Long Chain Alkanoic and Alkenoic Acids with Perfluoroalkyl Terminal Segments[1]

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In order to study the nature of the theoretically interesting and potentially useful long chain alkanoic and alkenoic acids having terminal perfluoroalkyl segments, synthetic routes to R_f(alkylene)COOH have been devised. Free radical chain reaction of iodoperfluoroalkanes and terminal unsaturated acids gave 90–100% yields of $R_fCH_2CHI(CH_2)_nCOOH$ which were reduced to alkanoic acids or hydrolyzed to alkenoic acids having a terminal R_f "tail." Three series of the so-called segmented acids were synthesized, in which R_f is normal, *iso*- or *sec*-perfluoroalkyl and the alkylene segment is two to sixteen carbons long. These alkanoic acids are similar to nonfluorinated compounds in reactivity but have unique surface-active and wettability properties. The enhancing effect of $CF_3(CF_2)_6$— on the ionization of the acids is transmitted through alkylene segments as long as five carbons.

Perfluoroalkanoic acids and their derivatives are noted for unusual chemical and physical properties.[2,3] For example, monolayers of perfluorodecanoic acid are nonwettable by any known class of liquids.[4] Long chain ω-trifluoroalkanoic acids,[5] surprisingly, failed to show such unusual effects,[6] and in wetting phenomena actually were inferior to alkanoic acids. We were interested in learning the effect of variations in the ω-perfluoroalkyl (R_f) group on the properties of alkanoic acids, having both longer and more complex R_f segments.

A convenient and high yield, 2-step synthesis

$$R_FI + CH_2{=}CH(CH_2)_{m-2}COOR \xrightarrow{R\cdot}$$
$$R_fCH_2CHI(CH_2)_{m-2}COOR \xrightarrow[alc]{Zn} R_f(CH_2)_mCOOR$$

was discovered[7] which provided a homologous series of long chain alkanoic acids and derivatives with terminal perfluoroalkyl segments. Iodoperfluoroalkanes with an even or odd number of carbons were obtained by telomerization of tetrafluoroethylene with pentafluoroiodoethane or 1-iodoperfluoropropane at 200–220°; those with branching at the end were prepared in this way from 2-iodoperfluoropropane.[8] This compound and 2-iodoperfluorohexane were two secondary iodides used in the addition reaction. During this work a related synthesis based on the addition of perfluoroalkanesulfonyl chlorides to unsaturated acids appeared.[9] Short chain homologs of $R_f(CH_2)_mCOOH$ are known.[10]

Results

Peroxide- or azonitrile-induced addition at 80–150° of iodoperfluoroalkanes to unsaturated acids proved to be far superior to thermally or ultraviolet light-induced reactions.[11] The initial adduct was obtained in excellent yield and high conversion in a short reaction time; those listed in Table I were distilled or crystallized. In most cases the rather sensitive iodo compound was not purified further but was converted directly to the solid, saturated acid derivative by reduction with zinc in alcohol.

Many of the adducts and esters of the reduced acids were high boiling viscous oils which could not be readily purified, even by precision fractionating columns. However, the solid acids were in each case recrystallized to a constant m.p., and were obtained in pure condition. All of the new alkanoic acids with perfluoroalkyl segments are listed in Table II, while the alternative methods used and *alkenoic* acids prepared are described in the Experimental.

Although the free radical addition of CF_3I to olefinic compounds is well known,[8-11] long chain terminal olefins have not been used previously and present special problems. The reaction is deceptively simple. In common with free radical chain reactions, traces of inhibitory substances completely prevented addition from occurring, and at the same time only a small amount of a free radical initiator (peroxide or azonitrile) was required to give complete conversion of pure reactants to adduct (Table I). The exothermic reaction was controlled by addition of one reactant to the other, and by external cooling. The react-

(1) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 3–8, 1961; Abstracts, p. 6M.

(2) (a) E. A. Kauck and A. R. Diesslin, *Ind. Eng. Chem.*, **42**, 2332 (1951); (b) G. B. Blake, A. H. Ahlbrecht, and H. G. Bryce (presented at the 126th National Meeting of the American Chemical Society, New York, N. Y.), *Div. Petrol. Chem., Gen. Papers*, **32**, 131–42 (1954).

(3) N. L. Jarvis and W. A. Zisman, *J. Phys. Chem.*, **63**, 727 (1959); *ibid.*, **64**, 150 (1960); *ibid.*, **64**, 157 (1960).

(4) F. Shulman and W. A. Zisman, *J. Am. Chem. Soc.*, **74**, 2123 (1952); *J. Colloid Sci.*, **7**, 465 (1952).

(5)(a) G. Gavlin and R. G. Maquire, *J. Org. Chem.*, **21**, 1342 (1956); (b) N. O. Brace and G. J. Mantell, *ibid.*, **26**, 5176 (1961).

(6) (a) H. W. Fox, *J. Phys. Chem.*, **61**, 1058 (1957); (b) E. G. Shafrin and W. A. Zisman, *ibid.*, **61**, 1016 (1957).

(7) N. O. Brace, *J. Org. Chem.*, **27**, 3023, 3027 (1962).

(8) (a) R. N. Haszeldine, *J. Chem. Soc.*, 3761 (1953); (b) the author is indebted to Dr. J. F. Harris for samples of $(CF_3)_2CF(CF_2CF_2)_nI$ (n = 1, 2, and 3) which were prepared by this method. This work will be reported separately.

(9) G. V. D. Tiers, U. S. Patent 2,951,051 (August 30, 1960).

(10) J. D. Park, E. R. Larsen, H. V. Holler, and J. R. Lacher, *J. Org. Chem.*, **23**, 1166 (1958).

(11) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953); K. Leedham and R. N. Haszeldine, *ibid.*, 1634 (1954).

TABLE I

SYNTHESES OF IODOALKANOIC ACIDS AND ESTERS WITH TERMINAL PERFLUOROALKYL SEGMENTS

Compound	Reaction conditions: Moles Olefin	Moles R_fI	Initiator[a] (mmoles)		Time, hr.	Temp.	Product: % of theory Conv.	Yield	Properties: B.p./mm.	$n^{25}D$	Calcd. C	Calcd. F	Calcd. H	Calcd. I	Found C	Found F	Found H	Found I
$(CF_3)_2CFCH_2CHI(CH_2)_8COOC_2H_5$	0.2	0.2	A	3.0	3	55–115	85	95	125°/0.57	1.4300	37.8	26.2	4.8	25.0	37.8	25.8	4.8	24.7
$CF_3(CF_2)_5CH_2CHI(CH_2)_8COOC_2H_5$	.1	.13	A	1.2	8	82–86	71	98	90°/0.9	1.4099	29.5		2.9		29.7		3.0	
$CF_3(CF_2)_6CH_2CHICH_2COOC_2H_5$	.05	.10	A	1.8	14	81	90	100	82°/0.15	1.3809	25.6		1.7	20.8	25.7		1.7	20.7
$CF_3(CF_2)_6CH_2CHI(CH_2)_2COOH$	.2	.24	A	2.4	2	80–150[b]	42	100	M.p. 76–77°		24.2		1.35	21.2	24.4		1.4	21.4
$CF_3(CF_2)_6CH_2CHI(CH_2)_8COOC_2H_5$	.24	.2	D	5.5	7.5	140–145	92	95	136°/0.2[c]	1.4022	33.9	40.2	3.4	17.9	34.8	40.5	3.4	16.2
$CF_3(CF_2)_6CH_2CHI(CH_2)_{14}COOH$	.05	.05	A	1.2	7.0	80–100	98	98	M.p. 47.5–49°[d]		37.3			16.6		35.0[e]		15.9[e]

