f.p. $-128°$, mol. wt. 166 (calcd. 166) in exact agreement with Ruff.[12]

Fraction 6.—Central cut was pure $CF_3N=NCF_3$, b.p. $-32°$, f.p. $-133°$, mol. wt. 166; known[13] b.p. $-32°$, f.p. $-132°$, mol. wt. calcd. 166.

Fraction 7.—This portion may have contained $(CNF_4)_2$ as $CF_3NF-NFCF_3$ or isomer.

The above run was then repeated using helium as diluent and the stabilized exit gases tested for N_2 by the lithium method.[4] In this case it was found that 9.8% of the nitrogen entering the reactor had been evolved as N_2 during the fluorination. In a blank run 40% of the N_2 in a known gas sample could be recovered by this method; and this factor was used in the calculations.

The Fluorination of Ethyleneimine.—Purified ethyleneimine was fluorinated in the jet reactor with the top half at $120°$ and the secondary reactor at $100°$. The sample diluted with 5.1 l./hr. of N_2 was carried from a glass saturator similar to that previously described[8] maintained at $0°$ at the rate of 0.028 mole/hr., and then further diluted by 1.8 l./hr. of N_2, after which it passed into the reactor through the turbulent jet, where it met and reacted with 0.140 mole/hr. of fluorine such that the molar reaction ratio was $5:1:10$. After 12 hr. the crude product, amounting to 28 cc., was collected, stabilized by alkaline bisulfite, and rectified in the usual manner, with the results shown in Table III; while a similar run at the ratio of $4:1:8$ gave much the same results.

TABLE III

THE RECTIFICATION OF FLUORINATED ETHYLENEIMINE

Fract.	Chief product	Boiling range, °C.	Molecular wt. Obsd.	Molecular wt. Calcd.	Liq. vol. % of total condensate
1	CF_4	-129 to -116	77–89	88	7
2	....	-90 to -68	90–132	..	9
3	$(CF_3)_2NF$	-55 to -37	132–179	171	18
4	$CF_3N=NCF_3$	-36 to -27	161–173	166	20
5	....	-23 to -5	178–218	..	16
6	$(CF_3)_2N-N(CF_3)_2$	-32 to 0 (200 mm.)	229–327	304	14
7	Stbln. loss	....	.....	..	11
8	Residue	....	.....	..	5

Fraction 2.—This portion boiled mostly at $-76°$ and consisted essentially of the inseparable mixture of $CF_3NF_2 + C_2F_6$.

(12) O. Ruff and F. Giese, *Ber.*, **69B**, 604 (1936).

(13) O. Ruff and W. Willenberg, *ibid.*, **73B**, 724 (1940).

Fraction 3.—About two-thirds of this fraction was pure $(CF_3)_2NF$, b.p. $-38°$, f.p. $-171°$, mol. wt. 170–173; known b.p. $-38°$,[14] f.p. $-171°$,[4] mol. wt. calcd. 171.

Fraction 4.—At least half of this material had b.p. -33 to $-32°$, with an average mol. wt. 165 (see above).

Fraction 5.—About one-third of this sample had b.p. -16 to $-14.5°$, average mol. wt. 188 (see Paper XXI).

Fraction 6.—About half of this portion was pure $(CF_3)_2N-N(CF_3)_2$, b.p. -3 to $-1°$ at 200 mm., f.p. $-61°$, average mol. wt. 305 (see above).

The Fluorination of Hexafluoroazomethane.—Purified $CF_3N=NCF_3$, b.p. -33 to $-31°$, contained in a small cylinder, was metered at the rate of 0.099 mole/hr., diluted with N_2 at the rate of 7.3 l./hr., and the mixture passed into the high temperature reactor described above maintained at $275°$, where it met with undiluted fluorine entering at the rate of 0.099 mole/hr., such that the molar reaction ratio was $1:1:3$. The product was passed over sodium fluoride at $100°$, and after 1 hr. 15 cc. of material had been condensed, which was stabilized by 5% NaOH and rectified in the usual manner; but the unchanged sample was recovered in 92% yield. Similar runs were made at the ratio of $1:1:0$ at both $275°$ and $400°$, with the same result, although the contact was short. Finally a run was made at $1:1:0$ and $500°$, when a reaction took place, and the crude product (9 cc.) was stabilized and rectified in the usual manner with the results shown in Table IV.

