Tetraethylammonium perchlorate (230 g, 1 mol) was dissolved in acetonitrile and added to a stirred solution of $(CF_3)_2CO$–KF adduct, prepared according to the above procedure. Potassium perchlorate precipitated out leaving a solution of the desired adduct, which was then isolated as described previously.

Elemental analysis showed contamination by $KClO_4$, and considerable decomposition occurred through the loss of hexafluoroacetone.

Formation of Metal Fluoride Adducts with Hexafluoroacetone in Different Solvents.—The reaction of hexafluoroacetone and a metal fluoride was run in different solvents according to the method described above for the preparation of $(CF_3)_2CO$–KF adduct in acetonitrile. No attempts were made to isolate the adduct, but its formation was shown by further reaction yielding stable derivatives.[3] All solvents were carefully dried and distilled shortly before use.

Calorimetric Measurements of Heats of Solution of Hexafluoroacetone in Different Solvents.—The calorimeter used in these experiments was equipped with a Dry Ice condenser, thermistor, stirrer, gas inlet with a flow meter attached to measure the amount of hexafluoroacetone added, and an opening for the addition of solid material. The apparatus was kept in a dewar flask to prevent any heat loss. The calorimeter was calibrated by the determination of the heat of solution of potassium chloride in water.

The calorimeter was charged with 250 cc of the purified solvent and hexafluoroacetone was added at a rate of about 1.3 g/min until a saturated solution was obtained. The addition times were between 15 and 20 min. The evolution of heat was followed with the thermistor and the heat of solution calculated by use of the calibration curve.

Registry No.—CsF, 13400-13-0; KF, 7789-23-3; AgF, 7775-41-9; $(C_2H_5)_4NF$, 665-46-3; NaF, 7681-49-4; LiF, 7789-24-4; BeF_2, 7787-49-7; SnF_2, 7783-47-3; MgF_2, 7783-40-6; CuF_2, 7789-19-7; HgF_2, 7783-39-3; hexafluoroacetone, 684-16-2; CF_3COCF_2Cl, 79-53-8; $(CF_2Cl)_2CO$, 127-21-9; $CF_2ClCOCFCl_2$, 79-52-7; perfluorocyclohexanone, 1898-91-5; perfluorocyclopentanone, 376-66-9.

Formation of Fluorinated Ethers in a Modified Halohydrin Reaction[1]

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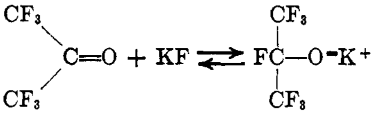
Received July 21, 1967

Fluorinated ethers have been prepared in a three-component reaction involving an adduct of a perhalogenated ketone or acid fluoride with a metal fluoride, an olefin, and a halogen. The reaction was shown to be general in that all three reactants could be varied. The reaction is analogous to a halohydrin reaction with the attack of a fluorinated alkoxide ion on a halonium ion or an olefin–halogen complex.

The formation of an adduct between fluorinated carbonyl compounds and a metal fluoride has been reported in the literature[3,4] (eq 1). At room temperature,



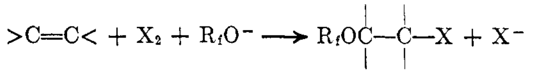
$$(CF_3)_2C{=}O + KF \rightleftharpoons FC(CF_3)_2{-}O^-K^+ \qquad (1)$$

the equilibrium in eq 1 lies very much in favor of the adduct of hexafluoroacetone. The heptafluoroisopropoxide ion has been used successfully in nucleophilic displacement reactions.[3,5] However, it is too weak a nucleophile to give nucleophilic attack on fluoroolefins.

Thus on reaction with a fluoro olefin at room temperature, the $(CF_3)_2CO$–CsF adduct was reported to give a perfluorinated alcohol.[6] Initial attack on the olefin by the fluoride ion was followed by a reaction with the free ketone present in equilibrium with the adduct (eq 2). No evidence of the formation of an ether was found.

$$CF_2{=}CF_2 + F^- \rightleftharpoons CF_3CF_2^- \xrightarrow{(CF_3)_2CO} CF_3CF_2C(CF_3)_2O^- \qquad (2)$$

We have found that, if an adduct of a perhalogenated carbonyl compound and a metal fluoride reacted with an olefin in the presence of a *halogen*, the reaction takes a different path and a fluorinated ether is formed (eq 3). This paper describes our investigation of the scope of this reaction.



$$>C{=}C< + X_2 + R_fO^- \longrightarrow R_fOC{-}C{-}X + X^- \qquad (3)$$

Results and Discussion

The reaction procedure can be described briefly as follows. The carbonyl compound was added to a slurry of the metal fluoride in an aprotic solvent. The olefin and halogen were added at room temperature to the adduct thus formed. The mixture was poured on ice and excess halogen reduced. The product separated out as a heavy layer.

The reaction is of a general type, in that all three reaction components can be varied, giving a large selection of this class of compounds. The scope of the reaction includes nonfluorinated as well as fluorinated olefins, and perfluorinated ketones and acyl fluorides, as well as chlorofluoro-substituted ketones. The results obtained with different ketones, olefins, and halogens will be discussed, each reactant being considered separately, and a mechanism for the reaction will be suggested.

Reactions of Different Carbonyl Compounds

In order for the ketone or acid fluoride to react, it must form an adduct with a metal fluoride (eq 1). The various factors affecting the formation of these adducts were discussed in another paper.[4] It was concluded that the carbonyl compound has to be at least partially fluorinated to give an adduct. Thus hexafluoroacetone, CF_3COCF_2Cl, $(CF_2Cl)_2CO$, perfluoro-

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[1] Paper presented at the Fourth International Symposium on Fluorine Chemistry in Estes Park, Colo., 1967.