[a] A = azobisisobutyronitrile; D = di-*t*-butyl peroxide. [b] Exothermic reaction gave some free iodine and low conversion. [c] Too unstable and high boiling to fractionate in an efficient column; probably contained a small amount of $CH_2{=}CH(CH_2)_8COOC_2H_5$. [d] Not recrystallized, probably contained a small amount of $CH_2{=}CH(CH_2)_{14}COOH$; converted to pure $CF_3(CF_2)_6(CH_2)_{16}COOH$; see Table II.

ant ratio was not critical in those cases where the terminal olefin does not readily polymerize. With acrylates and to a lesser degree with ethyl 3-butenoate (an allyl compound) telomerization occurred, which afforded products having structures

such as $R_f(CH_2\underset{|}{C}HCOOR)_nI$ (n = 1, 2, 3). By employing an excess of the iodoperfluoroalkane, it was possible to keep n small.

Our first attempts to synthesize these adducts using the known methods of ultraviolet light initiation at 30° or thermally induced reaction at 200–225° resulted in complex mixtures from which the desired product could be isolated only with much difficulty in an impure condition. Iodine and hydrogen iodide were produced by photolysis or thermal cracking, also giving olefins which further degraded under these conditions to tarry materials. The terminal olefin which did not react was rearranged to an internal olefin, which of course could then lead to isomeric adducts, as well as to a reduced yield, through chain terminating reactions. To a certain extent these difficulties could be surmounted in thermal reactions by the addition of an ester such as ethyl acetate which reacted with hydrogen iodide to give ethyl iodide and acetic acid.[12] The amount of tar was greatly reduced and the conversion to product was increased; nevertheless, an unsaturated mixture having a lower melting point and higher refractive index than pure material could not be avoided by this procedure (see Table II).

Reduction of the iodo addition compound with zinc and hydrogen chloride in alcohol solution proceeded readily in good yield. A small amount of coupling to "dimeric" compounds was usually observed.[7] Dehydrohalogenation of the iodo addition compound to the alkenoic acid by alkali, and hydrogenation to the saturated segmented acid

$$R_fCH_2CHI(CH_2)_{m-2}COOR \xrightarrow{OH^-} R_fCH{=}CH(CH_2)_{m-2}COOH \xrightarrow[PtO_2]{H_2} R_f(CH_2)_mCOOH$$

using platinum oxide catalyst (hydrogen at 45 p.s.i.), also gave good yields, and coupling was avoided. The segmented acids were prepared by hydrolysis of the nitrile in certain cases, and esters and amides were prepared by known methods.

An alternate route to an all *trans*-alkenoic acid in which the unsaturation was unequivocally adjacent to the R_f group employed the free radical addition of 1-iodoperfluoropropane to 10-hendecynoic acid.

$$CF_3(CF_2)_2I + HC{\equiv}C{-}(CH_2)_8COOH \xrightarrow{R\cdot} CF_3(CF_2)_2CH{=}\underset{\underset{I}{|}}{C}(CH_2)_8COOH \xrightarrow[HOAC]{Zn} C_2F_7CH{=}CH(CH_2)_8COOH$$

(12) N. O. Brace, U. S. Patent 3,016406, (January 9, 1962).

Smooth addition occurred using an azonitrile initiator; reduction of the *trans*-(perfluoropropyl)-10-iodo-10-hendecenoic acid by zinc and acid, previously reported to be stereospecific,[11] gave a single compound according to gas–liquid chromatography. The infrared spectrum showed a strong absorption band of the *trans* internal olefin structure at 10.30 μ. A weaker band at 5.95 μ appeared in this case, and also in the spectra of the alkenoic acids, which has been attributed to the $R_fCH{=}CH-$ group.[11]

16-Heptadecenoic acid (required for synthesis of long chain acids) was prepared from 10-hendecenoic acid by a chain lengthening sequence reported by Hünig and co-workers.[13] Improved conditions for the Wolff–Kishner reduction of 7-keto-16-heptadecenoic acid without isomerization to 15-heptadecenoic acid were worked out. Fractional crystallization of the isomeric mixture obtained under ordinary conditions[13] did not afford the pure compounds.

Properties of Long Chain Terminal Perfluoroalkylalkanoic Acids

Since an alkylene segment separates the strongly electron-withdrawing perfluoroalkyl group from the carboxylic acid function, these compounds undergo reactions typical of acids under normal conditions, in contrast to the somewhat modified chemistry of perfluoroalkanoic acids.[2] Our interest in the new segmented acids stems from the fact, however, that some of the unusual physical properties of perfluoroalkanoic acids and their derivatives may be carried over into the new series, possibly even with heightened effect. This expectation was fulfilled. We have compared the melting point, surface activity, and ionization constants of these new acids with alkanoic and perfluoroalkanoic acids. Other physical properties will be reported separately.

To a marked degree the length of the terminal R_f segment influences the melting point and surface activity of the new segmented acids. Branching in the R_f segment has an important effect also. To a lesser extent the relative lengths of the two dissimilar segments and the total chain length affect the m.p. behavior. In Fig. 1 are plotted the m.p. *vs.* chain lengths of three homologous series of segmented saturated acids along with dotted-in curves for the analogous alkanoic acids and perfluoroalkanoic acids. The segmented nature of the new acids is evident from the shape of the curves. In each series of the segmented acids, one part of the melting point curve parallels the curve for perfluoroalkanoic acids and another part the melting point curves of the alkanoic acids. The transition which may be abrupt or gradual occurs with a

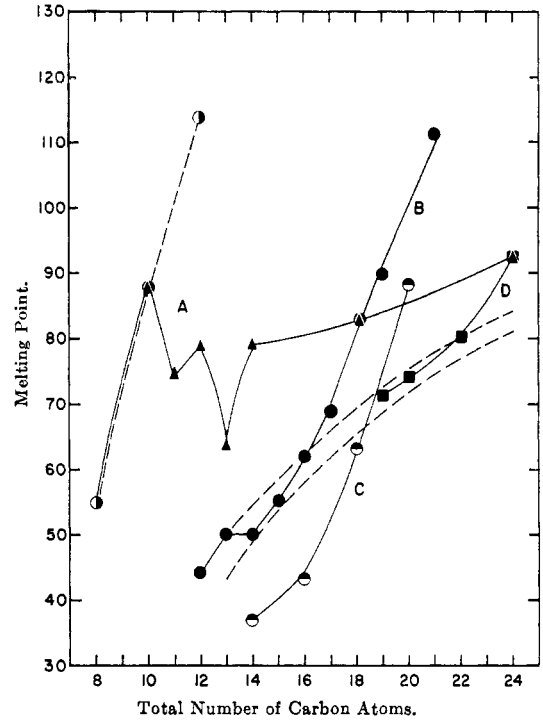

Fig. 1.—Melting point curves of alkanoic, perfluoroalkanoic, and segmented perfluoroalkylalkanoic acids. ◑—$CF_3(CF_2)_{n-2}COOH$; ▲ $CF_3(CF_2)_6(CH_2)_mCOOH$; ● $CF_3(CF_2)_n(CH_2)_{10}COOH$, ($n$ = 0 to 10); ■ $CF_3(CF_2)_n(CH_2)_{16}COOH$, ($n$ = 0 to 6); ◓ $CF_3CF(CF_3)(CF_2)_n(CH_2)_{10}COOH$, ($n$ = 0 to 6); — — — even-carbon alkanoic acids (upper curve) and odd-carbon alkanoic acids (lower curve).