TABLE IV

THE RECTIFICATION OF FLUORINATED $CF_3N=NCF_3$

Chief product	Boiling range, °C.	Molecular wt. Obsd.	Molecular wt. Calcd.	Liq. vol. % of total condensate
CF_4	-129 to -123	86–89	88	83
C_2F_6	-82 to -75	134–140	138	6
$CF_3N=NCF_3$	-34 to -28	161–167	166	11

In the above run the final exit gases, swept along by a little diluent helium which had been introduced into the crude product, were stabilized over 10% NaOH $+ 10\%$ NaHSO$_3$, dried by liquid air, and then passed directly over lithium at $60°$ for the subsequent determination of their N_2 content in the usual manner. In this way 79% of the N_2 in the original sample was accounted for as ammonia.

(14) J. Thompson and J. H. Emeleus, *J. Chem. Soc.*, 3080 (1949).

DURHAM, N. C.

[CONTRIBUTION FROM THE CARVER FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, TUSKEGEE INSTITUTE]

Preparation and Properties of Some α-Fluoroethers[1,2]

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Various metal fluorides were examined as fluorine-for-chlorine exchange agents with $CCl_3CHClOR$. The efficiency of the exchange was found to descend in approximately the order HgF_2, TlF, AgF, KF, Al_2F_6, CrF_3. Compounds of the general formula CCl_3CHFOR and CH_2FOR (where R is Me, Et, Pr, Bu and allyl) were prepared using HgF_2 and their physical and chemical properties examined. All attempts to prepare CH_3CHFOR and $CH_2FOCH_2CH=CH_2$ were unsuccessful.

While references in the literature are abundant for di- and polyfluoroethers, information on the monofluoroethers is very scarce, and no work at all seems to have been reported on the α-fluoroethers. The purpose of this work was therefore to investigate the preparation and properties of α-fluoroethers.

When heated, the α-halogenated ethers decom-

pose and polymerize into dark viscous mixtures. In exchange reactions between a metal fluoride and halogenated ethers, the difficulty is in finding a metal fluoride which will exchange its fluorine for halogen at a temperature low enough so as to minimize the decomposition of both the reactant and product. Mercuric fluoride was found to exchange its fluorine for the α-chlorine in some halogenated ethers. The reaction was smooth, and little decomposition took place. Compounds of the type CCl_3CHFOR and CH_2FOR (Tables I and II) were prepared.

TABLE I
CCl$_3$CHFOR

R	B.p. °C.	Mm.	Yield, %	d^{20}_4	Fluorine, % Calcd.	Found	Chlorine, % Calcd.	Found
CH$_3$	48–50	100	42	1.4880	10.5	10.1	58.7	58.6
C$_2$H$_5$	61–63	35	37	1.4012	9.72	9.42	54.4	54.5
C$_3$H$_7$	95–97	30	31	1.2987	9.07	8.90	50.8	50.4
C$_4$H$_9$	112–113	41	39	1.2579	8.50	8.09	47.6	47.2
CH$_2$CH=CH$_2$	52–54	3.6	38	1.3542	9.16	9.27	51.3	51.3

TABLE II
CH$_2$FOR

R	B.p. °C.	Mm.	Yield, %	d^{20}_4	Fluorine, % Calcd.	Found
CH$_3$	ca. 19	757	22		29.7	29.0
C$_2$H$_5$	40–44	749	33	0.9044	24.3	24.3
C$_3$H$_7$	43	326	20	.8983	20.6	20.3
C$_4$H$_9$	62–63	188	12	.8967	17.9	17.4
i-C$_3$H$_7$	58–60	752	18	.8948	20.6	20.3

In trying to find the most efficient fluoride for the exchange reaction, various metal fluorides were allowed to react with CCl$_3$CHClOR. This compound was chosen because it is easily prepared, because the α-chlorine is much more reactive than the β-, and because it was believed that the three β-chlorine atoms would stabilize the fluorine atom, inasmuch as dehydrofluorination of the fluoroether could be expected to be difficult. The CCl$_3$CHClOR was heated with equivalent amounts of various metal fluorides, the resulting fluoroether isolated by distillation, and the efficiency of the inorganic fluoride evaluated by consideration of yield, the amount of decomposition in the reaction, and the ease with which the product was isolated.

