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Nucleophilic Reactions of Fluoroolefins

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The scope of a number of base-catalyzed additions to fluoroolefins has been greatly extended. Thus, a wide variety of polyhydric alcohols and phenols, oximes, amines and amides have been added under moderate conditions of temperature and pressure. Certain of these reactions have been greatly facilitated by use of such solvents as dimethylformamide and dioxane. α,α -Difluoroamines, obtained by addition of strongly basic secondary amines to fluoroolefins, react readily with hydrogen cyanide to give the new α,α -dicyanoamines. Triphenylsilylpotassium, and sodium derivatives of diethyl malonate, diphenylacetone, 1-hexyne and phenylacetylene reacted with tetrafluoroethylene to give 1,2-disubstituted-1,2-difluoroethylenes.

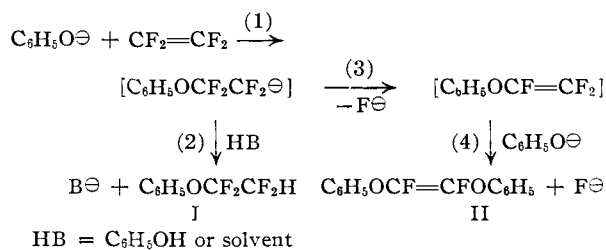
Nucleophilic additions to fluoroolefins are well known, but in many cases have been of rather limited scope, either with respect to the fluoroolefin or the nucleophile. We wish to report a greatly broadened scope for such reactions and, in addition, a novel reaction of certain α,α -difluoroamines with hydrogen cyanide to give the corresponding α,α -dicyanoamines. Several new "addition-elimination" reactions with organosodium derivatives also have been accomplished. Reactions of the various classes of nucleophiles are discussed in the following sections.

Hydroxy and Thiol Compounds (Table I).—Although alcohols have been added to a number of fluoroolefins at essentially atmospheric pressure,^{1a-d} such reactions with tetrafluoroethylene (TFE) have been accomplished only at appreciably higher pressures.^{2a,b,c} Furthermore, only in the case of the reaction of TFE with ethylene glycol^{2b} has a product derived from a fluoroolefin and a polyhydric alcohol been described and no products from phenols have been characterized.

We have found that base-catalyzed reactions of TFE with a variety of hydroxy compounds including polyhydric alcohols, phenols and oximes proceed rapidly at pressures of about four atmospheres when the reactions are conducted in such solvents as dimethylformamide (DMF), dioxane or dimethoxyethane. The reactions are conveniently carried out in a modified Parr low-pressure hydrogenation apparatus; DMF is the preferred solvent, since several reactions which went smoothly in DMF failed to proceed in dioxane. In the absence of solvent, many of these hydroxy compounds react sluggishly with TFE, even in sealed bombs under high pressure.

The polyfluoroalkyl ethers that have been prepared are listed in Table I. The advantages of the new procedure are strikingly demonstrated by the reaction of all hydroxyl groups in such compounds as pentaerythritol and dipentaerythritol, and by the smooth reactions with phenols. In the reaction of TFE with sodium phenoxide, a small amount of 1,2-difluoro-1,2-diphenoxyethyl-

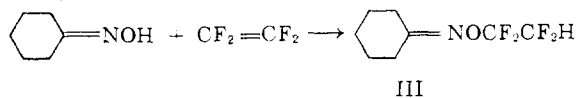
ene (II) also was obtained. This type of product arises from an addition-elimination process (steps 3 and 4), whereas the major reaction, which is favored by the presence of excess hydroxy compound, proceeds *via* step 2. Similar addition-elimination reactions of alkoxides with chlorotrifluoroethylene have been reported by Meier and Böhler.³ The saturated ether I was the only prod-



uct isolated when the amount of sodium was restricted to one-half gram atom per mole of phenol.

t-Butyl alcohol reacted exothermally with TFE in dimethylformamide at 2.7 atmospheres gauge pressure to give a 55% yield of *t*-butyl tetrafluoroethyl ether. Like the corresponding ether from chlorotrifluoroethylene,^{1c} this product was thermally unstable. In one experiment, during fractional distillation of the product, the final distillation fraction decomposed and formed two layers. Addition of a drop of this distillate to a previous fraction initiated an exothermic decomposition. The decomposition products were not examined, but presumably comprised mixtures of acyl and alkyl fluorides and polybutenes analogous to those reported for the chlorotrifluoroethylene product.^{1d} The ether obtained by reaction of propargyl alcohol with TFE in dimethoxyethane was also thermally unstable.

A new class of compounds, the polyfluoroethyl oximino ethers, were prepared by addition of ketoximes to TFE and chlorotrifluoroethylene.⁴ For example, cyclohexanoneoxime in the presence of its sodium salt reacted with TFE to give III in 44% yield.



(3) R. Meier and F. Böhler, *Chem. Ber.*, **90**, 2342 (1957).

(4) D. C. England, U. S. Patent 2,770,652 (1956). NOTE ADDED IN PROOF.—While this article was in proof, A. P. Stefani, J. R. Lacher and J. D. Park, *J. Org. Chem.*, **25**, 676 (1960), reported the addition of oximes to fluoroolefins to form oxime ethers of the type described above.

(1) (a) W. T. Miller, E. W. Fager and P. H. Griswold, *THIS JOURNAL*, **70**, 431 (1948); (b) J. D. Park, D. K. Vail, K. R. Lea and L. R. Lacher, *ibid.*, **70**, 1550 (1948); (c) J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **72**, 4480 (1950); (d) P. Tarrant and Henry C. Brown, *ibid.*, **73**, 1781 (1951).

