added 25 g. of the distilled reduction mixture of boiling range 85–95° obtained from the lithium aluminum hydride reduction of the perfluorobutyric acid, 25 g. (0.245 mole) of acetic anhydride and 10 ml. of pyridine. The mixture was refluxed overnight. The solution was transferred to a separatory funnel and washed with water, 10% sodium bicarbonate, again with water, and then dried over Drierite for 24 hours. The liquid was decanted from the Drierite and distilled through a semi-micro column of 8–10 theoretical plates. The acetate of 1,1-dihydroperfluorobutyl alcohol was separated by distillation at 105° (745 mm.) and the desired diacetate collected by distillation at 164° (743 mm.), yield 8 g. It had the following properties: n^{20}_{D} 1.3378, d^{20}_{4} 1.431.

Perfluorobutyraldehydrol.—In a 100-ml. flask fitted with dropping funnel and a reflux condenser cooled with a Dry Ice–acetone mixture was placed 30 g. (0.151 mole) of pure perfluorobutyraldehyde. While shaking the flask, 2.70 g. (0.150 mole) of water was added dropwise. After standing for one hour, the reaction mixture had completely crystallized. The crystals were removed and dried in air for two hours, during which time the pure aldehyde originally present in slight molar excess evaporated. Further purification was unnecessary; yield about 27–28 g. (90%), m.p. 61°, b.p. 93.5° (737.5 mm.) (micro); soluble in benzene, ether, methanol, toluene, ethyl acetate, hot carbon tetrachloride and hot heptane. *Anal.* Calcd. for $C_4H_3O_2F_7$: F, 61.6; C, 22.2; sapn. equiv., 216. Found: F, 61.3; C, 22.2; sapn. equiv., 212. Infrared absorption curve (Fig. 2) shows bands characteristic of CF, CH, C–OH groups, but no bands characteristic of the C=O group. A band appeared in the curves of all samples at 963 cm.$^{-1}$, but of varying intensity. This band is indicated as a dotted line since its significance is subject to doubt.

Alkaline Hydrolysis of Perfluorobutyraldehydrol.—In a 120-ml. round-bottomed flask fitted with a reflux condenser vented to a liquid air cooled trap was placed a 5.0 g. (0.0246 mole) of perfluorobutyraldehydrol and 20 ml. of a 10% solution of sodium hydroxide. After refluxing for 90 minutes, the reaction appeared to be complete. The *n*-heptafluoropropane produced, C_3F_7H, 3.69 g., 88.5% had condensed in the liquid air trap and was identified by its boiling point −17 to −19° (740 mm.) and infrared absorption spectrogram showing the characteristic peaks of *n*-heptafluoropropane at 12.03, 13.35, 13.44, 9.72 and 3.33 μ (C–H).

The empty volume of the system which was not flushed was 112 ml. and was sufficient to hold enough heptafluoropropane to account for the loss of material that should have been obtained from a quantitative reaction.

Perfluorobutyraldehyde by the Rosenmund Reduction.—To a dry three-necked flask fitted with a stirrer, Dry Ice–acetone cooled condenser and a gas inlet tube long enough to dip under the liquid in the flask were added 80 ml. of ether, 23.2 g. (0.1 mole) of perfluorobutyryl chloride,[1] 2 g. of palladium–charcoal catalyst[14] and six drops of quinoline-S regulator.[15] Hydrogen was passed in slowly with vigorous stirring for 8 to 12 hours at the reflux temperature of the ether At the end of the reaction period, the catalyst was removed by filtration and the filtrate distilled. The fraction boiling at 40–53° was removed and an excess of water (about 18 g., 1 mole) added. The ether was distilled off. The residue consisted largely of a mixture of 1,1-dihydroperfluorobutanol and perfluorobutyraldehydrol from which the aldehyde was recovered upon treatment with sulfuric acid in the manner described above; yield about 6.3 g. (31.8%).

The course of the reaction cannot be followed, as is customary, by the evolution of hydrogen chloride. The latter forms with the aldehyde and ether a distillable molecular complex or ternary azeotrope having the composition corresponding approximately to the formula $C_3F_7CHO \cdot C_2H_5OC_2H_5 \cdot HCl$, b.p. 52–52.5° (737 mm.), n^{25}D 1.3303. *Anal.* Calcd. for $C_8H_{12}O_2ClF_7$: Cl, 11.45. Found: Cl, 10.1.

The distillable complex can also be synthesized by direct addition of hydrogen chloride to an ether solution of perfluorobutyraldehyde.

By very careful addition of a small amount of water it is possible to isolate the free aldehyde from the complex, but the conversion to the aldehydrol is recommended as being more satisfactory and giving a higher over-all yield of aldehyde.

Perfluorobutyraldehyde by the Rosenmund Reduction (Low Pressure Reaction).—In a dry "citrate" pressure bottle were placed 23 g. (0.1 mole) of perfluorobutyryl chloride,[1] 1 g. of palladium–charcoal catalyst[14] and four drops of quinoline-S regulator.[15] The bottle was clamped into a Parr low pressure hydrogenation apparatus[16] and the bottle was "popped" twice (50 p.s.i. hydrogen pressure applied, the bottle opened) to remove the air from the bottle. Hydrogen was then run into the bottle to 50 p.s.i. and the container shaken at room temperature for one week. The pressure drop was about 8 pounds.

