

Aqueous Fluorination of Carboxylic Acid Salts

V. GRAKAUSKAS

Environmental Systems Division, Aerojet-General Corporation, Azusa, California 91702

Received February 19, 1969

Direct fluorination of aqueous alkali salts of malonic, succinic, glutaric, adipic, azelaic, and sebacic acids proceeded with decarboxylation yielding ω -fluorocarboxylic acids and α,ω -difluoroalkanes. Monocarboxylic acids yielded 1-fluoroalkanes. Nonanoic acid, decanoic acid, and monomethyl adipate were used as substrates. 1-Fluoroalkanes and α,ω -difluoroalkanes underwent additional random fluorination. Fluorination of aqueous sodium *p*-nitrobenzoate gave *p*-fluoronitrobenzene. An ionic mechanism is proposed for these decarboxylative fluorination reactions.

As a part of a program on direct liquid phase fluorination of organic compounds in progress at this laboratory for the past several years, the fluorination of aqueous alkali salts of aliphatic carboxylic acids was investigated. The primary objective of this work was to extend the scope of liquid phase fluorination technique, previously applied in the fluorination of nitrogenous compounds,^{1,2} nitronate salts,³ aromatic compounds,^{4,5} and aliphatic esters,⁶ to other classes of organic compounds.

Electrochemical fluorination of short-chain carboxylic acids yields predominantly perfluoroalkanes,⁷ but small amounts of the corresponding perfluoroacyl fluorides have also been obtained.⁸ Carboxylic acids with six or more carbon atoms yield cyclic ethers as the major products.⁹ The electrochemical fluorination of acyl halides to perfluoro acid fluorides is one of the most important applications of the electrochemical method. Dibasic acid fluorides, such as adipoyl and succinoyl, have been fluorinated in this manner to give dibasic perfluoro acid fluorides and monoacid fluorides.⁸ The partial electrochemical fluorination of propionic and butyric acids was reported¹⁰ to give mixtures of mono-fluoro derivatives in very low yields.

Very little work has been reported on direct fluorination of carboxylic acids. Bockemuller¹¹ obtained β - and γ -fluoro derivatives in the liquid phase fluorination of *n*-butyric acid, its anhydride, and chloride, and β -fluoroisobutyric acid in the fluorination of isobutyric acid. Bockemuller also investigated direct fluorination of acetic, succinic, and glutaric anhydrides, and acetic acid, in carbon tetrachloride, but found that all these substrates were unreactive. Miller and Prober¹² studied exhaustive fluorination of acetyl fluoride in the vapor phase at 100° and reported low yields of fluoroacetyl fluoride and difluoroacetyl fluoride. Liquid phase fluorination of acetic anhydride gave fluoroacetic acid and difluoroacetic acid.⁶

Fichter and Brunner,¹³ whose work comes closest to

the present study as far as the experimental technique is concerned, investigated the fluorination of aqueous potassium acetate in the presence of potassium carbonate and obtained methanol, formaldehyde, carbon dioxide, and ethylene. Fluorination of potassium propionate gave ethanol, acetaldehyde, and ethylene.

In the present work the fluorinations were conducted by passing fluorine diluted with nitrogen into aqueous solutions of alkali salts of carboxylic acids at 0–5° and, in some cases, at ambient temperatures. Thus, the fluorination of aqueous disodium adipate using 2 mol of fluorine at 0–5° was completed in 5 hr. The reaction proceeded smoothly and fluorine was well consumed. At the end of the reaction *ca.* 40% of the adipic acid was recovered. The major reaction product, obtained in 40% yield (23% conversion), was identified as 5-fluoropentanoic acid on the basis of its elemental analysis, nmr spectra (see Experimental Section for details), and the reported¹⁴ physical properties for the compound. The acid was also esterified to the known methyl 5-fluoropentanoate.

A small amount of a volatile liquid obtained in the above experiment analyzed for approximately C₄H₇F₃. Its infrared spectrum showed a typical fluoroalkane structure, and gas chromatographic analysis indicated that the material was a mixture of several compounds. Based on the analytical data and its physical properties (bp 75–80°), the material appeared to be a mixture of randomly fluorinated butanes. The individual components were not isolated in this case, and it is possible that some of the more volatile fluorobutane isomers were lost during the process of fluorination.