(2) (a) W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (1946); (b) D. D. Coffman, M. S. Raasch, G. W. Rigby, P. L. Barrick and W. E. Hanford, *J. Org. Chem.*, **14**, 747 (1949); (c) J. D. Park, M. L. Sharrah, W. H. Breen and J. R. Lacher, *THIS JOURNAL*, **73**, 1329 (1951).

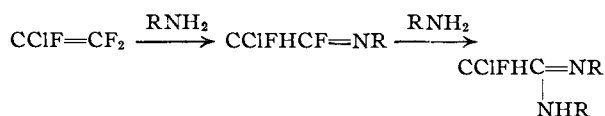
TABLE I
 REACTIONS OF HYDROXY AND THIOL COMPOUNDS WITH TFE^a

Compound, mole	Solvent, ml.	Sodium g. atom.	Product	Yield, %	B.p. °C. (mm.)	<i>n</i> _D ²⁰	Analyses, %					
							Calculated			Found		
							C	H (or other)	F	C	H (or other)	F
<i>t</i> -Butyl alcohol, 0.4	DMF (50)	0.2	(CH ₃) ₃ COCF ₂ CF ₂ H	55	87	1.3282	41.4	5.7	43.6	41.3	6.0	43.5
Propargyl alcohol, ^b 0.5	(CH ₃ OCH ₂) ₂ (100)	.1	HC≡CCH ₂ OCF ₂ CF ₂ H	40	87	1.3325			48.7			48.9
2,2-Dimethyl-1,3-propanediol, 0.1	Dioxane (50) DMF (50)	.05	(CH ₃) ₂ C(CH ₂ OCF ₂ CF ₂ H) ₂	75	80 (33)	1.3346	35.6	4.0	50.0	35.6	4.3	50.6
Pentaerythritol, 0.1	DMF (50)	.1	C(CH ₂ OCF ₂ CF ₂ H) ₄	65	113 (5)	1.3358	29.1	2.2	56.8	29.2	2.4	55.7
Dipentaerythritol, 0.1	DMF (100)	.1	[(HCF ₂ CF ₂ OCH ₂) ₃ CCH ₂] ₂ O	46	150-152 (1)	1.3519	30.9	2.6	53.4	31.8	2.9	53.7
Ethylene glycol monomethyl ether, 0.5	DMF (50)	.1	HCF ₂ CF ₂ OCH ₂ CH ₂ OCH ₃	75	117 (760)	1.3371	34.1	4.5	43.1	35.7	4.8	43.6
Phenol, 0.5	DMF (50)	.1	C ₆ H ₅ OCF ₂ CF ₂ H	50	147 (760)	1.4218	49.5	3.1	39.2	49.9	3.4	39.2
Phenol, 0.2	DMF (50)	.2	C ₆ H ₅ OCF ₂ CF ₂ H (30%) and (C ₆ H ₅ OCF ₂) ₂ =	3	134-139 (8) ^c		67.7	4.0	15.3	67.9	4.2	15.0
Catechol, 0.1	Dioxane (50) DMF (50)	.05	1,2-(HCF ₂ CF ₂ O) ₂ C ₆ H ₄	55	97-100 (32)	1.3859	38.7	1.9	49.0	38.7	2.2	51.8
Resorcinol, 0.1	Dioxane (50) DMF (50)	.05	1,3-(HCF ₂ CF ₂ O) ₂ C ₆ H ₄	55	78 (10)	1.3846	38.7	1.9	49.0	38.5	2.2	50.7
Hydroquinone, 0.1	Dioxane (50) DMF (50)	.05	1,4-(HCF ₂ CF ₂ O) ₂ C ₆ H ₄	58	81-83 (10)	1.3845	38.7	1.9	49.0	38.9	2.0	49.1
1-Naphthol, 0.1	Dioxane (50) DMF (50)	.025	1-(HCF ₂ CF ₂ O)C ₁₀ H ₇	57	87 (1.2-2.2)	1.5072	59.0	3.3	31.1	59.1	3.6	30.7
2-Naphthol, 0.1	Dioxane (50) DMF (50)	.025	2-(HCF ₂ CF ₂ O)C ₁₀ H ₇	52	75-76 (0.7)	1.5022	59.0	3.3	31.1	58.7	3.5	28.7
1,6-Naphthalenediol, 0.1	Dioxane (50) DMF (50)	.05	1,6-(HCF ₂ CF ₂ O) ₂ C ₁₀ H ₆	68	97 (0.5)	1.4605	46.7	2.2	42.1	47.1	2.4	42.1
Bis-(2-hydroxy-1-naphthyl)-methane, 0.1	Dioxane (50) DMF (50)	.05	[2-HCF ₂ CF ₂ O-1-C ₁₀ H ₆] ₂ CH ₂	47	M.p. 127-128 ^d		60.0	3.2	30.4	60.1	3.4	31.4
2,2'-Dihydroxy-bi-1-naphthyl, 0.1	Dioxane (50) DMF (50)	.05	[2-HCF ₂ CF ₂ O-1-C ₁₀ H ₆] ₂ -	29	M.p. 118-119 ^e		59.3	2.9	31.3	58.3	3.1	31.5
2,2-Bis-(4-hydroxyphenyl)-propane, 0.1	Dioxane (50) DMF (50)	.05	[<i>p</i> -(HCF ₂ CF ₂ O)C ₆ H ₄] ₂ C(CH ₃) ₂	63	136 (0.9)	1.4640	53.3	3.8		52.9	4.0	
2,2-Bis-(4-hydroxyphenyl)-propane, 0.1	Dioxane (50) DMF (50)	.05	[<i>p</i> -(HCClCF ₂ O)C ₆ H ₄] ₂ C(CH ₃) ₂ ^f	56	164-165 (0.3-0.5)	1.4928	49.5	3.5	24.8	49.5	3.6	24.6
Cyclohexanoneoxime, 0.1	Dioxane (50)	.05	HCF ₂ CF ₂ ON=C ₆ H ₁₀	44	77 (10)	1.4060	45.1	5.2	35.6	44.9	5.6	35.2
Cyclohexanoneoxime, 1.0	Dioxane (50)	.6	HCClCF ₂ ON=C ₆ H ₁₀ ^f	21	72-73 (4)	1.4355		6.1 (N)	24.8		6.1 (N)	25.4
Acetophenoneoxime, 1.0	Dioxane (50)	.87	C ₆ H ₅ C(CH ₃)=NOCF ₂ CF ₂ H	50	88-89 (6)			6.0 (N)	32.3		5.7 (N)	30.4
2-Ethylhexylmercaptan, 0.5	Dioxane (50)		(C ₂ H ₅)(C ₄ H ₉)CHCH ₂ SCF ₂ CF ₂ H	83	122-123 (65)	1.4088		12.8 (S)	29.1		13.0 (S)	30.9
Mercaptoacetic acid, 1.0	(Et) ₃ N (50)	. ^g	HCF ₂ CF ₂ SCH ₂ COOH	52	93-94 (4)	1.4083		16.7 (S)	39.6		16.9 (S)	40.3
Thiophenol, 1.0	Dioxane (50)	.04	C ₆ H ₅ SCF ₂ CF ₂ H	91	104-107 (72-76)	1.4672		15.2 (S)	36.2		15.4 (S)	37.3
<i>o</i> -Aminobenzenethiol, 0.3	Dioxane (50)	.06	1-HCF ₂ CF ₂ S-2-NH ₂ C ₆ H ₄	78	80-83 (3)	1.5138		14.2 (S)	33.8		13.9 (S)	33.8

