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Fluorocarboxylic Acids and Amides from Fluoroölefins and Sodium Cyanide

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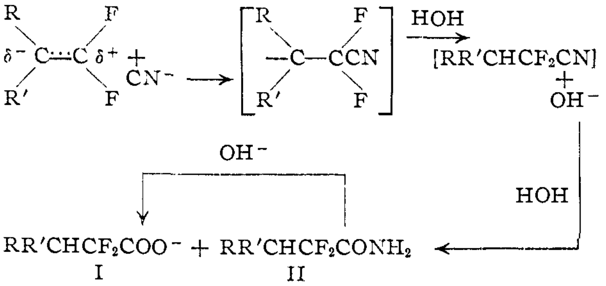
A variety of 1,1-difluoroölefins has been found to react with aqueous sodium cyanide in selected solvents under mild conditions to give fluorinated alkanoic acids and amides. For example, bromotrifluoroethylene, chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene and tetrafluoroethylene reacted exothermally, at less than four atmospheres pressure, with sodium cyanide and water in acetonitrile to give 40 to 90% yields of mixtures of the corresponding 1,1-difluoropropionic acids and amides. The acids from chlorotrifluoro- and dichlorodifluoroethylene were chlorinated and the resulting perhalopropionic acids hydrolyzed in fuming sulfuric acid to difluoromalonic acid. A variety of other derivatives of the fluoro acids were prepared.

The nucleophilic addition of alcohols[1] and amines[2] to polyfluoroölefins is well known. However, the addition of cyanide ion has not heretofore been demonstrated. We have found that a number of fluoroölefins, at four atmospheres pressure or less, react rapidly and exothermally with sodium cyanide and water in selected solvents to form mixtures of fluorocarboxylic acids and amides.[3] For example, when a solution of sodium cyanide and water in acetonitrile was shaken with chlorotrifluoroethylene at 3.7 atmospheres pressure, a reaction proceeded exothermally until one mole of olefin had been absorbed per mole of cyanide charged. Acidification of the alkaline mixture and extraction with ether afforded 70–80% yields of a mixture of the known 2-chloro-1,1,2-trifluoropropionic acid[3] (I, R = F, R′ = Cl) and the corresponding new amide in a ratio of about 3:1.

The olefins examined were all 1,1-difluoro alkenes which possess an electron deficient carbon atom susceptible to nucleophilic attack by cyanide ion. Thus, the reaction presumably proceeds by formation of a nitrile which is hydrolyzed *in situ* to a mixture of the amide and a salt of the corresponding acid.



Other fluoroölefins operable at low pressures and temperatures included bromotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene and tetrafluoroethylene (TFE).[3] Hexafluoropropene did not react under these mild conditions, but did form hexafluorobutyric acid when heated at 130° in a sealed tube with sodium cyanide and water.[3] On the other hand, when the propene was treated under similar conditions with potassium cyanide and acetone in the absence of water, hexafluorobutyramide was obtained in 12% yield. The intermediate nitrile was no doubt hydrolyzed to the amide during the isolation procedure. These results are summarized in Table I.

Acetonitrile was the preferred solvent for the sodium cyanide reaction and gave good yields of easily purified acids and amides. When dimethylformamide (DMF) was used as the solvent, the reaction proceeded with greater ease and rapidity, but the products were difficult to purify because of the tendency of DMF to complex with the products. For example, in runs with TFE, some of the acid and amide codistilled with the solvent and, in fact, portions of the acid and amide were isolated as 1:1 azeotropes with DMF.[3] The reaction was also carried out in acetone, dimethoxyethane, dimethyl sulfoxide, and the monomethyl or monobutyl ethers of ethylene glycol.

Although fluoronitriles are postulated as intermediates in the reactions described above, none were isolated in free form. This is not unexpected in view of the high alkalinity of the reaction mixtures and the known ease of alkaline hydrolysis of fluoronitriles.[4] However, in one experiment in which dimethylformamide (DMF) and a limited amount of water was used in the cyanide reaction with TFE, a small amount of 2,4,6-tris-(1,1,2,2-tetrafluoroethyl)-triazine (III), the trimer of tetrafluoropropionitrile, was obtained. It crystallized out of a portion of DMF distillate which had been distilled directly from the reaction mixture without prior acidification. This trimer probably was not formed directly from the nitrile, since a sample of the latter, prepared by dehydration of the amide, gave no trimer when heated in a sealed tube at 200° for four hours. Furthermore, the triazine was not formed by cyclodehydration of the amide, since the amide was recovered unchanged after being refluxed at 169° for six hours. In all probability, the triazine was formed from the corresponding amidine. This reaction has been shown to occur with perfluoroamidines under relatively mild conditions.[5] The amidine could arise from reaction of the nitrile with ammonia, which was always detected in the reaction mixtures.