structure having maximum interaction of the R_f and alkylene segments.[14]

As might be expected, a long chain acid with an internal-branched R_f segment, $CF_3(CF_2)_3CF(CF_3)(CH_2)_{10}COOH$, melts much lower than do straight chain analogs. This is also true of segmented acids with unsaturated alkylene segments. The greater stiffness of a $(CF_2)_n$- than a $(CH_2)_n$- sequence is apparent from a comparison of the melting points of the two known homologous series of acids. This and other differences between polytetrafluoroethylene and polymethylene such as the larger cross-sectional area, 29Å.^{2} for $(CF_2)_n$[15] *vs.* 20Å.^{2} [2] for $(CH_2)_n$ are factors responsible for the unusual melting point behavior in our three series of acids.

(13) (a) S. Hünig, E. Benzing, and E. Lücke, *Chem. Ber.*, **90**, 2833 (1957); (b) S. Hünig, E. Lücke, and E. Benzing, *ibid.*, **91**, 129 (1958); (c) S. Hünig and G. Eckardt, *Angew. Chem.*, **72**, 269 (1960).

(14) In the $CF_3(CF_2)_6(CH_2)_mCOOH$ series (curve A) as m is increased, there is first an increase and then an abrupt drop in m.p. to a minimum at $CF_3(CF_2)_6(CH_2)_5COOH$. Further extension of the paraffinic segment gives a curve roughly paralleling the alkanoic acids. For the series having a constant length alkylene segment [—$(CH_2)_{10}$—; curve B] as the R_f group is increased in length, a transition from alkyl- to perfluoroalkyl-like slope occurs near $CF_3(CF_2)_4(CH_2)_{10}COOH$. This corresponds to a similar attainment of maximum perfluoroalkyl-like surface activity in this series of acids.[17] The m.p. curve of the iso series in which R_f is branched at the end of the chain (curve C) also shows a transition, which is less abrupt than that of curve B. The iso acids with short R_f segments have melting points which are below rather than above the corresponding alkanoic acids. (The analogous iso-alkanoic acid melting point curve is nearly superimposable on the *n*-alkanoic acid curve.) The $R_f(CH_2)_{16}COOH$ series (curve D) illustrates the same concept.

(15) C. H. Arrington, Jr., and G. D. Patterson, *J. Phys. Chem.*, **57**, 247 (1953).

TABLE II

SYNTHESES OF TERMINAL PERFLUOROALKYL SEGMENTED ALKANOIC ACIDS

	Product, yield, and properties								
	Conditions[a]			R_fI adduct		$R_f(CH_2)_mCOOC_2H_5$			
Compound	Temp., °C.	Time, hr.	Method	Conv.[b] %	Yield,[b] %	Yield, %	M.p., °C.	B.p., °C./mm.	$n^{25}D$
$CF_3CF_2(CH_2)_{10}COOH$	225	8	T			85[d]	28–28.5	168/10	1.4128
$CF_3CF_2(CH_2)_{16}COOH$	200	6	T			84[e]			
$CF_3(CF_2)_2(CH_2)_{10}COOH$	30	48	L	50[f]	70[f]	70[f]		152/10[d]	1.3944[d]
$CF_3(CF_2)_2(CH_2)_{10}COOH$	260	15	T			50[f]	30–30.5	156/10	1.3872
$CF_3(CF_2)_2(CH_2)_{10}COOH$	215	6	T			62[d,f]		172/20	1.3882[d]
$CF_3(CF_2)_2(CH_2)_{10}COOH$	200	6	TE			95[f,g]			
$CF_3(CF_2)_2(CH_2)_{10}COOH$	145	8	D	86	95	76[h]		96/0.4	
$(CF_3)_2CF(CH_2)_{10}COOH$	55–115	3	A	85	95	80[i]		150/10	1.3884
$CF_3(CF_2)_2(CH_2)_{16}COOH$	200	6	TE			77[d]	52–53	150/0.5	
$CF_3(CF_2)_3(CH_2)_5COOH$	80	8	A	71	98				
$CF_3(CF_2)_3(CH_2)_{10}COOH$	200	6	TE			72		151/10	1.3824
$CF_3(CF_2)_4(CH_2)_{10}COOH$	200	6	TE		100[d]				
$(CF_3)_2CF(CF_2)_2(CH_2)_{10}COOH$	70–75	11	A	87	95	71		123/0.4	1.3803
$CF_3(CF_2)_4(CH_2)_{16}COOH$	200	6	TE			75	51–53	145/0.25	
$CF_3(CF_2)_5(CH_2)_{10}COOH$	85	17	A	70	95	85			
$CF_3(CF_2)_3CF(CF_3)(CH_2)_{10}COOH$	80–90	5	A	95	100	65		129/1.0	1.3744
$CF_3(CF_2)_6(CH_2)_2COOH$	200	6	TE	38[l]		38[l]		99/10	1.3291
$CF_3(CF_2)_6(CH_2)_3COOH$	81	14	A	90	100	86		107/10	1.3362
$CF_3(CF_2)_6(CH_2)_4COOH$	80–155	2	A	42	100				
$CF_3(CF_2)_6(CH_2)_5COOH$	80	7	A	76	95	80		134/10	1.3491
$CF_3(CF_2)_6(CH_2)_6COOH$[j]									
$CF_3(CF_2)_6(CH_2)_{10}COOH$	215	6	T			85[d]	25–28	156/2.5	
$CF_3(CF_2)_6(CH_2)_{10}COOH$	145	7.5	D	92	95	100	36–38		
$(CF_3)_2CF(CF_2)_4(CH_2)_{10}COOH$	75–84	10	A	95	95	75		153/0.6	1.3730
$CF_3(CF_2)_6(CH_2)_{16}COOH$	80–90	7	A	95	95	100	59–59.5		
$CF_3(CF_2)_7(CH_2)_{10}COOH$[m]	140	7	D	100	100	100	42–42.5		
$(CF_3)_2CF(CF_2)_6(CH_2)_{10}COOH$	71–85	10	A	95	95	85	40		
$CF_3(CF_2)_9(CH_2)_{10}COOH$	130–150	9	D	95	95	99	64.5–65		

[a] From equimolar amounts of R_fI and $CH_2{=}CH(CH_2)_{m-2}COOR$ unless otherwise noted. Method indicated: A, α,α'-azobisisobutyronitrile initiator; D, di-*t*-butyl peroxide; T, thermal reaction in shaker tube; TE, thermal reaction in ethyl acetate solution in shaker tube; L, ultraviolet light from internal quartz coil mercury vapor cell. [b] Conversion, yield based on R_fI used up and of $R_f(CH_2)_mCOOR$ obtained from zinc reduction unless otherwise noted. Isolated yields and analyses of R_fI adducts are listed in Table I; many of the compounds were high boiling, viscous oils which could not be readily purified. [c] Yield of compound by hydrolysis of $R_f(CH_2)_mCOOR$ unless otherwise noted; the acids were purified carefully in each instance. [d] Mixture of unsatd. compounds by infrared and hydrolysis to oil. [e] Combined solid and oil fractions. [f] See Experimental. [g] 95% of the product mixture distilled over the range of 100–130°/2.0 mm.; no tar; reduced to CF_3CF_2-$(CF_2CF_2)_n(CH_2)_{10}COONa$ (n = 0, 1, 2; n = 3 was too insoluble to measure) were not so effective in reducing surface tension of water as was the liquid *internal*-branched acid $CF_3(CF_2)_3CF(CF_3)(CH_2)_{10}$-$COONa$ (Fig. 2). Further details of surface activity and liquid contact angle data will be reported separately.