^a Unless otherwise indicated, the fluoroolefin used was TFE. It was added slowly enough to keep the temperature at 60-100° until absorption was complete. A maximum gauge pressure of 2.7 atm. was used. ^b The temperature of this reaction was kept below 80° to avoid decomposition of the product. ^c Melting point 98-99° from methanol. ^d Recrystallized from ethanol. ^e Recrystallized from cyclohexane. ^f Fluoroolefin was chlorotrifluoroethylene. ^g Twelve grams of 40% aqueous Triton B used as catalyst.

Several thiols also were found to add to TFE at low pressures in triethylamine or in dioxane containing a catalytic amount of the corresponding sodium salts to give tetrafluoroethyl sulfides (see Table I). Rapp, *et al.*,⁵ previously reported similar reactions with chlorotrifluoroethylene in sealed tubes at autogenous pressure.

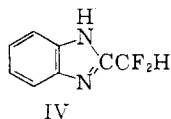
Primary Amines (Table II).—Chlorotrifluoroethylene reacts with primary amines to give imidyl fluorides which may be isolated, and which will react further with amine to give α -chloro- α -fluoroacetamidines.⁶



We have found that TFE reacts similarly to form difluoroamidines. Although imidyl fluorides were not isolated, their formation was indicated. Thus, in the reaction with cyclohexylamine, one of the products isolated was the *gem*-diamine, $\text{HCF}_2\text{CF}(\text{NHC}_6\text{H}_{11})_2$, presumably formed by addition of cyclohexylamine to the intermediate imidyl fluoride. On treatment with dilute alkali, the diamine readily lost hydrogen fluoride to form the corresponding amidine.

Reactions of primary amines with TFE in the presence of borax previously have been reported⁷ to give high yields of N-substituted α, α -difluoroacetamides. Undoubtedly, the fluoroamides were produced by hydrolysis of intermediate amidines, the borax serving as the source of water.

Most of the reactions of TFE with primary amines were carried out in the modified Parr apparatus. Low molecular weight amines reacted exothermally, and the reactions were controlled by regulating the rate of addition of TFE or by dilution with a solvent such as dioxane. With higher molecular weight aliphatic amines, heating was necessary to complete the reaction. Aromatic amines required higher temperatures and pressures and these reactions were run in an autoclave under autogenous pressure. Cyclic amidines were obtained from ethylenediamine, 1,3-propanediamine and *o*-phenylenediamine. For example, *o*-phenylenediamine gave a 50% yield of 2-difluoromethylbenzimidazole (IV).



The products that have been prepared from TFE, and primary amines are listed in Table II.

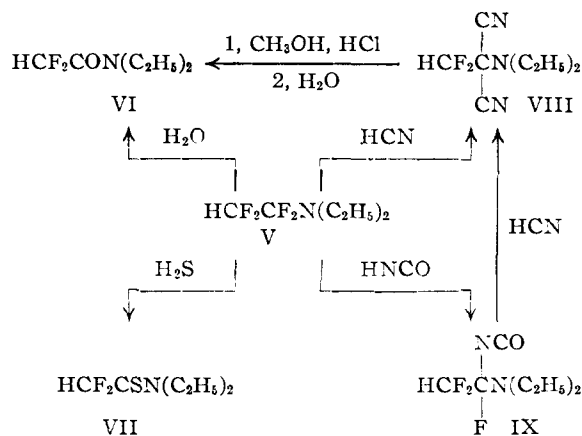
Secondary Amines (Table III).—The addition of diethylamine to chlorotrifluoroethylene reported by Pruett and co-workers⁵ has been extended to other aliphatic and alicyclic secondary amines and to other fluoroolefins. The reaction is very exothermic with strongly basic amines and, in some

(5) K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *THIS JOURNAL*, **72**, 3642 (1950).

(6) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **72**, 3646 (1950).