[2] Sandoz Pharmaceutical Co., Basel, Switzerland.

[3] (a) A. G. Pittman and D. L. Sharp, *Textile Res. J.*, **35**, 190 (1965); (b) A. G. Pittman and D. L. Sharp, *J. Polym. Sci., Part B*, **3**, 379 (1965); (c) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **45**, 389 (1967).

[4] F. W. Evans, M. H. Litt, A-M. Weidler-Kubanek, and F. P. Avonda, *J. Org. Chem.*, **33**, 1837 (1968).

[5] A. G. Pittman, D. L. Sharp, and R. E. Lundin, *J. Polym. Sci., Part A-1*, **4**, 2637 (1966).

[6] D. P. Graham and V. Weinmayr, *J. Org. Chem.*, **31**, 957 (1966).

cyclohexanone, perfluorocyclopentanone, perfluoroethyl isopropyl ketone, and perfluoropropionyl fluoride reacted, in the form of its adduct, with olefins to give fluorinated ethers (Tables I and II).

TABLE I

REACTIONS OF DIFFERENT CARBONYL COMPOUND–METAL FLUORIDE ADDUCTS WITH TETRAFLUOROETHYLENE TO GIVE $R_fOCF_2CF_2X$

Carbonyl compound	Metal fluoride	Halogen (X_2)	Conversion to ether, %	Yield of ether, %[a]
$(CF_3)_2CO$	KF	I_2	17	~98
CF_3COCF_2Cl	KF	I_2	25	~100
$(CF_2Cl)_2CO$	KF	I_2	24	~100
$CF_2ClCOCFCl_2$	CsF[b]	I_2	15	50[c]
Perfluorocyclopentanone[d]	CsF[b]	Br_2	40	40[e]

[a] Based on reacted halogen. [b] No complex forms with KF. [c] Many unidentified side products formed. [d] E. P. Moore, A. S. Milan, Jr., British Patent 1,019,788 (1966). Samples were kindly provided by A. Price, Industrial Chemicals Division, Allied Chemical Corp. [e] $C_2F_4Br_2$ was isolated in 19% yield.

TABLE II

REACTIONS OF DIFFERENT CARBONYL COMPOUND–METAL FLUORIDE ADDUCTS WITH VINYLIDENE FLUORIDE TO GIVE $R_fOCF_2CH_2X$[a]

Carbonyl compound	Metal fluoride	Halogen	Conversion to ether, %	Yield of ether, %[b]
$(CF_3)_2CO$	KF	ICl	52	60
Perfluorocyclohexanone[c]	CsF[d]	ICl	60	~75
$(CF_3)_2CFCOC_2F_5$[e]	CsF[d]	Br_2	8	8[f]
C_2F_5COF	CsF	ICI	20	40

[a] X = I with ICl. [b] Based on reacted halogen. [c] See Table I, footnote *d*. [d] No complex forms with KF. [e] R. D. Smith, F. S. Fawcett, D. D. Coffman, *J. Amer. Chem. Soc.*, **84,** 4285 (1962). [f] About 18% of $C_2F_2H_2Br_2$ formed.

The yields reported for this reaction were based on the amount of reacted halogen for the following reasons. Equimolar amounts of carbonyl compound and halogen were used in all experiments. Low conversions to the ether were found when iodine was used and a large amount of carbonyl compound, olefin, and halogen remained unreacted in the reaction mixture. As it was most convenient to determine the amount of unreacted halogen, the yield was based on this reagent. Bromine and chlorine always reacted completely and therefore the yield of ether based on halogen and the conversion to ether were the same. When the latter halogens were used, the dihalogenated olefin was formed. As this side reaction partly destroyed one of the major reactants, we found it justified to base the yield on reacted halogen in all cases.

Hexafluoroacetone, CF_3COCF_2Cl, and $(CF_2Cl)_2CO$ all gave high yields of fluorinated ethers. However, on further substitution of a fluorine by chlorine as in $CF_2ClCOCFCl_2$ a significant drop in yield was observed. This can be attributed to the low electrophilicity of the carbonyl carbon which affects the equilibrium between the adduct, free ketone, and fluoride ion. In addition the formation of many side products indicates significant amount of cleavage and further reaction of the cleavage products.

Cyclic ketones–CsF adducts reacted about as readily as the $(CF_3)_2CO$–KF adduct, while acid fluorides gave lower yields. The adducts of longer chain ketones were less soluble in acetonitrile. With a lower concentration of the adduct, side reactions became favored, and the yield of the desired product was reduced.

Ketones which were not perhalogenated as well as aldehydes did not seem to give ethers under these experimental conditions. Compounds tested were CF_3CHO and $CHF_2C(=O)CF_2H$.

Reactions of Different Olefins

An interesting aspect of this reaction is its applicability to a wide range of olefins. Perfluorinated and partially fluorinated as well as nonfluorinated olefins have been used successfully in this reaction (Table III).