Surface activity of salts of perfluoroalkyl-segmented alkanoic and alkenoic acids in aqueous solution was determined over a range of concentrations as shown in Fig. 2. As the length of the R_f segment in $R_f(CH_2)_mCOONa$ was increased up to seven carbons, the minimum surface tension obtainable dropped from 27 dynes/cm. to 14.8 dynes/cm. The latter value was observed for 0.3% by weight of $CF_3(CF_2)_6(CH_2)_5COONa$ or of $CF_3(CF_2)_6CH{=}CH(CH_2)_3COONa$ in water at 25°, the unsaturated acid being more effective at lower concentrations. Conventional surfactants, including soaps of fatty acids, do not lower the surface tension of water below 26 dynes/cm.[16,17] Acids

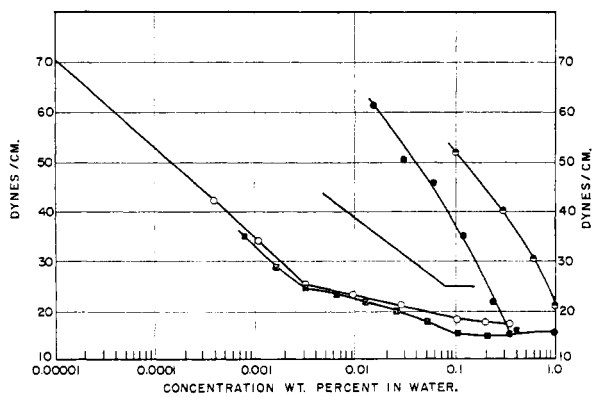

Fig. 2.—Surface tension of aqueous solutions of perfluorooctanoic acid, alkanoic acids, and terminal perfluoroalkyl segmented alkanoic acids at 25°. —● $CF_3(CF_2)_6COONH_4$; ● $CF_3(CF_2)_6COOH$ (ref. 16a); —tetradecanoic acid (ref. 16b); ○ $CF_3(CF_2)_3CF(CF_3)(CH_2)_{10}COONa$; ■ $CF_3(CF_2)_6$-$CH{=}CH(CH_2)_3COONa$.

(16) (a) M. K. Bernett and W. A. Zisman, *J. Phys. Chem.*, **63**, 1911 (1959); (b) A. Lottermoser and B. Baumguertel, *Trans. Faraday Soc.*, **31**, 200 (1935); (c) J. Powney, *ibid.*, **31**, 151 (1935).

(17) Perfluoroöctanoic acid does lower the surface tension of water to 15.3 dynes/cm. at 0.4% conc.; a solution of the ammonium salt, however, measures 37 dynes/cm. at this concentration and does not reach a value below 20 dynes/cm. (Fig. 2) up to 1% concentration. The longer the alkylene segment of $R_f(CH_2)_mCOOH$, the smaller the concentration required to reduce the surface tension to a given value; however, salts of $CF_3(CF_2)_6(CH_2)_mCOOH$ (m = 10 or 16) were too insoluble in water to be measured. The iso series, $(CF_3)_2CF$-

TABLE II (*Continued*)

$R_f(CH_2)_mCOOH$		Analyses											
		$R_f(CH_2)_mCOOC_2H_5$						$R_f(CH_2)_mCOOH$					
		Calcd.			Found			Calcd.			Found		
Yield, %[e]	M.p., °C.	C	H	F	C	H	F	C	H	F	C	H	F
70	48.5–50	54.2	7.6		54.7	7.6		51.3	6.95	31.2	51.2	6.9	31.2
37[f]	70–71							58.8	8.56	24.5	58.8	8.4	24.2
50[f]	49–50	50.3	6.6	34.8	50.0	6.5	34.8	47.45	5.98	37.5	47.4	6.0	38.0
90	36–37	50.3	6.59	34.8	50.5	6.7	34.6	47.45	5.98	37.5	47.5	5.9	37.1
95	73–74.5	56.6	8.0		57.2	8.0		54.8	7.6	30.3	54.4	7.8	29.8
50[j]	41–42							35.94	3.32	51.2	36.0	3.5	50.9
97	55	47.1	6.05	39.5	47.3	5.9	39.3	44.6	5.2	42.3	44.6	5.2	42.5
46[f]	58–59.8							42.3	4.66	46.0	42.0	4.7	46.3
81	43							42.3	4.66	46.0	42.4	4.7	45.8
25[f]	77–79	50.8	6.6	36.9	51.2	6.8	36.3	49.1	6.2	38.9	49.3	6.2	39.3
85	67–69							40.5	4.2	49.0	40.5	4.3	49.1
95	[k]	42.9	4.7		43.2	4.6		40.5	4.2	49.0	40.8	4.2	48.9
95	86–88	30.65	1.93	60.6	30.9	2.2	61.0	27.2	1.1	64.6	27.5	1.5	64.6
93	73							29.0	1.6	62.5	28.9	1.6	62.5
100[f]	79–80							30.6	1.9	60.5	30.6	2.0	60.4
95	64–65	35.15	2.95		35.8	2.8		32.2	2.3	58.9	32.2	2.3	58.8
100[f]	79.5–80							33.75	2.6	57.2	34.1	2.8	57.2
	82–83												
85	82–83	41.3	4.3		41.3	4.4		39.0	3.8	51.4	39.4	4.2	51.4
90	63	41.3	4.3		41.3	4.6		39.0	3.8	51.4	39.2	3.9	51.5
100	91.5–92	46.9	5.6		46.9	5.5		45.2	5.2	44.6	45.2	5.5	44.5
80	89–90							37.8	3.5	53.4	37.8	3.5	53.7
88	88							36.7	3.2	55.2	37.1	3.4	54.7
100	111–112	37.7	3.44	54.5	37.7	3.6	54.8	35.8	3.0	56.65	35.8	3.1	57.1