(7) H. E. Schroder and G. W. Rigby, U. S. Patent 2,409,315 (1946).

cases, *e.g.*, TFE and pyrrolidine, difficult to control without a solvent such as dioxane or ether. Although the products could be isolated by distillation at reduced pressure, they were not stable to heat and were hydrolyzed very easily to the corresponding α, α -difluoroacetamides. For example, tetrafluoroethyldiethylamine (V) from TFE and diethylamine was quantitatively (titration) hydrolyzed to N,N-diethyl- α, α -difluoroacetamide (VI).⁸ It also reacted with hydrogen sulfide under more vigorous conditions to give N,N-diethyl- α, α -difluorothioacetamide (VII).



The fluoroolefin-secondary amine adducts were found to undergo a remarkable displacement reaction with liquid hydrogen cyanide at 0° to give the corresponding α, α -dicyanoamines,⁹ as illustrated by the conversion of V to VIII. A number of such compounds are described in Table III. These compounds are quite stable and are not hydrolyzed by water. However, when a sample of VIII was refluxed in aqueous acid or base only tarry products were obtained, whereas treatment with methanolic hydrogen chloride followed by water gave VI as the only isolable product. Compound V also reacted with isocyanic acid but only one fluorine atom was replaced to give IX, which still contained a readily hydrolyzable fluorine atom. Reaction of IX with hydrogen cyanide resulted in replacement of this fluorine atom and the isocyanate group to give VIII.

Weakly Basic Secondary Amines and Amides (Table IV).—Pruett⁵ and co-workers reported that diphenylamine did not react with chlorotrifluoroethylene even under forcing conditions. We have been able to accomplish this reaction and similar reactions of weakly basic secondary amines with fluoroolefins by using catalytic amounts of the sodium or potassium salts of the amines.¹⁰ The use of dimethylformamide as solvent greatly facilitated these reactions. The products from diphenylamine were hydrolyzed quite easily to the corresponding amides by dilute acid or base. However, N-tetrafluoroethylpyrrole was stable to

(8) After the completion of our studies, the addition of diethylamine to TFE and hydrolysis of the product was reported by N. N. Yarovenko, M. A. Raksha, V. N. Shemanina and A. S. Vasileva, *Zhur. Obshchei Khim.*, **27**, 2246 (1957); *C. A.*, **52**, 6176a (1958).

(9) D. C. England, U. S. Patent 2,883,388 (1958).

(10) C. S. Cleaver and D. C. England, U. S. Patent 2,861,990 (1958).

TABLE II
 REACTIONS OF PRIMARY AMINES WITH TFE^a

Amine, ^b moles	Formula	Yield, %	B.p. °C. (mm.)	<i>n</i> _D ²⁰	Product					
					Calculated			Analyses, %		
					F	N	N.E. (or other)	F	N	N.E. (or other)
Ethylamine, ^c 1.1	HCF ₂ C(=NC ₂ H ₅)(NHC ₂ H ₅) ^d	53	149-150 (760)	1.4284	26.0	17.8	150	25.3	18.7	155
<i>n</i> -Butylamine, 1.0	HCF ₂ C(=N- <i>n</i> -C ₄ H ₉)(NH- <i>n</i> -C ₄ H ₉)	55	79-80 (4.5)	1.4360			206			209
Isobutylamine, 1.0	HCF ₂ C(=N- <i>i</i> -C ₄ H ₉)(NH- <i>i</i> -C ₄ H ₉)	54	80-81 (8)	1.4298			206			208
Cyclohexylamine, ^e 0.25	HCF ₂ CF(NHC ₆ H ₁₁) ^f	10	130 (2)	119-120 ^g (acetone)	10.1	60.4 (C)	9.0 (H)		10.0	60.0 9.4
	HCF ₂ C(=NC ₆ H ₁₁)(NHC ₆ H ₁₁) ^g	70	122-123 (4)	41-42 ^h (CH ₃ OH)			258			258
<i>n</i> -Octylamine, ^e 1.2	HCF ₂ C(=NC ₈ H ₁₇)(NHC ₈ H ₁₇)	56	158-160 (3)	1.4480	12.0	8.8	319	13.0	8.8	318
<i>n</i> -Octylamine, ^h 0.7	HCF ₂ CONHC ₈ H ₁₇ ⁱ	95	167-170 (38)	1.4289	18.4			18.3		
<i>n</i> -Dodecylamine, ^e 0.8	HCF ₂ C(=NC ₁₂ H ₂₅)(NHC ₁₂ H ₂₅)	90 ^j		1.4459	8.8	6.5	430	7.9	5.5	484
Benzylamine, 1.5	HCF ₂ C(=NCH ₂ C ₆ H ₅)(NHCH ₂ C ₆ H ₅)	70	175-176 (3) ^k	1.5609	13.9	10.2	274	14.1	9.7	280
Ethylenediamine, ^c 1.0	HCF ₂ C(=NCH ₂ CH ₂ NH-)	50	88-89		31.7	23.3	120	32.4	23.2	120.6
1,3-Propanediamine, ^c 1.2	HCF ₂ C(=NCH ₂ CH ₂ CH ₂ NH-)	56	41-42		28.4		134	28.7		134.5
Aniline, ^l 0.33	HCF ₂ C(=NC ₆ H ₅)(NCH ₆ H ₅)	85	32-34		15.5	11.4		16.1	11.7	
<i>o</i> -Phenylenediamine, ^m 0.3	HCF ₂ (=NC ₆ H ₄ -2-NH-)	50	155-156		22.6	16.7		22.0	16.7	

