[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Ionization Constants of Fluorinated Acids. III. Unsaturated Acids

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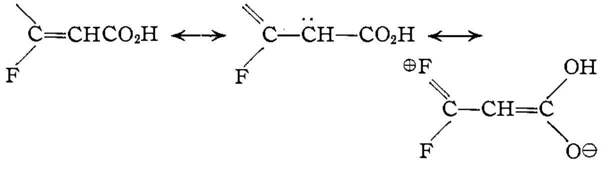
The unsaturated acids $CF_3CH=CHCO_2H$, $CH_2=CF-CO_2H$, $CF_2=CH-CO_2H$ and $CF_2=CF-CO_2H$ were synthesized, and their average $K_A \times 10^5$ determined as 45, 280, 68 and 1580. An interpretation of these low values is proposed.

The effect of a CF_3 group on the ionization of the $CF_3(CH_2)_nCO_2H$ series has been reported in a previous paper[1] and in a note[2]; it was found substantially proportional to the square of the distance separating the CF_3 from the CO_2H.

In the present paper, fluorinated acids with unsaturation in the alpha position have been synthesized and their dissociation constants measured. Two groups have been considered: (1) trifluorocrotonic acid, $CF_3CH=CHCO_2H$, where the fluorine is outside the double bond system, *i.e.*, is not vinylic; (2) fluorinated acrylic acids, $CH_2=CF-CO_2H$, $CF_2=CH-CO_2H$ and $CF_2=CF-CO_2H$, in which all fluorines are vinylic, and which are not complicated by geometrical isomerism.

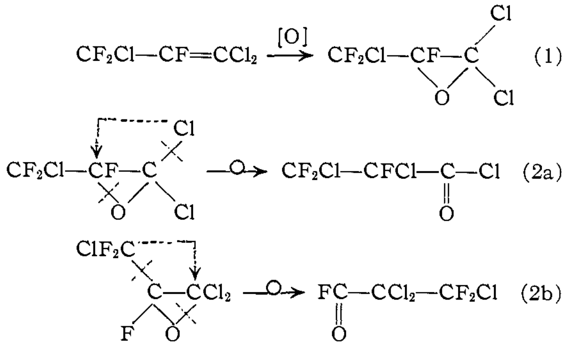
The results, expressed as $K_A \times 10^5$, have been interpreted as follows: (1) $CF_3CH=CHCO_2H$, with a value of 45 cannot be regarded as a mere vinylog of CF_3CO_2H, 55,000. Three other recent determinations[3-5] of this K_A were reported as 70, 71 and 33, respectively, values which confirm by their order of magnitude that vinylogy is out of the question. Clearly the inductive effect of the CF_3 is poorly relayed by the adjacent double bond. As the samples might differ by geometrical isomerism (see Experimental) a finer interpretation would be unwarranted. Chlorinated *cis-trans* analogs are known[6] to differ by similar ratios. (2) The fluorinated acrylic acids showed the following order of magnitude for $K_A \times 10^5$ (with details in Table I): $CH_2=CF-CO_2H$, 280; $CF_2=CH-CO_2H$, 68 and $CF_2=CF-CO_2H$, 1580. Remembering that acrylic acid (5.6) is only slightly more acidic than propionic acid (1.3), one can consider a somewhat similar relationship between $CH_2=CF-CO_2H$ (280) and CH_2FCO_2H (220), and regard the main effect of fluorine in the alpha position as induction. The very low value for $CF_2=CH-CO_2H$ (68) is however better explained by overriding mesomerism, conventionally symbolized as



In perfluorinated acrylic acid, $CF_2=CF-CO_2H$, the higher value (1580) shows an induction of greater importance, with mesomerism probably interfered with; mesomerism, however, must still be of consequence, because $CF_2=CF-CO_2H$ (1580) is a much weaker acid than $CCl_2=CCl-CO_2H$ (6200).