$CF_2(CH_2)_{10}COOC_2H_5$. [h] Coupled product: $[CF_3(CF_2)_2CH_2\underset{|}{C}H—(CH_2)_8COOC_2H_5]_2$; $n^{25}D$ 1.4047; b.p. 180–195°/0.3 mm.; also obtained in 13% yield. See Ref. *i* and Experimental for identification of similar product. [i] $[(CF_3)_2CF-CH_2\underset{|}{C}H(CH_2)_8COOC_2H_5]_2$; b.p. 175°/0.2; $n^{25}D$ 1.4057; also obtained in 20% yield. Hydrolyzed to dibasic acid. See Experimental. [j] B.p. 121°/4.3 mm.; hydrogenation of $CF_3(CF_2)_3CH=CH(CH_2)_3COOH$ by Raney Ni/H_2 at 4,000 p.s.i., 150° gave some hydrogenolysis and low yield. [k] B.p. 151°/1.0 mm.; $n^{25}D$ 1.3771. [l] Yield of products after reduction. Poor conv. of $CF_3(CF_2)_6I$; 17% of $CF_3(CF_2)_6CH_2CH_2COOC_2H_5$ and 21% of a telomeric product; b.p. 127°/0.4 mm.; m.p, 83–84°; details to be reported later. [m] Preparation by M. J. Griffin; reported (ref. 9), m.p. 83.5–84°.

with straight chain perfluoroalkyl segments were superior to those having branched chain R_f groups in surface active and wettability properties.[18]

Ionization constants of the long chain alkanoic and alkenoic acids with perfluoroalkyl terminal segments were determined by titration in 50% aqueous ethanol solution, since water did not dissolve a sufficient amount of material. Perfluorooctanoic acid and comparable alkanoic acids also were measured. The data in Table III show that the effect of the strong electron-withdrawing perfluoroalkyl group is transmitted through alkylene segments of two to five carbons with decreasing force. The short chain homologs having CF_3 or $CF_3(CF_2)_2$- segments showed a comparable effect,[19] but induction through alkylene segments greater than three methylenes has not been observed. The alkenoic acids were more highly ionized than their saturated analogs.

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(19) (a) E. T. McBee, O. R. Pierce, and D. D. Smith, *J. Am. Chem. Soc.*, **76**, 3722 (1954); (b) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 202; (c) *ibid.*, p. 48.

Experimental

Starting materials used were either synthesized by known methods or obtained from commercial sources and redistilled. The infrared spectra were obtained to confirm purity. The azonitrile initiators were solids having the correct melting point. Physical constants and sources of the various compounds are listed in Table IV.[20-23] Gas–liquid phase chromatography (g.l.c.) was used where appropriate to analyze liquids.

Perfluoroalkyl-terminated Alkanoic Acids.—A typical procedure is illustrated by the preparation of $(CF_3)_2CF-(CH_2)_{10}COOH$. In a flask, fitted with a nitrogen inlet and a reflux condenser filled with Dry Ice, and which was heated in an oil bath at 60–70°, was placed 2-iodoperfluoropropane[23] (66.9 g.; 0.23 mole), ethyl 10-hendecenoate (42 g.; 0.20 mole) and azobisisobutyronitrile[22] (0.50 g.; 0.003 mole). As refluxing and exothermic heat was observed, the flask was removed from the bath and cooled to 50°, momentarily. After 3 hr. heating, the orange solution was distilled in a 3-ft. platinum spinning band column (Column A). A fore-

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(21) N. A. Khan, *Org. Syn.* **32**, 104 (1952).

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(23) M. Hauptschein, M. Braid, and F. E. Lawlor, *ibid.*, **79**, 2549 (1957); M. Hauptschein, M. Braid, and A. H. Fainberg, *ibid.*, **83**, 2495 (1961); *Cf.* M. Hauptschein and M. Braid, Belgium Patent 612,520 (January 11, 1962).

TABLE III

APPARENT DISSOCIATION CONSTANTS FOR PERFLUOROÖCTANOIC ACID, PERFLUOROALKYL-SEGMENTED ALKANOIC AND ALKENOIC ACIDS, AND ALKANOIC ACIDS IN 50% AQUEOUS ETHANOL[a]

Compound	Concn., *M*	pK_a	$K \times 10^{-4}$
$CF_3(CF_2)_6COOH$	0.005	2.80 ± 0.03	159
$CF_3(CF_2)_6(CH_2)_2COOH$	.002	5.12 ± .06	0.76
$CF_3(CF_2)_6(CH_2)_3COOH$	.002	5.63 ± .03	.22
$CF_3(CF_2)_6(CH_2)_4COOH$	.002	5.81 ± .06	.16
$CF_3(CF_2)_6(CH_2)_5COOH$	.002	5.95 ± .005	.11
$CF_3(CF_2)_6(CH_2)_6COOH$	.002	6.26 ± .08	.06
$CF_3(CF_2)_6CH{=}CH(CH_2)_2COOH$	.004	5.40 ± .05	.38
$CF_3(CF_2)_6CH{=}CH(CH_2)_3COOH$	.003	5.83 ± .01	.15
$CH_3(CH_2)_8COOH$	0.002, 0.005	6.17 ± .01	.068
$CH_3(CH_2)_{10}COOH$	0.002, 0.005	6.13 ± .01	.074

[a] pK_a calcd. at five points on pH titration curve at 25° of two to four samples using a Beckman pH meter Model G with glass and calomel electrodes. The titrant was 0.1 *N* sodium hydroxide in 50% aqueous ethanol. Assistance by Dr. J. R. Martin is gratefully acknowledged.

TABLE IV

SOURCES AND PHYSICAL CONSTANTS OF STARTING MATERIALS

Compound	B.p.	$n^{25}D$	Source
$CH_2{=}CHCOOC_2H_5$	100°/atm.	1.4036	Carbide and Carbon Co.
$CH_2{=}CHCH_2COOC_2H_5$	126°/atm.	1.4092	Columbia Organic Chem. Co.
$CH_2{=}CH(CH_2)_2COOH$	129°/100 mm.	1.4285	Peninsular Chem-Research Co.
$CH_2{=}CH(CH_2)_3COOH$	109°/20.0 mm.	1.4359	Ref. 20
$CH_2{=}CH(CH_2)_8COOC_2H_5$	168°/atm. 80°/100 mm.	1.4198	Ref. 20
$CH_2{=}CH(CH_2)_8COOC_2H_5$	146°/20 mm.	1.4354	Eastman Kodak Co.
$CH_2{=}CH(CH_2)_{16}COOH$	M.p. 57–58°		This paper
$CH{\equiv}C(CH_2)_8COOH$	M.p. 43°		Ref. 21
$(CH_3)_2C(CN)N{=}NC(CN)(CH_3)_2$	M.p. 102° dec.		Ref. 22
$[(CH_3)_2CHCH_2C(CH_3)(CN)N{=}]_2$	M.p. 74–76° dec.		Ref. 22
$CF_3CF_2CF_2I$	41°/atm.	1.3250	Columbia Organic Chem. Co.
$(CF_3)_2CFI$	41°/atm.	1.3260	Ref. 23
$CF_3(CF_2)_3I$	67°/atm.	1.3252	Ref. 8a, 19c
$CF_3(CF_2)_4I$	66°/300 mm.	1.3268	Ref. 8a, 19c
$CF_3(CF_2)_5I$	84°/285 mm.	1.3258	Ref. 8a, 19c
$CF_3(CF_2)_6I$	77°/100 mm. 70°/70 mm.	1.3270[a]	Ref. 8a, 19c; also Columbia Organic Chem. Co.
$CF_3(CF_2)_7I$	79–80°/50 mm.	1.3284	Ref. 8a
$CF_3(CF_2)_8I$	112°/98 mm. M.p. 44–45.5°		Ref. 8a, 19c
$CF_3(CF_2)_9I$	105°/10 mm. M.p. 77–79.5°		Ref. 8a, 19c
$CF_3(CF_2)_3CF(CF_3)I$	115°/atm.	1.3287	Ref. 23
$(CF_3)_2CF(CF_2)_2I$	94°/atm.	1.3348	Ref. 8b, 23
$(CF_3)_2CF(CF_2)_4I$	134°/atm.	1.3327	Ref. 8b, 23
$(CF_3)_2CF(CF_2)_6I$	174°/atm.	1.3318	Ref. 8b, 23
$CF_3(CF_2)_6(CH_2)_6I$[b]	130°/9 mm. M.p. 38–40°		Ref. 28