A variety of derivatives were prepared from the fluoroacids and amides. Chlorination of the acids brought about replacement of the β-hydrogen atom by chlorine. Yields were low from 2,2,3,3-tetrafluoropropionic acid and from 3,3-dichloro-

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[1] (a) J. D. Park, C. M. Snow and J. R. Lacher, THIS JOURNAL, **73**, 861 (1951); (b) W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (1946).

[2] (a) R. L. Pruett, *et al.*, THIS JOURNAL, **72**, 3646 (1950); (b) G. W. Rigby and H. E. Schroeder, U. S. Patent 2,409,315 (1946).

[3] (a) D. C. England, U. S. Patent 2,802,028 (1957); (b) *C. A.*, **52**, 2052e (1958).

[4] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 493.

[5] W. L. Reilly and Henry C. Brown, *J. Org. Chem.*, **22**, 698 (1957).

TABLE I

FLUOROACIDS AND AMIDES

Olefin	Formula Structural	Formula Empirical	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Fluorine, % Calcd.	Fluorine, % Found
$F_2C{=}CF_2$[a]	HCF_2CF_2COOH[c]	$C_3H_2F_4O_2$	70–80	133–135		.....	1.3208						
	$HCF_2CF_2CONH_2$[c]	$C_3H_3F_4NO$	15–20	169		56–57[d]	....						
$ClFC{=}CF_2$[a]	$HCClFCF_2COOH$[c]	$C_3H_2ClF_3O_2$	60–70	159–160		......	1.3698						
	$HCClFCF_2CONH_2$	$C_3H_3ClF_3NO$	10–20	198–200		41–42[e]	....	22.3	22.3	1.9	2.2	..	..
$Cl_2C{=}CF_2$[a]	$HCCl_2CF_2COOH$	$C_3H_2Cl_2F_2O_2$	32	90–91	22	......	1.4228	20.1	20.3	1.1	1.7	21.2	19.3
	$HCCl_2CF_2CONH_2$	$C_3H_3Cl_2F_2NO$	9	.....		105–106[e]	....	20.2	20.2	1.7	1.8	21.4	21.0
$BrCF{=}CF_2$[a]	$HCBrFCF_2COOH$	$C_3H_2BrF_3O_2$	70–80	57–69	20	......	1.3980	17.4	18.0	1.0	1.3	27.5	27.2
$CF_3CF{=}CF_2$[b]	CF_3CFHCF_2COOH[c]	$C_4H_2F_6O_2$	23	138–142		......	....						
	$CF_3CFHCF_2CONH_2$[f]	$C_4H_3F_6NO$	12	76	1	......	....	..	..	..	..	58.4	57.3

[a] Run on 0.4 to 0.8 mole scale in acetonitrile with olefin pressure of four atmospheres or less and temperature of 80° or less. [b] Run in stainless steel shaker tube at 120–130° and autogenous pressure. [c] See ref. 3. [d] Recrystallized from benzene. [e] Recrystallized from carbon tetrachloride. [f] Calcd.: N, 7.2. Found: N, 7.3.

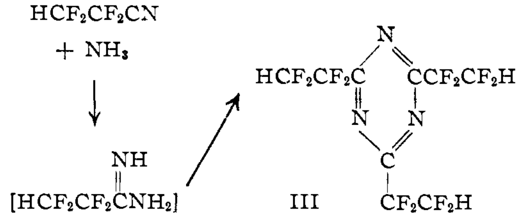
TABLE II

p-CHLOROANILINE SALTS

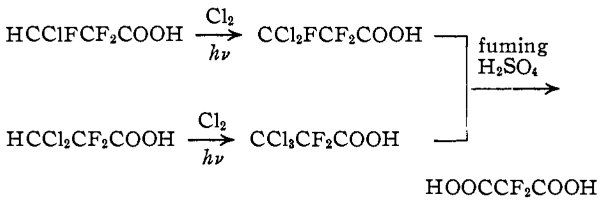
Parent acid	Salt formula	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
HCF_2CF_2COOH	$C_9H_8ClF_4NO_2$	118–119	39.6	39.4	3.0	3.1	274	276
$HCClFCF_2COOH$	$C_9H_8Cl_2F_3NO_2$	94	37.2	37.4	3.1	3.0	290	288
$HCCl_2CF_2COOH$	$C_8H_8Cl_3F_2NO_2$[a]	119					306	307
$HCBrFCF_2COOH$	$C_9H_8BrClF_3NO_2$	99	32.3	32.7	2.4	2.7	335	341
CF_3CFHCF_2COOH	$C_{10}H_8ClF_6NO_2$	107	37.2	37.4	2.5	2.7	324	322

[a] Calcd.: F, 12.4. Found: F, 12.5.

2,2-difluoropropionic acid, but the yield of 3,3-dichloro-2,2,3-trifluoropropionic acid from 3-chloro-2,2,3-trifluoropropionic acid was about 80%. Both this acid and 3,3,3-trichloro-2,2-difluoropropionic acid could be hydrolyzed to difluoromalonic acid with fuming sulfuric acid at 150–175°. Yields from the dichloro acid were about 50%. The formation of difluoromalonic acid from these compounds establishes that in the original reaction the cyanide ion adds to the most highly fluorinated carbon atom of the starting olefin.



