

TABLE I
 PHYSICAL CONSTANTS

Compound	B. p., °C.	Mm.	F. p., °C.	t, °C.	d ₄	n _D	MR	
							Found	Calcd.
CHCl ₂ CCl ₂ CHClCFCl ₂	123	11	Glass	20	1.7729	1.5230	54.7	54.7
CHCl ₂ CCl ₂ CHClCF ₂ Cl	99.3	11	Glass	25	1.7550	1.4905	49.6	49.7
CHCl ₂ CCl=CClCF ₂ Cl	140.9	23	-51	20	1.6830	1.4838	44.9	44.5
CHCl ₂ CCl ₂ CCl ₂ CF ₂ Cl	158	48	Glass	25	1.8476	1.5112	54.5	54.7
CCl ₂ =CClCCl ₂ CF ₂ Cl	125.8	47	-50.7	25	1.8047	1.5073	49.3	49.3
CCl ₃ CCl ₂ CCl ₂ CF ₂ Cl	161	25	41.9-42.4					
CF ₂ -CCl ₂	131.6	762	84.8					
CF ₂ -CCl ₂								
CF ₂ -CCl	67.1	61.5	-43.4	25	1.5340	1.3699	28.8	28.8
CF ₂ -CCl								
CF ₂ -CFCI	59.87		-24	20	1.6441	1.3340	29.2	29.2
CF ₂ -CFCI								
CF ₂ -CF	1.13		-60.37					
CF ₂ -CF								

therefore proceeds by junction of "head to head" and "tail to tail" exclusively.

CCl₂=CF₂ Dimer.—The dimer C₄F₄Cl₄ is quantitatively transformed into C₄F₄Cl₂ by zinc in alcohol.⁴ The latter, by permanganate oxidation,⁴ yields exclusively perfluorosuccinic acid;

its formula must therefore be $\overline{\text{CCl}=\text{CClCF}_2\text{CF}_2}$,

and the original dimer must be $\overline{\text{CCl}_2\text{CCl}_2\text{CF}_2\text{CF}_2}$,

uncontaminated with isomeric $\overline{\text{CCl}_2\text{CF}_2\text{CCl}_2\text{CF}_2}$. The cyclic dimerization proceeded therefore exclusively by "head to head" and "tail to tail" junctions.

Experimental

Dimerization of CHCl=CCl₂.—This was done by refluxing over benzoyl peroxide in bright illumination.⁵ The dimer is also available commercially.

Dimerization of CCl₂=CF₂.—The olefin (400 g.) was agitated at 200° for twelve hours in a stainless steel bomb.

(5) French Patents 814,423 and 840,867; British Patent 417,195.

The unchanged monomer (75 g.) was recovered by distilling it off. The residue was dissolved in ether, then distilled to give 313 g. of crystalline dimer, b. p. 131-132°, in about 80-85% yield which is about 80% conversion and 92% net yield.

Dimerization of CFCI=CF₂.—The olefin (48 g.) was agitated at 200° for eight hours in a stainless steel bomb. Distillation of the reaction mixture gave 28 g. of recovered starting material, and 16 g. of crude dimer, b. p. 47 to 60° (33% conversion, 80% yield).

Summary

Dimerization of CHCl=CCl₂ leads by a "head to tail" type of polymerization to a chain halogenated butene, the formula of which is demonstrated. In contrast, the dimerization of CCIF=CF₂ and of CCl₂=CF₂ lead to stable cyclo-

butane rings $\overline{\text{CClFCClF}_2\text{CF}_2}$ and $\overline{\text{CCl}_2\text{CCl}_2\text{CF}_2\text{CF}_2}$ respectively; no isomer is present and the cyclization process is exclusively a "head to head," "tail to tail" joining.

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Fluorinated Acids

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A few fluorinated acids are known, all of which have the fluorine atoms located on the carbon adjacent to the acid group. The pronounced electronegative effect of the fluorinated cluster causes these acids to be very strong. The same exaltation of the acidity has been observed in alcohols bearing a fluorinated group next to the alcohol function. We have now attempted to prepare a series of acids in which the fluorinated group would be located at increasing distances from the acid function, in order to permit a measurement of the electronegative influence in terms

of the distances. The present paper reports the synthetic work.

Alpha fluorinated acids (CH₃CF₂CO₂H and C₂H₅CF₂CO₂H) were made by the alkaline oxidation procedure¹ reported for the preparation of trifluoroacetic acid.