TABLE III

REACTIONS OF $(CF_3)_2CO$–KF ADDUCT AND IODINE WITH DIFFERENT OLEFINS TO GIVE $(CF_3)_2CFO\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}I$[a]

Olefin	Conversion to ether, %	Yield of ether,[b] %
$CF_2{=}CF_2$	17	~98
$CF_2{=}CH_2$	34	~100
$CFH{=}CH_2$	31	~100
$CH_2{=}CH_2$	15	30[c]
$CF_2{=}CFCl$	27	~100
$CF_2{=}CFBr$	27	~100
$CH_2{=}CHCl$	14	~100[d]

[a] The proportions of reactants were 2 mol of KF/1 mol of $(CF_3)_2CO$/1 mol of I_2. [b] Based on reacted halogen. [c] ~35% of $C_2H_4I_2$ formed. [d] Both isomers R_fOCH_2CHICl and R_fOCHCl-CH_2I formed in the ratio 1:2.

Partially fluorinated olefins gave higher conversions than tetrafluoroethylene, while with ethylene extensive amount of side reactions decreased the conversion to ether. With unsymmetrically substituted olefins usually only one isomer was formed, that is the isomer expected to form if only electronic factors were considered. However, as the heptafluoroisopropide anion is very bulky, steric factors are quite important and, in some cases as with butene-1 and vinyl chloride, both isomers were formed.

Also mainly owing to steric hindrance, the following olefins were unreactive or gave other reaction products than expected: hexafluorocyclobutene, 1,2-dichlorotetrafluorocyclobutene, octafluorobutene-2, trichloroethylene, and isobutylene.

The reaction with perfluoropropene using excess KF resulted mainly in the formation of perfluoroisopropyl iodide, which involved the addition of F^- rather than $C_3F_7O^-$ to the olefin (Table IV). Perfluoropropene is very susceptible to nucleophilic attack. Also, this olefin probably forms a very weak complex with the halogen and thus nucleophilic at-

TABLE IV

REACTIONS OF HEXAFLUOROACETONE, PERFLUOROPROPENE, AND IODINE AT DIFFERENT METAL FLUORIDE/$(CF_3)_2CO$ RATIOS

Ratio CsF(or KF)/$(CF_3)_2CO$	Ratio C_3F_7I formed/$C_3F_7OC_3F_6I$ formed
2.0[a]	Very large
1.0[b]	1.5
0.92[b]	0.4

[a] KF. [b] CsF.

tack by fluoride ion on the free olefin can compete successfully with the ether formation.[7] However, when the fluoride ion concentration is decreased by the use of an excess of hexafluoroacetone, the ether is formed predominately.

One reaction was performed using acetylene, which produced a mixture of products. One of these was identified as $CI_2{=}CI_2$; the remainder exploded on distillation and the reaction was not repeated.

Reactions of Different Halogens

Iodine, iodine monochloride, bromine, and chlorine have all been used successfully as reactants in the preparation of various iodides, bromides, and chlorides (Table V).

TABLE V

REACTIONS OF $(CF_3)_2CO$-KF ADDUCT AND $CF_2{=}CH_2$ WITH DIFFERENT HALOGENS TO FORM $(CF_3)_2CFOCF_2CH_2X^a$ IN ACETONITRILE

Halogen	Conversion to ether, %	Halogen reacted, %	Dihalogenated product, %	Reaction with solvent, %
I_2	33	33	Very small	None
ICl^a	52	84	27	5
Br_2	51	100	18	31
Cl_2	42	100	Very small	58

[a] X = I with ICl.

Iodine is the least reactive but also the most suitable halogen for this reaction, as it generally does not add to fluoro olefins to form diiodides. It is also unreactive toward most solvents, and for this reason the amount of side products is very small and yields are high. However, it has a disadvantage in that low conversions are obtained. This is due to the formation of soluble KI which inhibits the reaction through the formation of polyiodides, thus removing iodine effectively from the reaction.

Both iodine monochloride and bromine are better reactants in this respect, as potassium chloride and bromide are quite insoluble in the solvents used and precipitate out. Also the polyhalide ions are less stable in these cases. Thus no polyhalides are formed and higher conversions are obtained. However, both iodine monochloride and bromine add directly to the olefin and also react with the solvents, as may be seen in Table V. Large amounts of by-products are formed especially in the reactions of nonhalogenated olefins (Table VI).

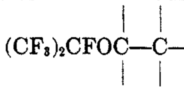
Chlorine is even more reactive, and side reactions tended to dominate. The best results were generally obtained with a mixture of iodine and iodine monochloride.

Effect of Different Solvents

All the reactions described so far were carried out in acetonitrile. The solvent has to be aprotic and polar in order to stabilize the adduct. The main problem is the formation of an intermediate halonium ion, which is a very reactive species and will attack most solvents, including benzene.[8] Acetonitrile which is relatively basic, is readily attacked by a halonium ion to give a secondary amide after hydrolysis.[9,10]

TABLE VI

REACTIONS OF $(CF_3)_2CO$-CsF ADDUCT AND Br_2 OR ICl WITH DIFFERENT NONHALOGENATED[a] OLEFINS TO FORM



$(CF_3)_2CFOC{-}C{-}X^b$ IN ACETONITRILE

Halogen	Olefin	Conversion to ether, %	Halogen reacted, %	Dihalogenated product, %	Reaction with solvent, %
ICl	Cyclohexene	42	95	28	25
Br_2	Cyclohexene	22	100	23	55
Br_2	$C_2H_5CH{=}CH_2$	15^c	100	26	59
Br_2	$C_8H_{17}CH{=}CH_2$	5	100	Very small	~95

[a] In a corresponding reaction with TFE and bromine, 28% ether, 43% dibromide, and 25% solvent attack was found. [b] X = I with ICl. [c] Two isomers formed.