III



$$HCClFCF_2COOH \xrightarrow[h\nu]{Cl_2} CCl_2FCF_2COOH$$

$$HCCl_2CF_2COOH \xrightarrow[h\nu]{Cl_2} CCl_3CF_2COOH$$

$$\xrightarrow{\text{fuming } H_2SO_4} HOOCCF_2COOH$$

In boiling aqueous alkali, 3,3-dichloro-2,2-difluoropropionic acid underwent facile elimination of hydrogen fluoride to form 3,3-dichloro-2-fluoroacrylic acid in over 80% yield. Under similar circumstances, 3-chloro-2,2,3-trifluoropropionic acid was degraded completely, whereas tetrafluoropropionic acid was unaffected.

$$HCCl_2CF_2COOH \xrightarrow[H_2O]{KOH} CCl_2{=}CFCOOH$$

The fluoroacids were converted to their crystalline *p*-chloroaniline salts (Table II). Azeotropic distillation of water from xylene solutions of the acids and amines, hydrazines or alcohols gave the corresponding anilides, hydrazides and esters (Table III). Reaction of certain of the amides with phosphorus pentachloride according to the method of Kirsanov[6] gave the corresponding N-(fluoroacyl)-trichlorophosphine imides (*e.g.*, IV) which were converted by formic acid to N-(fluoroacyl)-phosphoramidic dichlorides (*e.g.*, V). The amidic dichloride V reacted with sodium *p*-chlorophenoxide to form the *p*-chlorophenyl ester VI.

$$HCF_2CF_2CONH_2 \xrightarrow{PCl} \underset{IV}{HCF_2CF_2CON{=}PCl_3} \xrightarrow{HCOOH}$$

$$\underset{V}{HCF_2CF_2CONHPOCl_2} \xrightarrow[p\text{-}ClC_6H_4ONa]{}$$

$$\underset{VI}{HCF_2CF_2CONHPO(OC_6H_4Cl\text{-}p)_2}$$

Addition of acetylene to tetrafluoropropionic acid in the presence of mercuric tetrafluoropropionate according to a published procedure[7] gave vinyl tetrafluoropropionate in 70–80% yields. The vinyl ester readily was polymerized by free-radical catalysts to a clear, tough, low-softening polymer.

Experimental[7a]

Reaction of Chlorotrifluoroethylene with Sodium Cyanide and Water.—This reaction, carried out in dimethylformamide solvent, has been described.[3] However, by using acetonitrile as the solvent, the previously unknown 2-chloro-1,1,2-trifluoropropionamide has been obtained in addition to improved yields of more readily purified chlorotrifluoropropionic acid. Thus, the bottle of a low-pressure Parr hydrogenation apparatus was charged with 30 g. (0.51 mole) of sodium cyanide, 60 ml. of water and 60 ml. of acetonitrile. The apparatus was assembled, the bottle evacuated and filled with chlorotrifluoroethylene to a gauge pressure of 2.7 atmospheres. When shaking was started, absorption began immediately and the temperature of the reaction mixture rose to 70–80°. The rate of delivery of

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(6) A. V. Kirsanov, *Bull. Acad. Sci. (USSR), Div. Chem. Sci.*, 551 (1954).

(7) T. S. Reid, D. W. Codding and F. A. Bovey, *J. Polymer Sci.*, **18**, 417 (1955).

(7a) All melting points and boiling points are uncorrected.