^a The TFE was added slowly enough to keep the temperature below 80° until absorption was complete unless noted otherwise. A maximum gauge pressure of 2.7 atm. was used. ^b No solvent was used unless otherwise indicated. ^c One hundred ml. of dioxane solvent. ^d Warming this amidine in 10% sodium carbonate gave N-ethylidifluoroacetamide (b.p. 57-62° (5 mm.)) in 95% yield. *Anal.* Calcd. for C₄H₇NOF₂: F, 30.9; N, 11.4. Found: F, 30.6; N, 11.2. ^e Heated to 100°. ^f This diamine was separated from the amidine shown on the line below by crystallization from acetone, the amidine remaining in the filtrate. The diamine was converted easily to the amine by treatment with cold 10% KOH. ^g Treatment of this amidine with warm 15% H₂SO₄ precipitated a salt which could be recrystallized from nitromethane (m.p. 205-207°). *Anal.* Calcd. for C₁₄H₂₄N₂F₂·H₂SO₄: C, 47.2; H, 7.3; N, 7.9; F, 10.7; S, 9.0. Found: C, 46.4; H, 7.5; N, 7.5; F, 11.2; S, 8.7. When the amidine was refluxed in dilute acid or alkali, it was hydrolyzed to N-cyclohexylidifluoroacetamide, m.p. 70-72° (*ex* methylcyclohexane). *Anal.* Calcd. for C₈H₁₂NOF₂: C, 54.2; H, 7.3; N, 7.9; F, 21.5. Found: C, 54.2; H, 7.3; N, 7.9; F, 20.9. ^h Ten grams of 10% aq. sodium carbonate added. ⁱ Previously reported (Rigby and Schroeder, U. S. Patent 2,409,315), b.p. 105° (5 mm.), *n*_D²⁰ 1.4300. ^j This impure product was not stable to distillation. ^k Solidified on standing. ^l In a stainless steel bomb with 0.25 mole of TFE at 135°; maximum pressure 82 atm. ^m In a bomb with 0.3 mole of TFE at 136°; maximum pressure 135 atm. ⁿ Melting points.

 TABLE III
 ADDITION OF SECONDARY AMINES TO FLUOROOLEFINS^a AND REACTION OF THE PRODUCTS WITH HYDROGEN CYANIDE^b

Fluoroolefin	Secondary amine	Fluoroamine intermediates		Malononitriles										
		Product	Yield, %	B.p. °C. (mm.)	Identity	B.p. °C. (mm.)	Yield, %	<i>n</i> _D ²⁰	Calculated			Analyses, %		
								N	F	Other	N	F	Other	
CF ₂ =CF ₂	(C ₂ H ₅) ₂ NH	HCF ₂ CF ₂ N(C ₂ H ₅) ₂	77	64 (110) ^c	HCF ₂ C(CN) ₂ N(C ₂ H ₅) ₂	52 (1)	91	1.4091	22.4	20.3	51.4 (C)	20.9	20.0	51.5 (C)
										5.9 (H)				5.8 (H)
CF ₂ =CF ₂	Pyrrolidine	HCF ₂ CF ₂ N(CH ₂) ₄	60	70 (100)	HCF ₂ C(CN) ₂ N(CH ₂) ₄	66 (2)	83		22.7	20.5		22.2	20.6	
CF ₂ =CF ₂	Piperidine	HCF ₂ CF ₂ N(CH ₂) ₅	85	84 (100)	HCF ₂ C(CN) ₂ N(CH ₂) ₅	72 (2)	85	1.4378	21.1	19.1		20.3	19.0	
CF ₂ =CFCI	(C ₂ H ₅) ₂ NH	HCFCICF ₂ N(C ₂ H ₅) ₂	70	37 (10)	HCFCIC(CN) ₂ N(C ₂ H ₅) ₂	66 (2)	70		20.6	9.1	17.4 (Cl)	20.8	9.3	17.4 (Cl)
CF ₂ =CCl ₂	(CH ₃) ₂ NH ^d	HCCl ₂ CF ₂ N(CH ₃) ₂	18	42 (10)	HCCl ₂ C(CN) ₂ N(CH ₃) ₂	M.p. 105	76		21.9		36.9 (Cl)	21.8		36.6 (Cl)
CF ₂ =CFCF ₃	(C ₂ H ₅) ₂ NH	CF ₃ CHFCF ₂ N(C ₂ H ₅) ₂	75	54 (50)	CF ₃ CHFC(CN) ₂ N(C ₂ H ₅) ₂	59 (1)	69	1.3930	17.7	32.1		17.8	32.4	
CF ₂ =CFCF ₃	Pyrrolidine	CF ₃ CHFCF ₂ N(CH ₂) ₄	34	65 (50)	CF ₃ CHFC(CN) ₂ N(CH ₂) ₄	66 (2)	43	1.4082		32.3		Low	32.8	

^a Unless otherwise stated, the fluoroolefin was added slowly to the amine, keeping the temperature below 60°. A maximum pressure of 2.7 atm. was used. ^b Reactions with hydrogen cyanide were at 0° in a platinum or polyethylene container. ^c Reference 8 reported b.p. 31° (15 mm.). ^d The amine addition was carried out in a sealed tube at 50°.