[a] There is some discrepancy in the literature value; *cf.* G. V. D. Tiers, *J. Org. Chem.*, 26, 3515 (1961); *ibid.*, 27, 2261 (1962). [b] *Anal.* Calcd. for $C_{13}H_{13}F_{15}I$: C, 26.9; H, 2.08; F, 49.2; I, 21.9. Found: C, 27.2; H, 2.3; F, 48.6; I, 22.0.

run of ethyl 10-hendecenoate (4.5 g.; $n^{25}D$ 1.4357) was obtained. $(CF_3)_2CFCH_2CHI(CH_2)_8COOC_2H_5$, b.p. 125°/0.5 mm.; $n^{25}D$ 1.4300; 85.9 g. (85% conversion) was collected in three fractions having the same physical constants. A residual oil of 1.1 g. remained. The cold trap contained 9.1 g. of 2-iodoperfluoropropane, $n^{25}D$ 1.3260. The yield of adduct was 95% on materials used up.

It was convenient with high boiling starting materials such as $CF_3(CF_2)_6I$ or $CF_3(CF_2)_9I$ and ethyl 10-hendecenoate to use di-*t*-butyl peroxide as initiator at 130–140°. Increments of the peroxide were added during a 1-hr. period to control the rate of reaction. The amounts used for a typical preparation and conditions are listed in Tables I and II.

Zinc Reduction to $(CF_3)_2CF(CH_2)_{10}COOC_2H_5$.—A solution of 75 g. (0.15 mole) of $(CF_3)_2CFCH_2CHI(CH_2)_8COOC_2H_5$ in 150 ml. of absolute ethanol was saturated with anhydrous hydrogen chloride, and 10 g. (0.15 g.-atom) of zinc (10 to 20 mesh) was added while stirring at 65°. Foaming and exothermic reaction were observed. After 1 hr. at 65 to 70°, another 10 g. of zinc was added, and the slurry was resaturated with hydrogen chloride; this was repeated in 1 hr. The colorless solution was cooled, filtered from excess zinc, and poured into 1 l. of water, extracted with ether and benzene and the organic extract washed with water. $(CF_3)_2CF(CH_2)_{10}CO_2C_2H_5$ was fractionated in Column A, b.p. 150°/10 mm.; $n^{25}D$ 1.3884; 46.0 g. (80%). Analyses are in Table II. A residue of 11.4 g. remained which was distilled, b.p. 175°/0.20 mm.; $n^{25}D$ 1.4055; 8.6 g., leaving a hold-up of 3.2 g. (20% conversion). The molecular weight and infrared spectrum of this material were in accord with a coupled "dimeric" structure, as was hydrolysis to a dibasic acid, b.p. 208°/0.3 mm. Coupled products were observed in other instances also.[7]

Anal. Calcd. for $C_{32}H_{48}F_{14}O_4$: C, 50.4; H, 6.6; F, 34.9; mol. wt. 762.7. Found: C, 50.1; H, 6.8; F, 35.0; mol. wt. 723. (ebullioscopic).

Anal. Calcd. for $C_{28}H_{40}F_{14}O_4$: C, 47.6; H, 5.7; F, 37.6; Acid no. 159. Found: C, 47.7; H, 5.7; F, 37.7; acid no. 150.

In place of hydrogen chloride 55% aqueous hydriodic acid could be used with equal success, but concentrated hydrochloric acid was inferior. See Table II for yields, properties and analyses of analogous products from zinc reductions.

Hydrolysis to $(CF_3)_2CF(CH_2)_{10}COOH$.—Reaction of $(CF_3)_2CF(CH_2)_{10}CO_2C_2H_5$ with potassium hydroxide in 90% aqueous alcohol solution at 60–70° for 5 to 10 hr. gave complete hydrolysis. The solution was acidified, the solid acid collected, air-dried and recrystallized from dichloromethane; m.p. 37–38°. See Table II for analyses. Attempted hydrolysis by hydrogen chloride in acetic acid[24] by aqueous alkali was unsatisfactory.

Amidation[25] of $CF_3(CF_2)_2(CH_2)_{10}COOC_2H_5$ in methanol solution with anhydrous ammonia at 125° in a shaker tube gave $CF_3(CF_2)_2(CH_2)_{10}CONH_2$, m.p. 91–91.5° (recrystallized from cyclohexane and then from acetone).

Anal. Calcd. for $C_{14}H_{22}F_7NO$: C, 47.6; H, 6.27. Found: C, 47.6; H, 6.3.

$CF_3(CF_2)_3(CH_2)_{10}CONH_2$, m.p. 84–85.5° (recrystallized from methylcyclohexane and then from methanol), was obtained *via* the acid chloride and concentrated ammonium hydroxide at 0–5°.[26]

Anal. Calcd. for $C_{15}H_{22}F_9N$: C, 44.7; H, 5.5; F, 42.4. Found: C, 44.5; H, 5.5; F, 42.4.

Telomerization of 1-Iodoperfluoroheptane and Ethyl Acrylate.—Ethyl acrylate (20.0 g., 0.20 mole; redistilled, kept cold in a dropping funnel with a Dry Ice-filled jacket) was added over an 8-hr. period at 70° to 1-iodoperfluoroheptane (49.6 g., 0.1 mole) and azobisisobutyronitrile (0.4 g., 0.0024 mole) which was stirred under a nitrogen atmosphere. The unchanged material (52.2 g.) was removed by distillation under reduced pressure; analysis by g.l.c. showed it to contain 27% of ethyl acrylate and 69% of $CF_3(CF_2)_6I$ by weight. The residue of $C_7F_{15}(CH_2\underset{|}{C}HCOOC_2H_5)_nI$ (15.2 g.; 26% conversion of I; 43% of ethyl acrylate) had a calculated n of 2.5 from analysis, and was therefore a mixture of adducts in which $n = 1, 2, 3$ (and 4). Reduction gave $C_7F_{15}CH_2CH_2COOH$ and higher telomers.

Anal. Calcd. for $C_{17}H_{16}F_{15}O_4I$ ($n = 2$): C, 29.3; H, 2.3; I, 18.2. Found: C, 31.7; H, 2.8; I, 17.3.