TABLE III

ESTERS AND ANILIDES

Formula		Yield, %	B.p., °C. (m.p., °C.)	$n^{25}D$	Carbon, %		Hydrogen, %		Fluorine, %	
Structural	Empirical				Calcd.	Found	Calcd.	Found	Calcd.	Found
HCF_2CF_2COOEt[a,b]	$C_5H_6F_4O_2$	40	106–107	1.3272					43.7	44.0[c]
$HCClFCF_2COOEt$[a]	$C_5H_6ClF_3O_2$	65	136–137	1.3670	31.5	32.0	3.2	3.3	. .	. .
$HCCl_2CF_2COOEt$[a]	$C_5H_6Cl_2F_2O_2$	. .	165–166	1.4070	29.0	29.6	2.9	3.1	18.4	17.1
$HCF_2CF_2COOCH_2CH{=}CH_2$[a]	$C_6H_6F_4O_2$	71	123–124	1.3509	38.7	38.6	3.2	3.6	40.8	41.0
$(HCF_2CF_2COOCH_2)_4C$[a]	$C_{17}H_{12}F_{16}O_8$	60	158–159 (1 mm.)	1.3810	31.5	31.8	1.9	2.5	46.9	45.5
$HCF_2CF_2COOCH{=}CH_2$[d]	$C_5H_4F_4O_2$	70	88–89	1.3391	34.9	35.2	2.3	2.5	44.2	44.3
$HCF_2CF_2CONHC_6H_5$[e]	$C_9H_7F_4NO$	. .	(67–68)[f]	. . . .	48.8	48.3	3.2	3.1	34.4	34.3
$HCF_2CF_2CONHC_6H_4Cl$ (*p*)[a]	$C_9H_6ClF_4NO$	21	(69–70)[f]	. . . .	42.3	42.0	2.4	2.5	29.7	29.7
$HCClFCF_2CONHC_6H_4Cl$ (*p*)[e]	$C_9H_5Cl_2F_3NO$	. .	(78–79)[f]	. . . .	39.8	39.3	2.2	2.1	. .	. .
$HCF_2CF_2CONHNHC_6H_3Cl_2$ (2,5)[a]	$C_9H_6Cl_2F_4N_2O$	18	(92)[f]	. . . .	35.4	35.9	2.0	2.2	23.2[g]	23.5[g]
$HCClFCF_2CONHNHC_6H_3Cl_2$ (2,5)[a]	$C_9H_6Cl_3F_3N_2O$	23	(91)[f]	. . . .	33.7	34.1	1.9	2.1	33.1[g]	33.1[g]

[a] Azeotropic distillation of water from xylene or benzene solutions of components. [b] K. E. Rapp, *et al.*, THIS JOURNAL, **74**, 749 (1952), reported ethyl 2,2,3,3-tetrafluoropropionate, b.p. 68–70° (32 mm.), $n^{25}D$ 1.3663, but did not further characterize the product. It was presumed to have been formed by decarboxylation of ethyl hydrogen tetrafluorosuccinate. [c] Calcd.: sapn. equiv., 174. Found: sapn. equiv., 175. [d] Reaction of acid with acetylene; see Experimental. [e] Reaction of acid chloride with amine in benzene. [f] Recrystallized from cyclohexane. [g] Chlorine analyses.

TABLE IV

PHOSPHORUS DERIVATIVES

Formula		Yield, %	M.p., °C.	Carbon, %		Hydrogen, %		Others, %	
Structural	Empirical			Calcd.	Found	Calcd.	Found	Calcd.	Found
$HCF_2CF_2CON{=}PCl_3$	$C_3HCl_3F_4NOP$	73	89 (12 mm.)[a]	12.9	13.4	0.4	0.5	F, 27.2	F, 27.2
$HCF_2CF_2CONHPOCl_2$	$C_3H_2Cl_2F_4NO_2P$	63	65–69[b]	13.8	14.6	0.8	0.9	F, 29.0 Cl, 27.2	F, 28.3 Cl, 26.8
$HCF_2CF_2CONHPO(OC_6H_4Cl\text{-}p)_2$	$C_{15}H_{10}Cl_2F_4NO_4P$	48	108[b]	40.4	40.7	2.2	2.4	F, 17.0	F, 17.6
$HCClFCF_2CONHPOCl_2$[c]	$C_3H_2Cl_3F_3NO_2P$	41	82–84[b]	12.9	13.4	0.7	0.9	F, 20.4 Cl, 38.2	F, 20.9 Cl, 37.8
$HCCl_2CF_2CONHPOCl_2$[c]	$C_3H_2Cl_4F_2NO_2P$	. .	104–106[b]	12.2	12.7	0.7	0.9	Cl, 48.0	Cl, 47.7

[a] Boiling point. [b] Recrystallized from cyclohexane. [c] Prepared without isolation of the intermediate phosphine imide.

the olefin was regulated to maintain this temperature. Absorption was complete in about two hours. The cooled reaction mixture was acidified with 50% sulfuric acid, whereupon the mixture separated into two layers. The heavy layer was apparently a mixture of chlorotrifluoropropionamide and acid, but no advantage was found in separating the layers at this stage. The mixture was extracted with ether and the ether extract was dried over anhydrous magnesium sulfate. The products from five such runs were combined and distilled at atmospheric pressure in a 10-inch helices-packed column of about 0.5-inch inside diameter. Three fractions were taken:

Fraction	B.p., °C.	Identity	G.	Yield, %
A	150–166	Crude acid	255	62.5
B	166–192	Acid + amide	33	
C	192–201	Crude amide	77	19

Refractionation gave the pure acid,[3] b.p. 159–160°, and amide, b.p. 198–200°, m.p. 41–42°.

Other Fluoroölefins (Table I). **Bromotrifluoroethylene.**—In acetonitrile this olefin reacted similarly to the chloro analog. Bromotrifluoropropionic acid was obtained in 70–80% yields, but no amide was isolated.[8]

1,1-Dichloro-2,2-trifluoroethylene.—Reactions with this olefin were carried out at about 0.35 atmosphere gauge pressure which is the maximum pressure developed by the gas at room temperature when delivered directly from the storage cylinder. Relatively low yields of acid and amide and considerable amounts of tar were obtained.