TABLE IV
REACTIONS OF FLUOROOLEFINS WITH WEAKLY BASIC SECONDARY AMINES AND AMIDES^a

Amine, moles	Solvent, ml.	Catalyst, g. atom	Olefin	Formula	Yield, %	B.p., °C. (mm.)	n _D ²⁰	Analyses, %				
								Calculated	Found	Other		
Pyrrole, 1.5	None	K, 0.1	TFE	HCF ₂ CF ₂ N-(C ₆ H ₅)	74	102 (760)	1.3898	45.5	43.1 (C)	44.9	43.9 (C)	3.0 (H)
Pyrrole, 0.79	None	K, 0.1	CClF=CF ₂	HCClFCF ₂ N-(C ₆ H ₅) ^b	68	70-75 (100)	1.4428	31.1	19.3 (Cl)	31.1	19.4 (Cl)	
Pyrrole, 0.79	DMF, 50	K, 0.13	CF ₃ CF=CF ₂	CClF=CFN-(C ₆ H ₅) ^{b,c}	59	70 (100)	1.4750	23.3	21.7 (Cl)	23.7	21.2 (Cl)	
Pyrrole, 0.2	DMF, 25	K, 0.05	C ₆ H ₅ CF=CF ₂ ^d	CF ₃ CHF ₂ N-(C ₆ H ₅)	58	90 (20)	1.4372	27.8	6.4 (N)	51.0	6.7 (N)	
Pyrrole, 0.2	None	K, 0.05	C ₆ H ₅ CF=CF ₂ ^e	(C ₆ H ₅) ₂ CHFCF ₂ N-(C ₆ H ₅)	50		81-82 ^f	7.5	11.1 (N)	7.3	11.0 (N)	
Indole, 0.3	DMF, 50	K, 0.05	CClF=CF ₂	HCF ₂ CF ₂ N-(C ₆ H ₅)	74.5	83 (10)	1.4961	35.0	6.4 (N)	33.9	6.4 (N)	
Indole, 0.3	DMF, 50	K, 0.05	CClF=CF ₂	HCClFCF ₂ N-(C ₆ H ₅)	88	79 (3)	1.5281	24.4	15.2 (Cl)	24.3	15.2 (Cl)	
Carbazole, 0.4	DMF, 100	K, 0.1	TFE	HCF ₂ CF ₂ N-(C ₆ H ₅)	62	133 (2)	48-49 ^g	28.4	63.0 (C)	29.1	63.7 (C)	3.5 (H)
Phenothiazine, 0.3	DMF, 75	Na, 0.1	TFE	HCF ₂ CF ₂ N-(C ₆ H ₅) ^h	69	148 (3)	58-59 ^h	25.4	10.7 (S)	25.5	10.7 (S)	
Diphenylamine, 0.4	DMF, 50	K, 0.1	TFE	(C ₆ H ₅) ₂ NCF ₂ CF ₂ H	63	98 (1)		28.3	62.5 (C)	27.0	64.5 (C)	4.5 (H)
Diphenylamine, 0.1	(CH ₃ OCH ₂) ₂ , 25 DMF, 25	K, 0.01	CClF=CF ₂	(C ₆ H ₅) ₂ NCOCF ₂ H ⁱ	65		90-91 ^f	15.4	5.7 (N)	15.2	5.8 (N)	68.2 (C)
Caprolactam, 0.2	(CH ₃ OCH ₂) ₂ , 150	Na, 0.1	TFE	(C ₆ H ₅) ₂ NCF ₂ CF ₂ H ⁱ	29	63 (2)	1.4108	35.7	6.6 (N)	35.6	7.1 (N)	
Caprolactam, 0.2	(CH ₃ OCH ₂) ₂ , 200	Na, 0.1	CClF=CF ₂	HCClFCF ₂ N-(COC ₆ H ₁₀)	52	85 (2)	1.4418	24.8	15.5 (Cl)	25.0	15.5 (Cl)	6.1 (N)
Acetamide, 0.2	(CH ₃ OCH ₂) ₂ , 100	Na, 0.1	TFE	C ₆ H ₅ N(COCH ₃)(CF ₂ CF ₂ H)	51	84 (4)	1.4511	32.3	6.0 (N)	31.6	6.0 (N)	
Acetamide, 0.3	(CH ₃ OCH ₂) ₂ , 100	Na, 0.1	CClF=CF ₂	C ₆ H ₅ N(COCH ₃)(CF ₂ CClFH)	47	93 (2)	1.4820	22.7	14.1 (Cl)	22.7	14.4 (Cl)	5.8 (N)

^a The olefin was added slowly enough to keep the temperature below 80° until absorption was complete. A maximum gauge pressure of 2.7 atm. was used. ^b Structure not proved; may be a mixture of isomers. ^c Formed from saturated precursor by treatment with sodium *t*-butoxide in *t*-butyl alcohol. ^d Prepared from TFE and butyl- (or phenyl)-lithium by the method of Dixon, ref. 11. ^e Structure not proved. ^f M.p.; recrystallized from methanol. ^g M.p.; recrystallized from low-boiling petroleum ether. ^h M.p.; recrystallized from cyclohexane. ⁱ Prepared from the preceding α,α -difluoroamine by treatment with cold 20% hydrochloric acid or potassium hydroxide. ^j Crude product converted directly to the amide by washing with 20% hydrochloric acid.

refluxing 20% potassium hydroxide. Under similar conditions, it was possible to add caprolactam and acetanilide to either TFE or chlorotrifluoroethylene. No prior additions of amides to fluoroolefins have been reported.

Butyltrifluoroethylene and trifluoroethylene were similar to other fluoroolefins in that pyrrole could be added in the presence of potassium pyrrole. However, the only product isolated from trifluoroethylene and potassium pyrrole, even in the presence of excess pyrrole, was an addition-elimination product, either $C_6H_5CF=C(NC_4H_4)_2$ or its isomer.