The synthesis of the acids proved difficult. $CF_3CH=CHCO_2H$ was made by adding CCl_3Br to $CF_3CH=CH_2$ under free radical conditions to obtain $CF_3CHBrCH_2CCl_3$, then heating the latter for 12 hours at 125° in 96% H_2SO_4 to cause simultaneous dehydrobromination and hydrolysis of the CCl_3 group; Haszeldine's synthesis[3] is equivalent. The fluorinated acrylic acids were all synthesized by sequences which ended with the creation of a double bond in the free acids; this was due to the fact that the β-fluorinated acrylic acids are quite sensitive to hydrolysis; to proceed by any sequence calling for liberation of the acid function as its last step, such as the saponification of a fluorinated acrylate or the hydrolysis of an acrylonitrile was therefore to be avoided. The sequences finally adopted, after many trials, were: (a) $CH_2=CH-CO_2Me \rightarrow CH_2Br\text{-}CHBr\text{-}CO_2Me \rightarrow CH_2=CBr\text{-}CO_2Me \rightarrow CH_2Br\text{-}CBr_2\text{-}CO_2Me \rightarrow CH_2Br\text{-}CBrF\text{-}CO_2Me \rightarrow CH_2Br\text{-}CBrF\text{-}CO_2H \rightarrow CH_2=CF\text{-}CO_2H$; (b) $CF_3\text{-}CH_2\text{-}CO_2H \rightarrow CF_2=CH\text{-}CO_2H$; (c) $CF_2=CFCl + CHCl_3 \rightarrow CF_2Cl\text{-}CFCl\text{-}CHCl_2 \rightarrow CF_2Cl\text{-}CF=CCl_2 \rightarrow CF_2Cl\text{-}CFBr-COCl \rightarrow CF_2Cl\text{-}CFBr\text{-}CO_2H \rightarrow CF_2=CF\text{-}CO_2H$.

In general these reactions were conventional. The main innovation was the oxidation–bromination of $CF_2Cl\text{-}CF=CCl_2$ to the acyl chloride $CF_2Cl\text{-}CFBr\text{-}COCl$. It has been postulated[7] that oxidation–chlorination proceeds through an epoxide formation (eq. 1) followed by a rearrangement (eq. 2a or 2b)



However, when oxidation–chlorination was tried, only $CF_2Cl\text{-}CFCl\text{-}CO_2H$ was obtained. It was then reasoned that the rearrangement of the epoxide might not be a strictly intramolecular process, but might involve an attack by a chlorine atom on the middle carbon followed by liberation

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[1] A. L. Henne and C. J. Fox, THIS JOURNAL, **73**, 2323 (1951).

[2] A. L. Henne and C. J. Fox, *ibid.*, **75**, 5750 (1953).

[3] R. N. Haszeldine, *J. Chem. Soc.*, 922 (1953).

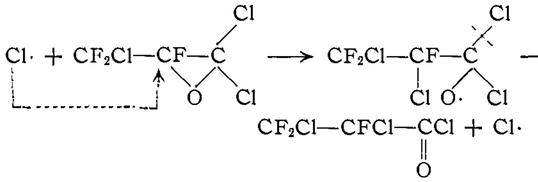
[4] H. N. Walborsky, THIS JOURNAL, **75**, 3241 (1953).

[5] E. T. McBee, O. R. Pierce and D. D. Smith, *ibid.*, paper in preparation. (1953).

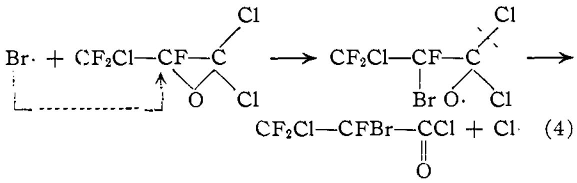
[6] H. J. Backer, *Rec. trav. chim.*, **54**, 167 (1935); also W. Ostwald, *Z. physik. Chem.*, **3**, 245 (1889).