Tetrafluoroethylene.—Acid and amide syntheses from tetrafluoroethylene have been described.[3] However, the reaction is best carried out in acetonitrile as described for chlorotrifluoroethylene. Preliminary external heating to about 60° was required to initiate the reaction.

Hexafluoropropene.—A 400-ml., stainless-steel shaker tube was charged with 32.5 g. (0.5 mole) of potassium cyanide, 80 ml. of acetone and 75 g. (0.5 mole) of hexafluoropropene. The tube was sealed and heated with shaking for three hours at 25° and three hours at 120°. The cooled reaction mixture was diluted with ether, filtered and extracted with water. The organic layer was dried and distilled to obtain 12 g. (12% yield) of hexafluorobutyramide, b.p. 76° (1 mm.). The amide set to a wax-like solid.[9]

The reaction of hexafluoropropene with sodium cyanide and water to form hexafluorobutyric acid has been described.[3]

Other Solvents.—The reaction rate in acetone, monomethyl or monobutyl ethers of ethylene glycol, dimethoxyethane, and dimethyl sulfoxide was comparable to that observed in acetonitrile. In dimethylformamide or dimethylacetamide, the reaction was very rapid and exothermic and no external heating was required. However, it was more difficult to isolate pure products from these solvents than from acetonitrile.

2,4,6-Tris-(1,1,2,2-tetrafluoroethyl)-triazine.—A mixture of 20.1 g. of disodium hydrogen phosphate heptahydrate, 30 g. of sodium cyanide and 75 ml. of dimethylformamide exothermally absorbed 58 g. of tetrafluoroethylene at a pressure of 2.7 atmospheres gauge. The material was distilled directly without prior acidification. After removal of DMF, a fraction was obtained boiling largely at 75° (10 mm.), $n^{25}D$ 1.3830, which was primarily the 1:1 azeotrope of DMF and tetrafluoropropionamide.[3] However, the infrared absorption spectrum showed the presence of small amounts of other components. After standing for several weeks, the mixture deposited crystals (0.5 g.) which were separated and recrystallized from carbon tetrachloride, m.p. 91–92°. Infrared, nuclear magnetic resonance and elemental analyses were in agreement for the cyclic trimer of tetrafluoropropionitrile, 2,4,6-tris-(1,1,2,2-tetrafluoroethyl)-triazine.

Anal. Calcd. for $C_9H_3F_{12}N_3$: C, 28.3; H, 0.89; N, 11.0; F, 59.8. Found: C, 28.4; H, 0.89; N, 10.9; F, 61.2.

***p*-Chloroaniline Salts** (Table II).—To a solution of about 0.5 g. of *p*-chloroaniline in 10 ml. of benzene was added an equivalent amount of the acid. On standing, the solution deposited an almost quantitative yield of the white crystalline salt. The salt was collected on a funnel and washed with low-boiling petroleum ether to obtain directly analytically pure material. Neutral equivalents were determined by dissolving the salts in water and titrating with 0.1 *N* sodium hydroxide.

Esters (Table III).—Esters were most conveniently prepared by dissolving equimolar quantities of acid and alco-

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[8] The reactions with this olefin were carried out by Dr. R. E. Putnam of this Laboratory.

[9] This reaction was carried out by Dr. R. A. Carboni of this Laboratory.

hol in an excess of benzene and refluxing under a water separator until the theoretical amount of water had been collected. For example, the esterification of 58 g. of tetrafluoropropionic acid with ethyl alcohol in 100 ml. of benzene was completed in two hours. The esters were isolated by direct distillation of the crude reaction mixtures.

Anilides and phenylhydrazides (Table III) were prepared by azeotropic distillation of water from xylene solutions of the components as illustrated by the preparation of the 2,5-dichlorophenyl hydrazide of 2,2,3,3-tetrafluoropropionic acid. A solution of 5.0 g. of 2,5-dichlorophenylhydrazine[10] and 6.0 g. of the acid in 50 ml. of xylene was refluxed under a water separator for four hours. The mixture was concentrated to half its original volume and diluted with petroleum ether to precipitate the hydrazide. The product was recrystallized from cyclohexane.

Anilides also were prepared by reaction of the amine with the appropriate acid chloride or anhydride in benzene.[11]

2,2,3,3-Tetrafluoropropionitrile.—2,2,3,3-Tetrafluoropropionamide (105 g.) was intimately mixed with 125 g. of phosphorus pentoxide by shaking in a flask which was then attached to a short still and heated to obtain 83.5 g. (90.6%) of tetrafluoropropionitrile, b.p. 14° (condenser cooled with ice-water). It was characterized by nuclear magnetic resonance.

The nitrile (12.7 g.) in an ice-cold solution of 20 g. of concentrated sulfuric acid in 80 ml. of water was treated dropwise with stirring with a solution of 46 g. of potassium permanganate in 35 ml. of water. The mixture was extracted with ether, dried and distilled to give 11 g. of 2,2,3,3-tetrafluoropropionic acid, b.p. 130–135°, $n^{25}\mathrm{D}$ 1.3268.