Since the characterization of the fluoroalkane mixture obtained in the fluorination of disodium adipate presented some experimental problems, the fluorination of longer chain dicarboxylic acids was examined next with the primary objective of characterizing α,ω -difluoroalkanes. The fluorination of disodium sebacate using 2 mol of fluorine gave a liquid boiling in the range of fluoroalkanes. The gas chromatographic analysis showed that this material was a mixture of at least five components. The compound present in the mixture at *ca.* 60% concentration was separated by gas chromatography and identified as 1,8-difluoroalkane on the basis of elemental analysis and nmr spectra.

A small amount of a high-boiling liquid, isolated on further distillation of the crude reaction product, was identified as 9-fluorononanoic acid on the basis of reported¹⁴ physical properties. The acid was also esterified to the known¹⁴ ethyl 9-fluorononanoate. In this

(1) V. Grakauskas, Abstracts, the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 23M.

(2) V. Grakauskas, Third International Symposium on Fluorine Chemistry, Munich, Sept 1965.

(3) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).

(4) V. Grakauskas, *ibid.*, in press.

(5) V. Grakauskas, Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967.

(6) V. Grakauskas, *J. Org. Chem.*, **34**, 963 (1969).

(7) For general discussion, see M. Stacey, J. C. Tatlow, and A. G. Sharpe, *Advan. Fluorine Chem.*, **1**, 145 (1960).

(8) H. M. Scholberg and H. G. Brice, U. S. Patent 2,717,871 (1955).

(9) C. F. Irwin, R. G. Brenner, A. F. Benning, F. B. Downing, H. M. Parmelee, and W. V. Wirtz, *Ind. Eng. Chem.*, **39**, 350 (1947).

(10) C. Slesser and S. R. Schram, Ed., "Preparation, Properties, and Technology of Fluorine and Organic Fluorine Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p 485.

(11) W. Bockemuller, *Ann.*, **506**, 20 (1933).

(12) W. T. Miller and M. Prober, *J. Amer. Chem. Soc.*, **70**, 2602 (1948).

(13) F. Fichter and E. Brunner, *Helv. Chim. Acta*, **12**, 573 (1929).

(14) F. L. M. Pattison, S. B. D. Hunt, and J. B. Stothers, *J. Org. Chem.*, **21**, 883 (1950).

Anal. Calcd for $C_5H_8FO_2$: C, 50.0; H, 7.55; F, 15.8. Found: C, 50.2; H, 7.1; F, 15.4.

The fluorine nmr spectrum exhibited one signal at ϕ 219.5, a triplet, $J_{HF_{gem}} = 47.1$ cps, of triplets, $J_{HF_{vic}} = 25.9$ cps (superposition of triplets made the signal appear as a symmetrical quintet), with additional fine 1-3 H-F splitting. The proton nmr spectrum exhibited five signals: a singlet at δ 11.70 was assigned to the carboxylic proton; a doublet, $J_{HF} = 47.6$ cps of triplets, $J_{H-H} \cong 5.5$ cps, at δ 4.44 to the FCH_2 protons; a triplet at δ 2.41 to the $-CH_2CO_2H$ protons; and two partially superimposed complex multiplets centering at δ 1.62 and 1.87 to the protons of β and γ methylene groups. The area ratio of the signals was approximately 1:2:2:2:2.

Redistillation of methylene chloride removed in the isolation of the acid yielded 7.5 g of a colorless liquid, bp 75-80°. The infrared spectrum showed bands at 3.4 (m), 3.5 (m), 6.83 (w), 7.21 (m), and a broad absorption envelope at 8.9-9.7 μ .

Anal. Calcd for $C_4H_6F_3$: C, 42.9; H, 6.2; F, 50.9. Found: C, 41.8; H, 5.8; F, 51.8.