Beta fluorinated acids could not be made by the same procedure because the alkalinity caused a loss of hydrogen fluoride, to yield CF₂=CHCO₂H instead of CF₃CH₂CO₂H and CH₃CF=CHCO₂H instead of CH₃CF₂CH₂CO₂H. The addition of

(1) Henne, Alderson and Newman, *THIS JOURNAL*, **67**, 918 (1945).

hydrogen fluoride to $\text{CH}_3\text{C}\equiv\text{CCO}_2\text{R}$ gave the beta fluorinated ester $\text{CH}_3\text{CF}_2\text{CH}_2\text{CO}_2\text{R}$, but saponification gave only $\text{CH}_3\text{CF}=\text{CHCO}_2\text{H}$. All efforts to add hydrogen fluoride to $\text{CH}\equiv\text{CCO}_2\text{H}$ or its esters were defeated by resin formation.

In order to synthesize a gamma fluorinated acid, we tried to transform $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{Cl}$ into the corresponding nitrile $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CN}$, but could not overcome the easy loss of hydrogen chloride with formation of $\text{CH}_3\text{CF}_2\text{CH}=\text{CH}_2$. We also prepared $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, with three purposes in mind: (1) that dehydrohalogenation would yield $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}=\text{CH}_2$, the oxidation of which might give a beta acid, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CO}_2\text{H}$; (2) that hydrolysis would give $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, the oxidation of which would give a gamma acid $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$; and (3) that a reaction with potassium cyanide would lead to $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$, which by hydrolysis would give a delta acid, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$. Only the last sequence succeeded; the other failed because we could not dehydrohalogenate $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$, nor could we hydrolyze it to $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, and reaction with the solvent led to ethers of the $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{C}_2\text{H}_5$ type; efforts to oxidize the ethers to the corresponding gamma acid $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ate up the supply of material before workable conditions were found.

The delta acid $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ was made as shown in the preceding paragraph.

Only one fluorinated diacid has been reported,² perfluorinated glutaric acid made by oxidative opening of the ring of $\text{CCl}=\text{CClCF}_2\text{CF}_2$. Using a similar procedure, we now have made perfluorinated succinic acid by opening the ring of $\text{CF}=\text{CFCF}_2\text{CF}_2$ and that of $\text{CF}=\text{CFCF}_2\text{CF}_2$.

Experimental

Synthesis of $\text{CH}_3\text{CF}_2\text{CO}_2\text{H}$.—Into a 500-cc., three-necked flask fitted with a reflux condenser, a dropping funnel and a mercury-sealed stirrer were placed 79 g. (0.5 mole) of potassium permanganate, 14 g. (0.25 mole) of potassium hydroxide, and 200 cc. of water. The flask was heated on a steam-bath while 32 g. (0.25 mole) of $\text{CH}_3\text{CF}_2\text{CCl}=\text{CH}_2$ prepared from $\text{CH}_3\text{CF}_2\text{CHClCH}_2\text{Cl}$ as shown before³ was added dropwise. After seventy-five minutes, the purple color disappeared. The steam-bath was removed and the theoretical amount of sulfuric acid needed for neutralization was added to the reaction mixture. The brown manganese oxide was reduced to the pink divalent state by means of sulfur dioxide. The organic acid was isolated by a continuous ether extraction. The yield of crude acid was 21 g., corresponding to a conversion of 84.4%.

This acid is very hygroscopic; a slow distillation gave a series of semi-solid fractions, boiling from 130 to 140°, then 5 g. of good white crystalline material boiling 140–141°, with a freezing range of 38–44° and a neutral equivalent of 111, theory 110.

Synthesis of $\text{C}_2\text{H}_5\text{CF}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$.—The starting material was $\text{C}_2\text{H}_5\text{CF}_2\text{CH}_2\text{CH}_2\text{Cl}$, b. p. 117°, easily obtainable by di-

rected chlorination⁴ of $\text{C}_2\text{H}_5\text{CF}_2\text{C}_2\text{H}_5$,⁵ 50 g. (0.35 mole) of this crude material was treated with a boiling alcoholic solution containing 0.5 mole of potassium hydroxide, under a reflux condenser adjusted so that the resulting olefin $\text{C}_2\text{H}_5\text{CF}_2\text{CH}=\text{CH}_2$, b. p. 54–55°, would distil off while most of the alcohol would be retained. The crude olefin amounted to 28 g. (0.27 mole) from which rectification gave 22 g. of good material. Oxidation of this purified sample by the procedure described above yielded 18 g. of crude acid, the rectification of which gave 15 g. of good crystalline $\text{C}_2\text{H}_5\text{CF}_2\text{CO}_2\text{H}$, m. p. 8.1°, with a neutral equivalent of 125, theory 124. Esterification to the ethyl ester was practically quantitative, in the presence of a trace of *p*-toluenesulfonic acid, and with refluxing benzene to permit continuous removal of water as formed.