A sample of the nitrile heated in a sealed tube at 200° for four hours was recovered unchanged.

2,2,3,3-Tetrafluoropropionic Anhydride.—Slow distillation from a mixture of 50 g. of tetrafluoropropionic acid (prepared in acetonitrile solvent) and 30 g. of phosphorus pentoxide gave the anhydride, b.p. 122–123°, $n^{25}\mathrm{D}$ 1.3153, yield 30.0 g. (64%).

Anal. Calcd. for $C_6H_2F_8O_3$: C, 26.2; H, 0.7; F, 55.5; neut. equiv., 137. Found: C, 26.6; H, 1.3; F, 54.2; neut. equiv., 138.

It is interesting that only low yields of impure anhydride could be obtained from tetrafluoropropionic acid which had been prepared in dimethylformamide.

2,2,3,3-Tetrafluoropropionyl chloride, b.p. 38–40°, was prepared from the corresponding acid by distillation from an excess of benzoyl chloride or benzotrichloride. It was characterized by reaction with aniline in benzene to give the anilide, m.p. 67–68°.

Anal. Calcd. for C_3HClF_4O: Cl, 21.6; F, 45.9. Found: Cl, 20.8; F, 45.1.

3-Chloro-2,2,3-trifluoropropionyl Chloride.—A mixture of 33 g. of chlorotrifluoropropionic acid and 39 g. of benzotrichloride was placed in a flask attached to a 10-inch, helices-packed column. The mixture was stirred and heated to maintain a slow rate of distillation. There was obtained 21.4 g. (59%) of the acid chloride, b.p. 72–74°.

Anal. Calcd. for $C_3HCl_2F_3O$: Cl, 39.2; F, 31.5; neut. equiv., 90.3. Found: Cl, 39.3; F, 30.6; neut. equiv., 90.5.

3-Chloro-2,2,3,3-tetrafluoropropionic Acid.—Chlorine was bubbled through a sintered glass disk into tetrafluoropropionic acid (78 g.) in a quartz flask fitted with a well containing a GE H85-C3 mercury vapor lamp. A water condenser was attached to the flask. The inside temperature reached 110°. After reacting overnight only 43 g. remained in the flask and very little material was recovered from a wet-ice trap attached to the condenser. Apparently the loss in weight was due to decarboxylation. Nearly all of the recovered material boiled at 49° (18 mm.), $n^{26}\mathrm{D}$ 1.3380.

Anal. Calcd. for $C_3HClF_4O_2$: Cl, 19.7; neut. equiv., 180.5. Found: Cl, 19.7; neut. equiv., 181.

3,3,3-Trichloro-2,2-difluoropropionic Acid.—Chlorine was bubbled through dichlorodifluoropropionic acid (30 g.) in a flask equipped with a GE H85-C3 mercury vapor lamp. After two hours, the material was distilled to give recovered starting material and a trace of high-boiling solid. All of the distilled material was recombined in a quartz vessel in carbon tetrachloride, irradiated, and chlorinated as before for 18 hours. Distillation gave 14.7 g. of product boiling mostly at 104° (20 mm.) which solidified on cooling. This solid was recrystallized from hexane, m.p. 53–55°.

Anal. Calcd. for $C_3HCl_3F_2O_2$: Cl, 49.8. Found: Cl, 49.4.

3,3-Dichloro-2,2,3-trifluoropropionic Acid.—Chlorine was bubbled slowly through 3-chloro-2,2,3-trifluoropropionic acid (87 g.) in a Vycor tube for 15 hours while irradiating with a GE H85-C3 mercury vapor lamp. The liquid was then distilled to obtain 90 g. (85%) of 3,3-dichloro-2,2,3-trifluoropropionic acid, b.p. 168°, $n^{25}\mathrm{D}$ 1.3910.

Anal. Calcd. for $C_3HCl_2F_3O_2$: C, 18.3; H, 0.5; neut. equiv., 197. Found: C, 19.0; H, 1.1; neut. equiv., 194.

Difluoromalonic Acid.—A mixture of 3,3-dichloro-2,2,3-trifluoropropionic acid (6 ml., 10 g.) and 20% fuming sulfuric acid (10 ml.) was sealed in a Carius tube and heated to 175° for four hours. The tube was cooled in liquid nitrogen, opened, and inverted over about 25 g. of ice while the contents melted. The aqueous solution was saturated with sodium chloride and extracted several times with ether. The ether extract was dried and the ether removed to give 5 g. of impure crystalline difluoromalonic acid. This material was treated with aniline and the resulting salt recrystallized from acetone–chloroform to give 8.4 g. (51% based on dichlorotrifluoropropionic acid), m.p. 164–165° (lit. value[12] 160–161°). The acid could be purified directly by sublimation or by recrystallization from xylene. It melted at 117–118° (lit. value[11] 117–118°), was very hygroscopic and could be handled only in a relatively dry atmosphere.