In order to get a valid comparison of the effects of different solvents, we studied the reaction under standardized conditions using the cesium fluoride adduct of hexafluoroacetone, cyclohexene, and bromine as reactants and only varying the solvent. 1-Bromo-2-heptafluoroisopropoxycyclohexane (**1**) and 1,2-dibromocyclohexane (**2**) were formed, besides products originating from solvent reactions. The yields of the different products are given in Table VII.

TABLE VII

REACTION OF $(CF_3)_2CO$-CsF ADDUCT WITH CYCLOHEXENE AND BROMINE IN DIFFERENT SOLVENTS

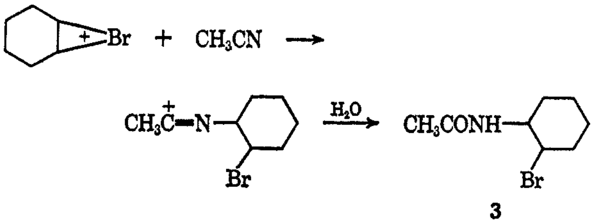
Solvent	Yield of 1	Yield of 2	Reaction with solvent, %[a]
Acetonitrile	22	26	48
Butyrolactone	5	25	70
Nitrobenzene	20^b	66^b	None
3-Methyl sulfolane	10	47	. . .

[a] Represents a maximum figure estimated from the total amount of isolated dibromide and ether. [b] Some product was probably lost on isolation.

Nitrobenzene was the only solvent not attacked by halonium ion. However, the adduct tended to precipitate out, and it was also difficult to purify the products as this solvent is not water miscible. Therefore, acetonitrile turned out to be the preferred solvent and with the use of iodine and iodine monochloride the side reactions were negligible.

Analyses of Side Reaction Products in Acetonitrile

When the reaction was run with bromine in acetonitrile, two major side reaction products were isolated. As reported by Cairns, *et al.*,[9] the halonium ion attacked acetonitrile to give a secondary amide (**3**) after hy-



3 (4)

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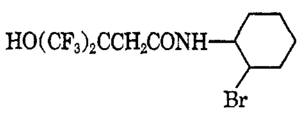
[7] See Table II, footnote *e*.

[8] G. Sumrell, R. G. Howell, B. M. Wyman, and M. C. Harvey, *J. Org. Chem.*, **30**, 84 (1965).

[9] T. L. Cairns, P. J. Graham, P. L. Barrick, and R. S. Schreiber, *ibid.*, **17**, 751 (1952).

[10] A. Hassner, L. A. Levy, and R. Gault, *Tetrahedron Lett.*, 3119 (1966).

drolysis (eq 4). However, in this run also a second amide was isolated and shown to have the structure **4**.



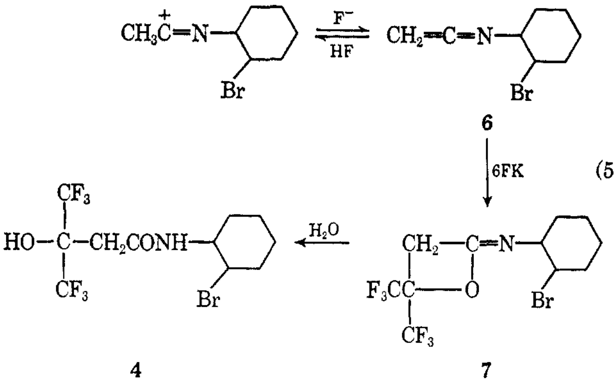
4

$HO(CF_3)_2CCH_2COOH$

5

Acid hydrolysis of **4** gave the hydroxy acid **5**, which was compared with an authentic sample, prepared from the corresponding β-lactone. The nmr spectrum of **4** was consistent with the proposed structure and comparison of the spectra of **3** and **4** showed that the parts of the spectra originating from the amine were identical.

Instead of an addition of hexafluoroacetone to the iminohalide we suggest the sequence of reactions given in eq 5. Addition of hexafluoroacetone to the ketenimine (**6**) which might exist in equilibrium with the imino bromide would give **7**. The iminooxetane would undergo ring opening upon hydrolysis to give the hydroxy amide (**4**). The reaction was studied further, supporting this reaction sequence.[11]



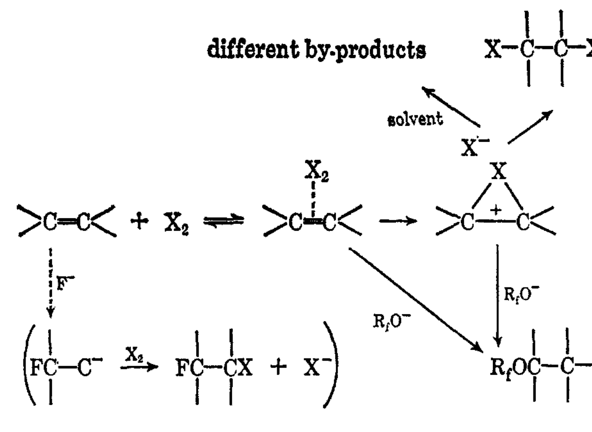
(5)

Mechanism

We observed that conversions tended to be higher when the olefin contained less fluorine, that is, was more basic (see Table III). Also, ethers were formed from fluorinated olefins under conditions where the weakly nucleophilic heptafluoroisopropoxide ion is known not to attack such olefins.[6]

We, therefore, feel that the same mechanism is operative with all olefins, and we can exclude a reaction path which involves a nucleophilic attack by the heptafluoroisopropoxide anion on the olefin, and *subsequent* reaction with halogen.