Methyl 5-Fluoropentanoate.—To a solution of 6.0 g of 5-fluoropentanoic acid above in 50 ml of methanol was added 2 drops of concentrated sulfuric acid and the mixture was refluxed for 5 hr. The solution was cooled to 10°, added to 200 ml of ice water, and extracted with three 50-ml portions of methylene chloride. The combined extracts were distilled to give 5.5 g of methyl 5-fluoropentanoate: bp 62-63° (18 mm); n_D^{25} 1.3975 [lit.¹⁷ bp 72-74° (25 mm); n_D^{25} 1.3973].

Fluorination of Sodium Methyl Adipate.—A solution of 80 g (0.5 mol) of monomethyl adipate in 750 ml of water containing 20 g (0.5 mol) of sodium hydroxide was fluorinated at 3-5° until 0.5 mol of fluorine was consumed. The fluorination mixture was made basic by adding 15 g of sodium hydroxide and the resulting solution was extracted with 100 ml of methylene chloride. The extract was distilled to give 19 g of a colorless liquid: bp 74-75° (25 mm); n_D^{25} 1.3979; identified as methyl 5-fluoropentanoate¹¹ [lit.¹⁴ bp 72-74° (25 mm); n_D^{25} 1.3973]; yield 14.2%.

The fluorine nmr spectrum in carbon tetrachloride exhibited a triplet, $J_{HF_{gem}} = 47.5$ cps, of triplets, $J_{HF_{vic}} = 25.7$ cps, at ϕ 219.5. The proton nmr spectrum exhibited five signals: a doublet, $J_{HF} = 47.4$ cps, of triplets, $J_{H-H} \cong 5.5$ cps, assigned to the FCH_2 protons; a singlet at δ 3.68, to the OCH_2 proton of the ester group; a triplet of δ 2.38, to the $-CH_2CO_2-$ protons; and two partially overlapping multiplets centered at δ 1.62 and δ 1.87, to the protons of β and γ methylenes. The area ratio of the above signals was 2:3:2:2:2. A very weak doublet of δ 5.70, $J_{HF} \cong 51$ cps, was assigned to the $-CO_2CH_2F$ protons of fluoromethyl 5-fluoropentanoate, present as an impurity, on the basis of reported⁶ proton nmr spectrum of fluoromethyl esters.

Fluorination of Disodium Sebaccate.—A solution of 101 g (0.5 mol) of sebaccic acid in 1500 ml of water containing 42 g (1.05 mol) of sodium hydroxide was fluorinated at $10 \pm 5^\circ$ until 1 mol of fluorine was consumed (3.5 hr). The fluorination mixture was made basic with 100 ml of 50% aqueous sodium hydroxide and extracted with three 100-ml portions of diethyl ether. The combined ether extracts were distilled to give 22 g of a colorless liquid: bp 34-36° (0.2 mm); n_D^{25} 1.3885 (lit.³⁰ for 1,8-difluorooctane, n_D^{25} 1.3933).

Anal. Calcd for $C_8H_{10}F_3$: C, 57.1; H, 8.8; F, 33.9. Found: C, 57.1; H, 8.7; F, 33.9.

The proton nmr spectrum in carbon tetrachloride exhibited a very intense broad signal centered at δ 1.6, a weak complex multiplet at δ 1.67, and two complex multiplets of equal area at δ 4.0 and 4.75. The chemical shift and the structure of the latter two multiplets suggested that they represented several superimposed doublets of triplets of FCH_2 groups. The fluorine nmr spectrum exhibited six complex multiplets at ϕ 116.2, 182.6, 185.0, 189.7, 219.5, 222.1, and 230.9, the most intense of which at ϕ 219.5, an overlapping triplet, $J_{HF_{gem}} = 47.6$ cps, of triplets, $J_{HF_{vic}} \cong 24$ cps, was assigned to the terminal FCH_2 fluorines of 1,8-difluorooctane based on analogy with the fluorine nmr spectra of 5-fluoropentanoic acid and methyl 5-fluoropentanoate (see above). The infrared spectrum indicated a typical fluoroalkane structure.