Organometallic Compounds (Table V).—Addition-elimination reactions of fluoroolefins with lithium alkyls^{11a} and Grignard reagents^{11b} to give substituted fluoroethylenes have been reported. Several additional examples of this type of reaction have now been found. For example, the sodium derivatives of 1-hexyne and phenylacetylene reacted with TFE to give low yields of products of the type $RC\equiv C-CF=CFC\equiv CR$ ($R = CH_3(CH_2)_3-$ and C_6H_5-). Similar reactions were carried out with sodiodiphenylacetonitrile and diethyl sodiomalonate. The product from the latter reaction was hydrolyzed and then decarboxylated to yield 3,4-difluoro-3-hexenedioic acid; TFE also reacted with triphenylsilylpotassium¹² to give 1,2-difluoro-1,2-bis-(triphenylsilyl)-ethylene.

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Experimental¹³

Apparatus.—Most of this work was carried out in a modified Parr low-pressure hydrogenation apparatus. The reservoir tank was removed from the apparatus, and the pressure gauge was attached to a manifold system with needle valves leading to a vacuum line, a nitrogen purge line, a storage cylinder of TFE and a bleed valve. The storage cylinder containing "Terpene-B" stabilized TFE was equipped with a reducing valve set for a maximum gauge pressure of 2.7 atmospheres (40 lb./sq. in.). The rubber stopper of the glass reaction vessel was equipped with a thermocouple retainer comprising a glass tube whose sealed end led almost to the bottom of the reaction vessel. A second opening in the stopper held a gas inlet tube of heavy-walled capillary glass attached by means of Tygon plastic pressure tubing to the pressure gauge. To the base plate of the reaction vessel was attached a commercially available disk heater, and this was connected to a Variac or Powerstat.

General Procedure.—To a solution or slurry of 0.1–0.5 mole of the hydroxy compound in 50–75 ml. of sodium-dried dioxane was added the appropriate amount of sodium, preferably as a 50% dispersion in xylene. In general, about 0.25 g. atom of sodium was used per mole of hydroxyl group. This mixture was stirred mechanically for 1 hour, diluted with 50 ml. of DMF and transferred to the reaction vessel. The vessel was placed in a gridded metal shield and secured in the apparatus. *Subsequent operations were carried out behind a protective shield.* The vessel was purged several times with nitrogen, then with TFE and, finally, pressured to 2.7 atmospheres and the main TFE valve closed. Shaking was begun and a rapid decrease in pressure to about 2 atmospheres occurred as the olefin dissolved in the solvent. In the case of non-spontaneous reactions, heat was applied at this point, and the fluoroolefin was bled off to maintain a pressure of 2.7 atmospheres during the heating process until pressure reduction occurred, indicating the onset of reaction. In the case of spontaneous re-

(11) (a) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956). (b) P. Tarrant and D. A. Warner, *THIS JOURNAL*, **76**, 1624 (1954).

(12) A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954).

(13) All boiling points and melting points are uncorrected.

TABLE V
REACTION OF ORGANOMETALLIC COMPOUNDS WITH TFE

Compound, mole	Solvent, ml.	Metal, g. atom	Olefin	Formula	Yield, %	B.p., °C. (mm.)	n_D^{20}	Product					
								Calculated, %			Analyses, %		
								C	H	F	C	H	F
Diethyl malonate, ^a 0.2	Dioxane, 100	Na, 0.2	TFE	$[=CFCH(COOEt)]_2$ ^b	48.5	150 (1)	1.4452	80.7	4.5	10.0	81.1	4.6	10.2
Diphenylacetonitrile, ^a 0.05	Dioxane, 50	Na, 0.05	TFE	$[(C_6H_5)_2C(CN)CF]_2$ ^c	46		1.66–1.67 ^e (EtOH)	75.0	8.0	8.5	6.3 (N)	8.2	6.5 (N)
1-Hexyne, 0.3	$(CH_3OCH_2)_2$, 250	Na, ^c 0.3	TFE ^d	$(C_6H_5C\equiv CCF)_2$ ^e	30	91 (1)	1.4842	74.3	8.0	17.0	74.3	8.2	16.4
Phenylacetylene, 0.2	$(CH_3OCH_2)_2$, 100	Na, ^c 0.2	TFE	$(C_6H_5C\equiv CCF)_2$ ^e	9		82–83 ^e (CH ₃ OH)	14.4		14.4			13.9
Hexaphenyldisilane, 0.01	Ether, 50	K, 0.02	TFE	$[(C_6H_5)_3SiCF=]_2$	7		253 ^e (acetone)			6.6			7.0

^a This reaction mixture heated at 125° for one hour. ^b This reaction was reported in British Patent 583,874, but the product was not characterized; see Experimental Section for conversion to 3,4-difluoro-3-hexenedioic acid. ^c The sodium acetylide was prepared in liquid ammonia and the ammonia was replaced by dimethoxyethane. ^d TFE was added slowly enough to keep the temperature at 40–45°; higher temperatures gave lower yields. ^e Melting point.

actions, reduction in pressure occurred exothermally. When reaction was evident and the gauge pressure registered less than about one atmosphere, the vessel was repressured to 2.7 atmospheres. Theoretical absorption of 0.1 mole of TFE within the pressure limits of 2.7 to 2 atmospheres required repressuring 7 to 8 times. After completion of reaction, the mixture was cooled to room temperature and poured into water. The organic layer was extracted with ether, washed first with water, then with dilute sodium hydroxide solution, dried over magnesium sulfate, and distilled or recrystallized.

Procedure Variations.—In some experiments (see Table I), either DMF or dioxane was used alone as solvent. In such cases the hydroxy compound was dissolved or suspended in the single solvent, treated with sodium dispersion and then manipulated as indicated above. Although sodium reacts with DMF, it apparently reacted preferentially with the hydroxylic substrates since no effective loss in catalyst activity was observed.

Reactions of fluoroolefins with weakly basic secondary amines and with amides were carried out as described for alcohols. Reactions with basic secondary amines and with primary amines were carried out in the same equipment without catalyst and usually without solvent. The products from primary amines were filtered from amine hydrofluoride and washed with 5% sodium hydroxide before distillation. Products from aliphatic secondary amines were distilled directly.