Instead we suggest that this anion reacts, in a modified halohydrin reaction, with an "olefin–halogen complex" which, depending on the structure of the olefin, can be a π complex, a halonium ion, or a carbonium ion. Alternatively this ion pair can collapse to form the dihalogenated olefin,[12] or attack the solvent to give a variety of side reaction products[8-10] (eq 6). In the case of fluoro olefins, iodine and iodine monochloride probably only produce a π complex. This species can apparently react rapidly with anions but is too stable to attack the very weakly basic acetonitrile. With nonfluorinated olefins, the initial π complex breaks down to an ion pair which involves a halonium ion. We then have an attack of the highly reactive halonium ion on the heptafluoroisopropoxide ion, on the solvent, or on a halide anion to give the products found.



(6)

As in the halohydrin reaction, the formation of the halonium ion is probably slow and rate determining, and is followed by a rapid reaction with any nucleophile present. The relative concentrations of the different nucleophiles will therefore be the most important factor in deciding the structure of the product. As the equilibrium between free ketone and metal fluoride adduct lies very much in favor of the adduct, exclusive reaction with heptafluoroisopropoxide ion is observed.

When the olefin is very electron deficient, as is perfluoropropylene, direct attack on the olefin by a fluoride ion can compete successfully with the ether formation (Table IV).

Experimental Section

Preparation of Fluorinated Ethers.—The same basic procedure was used in all reactions and a typical example will be described below.

Preparation of $(CF_3)_2CFOCF_2CH_2I$.—A round-bottomed flask, equipped with Dry Ice condenser, stirrer, gas inlet, and thermometer, was used in the experiments. Acetonitrile (1 l.) which had previously been distilled from phosphorous pentoxide was placed in the reaction vesel together with 58 g (1 mol)[13] of anhydrous potassium fluoride. This suspension was stirred and 166 g (1 mole) of hexafluoroacetone was added through a gas inlet. A temperature rise of 15° was noticed over the 50-min period needed to add the gas, and at the end of this time the potassium salt had dissolved. Iodine (254 g, 1 mol) was added and then 39 l. of vinylidene fluoride was bubbled through the mixture over a period of 5.5 hr (50–100% excess of gaseous olefin was generally used). The temperature of the solution during the addition of the olefin was in the neighborhood of 26°.

The reaction mixture was stirred overnight, then cooled to 0° and poured into 1 l. of an ice–water mixture. A 1.0 *M* solution of sodium sulfite was added slowly until all the iodine remaining in the solution had been reduced. A 670-cc sample of this sulfite solution was required, thus 0.33 mol or 33% of the iodine had reacted. The aqueous solution was diluted with 4 l. of water and a lower organic liquid separated out. This heavy liquid was collected and washed four times with 150 ml of water leaving 135 g (35% conversion) of a pale yellow liquid. Distillation at 300 mm yielded a middle fraction of 104 g of expected product, which was shown by vpc analysis to contain only 1.3%

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[11] A-M. Weidler-Kubanek and M. H. Litt, *J. Org. Chem.*, **33**, 1844 (1968).

[12] The dihalogenated compound can also be formed in a free-radical reaction.

[13] The ratio of moles of KF per mole of hexafluoroacetone was varied between 1 and 2 in the different experiments without any effect on the reaction.

TABLE VIII
ELEMENTAL ANALYSES OF COMPOUNDS

Compound	Formula	Calcd, %						Found, %					
		C	H	F[a]	I	Br	Cl	C	H	F[a]	I	Br	Cl
Perfluoroisopropyl 2'-iodotetrafluoroethyl ether	$C_5F_{11}IO$	14.6			30.8			14.7			30.2		
Perfluoroisopropyl 2'-iodo-1',1'-difluoroethyl ether	$C_5H_2F_9IO$	15.96	0.56	45.5	33.8			15.96	0.42	43.0	34.3		
Perfluoroisopropyl 2'-iodo-1'-fluoroethyl ether	$C_5H_3F_8IO$	16.8	0.84	42.4	35.5			16.8	0.81	41.0	34.8		
Perfluoroisopropyl 2'-iodoethyl ether	$C_5H_4F_7IO$	17.6	1.20	39.1	37.4			17.5	1.32	39.5	37.3		
Perfluoroisopropyl 2'-iodocyclohexyl ether	$C_9H_{10}F_7IO$	27.4	2.56		32.2			27.2	2.80		32.1		
Perfluoroisopropyl 2'-bromo-1'-ethylethyl ether	$C_7H_8F_7BrO$	26.2	2.49			24.9		26.6	2.75			26.9	
Perfluoroisopropyl 2'-bromo-1'-octylethyl ether	$C_{13}H_{20}F_7BrO$	38.5	4.9					37.8	4.3				
Perfluoroisopropyl 2'-iodohexafluoropropyl ether	$C_6F_{13}IO$	15.6			27.5			16.1			26.8		
Perfluoroisopropyl 2'-iodo-2'-chlorotrifluoroethyl ether	$C_5ClF_{10}IO$	14.0			29.6		8.3	13.9			28.6		8.8
Perfluoroisopropyl 2'-iodo-2'-bromotrifluoroethyl ether	$C_5BrF_{10}IO$	12.7		40.2	26.3			13.1		40.2	26.3		
Perfluoroisopropyl 2'-bromo-1',1'-difluoroethyl ether	$C_5H_2F_9BrO$	18.2	0.61			24.3		18.15	0.86			22.2	
Perfluoroisopropyl 2'-bromo-1'-fluoroethyl ether	$C_5H_3F_8BrO$	19.3	1.0			25.7		19.3	0.86			25.7	
Perfluoroisopropyl 2'-bromotetrafluoroethyl ether	$C_5F_{11}BrO$	16.4				21.9		16.4				19.7	
Perfluoroisopropyl 2'-chloro-1',1'-difluoroethyl ether	$C_5H_2F_9ClO$	21.1	0.70				12.5	21.5	1.18				11.9
Perfluoroisopropyl 2'-iodo-2'-chloroethyl ether	$C_5H_3F_7ClIO$	16.0	0.80		33.9			16.3	0.96		33.8		
1-Chlorohexafluoroisopropyl 2'-iodotetrafluoroethyl ether	$C_5ClF_{10}IO$	14.0		44.3	29.6		8.3	13.7		43.3	30.5		7.1
1,3-Dichloropentafluoroisopropyl 2'-iodotetrafluoroethyl ether	$C_5Cl_2F_9IO$	13.5		38.6	28.4		15.8	13.7		37.8	28.6		15.3
1,1,3-Trichlorotetrafluoroisopropyl 2-iodotetrafluoroethyl ether	$C_5Cl_3F_8IO$	13.0		32.9	27.5		23.1	13.4		35.5	26.3		23.8
Perfluoro-1-ethyl-3-methylpropyl 1',1'-difluoro-2'-bromoethyl ether	$C_8H_2F_{15}BrO$	20.0	0.42			16.7		20.1	0.54			16.1	
Perfluorocyclohexyl 2'-iodo-1',1'-difluoroethyl ether	$C_8H_2F_{13}IO$	19.7	0.41	50.6	26.0			19.4	0.48	51.8	26.1		
Perfluorocyclopentyl 2'-bromotetrafluoroethyl ether	$C_7F_{13}BrO$	19.6				18.7		19.0				18.2	
Perfluoropropyl 2'-bromoethyl ether	$C_5H_4F_7BrO$	20.5	1.40			27.3		20.9	1.74			29.9	
Perfluoropropyl 2'-iodo-1',1'-difluoroethyl ether	$C_5H_2F_9IO$	16.0	0.50					16.2	0.64				
Perfluoroisopropyl 2'-bromocyclohexyl ether	$C_9H_{10}F_7BrO$	31.1	2.90			23.0		31.8	2.96			23.0	