Gas chromatographic analysis using 24 ft \times 1/4 in. column of 10% Carbowax 4000 on Fluoropak 80, 95°, He flow rate 50 cc/min, showed that the mixture at ca. 60% concentration was sep-

arated (retention time 42 min) and identified as 1,8-difluorooctane.

Anal. Calcd for $C_8H_{16}F_2$: C, 63.96; H, 10.74; F, 25.30. Found: C, 63.4; H, 10.4; F, 25.4.

The proton nmr spectrum (in microcell) exhibited a doublet, $J_{HF} = 47.7$ cps, of triplets at δ 4.35 assigned to the FCH_2 protons (the high-field triplet was broadened). A poorly resolved multiplet at δ 1.85 was assigned to the FCH_2CH_2- methylene protons, and a broadened signal at δ 1.39 to the remaining protons in the chain. The area ratio of the signals agreed well with the required 1:1:2.

The alkaline aqueous phase was acidified with 50% aqueous sulfuric acid. A white solid which precipitated on acidification was filtered, washed with three 100-ml portions of diethyl ether, and dried in air: weight 48.5 g; mp 133-135°, alone or when mixed with an authentic sample of sebaccic acid. The filtrate was extracted with four 100-ml portions of diethyl ether. The etheral extracts, combined with the ether washings above, were distilled to give 3.5 g of a colorless liquid, bp 102-104° (0.2 mm), n_D^{25} 1.4285, which was identified as 9-fluorononanoic acid on the basis of the reported¹⁴ boiling point, 100-101° (0.15 mm), and refractive index, n_D^{25} 1.4289, for the compound.

9-Fluorononanoic acid above, 2.5 g, was dissolved in 10 ml of absolute ethanol, 1 drop of concentrated sulfuric acid added, and the mixture was refluxed for 4.0 hr. The solution was cooled, added to 50 g of crushed ice, and the resulting mixture was extracted with 15 ml of methylene chloride. The extract was distilled to give 2.5 g of colorless liquid: bp 76-78° (0.2 mm); n_D^{25} 1.4190. The compound was identified as ethyl 9-fluorononanoate on the basis of the reported¹⁴ boiling point, 87-88° (1 mm), and refractive index, 1.4191, for the ester.

In another experiment, a solution of 162 g (0.8 mol) of sebaccic acid in 1500 ml of water containing 132 g of 85% potassium hydroxide (2.0 mol of KOH) was fluorinated at 25-30° until 1.5 mol of fluorine was consumed. At this stage, the fluorination was interrupted, another 1.0 mol of potassium hydroxide added to the reaction mixture, and the fluorination was resumed and continued until an additional 1.0 mol of fluorine was consumed. The pH of the reaction mixture at the end of fluorination was 6-7, and a large amount of water-insoluble heavy liquid was present. The mixture was acidified with 50% sulfuric acid to pH 1-2, and extracted with three 200-ml portions of methylene chloride. The combined extracts were distilled to give (1) 91 g of colorless liquid, bp 33-36° (0.2 mm); (2) 20 g of slightly dark liquid, bp 101-105° (0.1 mm); and (3) dark, viscous distillation residue amounting to 20 g.

Anal. of fraction 1. Calcd for $C_8H_{10}F_3$: C, 57.1; H, 8.8; F, 33.9. Found: C, 55.6; H, 8.2; F, 34.8.

The proton and fluorine nmr spectra were identical with those above, with the exception that the ϕ 116.4 signal in the fluorine spectrum was resolved into a doublet, $J_{HF_{gem}} = 56.8$ cps, of triplets, $J_{HF_{vic}} = 16.6$ cps, suggesting the presence of $-CHF_2$ groups.

The material of fraction 2 above was esterified with ethanol yielding 12.5 g of ethyl 9-fluorononanoate: bp 76-79° (0.2 mm); n_D^{25} 1.4190.

The distillation residue (3) was not characterized, but probably contained mainly unreacted sebaccic acid. The material crystallized at room temperature.