[7] D. W. Chaney, U. S. patents 2,456,768 (1946) and 2,514,473 (1948).

of another chlorine atom from the end carbon, equation 3


(3)

This new interpretation permitted the hope that the use of an attacking bromine atom would allow equation 4


(4)

The liberated chlorine atom could, of course, cause reaction (eq. 3). Actually, a mixture of $CF_2Cl-CFBrCO_2H$ and $CF_2ClCFClCO_2H$ was obtained in the molar ratio of 1:1.2.

The physical measurements were made as previously[1] described. The results are tabulated below. Thermodynamic ionization constants were calculated in a conventional manner.[8]

TABLE I

IONIZATION CONSTANTS IN WATER AT 25°, $K \times 10^5$

	From pH	Classical	Thermodynamic
$CF_3CH_2CO_2H$		93.9 ± 0.9[1]	84.8 ± 0.8[1]
$CF_3(CH_2)_2CO_2H$	7.0 ± 0.1[1]	6.98 ± 0.03[1]	6.62 ± 0.05[1]
$CF_3(CH_2)_3CO_2H$	3.2 ± 0.03[2]		
$CF_3CH{=}CH{-}CO_2H$	45 ± 0.6		
	70 ± 2[3]		70 ± 5[3]
	71 ± 1[4]		
	33[5]		
$CF_2{=}CH{-}CO_2H$	68 ± 1		
$CH_2{=}CF{-}CO_2H$	270 ± 3	306 ± 6	279 ± 3
$CF_2{=}CF{-}CO_2H$		1570 ± 10	1610 ± 70
$CH_2F{-}CO_2H$		218 ± 2	161 ± 2[9]
$CCl_2{=}CCl{-}CO_2H$		7000 ± 100	5440 ± 50[10]

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Experimental

1.0 Preparation of $CF_3CH{=}CHCO_2H$.—This synthesis was carried out by Dr. Maxwell Nager.[11] Hydrolysis of $CF_3CHBrCH_2CCl_3$ was carried out in 96% H_2SO_4 at 125° for 12 hours. Evolution of HCl, HBr and Br_2 was observed; no hydrolysis of the CF_3 group occurred. After quenching, the organic products are extracted with ether, and recrystallized from petroleum ether to give an insoluble fraction of $CF_3CHBrCH_2CO_2H$, m.p. 132–134°, and a soluble fraction of $CF_3CH{=}CHCO_2H$, m.p. 49.5–50.5°. *Anal.* Calcd.: C, 34.30; H, 2.16; neut. equiv., 140. Found: C, 33.74; H, 2.30; neut. equiv., 140.1. Haszeldine's sample was reported to melt at 51° and to show strong infrared bands at 6.00 and 10.28 μ attributed to the *trans* $-CH{=}CH-$ group. Walborsky's sample melted at 54–55°, and no claim was made as to its geometry. McBee's sample melted at 55–56°.

2.0 Preparation of 2-Fluoroacrylic Acid, $CH_2{=}CF{-}CO_2H$.

2.1 Preparation of $CH_2BrCHBrCO_2CH_3$.—Methyl acrylate containing hydroquinone (880 g., 10.2 moles) in CH_3OH (500 ml.) is brominated with commercial Br_2 (1630 g., 10.2 moles) as described in the literature.[12] Distillation gives $CH_2BrCHBrCO_2CH_3$ (2311 g., 9.4 moles, 92% yield) b.p. 96–102° at 21 mm.