[a] The fluorine determination by combustion was found to give up to 5% lower values than calculated, owing to incomplete combustion. Fluorine determination by wide-band nmr methods is much preferred.

impurity and was used for the various analyses. The ir spectrum showed the strong characteristic $-CF_3$ absorption at ~8.1 μ.

Some slight modifications were employed in certain cases. In the reactions with bromine and iodine monochloride the halogen was dissolved in the solvent used and added simultaneously with the olefin. Chlorine was diluted with five parts of nitrogen and bubbled through the mixture continuously during the reaction. If the olefin was a liquid, the equivalent amount of olefin was added to the adduct before the addition of halogen. When the solvent used was not water soluble (*e.g.*, nitrobenzene), the products were separated by distillation from the reaction mixture.

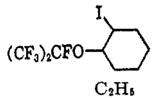
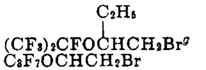
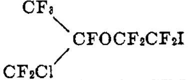
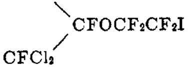
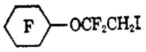
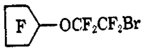
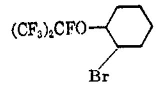
In the reactions with bromine, it was sometimes found difficult to separate the dibromide from the desired product by distillation. In these cases the dibromide was removed by reaction with zinc. The ether was recovered unchanged.

The structures of the products were determined by elemental analysis (Table VIII) and infrared and nmr spectroscopy (H^1 and F^{19}). The nmr spectra were recorded with a Varian A-56-60 spectrometer and will be reported separately. The purity of the products was checked by vpc analyses. The physical data of the purified ethers are given in Table IX.

Reaction in Different Solvents of $(CF_3)_2CO$–CsF Adduct with Cyclohexene and Bromine.—All solvents (acetonitrile, butyrolactone, 3-methyl sulfolane, nitrobenzene) were distilled from phosphorus pentoxide and then redistilled without a drying agent shortly before use. Cesium fluoride was dried at 150° (0.01 mm) and the water content determined by Karl Fischer titration (<0.08% H_2O). Cyclohexene of chromatographic grade (Matheson Coleman and Bell) and reagent grade bromine were used as obtained.

Cesium fluoride (0.25 mol) and solvent (250 cc) were added to the dry 1-l., three-necked reaction flask, equipped with stirrer, gas inlet, Dry Ice condenser, and thermometer (the system was previously flushed with nitrogen). Hexafluoroacetone (0.25 mol) was added through the gas inlet. A raise in temperature was observed and the flask was occasionally cooled in an ice bath to keep the temperature between 25 and 35°. Most of the cesium fluoride had reacted at the end of the addition (*ca.* 40 min). The solution was stirred at room temperature for 30 min and cyclohexene (0.25 mol) added. The bromine (0.25 mol) was dissolved in 50 cc of solvent and added slowly to the solution over a period of 2 hr. The temperature was kept between 20 and 25° through cooling in an ice bath. A heavy white precipitate was formed. The solution was colorless at the end of the addition, indicating that all bromine had reacted. The precipitate was filtered off, dissolved in 500 cc of water, and analyzed for bromide and fluoride ions. The filtrate was poured on ice and stirred for some time. The heavy oil was separated, washed with water, and dried. The combined water layers were analyzed for bromide