The contents of the bottle were placed in a still and the major portion distilling at 28–32° (740 mm.) removed. To this fraction water was added with cooling. The crystalline aldehydrol was recovered by filtration and dried in air; yield 6.87 g. (35%). The aldehyde was obtained by dehydration with concentrated sulfuric acid as described earlier.

Perfluoroacetaldehyde by the Rosenmund Reduction.—In a dry "citrate" pressure bottle was placed 42 g. (0.2 mole) of perfluoroacetic anhydride, 6 g. of diethyl ether saturated with hydrogen chloride, equivalent to 1% Cl^- based on the weight of anhydride used,[17] 2.4 g. of palladium–charcoal catalyst,[14] and 4–6 drops of quinoline-S regulator.[15] The bottle was clamped into a Parr low pressure hydrogenation apparatus[16] and without "popping" the bottle, 50 p.s.i. hydrogen pressure was applied and the container shaken at room temperature until the pressure dropped 12 p. s. i., or until the pressure no longer decreased. The pressure was released and the contents of the bottle were transferred to the pot of a semi-micro vacuum type still, the vacuum outlet attached to a Dry Ice–acetone cooled trap and the liquid portion distilled at atmospheric pressure. A portion of the trifluoroacetaldehyde present collected in the cold trap. The fraction boiling 36–68° (740 mm.) was redistilled in a similar still and a further amount of the aldehyde collected in the cold trap; yield 1.05 g. (5%), b.p. −19° (746 mm.). The fraction distilling at 50–55° (740 mm.) contains 1,1-dihydroperfluoroethyl perfluoroacetate (CF_3-$COOCH_2CF_3$), (5 g., 12%, b.p. 55–56° (741 mm.), n^{20}D 1.2772, $d^{20}{}_4$ 1.464) which lends support to Swarts'[3] claim of obtaining the same compound by the catalytic hydrogenation of perfluoroacetic anhydride. From it he prepared 1,1-dihydroperfluoroethanol by hydrolysis.

Acknowledgments.—We are indebted to B. W. Nippoldt, H. E. Freier and D. G. Weiblen and the Clark Microanalytical Laboratory for the analyses reported in this paper; and to Minnesota Mining & Manufacturing Co. for permission to publish this paper.[18]

---

[14] Catalyst may be obtained from the Wilkins–Anderson Company, 111 N. Canal Street, Chicago, Illinois.

[15] R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 368; E. B. Hershberg and J. Carson, *Org. Syntheses*, **21**, 84 (1941).

[16] Parr Catalytic Hydrogenation Apparatus, Model C. A., Parr Instrument Company, Moline, Illinois.

[17] C. Mannich and A. H. Nadelman, *Ber.*, **63B**, 796 (1930), state that under these conditions anhydrides are converted to the acid chloride, a reaction presumed to occur here also.

[18] Since the original filing date of this paper, U. S. Patents 2,568,500 covering the perfluoroaldehydes and aldehydrols, and 2,568,501 covering the alkylidene diesters have been issued to the authors and assigned to Minnesota Mining and Manufacturing Company.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY]

Migration Ratios in the Rearrangement of 2,2-Diarylethanols[1]

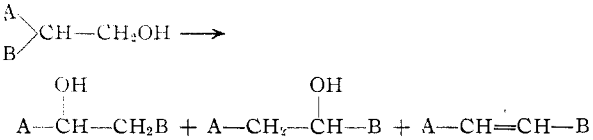
BY JOHN G. BURR, JR., AND LEON S. CIERESZKO[2]

RECEIVED JUNE 7, 1952

The migration ratios with reference to phenyl of eight substituted phenyl groups have been determined by the acid-catalyzed rearrangement of the corresponding 2,2-diarylethanol-1-C^{14}. The values were obtained by oxidation of the stilbene resulting from the rearrangement, and by radiochemical assay of the most easily isolated oxidation product, which in the above cases was a phthalic acid or a substituted benzoic acid. This method of obtaining migration ratios is characterized by lack of stereochemical complications, simplicity of system, easy availability of starting materials, operation on a semimicro scale, and precision in the determination of the ratios. The meaning of the values here reported is discussed in relation to other values of migration ratios, in terms of Hammett's σ-values, and with reference to the concept of neighboring group participation.

Introduction

One of the simplest possible systems available for investigating the relative migrations of aryl or alkyl groups may be represented as



$$\begin{matrix} A \\ B \end{matrix}\!\!>\!CH-CH_2OH \longrightarrow$$

$$A-\underset{}{\overset{OH}{\overset{|}{C}H}}-CH_2B + A-CH_2-\overset{OH}{\overset{|}{C}H}-B + A-CH{=}CH-B$$

Such systems consist only of the two groups, A and B, capable of migration; a two-carbon chain offering the opportunity of rearrangement; and the grouping, -OH, which offers a reactive site where a rearrangement reaction may be initiated with rea-

---

[1] This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory. Presented in part at the Milwaukee Meeting of the American Chemical Society, March 30–April 3, 1952.

[2] Member of the Research Participation program sponsored jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute of Nuclear Studies; permanent address: University of Oklahoma, Norman, Oklahoma.