Fluorination of Disodium Azelate.—A solution of 376.5 g (2.0 mol) of azelaic acid in 3500 ml of water containing 160 g (4.0 mol) of sodium hydroxide was fluorinated at 5° until 3.0 mol of fluorine was consumed (3.0 hr). The fluorination mixture was acidified with 200 g of concentrated sulfuric acid and filtered. The filter cake was washed with two 250-ml portions of methylene chloride and the white solid was dried: weight 150 g; mp 105-106°, alone or when mixed with an authentic sample of azelaic acid. The aqueous filtrate was extracted with two 400-ml portions of methylene chloride, the extracts were combined with the methylene chloride washings above, and the combined solution was distilled to give 60 g of a colorless liquid, bp 30-35° (0.2 mm). The material was redistilled to give (1) 4.5 g of colorless liquid, bp 23-25° (0.5 mm), and (2) 55 g of colorless liquid, bp 32-33° (0.1 mm).

Anal. of fraction 1. Calcd for $C_7H_{12}F_4$: C, 48.8; H, 7.0; F, 44.2. Found: C, 48.0; H, 6.8; F, 45.0.

Anal. of fraction 2. Calcd for $C_7H_{14}F_2$: C, 61.7; H, 10.4; F, 29.9. Calcd for $C_7H_{13}F_3$: C, 54.5; H, 8.5; F, 37.0. Found: C, 56.8; H, 9.2; F, 31.2.

(30) F. L. M. Pattison and R. G. Woolford, *J. Amer. Chem. Soc.*, **79**, 2308 (1957).

The proton nmr spectrum of fraction 2 exhibited five broadened, partially superimposed complex multiplets centered at approximately δ 4.4, 3.6, 2.3, 1.8, and 1.4. The δ 4.4 and δ 3.6 multiplets, equal in area, seem to represent the FCH_2 -protons of several α -fluoroalkanes, $J_{\text{HFgem}} = 47$ cps.

The distillation residue amounting to ca. 100 g, bp $> 80^\circ$ (0.1 mm), was dissolved in 250 ml of methanol, 2 drops of concentrated sulfuric acid added, and the resulting solution was refluxed for 6 hr. The mixture was cooled, added to 1200 ml of ice water, and extracted with 100 ml of methylene chloride. The extract was distilled to give 65 g of colorless liquid, bp 59 – 61° (0.1 mm), identified as methyl 8-fluorooctanoate on the basis of the reported¹⁴ boiling point, 106.5 – 107° (9 mm), for the ester.

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{FO}_2$: C, 61.3; H, 9.7; F, 10.8. Found: C, 60.9; H, 9.4; F, 11.4.

The proton nmr spectrum exhibited five signals. A doublet, $J_{\text{HF}} = 47.7$ cps, of triplets, $J_{\text{HH}} \cong 5.5$ cps, at δ 4.34 was assigned to the FCH_2 protons; a singlet of δ 3.64 to the $-\text{OCH}_3$ protons of the ester group; a triplet at δ 2.29 to the $-\text{CH}_2\text{CO}_2-$ protons; a poorly resolved multiplet at δ 1.75 to the $-\text{CH}_2\text{CH}_2\text{CO}_2-$ protons; and an intense broad signal centered at δ 1.38 to the protons of the internal methylene groups. The area ratio of the signals was approximately 2:3:2:2:8. The fluorine nmr spectrum exhibited a single signal, a triplet, $J_{\text{HFgem}} = 48$ cps, of triplets, $J_{\text{HFvic}} \cong 24$ cps, at ϕ 218.7. Additional fine splitting due to 1,3 H-F coupling was visible.

In another experiment, a solution of 94 g (0.5 mol) of azelaic acid in 1500 ml of water containing 44 g (1.1 mol) of sodium hydroxide was fluorinated at 0 – 5° until 1.1 mol of fluorine was consumed (2.5 hr) (very smooth fluorination); pH of reaction mixture at the end of the run was 5–6. The reaction mixture was extracted with two 150-ml portions of methylene chloride and the combined extracts were distilled to give 32 g of a colorless liquid, bp 33 – 35° (0.2 mm).

Anal. Found: C, 53.5; H, 7.8; F, 33.0.

Gas chromatographic analysis indicated that the material contained at least six components. The most predominant compound present in the mixture, 1,7-difluoroheptane, was separated by gas chromatography.