2.2 Preparation of $CH_2BrCBr_2CO_2CH_3$.—The dehydrohalogenation of $CH_2BrCHBrCO_2CH_3$ was best carried out by the method of Marvel.[12] Quinoline (129 g., 1 mole) and $CH_2BrCHBrCO_2CH_3$ (246 g., 1 mole) are mixed in a nitrogen atmosphere and the pressure reduced to 10 mm. When quinoline hydrobromide precipitates heat is applied and $CH_2{=}CBrCO_2CH_3$ distilled. The ester is dissolved in $CHCl_3$ (300 ml.) containing LiCl (0.5 g.) and hydroquinone, and Br_2 (160 g., 1 mole) is added slowly while stirring. The bromination reaction is initiated by illuminating with a "sun lamp" but this is not essential. The $CHCl_3$ solution is treated with aqueous Na_2SHO_3 to remove excess Br_2, washed with H_2O, saturated NaCl, and dried over anhydrous $MgSO_4$. Distillation gives $CH_2BrCBr_2CO_2CH_3$ (174 g., 0.535 mole, 56% over-all yield in 96% conversion), b.p. 93–95° at 5 mm.

2.3 Fluorination of $CH_2BrCBr_2CO_2CH_3$ with HgF_2.—Mercuric fluoride (91 g., 0.38 mole) and $CH_2BrCBr_2CO_2CH_3$ (278 g., 0.85 mole) are stirred at 5 mm. and heated slowly to 140° and the crude product distilled with no attempt to fractionate. The distillate (205 g.) is diluted with ether (100 ml.), washed with dilute HCl, H_2O and saturated NaCl, and dried over anhydrous $MgSO_4$. Distillation gives $CH_2BrCBrFCO_2CH_3$ (64 g., 0.24 mole, 24% yield on 66% conversion), b.p. 76–78° at 9 mm., $n^{27}D$ 1.4885, d^{27}_4 1.99, M_R 38.2, AR_F 1.44 and $CH_2BrCBr_2CO_2CH_3$ (92 g., 0.28 mole).

2.4 Saponification of $CH_2BrCBrFCO_2CH_3$.—Sodium bicarbonate (21.6 g., 0.26 mole) in H_2O (600 ml.) and $CH_2BrCBrFCO_2CH_3$ (64 g., 0.24 mole) are stirred at room temperature until one phase is present (10 days). The aqueous solution is acidified with dilute H_2SO_4 and continuously extracted with ether. Ether is removed, and H_2O is removed from the residue by azeotropic distillation with benzene. Distillation of the dark residue gives $CH_2BrCBrFCO_2H$ (45 g., 0.18 mole, 75% yield), b.p. 105° at 5 mm., sublimes under reduced pressure at *ca.* 70°, m.p. 71.0–72.5°, 247 neut. equiv. (calcd. 249.8).

2.5 Dehalogenation of $CH_2BrCBrFCO_2H$.—A solution of $CH_2BrCBrFCO_2H$ (10 g., 0.04 mole) in ether (300 ml.) is stirred with powdered Zn (3 g., 0.046 mole) and refluxed (8 hours). Appreciable precipitate is evident and the solution is filtered. Ether is removed under reduced pressure (H_2O aspirator) and carries some unsaturated product. The residue is placed in a sublimation apparatus and the product sublimed. Reduced pressure facilitates removal of the product from the viscous residue. $CH_2{=}CFCO_2H$ (2 g., 0.022 mole, 55% yield), resublimed three times, m.p. 51.5–52° found 20.65% F (calcd. 21.10% F), neut. equiv. 91.3 (calcd. 90.05), is obtained as colorless crystals which on fusion with Na give a negative test for Br^-. The yield is lowered by each sublimation. The residue after sublimation is quite viscous and after standing (7 days) at room temperature the sublimed product is an amorphous powder which softens and darkens at 130–140°.