TABLE IX
PHYSICAL PROPERTIES OF COMPOUNDS

No.[a]	Compound	n_D[b]	Bp °C (mm)	Purity, %
1	$(CF_3)_2CFOCF_2CF_2I$	1.3155[c]	86–87 (760)	...
2	$(CF_3)_2CFOCF_2CH_2I$	1.3426[d]	110 (760)	98.7
3	$(CF_3)_2CFOCFHCH_2I$	1.3600[e]	60–63 (100)	95.8
4	$(CF_3)_2CFOCH_2CH_2I$	1.3680[c]	45–47 (10)	99.5
5		1.4214[c]	49–49.5 (5.0)	97.5
6	 $(CF_3)_2CFOCH(C_2H_5)CH_2Br$[g]	1.3561[f]	50–51 (40)	94
7	 $C_3F_7OCH(C_8H_{17})CH_2Br$	1.4110[c]	59–61 (1.0)	95.0
8	 $(CF_3)_2CFOCF_2CF(CF_3)I$	1.3147[c]	110–111.5 (750)	99.5
9	$(CF_3)_2CFOCF_2CFClI$	1.3465[c]	19–21 (15)	99.7
10	$(CF_3)_2CFOCF_2CFBrI$	1.3665[c]	16–17 (6.0)	
11	$(CF_3)_2CFOCF_2CH_2Br$	1.3090[c]	92–94 (760)	99.5
12	$(CF_3)_2CFOCFHCH_2Br$	1.3215[c]	99.5–100 (760)	99.5
13	$(CF_3)_2CFOCF_2CF_2Br$	1.2850[f]	65–66 (760)	98.0
14	$(CF_3)_2CFOCF_2CH_2Cl$	1.2925[f]	76–77 (760)	99.0
15a	$(CF_3)_2CFOCHClCH_2I$[g]	1.3925[f]	51–52 (25)	99.5
15b	$(CF_3)_2CFOCH_2CHClI$[g]			
16		1.3516[d]	115–117 (760)	97.4
17	$(CF_2Cl)_2CFOCF_2CF_2I$	1.3764[c]	54.5–55.5 (28)	99.5
18		1.4008[c]	36–37 (50)	99.5
19		1.3192[c]	84–85 (85)	...
20		1.3566[c]	66–67 (20)	99.5
21		1.3082[c]	108–109 (760)	99.7
22	$CF_3CF_2CF_2OCH_2CH_2Br$	1.3458[f]	88–90 (760)	89
23	$CF_3CF_2CF_2OCF_2CH_2I$	1.3390[f]	51–52 (90)	99.5
24		1.3949[c]	51–53 (7)	...

[a] Registry no. are as follows: 1, 16005-38-2; 2, 16005-39-3; 3, 16005-40-6; 4, 16005-41-7; 5, 16005-42-8; 6, 16005-43-9; 7, 16005-44-0; 8, 16005-45-1; 9, 16031-04-2; 10, 16005-46-2; 11, 16005-47-3; 12, 16005-48-4; 13, 16005-49-5; 14, 16005-50-8; 15a, 16003-03-5; 15b, 16005-51-9; 16, 16005-52-0; 17, 16003-36-4; 18, 16003-37-5; 19, 16031-05-3; 20, 16031-06-4; 21, 16031-07-5; 22, 16003-38-6; 23, 16003-39-7; 24, 16003-40-0. [b] Indices of refraction were taken at the following temperatures: [c] 23°, [d] 22°, [e] 20°, [f] 24°. [g] Two isomers formed as shown by nmr analysis.

and fluoride ions. Distillation of the organic layer on spinning-band column separated the two main components, 1-heptafluoroisopropoxy-2-bromocyclohexane (1) and 1,2-dibromocyclohexane (2).[14] The purity of the products was checked by vpc analysis (Table X).

TABLE X

PHYSICAL CONSTANTS OF PURIFIED SAMPLES

Product	Bp, °C (mm)	n^{25}D	Yields, %
1	51-53 (7)	1.3949	22
2	41-41.5 (0.5)	1.5491	26
trans-Dibromocyclohexane	99.6-99.9 (13)[a]	1.5507	

[a] Literature boiling point: S. Winstein, *J. Amer. Chem. Soc.*, 69, 2488 (1947).

Isolation of N-(2-Bromocyclohexyl)acetamide (3) and N-(2-Bromocyclohexyl)-4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)-butyramide (4).—The reaction of $(CF_3)_2CO$-CsF adduct with cyclohexene and bromine was run in acetonitrile as described above. Emulsions formed on treatement of the acetonitrile solution with water. Methanol was added (*ca.* 250 cc of CH_3OH to 900 cc of water) giving good separation of the organic layer. The aqueous layer was stripped to remove all the methanol and some water, giving a white solid (10.1 g, 18%). Recrystallization from ethyl acetate or $CHCl_3$-CCl_4 gave N-(2-bromocyclohexyl)-acetamide (3): mp 105-108° (lit.[9] mp 109-110°) (the mixture melting point with authentic sample prepared according to Cairns[9] showed identity: mmp 105-108°); λ_{max} (KBr) 3.05, 6.05, 6.1, 6.4 μ; nmr[15] ($CDCl_3$), H^1, sharp singlet at δ 2.04 ppm (CH_3 protons), broad peak at 6.75 ppm (-NH-), multiplet at ~4.0 ppm (tertiary ring protons), multiplet at ~1.6 ppm (secondary ring protons).