Products from Fluoroolefins and Secondary Amines.—Products obtained from fluoroolefins and secondary amines fumed in moist air and were difficult to keep pure because of their reactivity. Most of them were not analyzed and were used immediately after distillation for the preparation of the dicyano derivatives (see Table III), which were very stable and easily handled. However, tetrafluoroethyl-diethylamine (V), prepared from diethylamine and TFE, was further characterized by a neutral equivalent. This was obtained by weighing a sample into a vial which was sealed and broken in standard 0.1 *N* sodium hydroxide. The solution then was back-titrated with 0.1 *N* hydrochloric acid.

Anal. Calcd. for $C_8H_{11}F_4N$: neut. equiv., 86.5. Found: neut. equiv., 88.0, 88.4.

The hydrolysis product, *N,N*-diethyl difluoroacetamide (VI), was prepared on a larger scale and isolated by ether extraction and distillation, b.p. 79° (25 mm.), n_D^{25} 1.4130 (lit. values⁸ b.p. 97° (60 mm.), n_D^{20} 1.4155).

Anal. Calcd. for $C_8H_{11}ONF_2$: C, 47.6; H, 7.3; F, 25.2. Found: C, 48.0; H, 7.4; F, 25.3.

***N,N*-Diethyl difluorothioacetamide (VII).**—Tetrafluoroethyl diethylamine (23 g.), hydrogen sulfide (12 g.) and diethyl ether (50 ml.) were sealed in a heavy-walled Carius tube and heated overnight on a steam-bath. The product was poured into water, extracted with ether, dried and distilled to give 14.9 g. (67%), b.p. 84–86° (20 mm.), n_D^{25} 1.4921. Infrared and nuclear magnetic resonance spectra supported the proposed structure.

Anal. Calcd. for $C_8H_{11}F_2NS$: F, 22.7; S, 19.2. Found: F, 23.0; S, 19.3.

(Diethylamino)-(difluoromethyl)-malononitrile (VIII).—The following is a typical procedure used for the preparation

of the compounds listed in Table III. To obtain the best yields, it is important to use *dry* hydrogen cyanide and to avoid the use of a glass reaction vessel, since hydrogen fluoride is evolved during the reaction. Hydrogen cyanide (50 ml., previously distilled from phosphorus pentoxide) was placed in a polyethylene bottle equipped with a magnetic stirrer and cooled in an ice-bath. Tetrafluoroethyl diethylamine (57 g.) was added dropwise with stirring. When the addition was complete, the mixture was warmed to room temperature and poured into ice-water. The lower layer was extracted with ether, dried and distilled to obtain 56.2 g. (91%) of product, b.p. 52° (1 mm.).

1,2-Trifluoro-1-(diethylamino)-ethyl Isocyanate.—To a solution of 40 g. (0.93 mole) of isocyanic acid in 100 ml. of ether cooled in a solid carbon dioxide-acetone mixture was added dropwise with stirring 54 g. (0.31 mole) of tetrafluoroethyl diethylamine (V). Stirring was continued while the mixture was allowed to warm to room temperature. It then was filtered to remove isocyanic acid polymer and distilled to give 42.7 g. (70%) of crude 1,2,2-trifluoro-1-(diethylamino)-ethyl isocyanate (IX) which, on redistillation, boiled mostly at 80° (1 mm.), n_D^{25} 1.4500. The product reacted readily with water to liberate fluoride ion. The nuclear magnetic resonance spectrum was in agreement with the proposed structure.

Anal. Calcd. for $C_7H_{11}N_2OF_3$: N, 14.3; F, 29.1. Found: N, 15.0; F, 28.8.

Compound IX (10 g.) was added to 20 ml. of dry hydrogen cyanide at 0° and the mixture was warmed to room temperature. A gummy solid separated (apparently isocyanic acid polymer) which was removed by filtration and the filtrate was distilled to give 3.4 g. of (diethylamino)-(difluoromethyl)-malononitrile (VIII), b.p. 60° (2 mm.), n_D^{25} 1.4090.

3,4-Difluoro-3-hexenedioic Acid.—The crude ester (90 g.) prepared from diethyl sodiomalonate and TFE (see Table V) was added to a solution of 115 g. of potassium hydroxide in 115 ml. of water and the mixture was stirred and heated. At first, a potassium salt formed which solidified. With continued heating, the salt began to dissolve and hydrolysis proceeded. The reaction soon became very vigorous so that some cooling was necessary to permit condensation of the refluxing alcohol. After stirring and refluxing for 0.5 hour, water (115 ml.) was added and a still head was attached to the reaction flask. About 55 ml. of ethanol (the theoretical amount) was distilled and the mixture was then cooled and stirred while a solution of 100 ml. of concentrated sulfuric acid in 250 ml. of water was added. Carbon dioxide was evolved. The mixture was refluxed for 0.5 hour, diluted to 800 ml. and continuously extracted with ether for 4 days. The ether extract was dried and the ether removed to give oily crystals which were washed with nitromethane. The solvent was removed from the filtrate and the solid obtained was recrystallized from nitromethane. This gave a total of 24.9 g. (58.5%) of nearly white 3,4-difluoro-3-hexenedioic acid. It was very soluble in water and most organic solvents. A sample recrystallized from xylene melted at 139–144° and probably was a mixture of *cis* and *trans* isomers.

Anal. Calcd. for $C_6H_8O_4F_2$: C, 40.0; H, 3.3; F, 21.1; neut. equiv., 90.0. Found: C, 40.1; H, 3.5; F, 21.1; neut. equiv., 90.5.