2.6 Alternate Attempt: Fluorination of $CH_2BrCHBrCO_2CH_3$ with HgF_2.—Mercuric fluoride (150 g., 0.63 mole) and $CH_2BrCHBrCO_2CH_3$ (150 g., 0.61 mole) are stirred at 150 mm. and the temperature raised slowly. Reaction starts vigorously at 130° and reducing pressure to 120 mm. causes evolution of fumes and solidification of the mixture. Distillation is interrupted, additional $CH_2BrCHBrCO_2CH_3$ (100 g., 0.4 mole) added and the crude product (156 g.), b.p. 100° at 120 mm., is distilled. The distillate is washed with dilute HCl, H_2O, saturated NaCl, and dried over anhydrous $MgSO_4$. Distillation gives a monofluorinated product (92 g., 0.5 mole, 56% yield on 88% conversion), b.p. 92–94° at 80 mm., $n^{30}D$ 1.4389, d^{30}_4 1.624, M_R 30.0, AR_F 1.01, which is assumed to be $CH_2BrCHFCO_2CH_3$, and $CH_2BrCHBrCO_2CH_3$ (30 g., 0.12 mole). All attempts to remove hydrogen bromide from $CH_2BrCHFCO_2CH_3$ failed to give $CH_2{=}CF{-}CO_2CH_3$.

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(8) S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 970.

(9) F. Swarts, *Bull. Acad. Roy. Belg.*, 681 (1896).

(10) J. Böeseken, *Rec. trav chim.*, **46**, 844 (1927).

(11) Maxwell Nager, Ph.D. thesis, The Ohio State University, 1951, and laboratory notes.

(12) C. S. Marvel, THIS JOURNAL, **62**, 3496 (1940).

3.0 Preparation of $CF_2{=}CH{-}CO_2H$.

3.1 Dehydrohalogenation of $CF_3CH_2CO_2H$.—$CF_3CH_2CO_2H$ (11 g., 0.086 mole) in 150 ml. of H_2O is stirred and NaOH (6.9 g., 0.17 mole) in 200 ml. of H_2O is added intermittently at room temperature over a period of 10 days to keep the solution slightly basic. The neutral solution is made acid with cold 10% H_2SO_4 and continuously extracted with ether. Ether is removed under reduced pressure. Well defined crystals separate; after removing excess ether in a stream of dry air analysis gives 25.08% F (calcd. for $CF_2{=}CHCO_2H$, 35.2% F, $CF_2{=}CHCO_2H{\cdot}H_2O$ 30.2% F, $CF_2{=}CHCO_2H{\cdot}2H_2O$ 26.4% F). These crystals gave a positive test for unsaturation with aqueous $KMnO_4$ and react with Br_2 in CCl_4. Distillation at 5 mm. gives a trace of saturated material with neut. equiv. 127, 129 (calcd. for $CF_3CH_2CO_2H$ 126) and unsaturated material containing 27.05% F with neut. equiv. 146 (calcd. for $CF_2{=}CHCO_2H{\cdot}3H_2O$ 144).