Perfluoroalkyl-terminated Alkenoic Acids.—(a). **Ethyl 6,6 to 12,12,12-pentadecafluoro-4-dodecenoate** was obtained by dehydrohalogenation and esterification of $CF_3(CF_2)_6CH_2CHI(CH_2)_2COOH$, b.p. 65° (0.2 mm.); or b.p. 103° (4 mm.); $n^{25}D$ 1.3744 in 85% yield. The ester had an infrared spectrum which contained the C=O band at 5.75 μ, $R_fCH{=}CH-$ at 5.95 and 10.30 μ and bands at 10.10 and 11.20 μ. Analysis by gas liquid chromatography showed it to be a single substance; only one peak was obtained.

Anal. Calcd. for $C_{14}F_{15}H_{11}O_2$: C, 33.9; F, 57.4; H, 2.2. Found: C, 33.8; F, 56.7; H, 2.3.

The ester was hydrolyzed to *6,6 to 12,12,12-pentadecafluoro-4-dodecenoic acid*, b.p. 138° (3 mm.); m.p. 24–26.4°; 28.3 g. (85% yield). An infrared spectrum showed C=O band at 5.85 μ, a weak $R_fCH{=}CH-$ band at 5.95 μ and bands at 10.10, 10.30 and 11.2 μ.

Anal. Calcd. for $C_{12}F_{15}H_7O_2$: C, 30.8; F, 60.9; H, 1.5. Found: C, 30.8; F, 60.5; H, 1.6.

A solution of 10.0 g. (0.021 mole) of 6,6 to 12,12,12-pentadecafluoro-4-dodecenoic acid in 60 ml. of 90% aqueous alcohol and 0.2 g. of platinum oxide was shaken at 3 atm. of hydrogen pressure in a Parr shaking apparatus for 18 hr. at 25°. A small pressure drop occurred. *6,6 to 12,12,12-Pentadecafluorododecanoic acid* recovered by filtration and evaporation of solvent weighed 10.0 g. (100%); m.p. 70–75°. It was recrystallized from methylene chloride; m.p. 79–80°; f.p. 78.5°.

$CF_3(CF_2)_6CH_2CHI(CH_2)_3COOC_2H_5$ was hydrolyzed to *7,7 to 13,13,13-pentadecafluoro-5-tridecenoic acid* with alkali, acidified, and the acid extracted into ether, treated with zinc dust to remove a trace of halogen and distilled in a 16-in. platinum spinning band column, b.p. 142° (3 mm.); $n^{25}D$ 1.3539 (82% yield). An infrared spectrum showed the carboxyl group carbonyl band at 5.82 μ, a weak 6.00 μ band and bands at 10.30 and 11.02 μ.

Anal. Calcd. for $C_{13}F_{15}H_9O_2$: C, 32.4; F, 59.1; H, 1.9; Acid No. 115. Found: C, 32.4; F, 59.5; H, 1.8; Acid No. 115.

Catalytic hydrogenation of 7,7- to 13,13,13-pentadecafluoro-5-tridecenoic acid gave $CF_3(CF_2)_6(CH_2)_5COOH$, m.p. 62–63° (100%) which was recrystallized from carbon tetrachloride, m.p. 63–64.8°. The m.p. was unchanged by repeated recrystallizations. Product of the same m.p. was obtained by zinc reduction in alcohol of ethyl 7,7- to 13,13,13-pentadecafluoro-5-iodotridecanoate, followed by hydrolysis. There was no depression observed in a mixed melting point determination. N.m.r. and infrared spectroscopy gave results which were consistent with the structure. Specifically, unsaturation and CH_3—C groups were not indicated.

(b) ***trans*-3-Perfluoropropyl-10-hendecenoic Acid.**—10-Hendecynoic acid (8.0 g., 0.04 mole), 1-iodoperfluoropropane (25.0 g., 0.085 mole) and azobis-α,γ-dimethylvalerylnitrile[22] (0.1 g., 0.0004 mole) was heated under reflux at 45–52° for 9 hr. Distillation gave the adduct as colorless liquid, b.p. 100–122°/0.15 mm. (18.6 g.; $n^{25}D$ 1.4442; 88% conversion) and $CF_3(CF_2)_6I$ (16.4 g.). The adduct was added to 50 ml. of glacial acetic acid and 6.5 g. (0.1 g.-atom) of zinc dust saturated with hydrogen chloride while stirring vigorously at 60–70°. After 3 hr., 2 g. of zinc was added and stirring continued for 2 hr. *trans*-3-(Perfluoropropyl)-10-hendecenoic acid, obtained after drowning in water and extraction, was distilled, b.p. 82°/0.1 mm.; $n^{25}D$ 1.4004; 9.2 g. (76%); residue, 1.0 g. Analysis by g.l.c. showed 97.3% of the total area was under a single peak.

Anal. Calcd. for $C_{14}H_{19}F_7O_2$: C, 47.8; H, 5.45. Found: C, 48.2; H, 5.6.

Ultraviolet Light-induced Addition of 1-Iodoperfluoropropane to Ethyl 10-Hendecenoate.—A mixture of 130 g. (0.44 mole) of 1-iodoperfluoropropane and 103.5 g. (0.49 mole) of ethyl 10-hendecenoate was irradiated at 31° for 48 hr. under an argon atmosphere in a 12-in. by 3-in. vessel having an internal quartz coil mercury vapor ultraviolet source and fitted with a Dry Ice reflux condenser. The liquid turned dark and a deposit (iodine) formed on the quartz coil in the reaction tube. Distillation of 223.4 g. (a loss of 10 g., some remaining in the vessel) gave 60.6 g. (46% recovery) of 1-iodoperfluoropropane. The residue remaining (159.8 g.) was heated to 180°, but no further attempt was made to distil it, because of evident decomposition. The crude iodo ester mixture was reduced with zinc, and fractionated in Column A.

Recovered ethyl hendecenoate (43.1 g.; b.p. 142–145°/18 mm., $n^{25}D$ 1.4283) was isomeric with the original ester according to physical properties and infrared spectra. The mixture of unsaturated fluorine-containing esters, b.p. 137–152°/10 mm.; $n^{25}D$ 1.4112 to 1.3944; 63 g., was hydrogenated. Fractionation in Column A gave 13.3 g. of ester (impure mixture), b.p. 153–154°/10.0 mm.; $n^{25}D$ 1.3901; and 48.0 g. of nearly pure ethyl 12,12,13,13,14,14,14-heptafluorotetradecanoate, b.p. 154–154.5°/10 mm.; $n^{25}D$ 1.3890. Isomeric impurities were present. Hydrolysis of 30.6 g. (0.08 mole) of this material gave 28.1 g. (99%) of an acid mixture, m.p. 40–43°. There was a negligible amount of fluoride cleavage. Recrystallization from cold methylene chloride gave 16.0 g. of pure acid, m.p. 47.5–48.5°; 4.2 g.

(24) M. A. Mitz, A. E. Axelrod, and K. Hofmann, *J. Am. Chem. Soc.*, **72**, 1231 (1956).

(25) P. B. Russell, *ibid.*, **72**, 1853 (1950).

(26) R. E. Kent and S. M. McElvain, *Org. Syn.*, **25**, 58 (1945).

of acid, m.p. 43–46° and 4.8 g. of soft solid and oil. The principal products from ultraviolet-initiated addition, therefore, were a mixture of unsaturated esters including $CF_3CF_2CF_2CH{=}CH(CH_2)_8COOC_2H_5$ formed by the dehydroiodination of the intermediate iodo-addition compound and isomerization of ethyl 10-hendecenoate.