In the manner described above, a 1-g. sample of 3,3,3-trichloro-2,2-difluoropropionic acid was sealed in a Carius tube with 5 ml. of 20% fuming sulfuric acid and heated to 150° for four hours. By the procedure noted above, there was obtained 0.3 g. of the aniline salt of difluoromalonic acid, m.p. 162–164°.

A sample of 3-chloro-2,2,3,3-tetrafluoropropionic acid was not hydrolyzed to difluoromalonic acid when heated to 200° with fuming sulfuric acid.

Diethyl Difluoromalonate.—A mixture of difluoromalonic acid (14 g.), ethyl alcohol (25 ml.) and benzene (100 ml.) was refluxed overnight while water was removed as an azeotrope. Distillation gave 17.7 g. (91%) of ethyl difluoromalonate, b.p. 58° (2 mm.), $n^{25}\mathrm{D}$ 1.3761.

Anal. Calcd. for $C_7H_{10}F_2O_4$: C, 42.9; H, 5.1; F, 19.4. Found: C, 43.5; H, 5.4; F, 19.0.

3,3-Dichloro-2-fluoroacrylic Acid.—3,3-Dichloro-2,2-difluoropropionic acid (45 g.) was refluxed in a solution of 33 g. of potassium hydroxide and 150 ml. of water for two hours. When cooled, the mixture set to a crystalline mass. It was treated with a cold solution of 25 ml. of concentrated sulfuric acid and 150 ml. of water and extracted with ether. The extracts were dried and distilled to obtain 33 g. (82%) of product boiling mostly at 72° (1 mm.). Recrystallization from water gave 30 g., m.p. 69–71°.

Anal. Calcd. for $C_3HCl_2FO_2$: C, 22.7; H, 0.6; Cl, 44.6; F, 12.0; neut. equiv., 159. Found: C, 23.0; H, 0.9; Cl, 44.5; F, 12.0; neut. equiv., 151.

An attempt to effect an analogous dehydrofluorination with 3-chloro-2,2,3-trifluoropropionic acid resulted in complete degradation of the acid. When 2,2,3,3-tetrafluoropropionic acid was subjected to this treatment, it was recovered unchanged.

Ethyl 3,3-Dichloro-2-fluoroacrylate.—A mixture of the acid (16 g.), ethyl alcohol (25 ml.), sulfuric acid (1 ml.) and benzene (100 ml.) was refluxed overnight while water was removed as the benzene azeotrope. Distillation of the reaction mixture gave the ester (14 g., 76%), b.p. 78° (30 mm.), $n^{25}\mathrm{D}$ 1.4550.

Anal. Calcd. for $C_5H_5Cl_2FO_2$: Cl, 37.9; F, 10.2. Found: Cl, 37.3; F, 10.0.

Vinyl 2,2,3,3-Tetrafluoropropionate.—In a 3-necked flask equipped with a stirrer, reflux condenser and gas inlet tube was placed 90 g. of tetrafluoropropionic acid, 7 g. of red mercuric oxide and 9 g. of tetrafluoropropionic anhydride. The mixture was stirred at 70° until a clear yellow solution was obtained. The solution was cooled to room temperature, blanketed with nitrogen and a stream of acetone-

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(10) Distillation Products Industries.

(11) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 132.

(12) D. E. M. Evans and J. C. Tatlow, *J. Chem. Soc.*, 3779 (1954).

stabilized acetylene bubbled into the well-stirred solution for 16 hours. A trace of hydroquinone was added and the product was distilled to obtain 74.0 g. (70%) of the vinyl ester (see Table III).

Polyvinyl 2,2,3,3-Tetrafluoropropionate.—A mixture of 6 g. of the vinyl ester and 0.01 g. of benzoyl peroxide in a sealed tube was heated at 80° for 12 hours. The solid plug of polymer was dissolved in acetone and reprecipitated by pouring into low-boiling petroleum ether. The polymer had an inherent viscosity of 1.09 (0.1% in dioxane at 25°) and could be pressed at 125° into a clear, colorless, colddrawable film.

Anal. Calcd. for $(C_5H_4F_4O_2)_n$: C, 34.9; H, 2.3; F, 44.2. Found: C, 34.3; H, 2.6; F, 44.3.

Phosphorus Derivatives (Table IV).—The preparation of these compounds is illustrated by the conversion of 2,2,3,3-tetrafluoropropionamide to a phosphoramidic ester, *via* the intermediate phosphine imide and phosphoramidic dichloride.

To a suspension of 25.5 g. of phosphorus pentachloride in 50 ml. of benzene was added, in small portions, 17.8 g. of tetrafluoropropionamide. An endothermic reaction occurred at each addition with vigorous evolution of hydrogen chloride. The benzene was evaporated under a stream of nitrogen and the residue was distilled at reduced pressure to afford 24.5 g. of the moisture-sensitive N-(tetrafluoropropionyl)-trichlorophosphine imide.