4.0 Preparation of Perfluoroacrylic Acid, $CF_2{=}CFCO_2H$.

4.1 Dehydrohalogenation of $CHCl_2CF_2CF_2Cl$.—$CHCl_{23}$ CF_2CF_2Cl[13] (438 g., 2 moles) obtained by addition of $CHCl$- to $CF_2{=}CF_2$ (75% yield, 90% conversion) is treated with $NaOC_2H_5$ (136 g., 2 moles) in C_2H_5OH (900 ml.) while heating at 110° and stirring. The product is removed at 72–73° as an azeotrope with C_2H_5OH and $CHCl_2CF_2CF_2Cl$ through a column 3″ long packed with glass helices. The azeotrope and residue are washed with water and insoluble material dried over $MgSO_4$. Separation of the olefin from $CHCl_2CF_2CF_2Cl$ is difficult. Using a 2″ column packed with Podbielniak 0.2 mm. nichrome helices, a good fraction is obtained, b.p. 86.2° at 745.2 mm., $n^{25}{}_D$ 1.3950, $d^{25}{}_4$ 1.576, M_R 30.2, AR_F 1.12, found 28.71% F (calcd. 28.59% F); total material, b.p. 86–89° (281 g., 70% as $CCl_2{=}CFCF_2Cl$ on 100% conversion). Less efficient separations gave material with less satisfactory AR_F and analysis, *e.g.*, material b.p. 85.5–85.6° has $n^{25}{}_D$ 1.4010, $d^{25}{}_4$ 1.585, M_R 30.6, AR_F 1.23, found 24.66% F, 51.88% Cl. Attempts to increase $CCl_2{=}CFCF_2Cl$ yield by decreasing the rate of take-off resulted in the formation of substantial amounts of substitution products. $CHCl_2CF_2CF_2Cl$ (502 g., 2.3 moles) with $NaOC_2H_5$ (136 g., 2 moles) in C_2H_5OH (900 ml.) gave $CCl_2{=}CFCF_2Cl$ (260 g., 1.3 moles, 62.5% yield on 91% conversion); material b.p. 154° (68 g.), $n^{28}{}_D$ 1.4209, $d^{28}{}_4$ 1.425, calcd. as $C_2H_5OCCl{=}CFCF_2Cl$ or $CCl_2{=}CFCF_2OC_2H_5$, M_R 37.28, AR_F 1.46; and material, b.p. 55° at 20 mm. (41 g.), which was not investigated. Dehydrohalogenation with alcoholic KOH gave 56% $CCl_2{=}CFCF_2Cl$ on 55% conversion; manipulation of rates during addition and distillation was difficult. An insignificant amount of olefin was obtained by distillation with alcohol from the H_2O wash solution.

4.2 Dehydrohalogenation of $CHCl_2CFClCF_2Cl$.—$CHCl_2CFClCF_2Cl$, b.p. 125–130°, $n^{29}{}_D$ 1.4141 (36 g., 0.15 mole) obtained by addition of $CHCl_3$ (1194 g., 10 moles) to $CF_2{=}CFCl$ (232 g., 2 moles) with $AlCl_3$ (30 g.) (10.2% yield on 73% conversion) is treated with $NaOC_2H_5$ (10.4 g., 0.15 mole) in C_2H_5OH (65 ml.). The azeotrope, b.p. 69–72°, is washed and dried: distillation gives $CCl_2{=}CFCF_2Cl$, b.p. 84.5–85.5° (12 g., 0.06 mole, 55% yield on 73% conversion), $n^{22}{}_D$ 1.4046, $d^{22}{}_4$ 1.590, M_R 30.75, AR_F 1.29, % Cl found 52.8, calcd. 53.4. This is much better than the 4.1 procedure.

4.3 Oxidation–Bromination of $CF_2ClCF{=}CCl_2$.—Oxygen is bubbled through $CF_2ClCF{=}CCl_2$ (100 g., 0.5 mole crude sample) while stirring and adding Br_2 (40 g., 0.25 mole) very slowly. The reaction is protected by a condenser followed by an ice and a Dry Ice trap; material collecting in the traps is recycled over a period of 96 hours at which point unreacted Br_2 returned to reaction is not decolorized. The mixture does not react with H_2O; added slowly to NaOH (20 g., 0.5 mole) in 100 ml. of H_2O while warming, reaction is vigorous. Insoluble material remains which, separated, washed, dried over $MgSO_4$ and distilled, is $CF_2ClCF_2CHCl_2$ and/or $CF_2ClCH{=}CCl_2$ (29 g., 0.14 mole). The basic solution is acidified with H_2SO_4 (50 ml.) and continuously extracted with ether for 12 hours. Water is removed by distillation with ether and benzene; distillation under reduced pressure gives $CF_2ClCFClCO_2H$ (23 g., 0.117 mole), b.p. 65° at 8 mm. or 83–85° at 30 mm., neut. equiv. 196 (calcd. 197), $n^{25}{}_D$ 1.3868, $d^{25}{}_4$ 1.591, M_R 29.08, AR_F 1.68 and $CF_2ClCFBrCO_2H$ (23 g., 0.095 mole), b.p. 75° at 7 mm. or 85–86° at 15 mm., m.p. 23.9° (cooling curve), $n^{25}{}_D$ 1.948, M_R 31.09, AR_F 1.39, neut. equiv. 240.5 (calcd. 241.5), found 24.45% F (calcd. 23.65% F). Combined amount of Cl and Br weighed as AgCl and AgBr is 98.5% of the theoretical amount. Correcting for entrainment of Cl and/or Br in F analysis gives 23.25% F found. Separation is clean using a 2″ column with "Podbielniak" nichrome packing; however, decomposition of $CF_2ClCFBrCO_2H$ occurs.