Thermally-induced Addition of Iodoperfluoroalkanes to Ethyl 10-Hendecenoate. (a). **At 215° for 6 Hr.**—Reaction of 150 g. (0.5 mole) of 1-iodoperfluoropropane and 125 g. (0.59 mole) of ethyl 10-hendecenoate at 215° for 6 hr. in a 400-ml. Hastelloy C-lined shaker tube gave 11.0 g. of volatile gas and 261 g. of fluid product which contained both the acid and the ester groups according to infrared analysis. Zinc reduction and distillation gave a black tarry residue (20.5 g.) and a partly crystalline distillate (163.8 g.). Fractionation in column A gave impure ethyl 12,12,13,13,14,14,14 - heptafluorotetradecanoate, b.p. 166–174°/20 mm.; $n^{25}D$ 1.4036 to 1.3888; 120 g. (62% yield, crude) which contained liquid isomeric unsaturated compounds (infrared absorption band at 5.77 μ) which were not completely separated by distillation in a 4-ft. by 0.5-in. Podbielniak column. Unchanged ethyl 10-hendecenoate been rearranged to an internal olefinic ester (10.30-μ absorption band; no 6.05-μ band) as in ultraviolet light-induced reaction. Pure $CF_3(CF_2)_2(CH_2)_{10}COOC_2H_5$, m.p. 30–30.5°, was obtained by pressing out the oil from the impure product. When ethyl acetate (1.5 moles) was used as a coreactant, the amount of tar formed was less than 1% and 95% of distilled products were obtained (see Table II).

Preparation of 8,8- to 14,14,14-Pentadecafluorotetradecanoic Acid *via* the Nitrile.[27]—Reaction of 4.9 g. (0.0086 mole) of 7,7- to 13,13,13-pentadecafluoro-1-iodotridecane[28] (b.p. 130°/9 mm.; m.p. 38–40°) and 1.5 g. (0.023 mole) of potassium cyanide in 15 cc. of 95% alcohol gave the nitrile which was hydrolyzed directly to the acid, m.p. 79.5–80°; f.p. 78°; 4.4 g. (90%); recrystallized in methylene chloride solution at 5°. Analyses are in Table II.

16-Heptadecenoic Acid. (a). **7-Keto-16-heptadecenoic Acid.**—2-(10-Undecenoyl)-1-cyclohexanone[13] (b.p. 145°/0.5 mm.; $n^{25}D$ 1.4938, 67.0 g.; 0.25 mole) was stirred with a steel rod at 100° in a steel beaker while a solution of 40 g. (0.71 mole) of potassium hydroxide in 28 g. of water was added. The liquid became thick and pasty in 3 to 5 min. as the temperature rose to 130° and fell. A solution made in 2 l. of water was acidified with concentrated hydrochloric acid at 40–45°; the precipitated acid was collected and washed with water. The yield was 68 g. (100%) of crude 7-keto-16-heptadecenoic acid, m.p. (sinter 58°) 62–67°. The reaction was repeated five times with identical results. Recrystallization of 136.3 g. of the keto acid from 1 l. of petroleum ether and hexane gave 101.7 g. (72%); m.p. (sinter 68°) 68.5–69.5°; 13.0 g. (9%), m.p. (60.5°) 61.5–66°; and 1.2 g., m.p. (54°) 59–62°. An infrared spectrum showed a COOH band at 5.82 μ; $H_2C{=}CH$ band at 6.03 μ; bands at 7.04, 7.68, 10.06, and 10.90 μ (CH deformation bands of $CH_2{=}CH-$); and two bands not in 16-heptadecenoic acid (see below) at 7.98 and 8.28 μ.

Anal. Calcd. for $C_{17}H_{30}O_3$: C, 72.3; H, 10.7. Found: C, 72.0; H, 10.6.

(b) **Wolff–Kishner Reduction.**—A mixture of 135 g. (0.25 mole) of the crude potassium salts of 7-keto-17-heptadecenoic acid (above), 400 ml. of diethylene glycol and 25 ml. of hydrazine hydrate was heated to 137° (caution: foaming occurred). Hydrazine hydrate (25 ml.) was added after 2 hr. and refluxing was continued at 137° for 2.5 hr. The condenser was removed and vapors driven off up to 185° in 43 min. The temperature was kept at 185–195°. A sample, when acidified, gave solid acid, m.p. (sinter 45.5°) 53–58.5°; recrystallized from acetone, m.p. (55°) 60.5–62.5°. It contained unreduced keto acid (infrared analysis). A sample after 2 hr. had m.p. 47.5–51°, and after 3 hr., m.p. 48–52°. Infrared analysis showed no unreduced keto acid was present and was identical to a recrystallized sample of 16-heptadecenoic acid. The mixture was cooled and worked up as above. The acid was recrystallized from 300 cc. of acetone and 30 cc. of water; total yield, 58 g. (88%) based on crude potassium salt mixture. When a longer heating time (14 hr.) at 195° was employed, as is customary,[13] isomerization of part of the product to 15-heptadecenoic acid occurred (infrared analysis). Attempts to separate the acids by fractional crystallization from alcohol failed.

In a second experiment twofold amounts were used. Samples taken after 1.5 hr. at 192–195° showed some unreduced keto acid, but after 3.0 hr. no keto acid and no isomerized olefinic acid. 16-Heptadecenoic acid, m.p. (54°) 55–56°; 124.5 g. (93%), was recrystallized after treatment with decolorizing carbon in petroleum ether, m.p. 57–58°.

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.1; H, 12.0. Found: C, 75.7; H, 12.0.

An infrared spectrum showed COOH (bonded OH) band, C=O band at 5.82 μ, $CH_2{=}CH$ (stretch) band at 6.08 μ and associated deformation bands at 7.06, 7.68, 10.08, and 11.0 μ. There were also present new bands not in 7-keto-16-heptadecenoic acid at 8.05, 8.20 (8.32), and 8.43 and 10.65 μ. These bands were useful in studying mixtures. There was no 10.36 μ band of —CH=CH— (*trans*) which was present in the infrared spectra of the mixtures of unsaturated acids prepared by 14 hr. refluxing at 195°.

(27) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1946, p. 292.

(28) Prepared by heating $CF_3(CF_2)_6I$ with an excess of ethylene at 200°; *cf.* R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949); 3761 (1953); and T. N. Bell, *ibid.*, 4973 (1961).

Ozonolysis of Dihydropyran. Reactions of 4-Hydroperoxy-4-methoxybutyl Formate

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Ozonolysis of dihydropyran in methanol readily afforded 4-hydroperoxy-4-methoxybutyl formate (II). The latter could be reduced smoothly to 4-formoxybutyraldehyde (VI) or dehydrated to methyl 4-formoxybutyrate (III). Products arising from thermal and ferrous ion-catalyzed decomposition of II have been determined.

The primary peroxidic product arising from the ozonolysis of cyclohexene in methanol has been shown by Bailey[1] to be essentially the aldehyde–hydroperoxide predicted by the Criegee[2] mechanism. A monomeric product could not be isolated as such because of facile intermolecular self-

(1) P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957).

(2) See P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).