Synthesis of $\text{CH}_3\text{CF}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$.—Tetrolic acid, $\text{CH}_3\text{C}\equiv\text{C}-\text{CO}_2\text{H}$, was prepared by interaction of sodium propynate with carbon dioxide under pressure; it was esterified to its ethyl ester. To 138 g. (1.23 mole) of this ester cooled to -70° was added 246 g. (12.3 moles) of hydrogen fluoride, in a steel bomb. The bomb was closed while cold, brought back to room temperature, then heated in live steam for five hours. The pressure rose to 15 atm., and dropped down to 5 atm. by cooling to room temperature. After bleeding off the gases (mostly ethyl fluoride), the bomb contents were emptied on cracked ice, washed and dried; the crude fluorinated ester amounted to 70 g. (35% conversion), from which 26 g. of material suitable for physical constants was obtained by distillation. That the formula was really $\text{CH}_3\text{CF}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ was shown by contrast with the physical properties of the isomer $\text{C}_2\text{H}_5\text{CF}_2\text{CO}_2\text{C}_2\text{H}_5$.

Saponification of $\text{CH}_3\text{CF}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$.—A series of saponifications with dilute aqueous caustic were attempted and led to acid samples with neutral equivalents intermediate between 124 ($\text{CH}_3\text{CF}_2\text{CH}_2\text{CO}_2\text{H}$) and 104 ($\text{CH}_3\text{CF}=\text{CH}-\text{CO}_2\text{H}$).

Synthesis of $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$.—The starting point was $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{Cl}$, obtained by condensing sodium acetylide with $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Cl}$. The addition of hydrogen fluoride across the triple bond was very violent, but was brought under control as follows. Into a copper vessel equipped with a dropping funnel, a mechanical stirrer and a reflux condenser maintained at -70°, were placed 60 g. (0.8 mole) of diethyl ether and 140 g. (7 moles) of hydrogen fluoride. The copper vessel was immersed in a water-bath maintained at 34°. From the dropping funnel, 80 g. (0.78 mole) of 5-chloro-1-pentyne was added at such rate that hydrogen fluoride fumes did not escape from the top of the reflux condenser. After completion of the addition, one mole of hydrogen fluoride was poured in, and the mixture was stirred for half an hour, then poured onto cracked ice, washed, dried and distilled. Several runs were made, which averaged from 40 to 50% yields of the desired $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$.

Into a flask fitted with stirrer and reflux condenser were placed 50 g. (0.35 mole) of $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, 37 g. (0.63 mole) of sodium cyanide, 50 g. of water and 50 cc. of ethyl alcohol. The mixture was refluxed for twenty-five hours. After washing out the alcohol and salt and drying, the reaction product weighed 37 g., of which 22 g. (0.165 mole) was the desired nitrile. The yields on several runs averaged 45–50%, and the balance of material was mostly an ether, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{C}_2\text{H}_5$.

A stirred mixture of 18 g. (0.135 mole) of nitrile with 55 cc. of absolute alcohol and 21 cc. of concentrated sulfuric acid was refluxed for four hours; after addition of water, ether extraction and distillation, 18.5 g. (0.1 mole) of ester was isolated. Ten grams of this ester and 80 cc. of a 25% solution of sodium hydroxide were refluxed for one hour; this brought about the complete disappearance of the organic layer. Ether extraction removed the alcohol. Acidifying with 85% phosphoric acid threw off the organic

(4) Henne and Hinkamp, *ibid.*, **67**, 1194, 1196 and 1906 (1945).

(5) Renoll, *ibid.*, **64**, 1115 (1942); Henne and Phueddeman, *ibid.*, **65**, 587 (1943).

(2) Henne and Zimmerschied, *THIS JOURNAL*, **67**, 1235 (1945).

(3) Henne and Hinkamp, *ibid.*, **67**, 1194 (1945).