The organic layer was distilled giving 1-heptafluoroisopropoxy-2-bromocyclohexane and 1,2-dibromocyclohexane. The brown distillation residue crystallized on standing (11.6 g). A 3-g sample of the solid was chromatographed on silica gel (80 g). Elution with 15% ethyl acetate in benzene gave a white solid, mp 119-121.5°. The crystals were dissolved in methanol and precipitated with water giving the pure N-(2-bromocyclohexyl)-4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)butyramide (4): mp 124-125°; total yield, 12%; λ_{max} (KBr) 2.97, 3.08, 6.08, 6.2, 6.45, 8.35-8.45 μ. *Anal.* Calcd for $C_{11}H_{14}BrF_6NO_2$: C, 34.30; H, 3.63; N, 3.63; Br, 20.7; F, 29.7. Found: C, 34.2; H, 3.96; N, 4.1; Br, 20.8; F, 30.1.[16]

Nmr[15] analysis follows (DMSO-d_6): F^{19}, singlet at +77.4 cps (CF_3 groups); H^1, broad peak at δ 8.9 ppm (-OH and -NH), broad peak at 2.9 ppm ($-CH_2-$), multiplet at ~4.0 ppm (tertiary ring protons), multiplet at ~1.6 ppm (secondary ring protons).

Hydrolysis of 4.—Amide 4 (1.34 g, 0.0035 mol) in 25 cc of 25% H_2SO_4 was heated to reflux for 2 hr. The clear water layer was decanted from some decomposition products and extracted with ether. Evaporation of the dried ether layer gave 0.5 g (64%) of white crystals, mp 72-80°. Sublimation at 50° (0.02 mm) gave the pure 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)-butyric acid (5), mp 83-84°, mmp 83.5-84° with sample prepared from hydrolysis of β,β-bistrifluoromethyl-β-propiolactone.

Hydrolysis of β,β-Bistrifluoromethyl-β-propiolactone.[17]—The lactone (2.66 g, 0.013 mol) was treated with 60% H_2SO_4 at reflux for 30 min. The clear water solution was distilled under vacuum (~50 mm). The distillate was extracted with ether. Evaporation of the ether solution gave 2.18 g (76%) of white crystals, mp 83-84.5°. Recrystallization from CCl_4 and sublimation gave the pure acid (5): mp 87-88° (lit.[17] mp 87-88°); λ_{max}^{neat} 5.9 μ; nmr[15] (acetone-d_6), F^{19}, equivalent CF_3 groups at +78.5 cps, $J_{CF_3CH_2}$ = 1 cps; H^1, -OH and -COOH protons gave a very broad peak at δ 8.5 ppm, two aliphatic protons appeared at 2.96 ppm.

Registry No.—2, 5401-62-7; 3, 16003-42-2; 4, 16003-43-3; 5, 1547-36-0.

Acknowledgments.—We are indebted to Drs. J. P. Sibilia and R. Ettinger for the nmr analyses, to Mrs. L. S. Komarowski for recording the ir spectra, and to Mr. S. Roth for technical assistance.

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[14] The absence of an absorption in the ir spectrum at 7.75 μ reported for the *cis* compound showed that the addition was predominantly *trans*.

[15] TMS was used for the H^1 and CCl_3F for the F^{19} spectra as standards.

[16] Nitrogen value is high owing to the formation of CF_4.

[17] I. L. Knunyants and Yu. A. Cheburkov, *Bull. Acad. Sci. SSSR, Div. Chem. Sci.*, 640 (1960).

Addition of Hexafluoroacetone to Ketenimines

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Received December 27, 1967

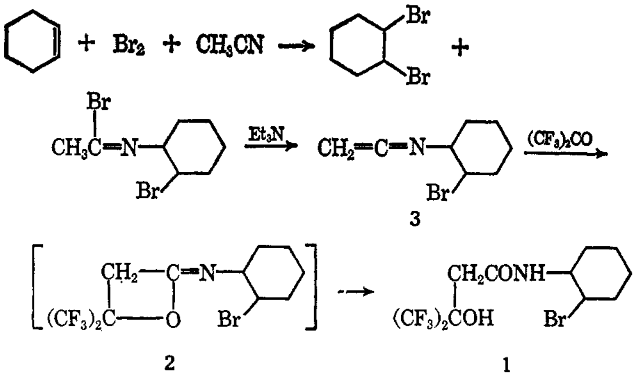
The ionic addition of hexafluoroacetone to ketenimines to give oxetanes was demonstrated in the reaction of diphenylketene-*p*-tolylimine and hexafluoroacetone. The structure of the very unreactive cyclic addition product was determined by mass spectroscopy. The same 1,2-addition mechanism was postulated in a reaction of cyclohexene, bromine, and acetonitrile with hexafluoroacetone. However, in this system, the hydrolysis product, a hydroxy amide, was isolated.

Recently we described the formation of a fluorine-substituted, secondary amide (1) in a reaction of the metal fluoride adduct of hexafluoroacetone with cyclohexene and bromine in acetonitrile.[1] An oxetane (2) was postulated as the intermediate, formed by the addition of hexafluoroacetone to a ketenimine (3).

Results and Discussion

In order to study the formation of 1 a reaction was run as described in Scheme I. Bromine was combined with cyclohexene in acetonitrile; triethylamine was added; and the precipitated hydrobromide was removed from the system. Subsequent reaction with hexafluoroacetone gave, after hydrolysis, 1,2-dibromocyclohexane and the amide (1) as the only products; no N-(2-bromocyclohexyl)acetamide was formed.

SCHEME I



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[1] F. W. Evans, M. H. Litt, A-M. Weidler-Kubanek, and F. P. Avonda, *J. Org. Chem.*, 33, 1839 (1968).