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{F}_2$: C, 61.73; H, 10.36; F, 27.90. Found: C, 60.9; H, 9.7; F, 28.5.

The proton nmr spectrum exhibited three signals. A doublet, $J_{\text{HF}} = 47.3$ cps, of triplets, $J_{\text{HF}} \cong 5.6$ cps, at δ 4.46 assigned to the FCH_2 protons, a complex multiplet centered at δ 1.88, assigned to the FCH_2CH_2- protons, a broad signal centered at δ 1.40, assigned to the protons of the three remaining methylene groups. The area ratio of the three signals was approximately 2:2:3.

On further distillation the crude reaction product yielded 35 g of a colorless liquid, bp 85 – 88° (0.05 mm), which partially solidified to a white crystalline solid at room temperature. The material was identified as 8-fluorooctanoic acid on the basis of reported¹⁴ physical properties: bp 145 – 148° (10 mm); mp 34 – 35° .

Anal. Calcd for $\text{C}_8\text{H}_{15}\text{FO}_2$: C, 59.2; H, 9.3; F, 11.7. Found: C, 58.6; H, 8.7; F, 13.5.

Fluorination of Disodium Malonate.—A solution of 208 g (2.0 mol) of malonic acid in 1600 ml of water containing 160 g (4.0 mol) of sodium hydroxide was fluorinated at 0 – 5° until 2.0 mol of fluorine was consumed. The solution was acidified with 50% sulfuric acid and extracted with six 100-ml portions of diethyl ether. The combined ether extracts were dried, filtered, and the filtrate was distilled to give 2.2 g of a colorless liquid, bp 37 – 39° (0.2 mm), $n_D^{25} 1.3800$, which solidified at room temperature. The differential thermal analysis showed an endotherm of 166° , indicating that this was the boiling point of the compound. The compound was identified as fluoroacetic acid on the basis of reported¹⁶ physical properties, bp 167 – 168.5 , mp 31 – 32° , for the acid.

The proton nmr spectrum in water exhibited a doublet, $J_{\text{HF}} = 47$ cps, at δ 5.00. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (SDSS) was used as internal reference.

4-Fluorobutyric Acid.—A solution of 33 g (0.25 mol) of glutaric acid in 450 ml of water containing 40 g of 85% potassium hydroxide (0.6 mol of KOH) was fluorinated at 10° until 0.3 mol of fluorine was consumed. The fluorination mixture was acidified with 50% sulfuric acid, extracted with three 100-ml portions of methylene chloride, and the combined extracts were distilled to give 4.5 g of 4-fluorobutyric acid: bp 62 – 63° (3 mm); $n_D^{25} 1.4010$ [lit.¹⁴ bp 60 – 62° (2 mm)].

3-Fluoropropionic Acid.—A solution of 23.6 g (0.2 mol) of succinic acid in 450 ml of water containing 0.5 mol of potassium hydroxide was fluorinated and the reaction product isolated as above to give 2.1 g of 3-fluoropropionic acid: bp 100 – 101° (25 mm); $n_D^{25} 1.3884$ [lit.¹⁴ bp 97° (29 mm); $n_D^{25} 1.3888$].

Fluorination of Sodium Nonanoate.—A solution of 79 g (0.5 mol) of nonanoic acid in 1400 ml of water containing 22 g (0.55 mol) of sodium hydroxide was fluorinated at 0 – 5° until 0.5 mol of fluorine was consumed (3.0 hr). The reaction mixture was extracted with two 150-ml portions of methylene chloride and the combined extracts were distilled to give 18 g of a colorless liquid, bp 50 – 60° (25 mm). Gas chromatographic analysis indicated that the material was a mixture of at least six components. The predominant component present in the mixture to the extent of ca. 50% was separated by gas chromatography and identified as 1-fluorooctane.

Anal. Calcd for $\text{C}_8\text{H}_{17}\text{F}$: C, 72.7; H, 13.0; F, 14.4. Found: C, 71.7; H, 12.6; F, 14.4.