TABLE I
PHYSICAL PROPERTIES

Compound	F. p., °C.	B. p., °C.	Mm.	T, °C.	d_4^t	n_D^t	MR^a	AR_F^b
CH ₃ CF ₂ COOH	38-44	141	
CH ₃ CH ₂ CF ₂ COOH	8.1	100-101	8.5	25	1.2201	1.3618	20.01	1.25
CH ₃ CH ₂ CF ₂ COOC ₂ H ₅	...	127-128		20	1.082	1.3665	31.46	1.05
CH ₃ CF ₂ CH ₂ COOC ₂ H ₅	(ca.) -96	135		25	1.1094	1.3680	30.84	0.74
CH ₃ CF=CH-COOH	83	108-110	8.5
CH ₃ CH ₂ CF ₂ CH=CH ₂	...	54-55		25	0.921	1.3438	24.4	.9
CH ₃ CF ₂ CH ₂ CH ₂ CH ₂ Cl	-74.98	80	149	20	1.1253	1.3870	29.83	.94
CH ₃ CF ₂ (CH ₂) ₃ CN	-37.96	197-198		20	1.0559	1.3848	29.51	1.03
CH ₃ CF ₂ (CH ₂) ₃ COOC ₂ H ₅	-50.2	102	40	20	1.0548	1.3901	40.50	0.95
CH ₃ CF ₂ (CH ₂) ₃ COOH	34-35	85-86	15
(CF ₂) ₂ (COOH) ₂	86.4-87.4	150	15
(CF ₂) ₂ (COOC ₂ H ₅) ₂	...	89	15	20	1.2640	1.3690	43.91	1.44
CH ₃ CF ₂ (CH ₂) ₃ -O-C ₄ H ₉	...	171.5		20	0.9336	1.3889		1.19

^a MR denotes the molecular refraction calculated by Lorentz-Lorenz formula. ^b AR_F is the atomic refraction for fluorine, obtained from MR by subtracting the customary increments for C, H, Cl, N, O and double bond.

TABLE II
ANALYTICAL DATA

Compound	% Chlorine		% Fluorine		Neut. equiv.	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
CH ₃ CF ₂ COOH	34.5	33.9	110	111
CH ₃ CH ₂ CF ₂ COOH	30.6	29.3	124	125
CH ₃ CF ₂ CH ₂ COOC ₂ H ₅	25.0	24.8
CH ₃ CF ₂ (CH ₂) ₂ CH ₂ Cl	24.9	25.0
CH ₃ CF ₂ (CH ₂) ₃ COOH	152	151.6
(CF ₂) ₂ (COOH) ₂	94	94.5
(CF ₂) ₂ (COOC ₂ H ₅) ₂	30.8	29.8
CF ₃ CH ₂ CCl ₂ CCl ₃	62.4	62.5

layer, which was decanted; the aqueous layer was extracted twice with ether. The combined organic materials were dried and distilled to yield 7 g. of crystalline acid, m. p. 34-35°, with a neutral equivalent of 151.6, calcd. 152.

Synthesis of HO₂CCF₂CF₂CO₂H.—The starting materials were $\overline{\text{CCl}_2\text{CCl}_2\text{CF}_2\text{CF}_2}$ and $\overline{\text{CClFCClFCF}_2\text{CF}_2}$ obtained as indicated in the preceding paper.⁶

The removal of two chlorine atoms from cyclo-C₄F₆Cl₂ was done with zinc in absolute alcohol; the reaction was very slow, but by refluxing the mixture for three days, and letting the resulting cycloolefin C₄F₆, b. p. 2 to 3°, escape through the reflux condenser, a quantitative transformation was obtained. Permanganate oxidation of C₄F₆ at atmospheric pressure in an open vessel proved unsatisfactory and was replaced by oxidation in a closed steel vessel. A 1.5 liter vessel was loaded at -70° with 150 g. (2.66 moles) of potassium hydroxide, 210 g. (1.33 moles) of potassium permanganate, 500 cc. of water and 120 g. (0.74 mole) of C₄F₆. After closing, the vessel was strapped to a mechanical shaker and agitated for ten hours. The exothermic reaction caused much heat evolution, and the pressure rose to 5 atm. After cooling, the reaction mixture was treated in the manner described above, and from the ether extract 48 g. of perfluorosuccinic acid was obtained. Esterification to the diethyl ester was per-

formed quantitatively, with *p*-toluenesulfonic acid as catalyst and continual removal of water by means of refluxing benzene.

Perfluorosuccinic acid was also obtained from cyclo-C₄F₆Cl₂ obtained quantitatively by zinc treatment of cyclo-C₄F₆Cl₄; this is the recommended synthesis,⁶ because the starting material is easily obtainable, and the oxidation can be performed in good yield in open equipment. The removal of two chlorine atoms with zinc in alcohol is very easy and leads to a quantitative yield of cyclo-

$\overline{\text{CCl}=\text{CClCF}_2\text{CF}_2}$. In a typical oxidation, 23 g. (0.17 mole) of cycloolefin fed progressively to a solution containing 27 g. (0.17 mole) of potassium permanganate and 0.35 mole of potassium hydroxide then refluxed until disappearance of the organic material gave after the customary working up a 70% yield of pure perfluorosuccinic acid with a neutral equivalent of 94.8, calcd. 95.

Summary

Fluorinated acids have been prepared, the fluorinated cluster of which is located at increasing distances from the acid function. Table I lists the compounds, with their physical properties. Preparative directions are detailed.

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(6) Henne and Ruh, *THIS JOURNAL*, **69**, 279 (1947).