A benzene solution of the phosphine imide was prepared as described above from 28 g. of tetrafluoropropionamide and 40 g. of phosphorus pentachloride. To this solution was added, dropwise with stirring, 9 g. of formic acid. Vigorous gas evolution occurred. The benzene was removed under reduced pressure and the solid residue was crystallized from cyclohexane to obtain N-(tetrafluoropropionyl)-phosphoramidic dichloride.

Sodium *p*-chlorophenoxide was prepared by azeotropic distillation (three hours) of water from a mixture of 0.067 mole each of sodium hydroxide and *p*-chlorophenol in benzene. To this mixture was added 9.0 g. of the phosphoramidic dichloride dissolved in 50 ml. of tetrahydrofuran. The mixture was stirred at room temperature for three hours, distilled to half-volume, treated with 100 ml. of low-boiling petroleum ether and filtered. The filtrate was concentrated to a sirupy consistency and was allowed to stand for two days during which time the mass crystallized. It was recrystallized once from a benzene–petroleum ether mixture and twice from cyclohexane to obtain the pure *p*-chlorophenyl ester.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

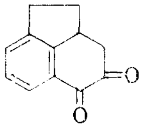
Acenaphthene Chemistry. III.[1] The Preparation and Reactions of 4,5-Acenaphthenequinonedibenzenesulfonimide[2]

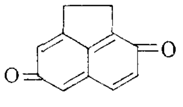
BY HENRY J. RICHTER AND BERTON C. WEBERG

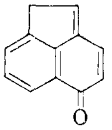
RECEIVED MAY 26, 1958

An acenaphthene derivative with a true quinoid structure has been prepared and characterized. Dark red 4,5-acenaphthenequinonedibenzenesulfonimide was prepared by the lead tetraacetate oxidation of 4,5-dibenzenesulfonamidoacenaphthene. Treatment of the quinone diimide with hydrochloric acid or hot pyridine caused isomerization to form the yellow 4,5-dibenzenesulfonamidoacenaphthylene. 4-Amino-5-benzenesulfonamidoacenaphthene when treated with nitrous acid gave 4,5-triazoloacenaphthene.

The literature on acenaphthenequinone, 1,2-diketoacenaphthene is quite extensive. However, acenaphthene derivatives in which the aromatic portion of the molecule is a part of the quinoid structure are unknown. The structural analogy to naphthalene would indicate acenaphthenequinone structures corresponding to







Two of these possibilities were considered by Sachs and Mosebach in 1911,[3] but no such derivative was described.

In 1920 Rowe and Davies[4] reported what they believed to be 4,5-acenaphthenequinone dioxime which they prepared by the oxidation of 4-nitro-5-aminoacenaphthene (I) with sodium hypochlorite followed by reduction with hydroxylamine. The dioxime of the quinone was described as a brown, amorphous, infusible powder. Although an analysis was reported which agrees with the calculated value, no characterization confirming this structure was described. The principal objective of the present work was the synthesis and characterization of an acenaphthene compound with a quinone structure.

4-Nitro-5-aminoacenaphthene (I), first described by Sachs and Mosebach,[3] was the derivative selected for the initial study. The amino nitro compound was reduced to 4,5-diaminoacenaphthene which proved to be too unstable for use in the proposed work. Adams[5–8] and his co-workers have shown that the sulfonimides of benzo- and naphthoquinones are characterized by greatly enhanced stability, and efforts were, therefore, directed to the synthesis of an appropriate acenaphthene disulfonamide for oxidation to a diimide possessing a quinoid structure. Treatment of I with benzenesulfonyl chloride afforded only a very low yield of 4-nitro-5-benzenesulfonamidoacenaphthene (II). With a large excess of benzenesulfonyl chloride, an N,N-disubstituted derivative was obtained. A more satisfactory approach to II was realized by nitrating 5-benzenesulfonamidoacenaphthene (III), which gave an 87% yield of II. Compound

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[1] Preceding papers: H. J. Richter, THIS JOURNAL, **75**, 2774 (1953), and H. J. Richter, *J. Org. Chem.*, **21**, 619 (1956).

[2] This work was supported by the National Institute of Health, Grant Cy-2997-Cy and by an Ohio Oil Co. Fellowship. It represents a portion of a thesis submitted by Berton C. Weberg in partial fulfillment of the requirements for the Ph.D. degree at the University of Colorado, 1958. Presented at the 134th National Meeting of the American Chemical Society at Chicago in September, 1958.

[3] F. Sachs and G. Mosebach, *Ber.*, **44**, 2852 (1911).

[4] F. M. Rowe and J. S. H. Davies, *J. Chem. Soc.*, 117, 1344 (1920).

[5] R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950).

[6] R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950).

[7] R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951).

[8] R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951).