The proton nmr spectrum exhibited a doublet, $J_{\text{HFgem}} = 47.5$ cps, of triplets, $J_{\text{HHvic}} \cong 5.6$ cps, at δ 4.38 assigned to the FCH_2- protons; a broad poorly resolved multiplet centered at δ 1.9 and an intense broad signal at δ 1.37 were assigned to the protons of the other six methylene groups; and a poorly resolved triplet at δ 0.88, assigned to the protons of the CH_3 group. The approximate area ratio of FCH_2- , $-\text{CH}_2-$, and $-\text{CH}_3$ signals was the required 2:12:3.

The aqueous solution was acidified with 50% sulfuric acid, extracted with four 150-ml portions of diethyl ether, and the combined extracts were distilled to give 51 g of colorless liquid, bp 85 – 86° (0.1 mm), which was identified as the starting material (65% recovery) by comparing its infrared spectrum with that of nonanoic acid. Elemental analysis indicated no fluorine.

Fluorination of Potassium Decanoate.—A solution of 43 g (0.25 mol) of decanoic acid in 350 ml of water containing 0.3 mol of potassium hydroxide was fluorinated at 15 – 20° until 0.25 mol of fluorine was consumed. At this stage, the fluorination was interrupted, another 0.2 mol of potassium hydroxide was added to the solution, and the fluorination was resumed and continued until another 0.25 mol of fluorine was consumed. Total fluorination time was 3.5 hr. The reaction mixture was made basic with 50% aqueous potassium hydroxide and extracted with 75 ml of methylene chloride. The extract was distilled to give 19 g of a colorless liquid: bp 30 – 40° (0.3 mm); $n_D^{25} 1.4015$.

Anal. Calcd for $\text{C}_9\text{H}_{19}\text{F}$: C, 74.0; H, 13.0; F, 13.0. Calcd for $\text{C}_9\text{H}_{18}\text{F}_2$: C, 65.8; H, 11.0; F, 23.2. Found: C, 67.8; H, 12.2; F, 19.7.

The infrared spectrum was typical for fluoroalkanes: at 3.4 and 3.5 μ , aliphatic CH stretching; at 6.85 and 7.23 μ , $-\text{CH}_2$ and CH_3 deformations; a broad absorption envelope with peaks at 8.9, 9.5, and 9.9 μ indicated CF bonding.

Fluorination of Sodium *p*-Nitrobenzoate.—A solution of 167.1 g (1.0 mol) of *p*-nitrobenzoic acid in 1200 ml of water containing 44 g (1.1 mol) of sodium hydroxide was fluorinated at 0 – 5° until ca. 0.5 mol of fluorine was consumed. The fluorination mixture was made strongly alkaline with 20 g (0.5 mol) of sodium hydroxide and the resulting solution was extracted with two 150-ml portions of methylene chloride. The combined extracts were distilled to give 2.8 g of *p*-fluoronitrobenzene: bp 202 – 204° ; $n_D^{25} 1.5350$ (lit.^{31,32} bp 203 – 204° ; $n_D^{25} 1.5340$).

Anal. Calcd for $\text{C}_6\text{H}_4\text{NFO}_2$: F, 13.5. Found: F, 14.1.

The infrared spectrum was identical with that of an authentic sample of *p*-fluoronitrobenzene.

Registry No.—Disodium adipate, 7486-38-6; sodium methyl adipate, 5877-45-2; disodium sebacate, 17265-14-4; disodium azelate, 17265-13-3; disodium malonate 141-95-7; sodium nonanoate, 14047-60-0; potassium decanoate, 13040-18-1; sodium *p*-nitrobenzoate, 3847-57-2.

Acknowledgment.—The author wishes to thank Mr. K. Inouye for the elemental analysis, Dr. H. M. Nelson for the nmr spectra, and Dr. K. Baum for useful discussions and help with the manuscript.

(31) G. C. Finger and C. W. Kruse, *J. Amer. Chem. Soc.*, **78**, 6034 (1956).

(32) N. N. Vorozhtsov and G. G. Yakobson, *Khim. Nauka i Promy.*, **3**, 403 (1958).