4.4 Dehalogenation of $CF_2ClCFBrCO_2H$; Preparation of $CF_2{=}CFCO_2H$.—$CF_2ClCFBrCO_2H$ (5 g., 0.02 mole) is heated at 40° with Zn (2 g.) in dry ether (300 ml.) for 3 hours while stirring; reflux is rapid for a short period and reaction is evident. The cool mixture is filtered and ether is removed under reduced pressure through a water cooled condenser. Very little residue is obtained from the ether distillate on redistillation at 1 atmosphere. The residue is placed in a 5-ml. flask and $CF_2{=}CFCO_2H$ (*ca.* 1.0 g.) sublimed under reduced pressure through an inverted U tube into an ice-water cooled receiver as a colorless crystalline solid, m.p. 35.5–36.5° (sealed tube), neut. equiv. 126.7 (calcd. 126), found 45.16% F (calcd. 45.25% F), qualitative analysis for bromine after Na fusion is negative. The residue is very viscous and polymerizes to a solid on standing. $CF_2{=}CFCO_2H$ is extremely hygroscopic and great care must be observed to obtain a high m.p.; all weighings are made by difference in a glass stoppered weighing bottle; neutral equivalents must be made immediately after solution since the F hydrolyzes. $CF_2{=}CFCO_2H$ polymerizes at room temperature (3 days) coating the vessel with a viscous film and liberating acidic fumes. Identical experiments in which heating at 40° was continued for 2 hours and 45 minutes gives, respectively, 0.7 g. and 0.3 g. and in the latter case is complicated by contamination with $CF_2ClCFBrCO_2H$. $CF_2ClCFBrCO_2H$ (3 g.) and Zn (1 g.) in ether (300 ml.) heated 1 hour at 40° gives 0.4 g. of $CF_2{=}CFCO_2H$.

4.5 Alternate Attempts.—Dechlorination of $CF_2ClCFClCO_2H$ (5 g.) with zinc (1.5 g.) in ether (300 ml.) for eight hours gave a mixture of $CF_2{=}CFCO_2H$ and $CF_2ClCFClCO_2H$, the separation of which proved impractical.

Chromic oxidation of $CF_2HCF_2CH_2OH$, b.p. 105–110° (a gift of E. I. du Pont de Nemours Company) gives a mixture of $CF_2HCF_2CO_2H{\cdot}0.5H_2O$, b.p. 131.5–2.5°, neut. equiv. 152 (calcd. 155) and $CF_2HCF_2CO_2H{\cdot}1H_2O$, b.p. 136–137°, the dehydration of which on P_2O_5 does not give a clean cut of the dry acid, but rather the anhydride, b.p. 122.5–123.5° at 744 mm., neut. equiv. 275, calcd. 274. The methyl ester $CF_2HCF_2CO_2CH_3$, b.p. 93–94° at 754 mm., $n^{29}{}_D$ 1.3152, % F 46.6) calcd. 47.5%), and the amide recrystallized from chloroform, m.p. 58.4–59.4° with sublimation. It proved impossible to remove a molecule of hydrogen with a base, $CHF_2{-}CF_2{-}CO_2R \rightarrow CF_2{=}CFCO_2R$.

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[13] R. Cramer, D. D. Coffman and G. W. Rigby, THIS JOURNAL, **71**, 979(1949).