The efficiency of the exchange was found to descend in roughly the following order: HgF$_2$, TlF, AgF, KF, Al$_2$F$_6$ and CrF$_3$·3.5H$_2$O. With the better reagents yields of the fluoroether varied from 15 to 42%. With Al$_2$F$_6$ and CrF$_3$·3.5H$_2$O, no reaction was observed. In other cases extensive polymerization resulted and in some instances the presence of low-boiling products was probably indicative of the exchange of some β-chlorine for fluorine. With HgF$_2$, however, a smooth exchange of the α-chlorine took place. Fluorosulfonic acid also was tried, but it did not act as an exchange reagent.

The method of producing the exchange reaction was modified in various ways in an effort to improve the yield of fluoroether. Temperature seemed to be an important factor. The exchange reaction took place more readily at higher temperature (i.e., 140°) but polymerization of the original chloroether (and probably of the product) was more extensive. To minimize this side reaction, the chloroether was dropped into potassium fluoride in Nujol at 140°. This temperature was sufficient to allow the product to be distilled off as it was formed. Even under these conditions polymerization (as indicated by the presence of solid organic products) occurred, and the method was not as efficient as that wherein the chloroether was dropped slowly into well-stirred HgF$_2$, the mixture stirred for half an hour, filtered and the filtrate fractionated. Ultraviolet light also was used in an attempt to reduce the temperature at which the exchange took place, but was ineffective. α-Bromoethers decompose at lower temperatures than their chlorine analogs, and are not as useful as the chloroethers in the preparation of fluoroethers.

The presence of free hydrochloric acid was detrimental to the yield of fluoroether. Hydrochloric acid is a product of the decomposition of the α-chloroethers and is always present after these ethers have been allowed to stand for even a short period. Stirring the freshly distilled chloroether with activated silica gel and using it immediately effectively removed the HCl, and this procedure resulted in higher yields of the fluoroether.

Neither CH$_3$CHClOMe nor CH$_2$ClCHClOEt could be used to prepare the corresponding α-fluoroethers. Mercuric fluoride, added to either of the above compounds at 0° appeared to give an exchange reaction inasmuch as HgCl$_2$ seemed to be formed. On coming to room temperature, however, the reaction mixture darkened, became viscous, and no identifiable products of the reaction could be isolated. When carried out at $-5°$ and using benzene as a diluent, the reaction took place in the same manner. In contrast with the above, the α-chlorine of CHCl$_2$CHClOR reacted smoothly with the mercuric fluoride to give the corresponding α-fluoroether. Thus the presence of two or three chlorine atoms in the β-position was sufficient to stabilize the α-fluorine atom, but the absence of chlorine or the presence of only one chlorine atom in the β-position led to instability, and the fluoroether could not be isolated. Presumably HF or HCl is split off and the product, in the presence of HF or HgF$_2$, polymerizes. Similarly, CCl$_3$CH-FOCH$_2$CH=CH$_2$ has been prepared, but all attempts to prepare CH$_2$FOCH$_2$CH=CH$_2$ have been unsuccessful, and have led only to solid polymeric products. At present we can assume that the fluorine in CH$_2$FOCH$_2$CH=CH$_2$, its stability not being increased by the presence of the trichloromethyl group, takes part in a polymerization which begins as

2CH$_2$FOCH$_2$CH=CH$_2$ $\longrightarrow$

CH$_2$FOCH$_2$CHFCH$_2$CH$_2$OCH$_2$CH=CH$_2$

This reaction will be investigated in the future.

Attempts were made to prepare the α-fluoromethyl alkyl ethers by a modification of the method of Henry.[3] The use of HF was avoided inasmuch as it would entail the use of complicated apparatus. Various combinations of (CH$_2$O)$_3$, KF, alcohols and acids were tried, however, to investigate the remote possibility that compounds of the type CH$_2$FOR could be formed. The fluoroethers could not be isolated, however. In some cases the starting materials were recovered, but when HCl was passed into a mixture of trioxymethylene, alcohol and KF, the chloromethyl alkyl ether was obtained.

(3) L. Henry, Bull. soc. chim. Belg., [2] 44, 458 (1885).

As would be expected, the α-fluoroethers boil about 40° lower than their chlorine counterparts. Like the other α-halogenated ethers, they fume in moist air and are lachrymatory. These α-fluoroethers will etch glass very easily. It has been found that the usual precaution of wiping and rinsing the chemical off the prisms of the Abbe refractometer immediately after taking a reading is not sufficient to prevent etching of the prisms. For this reason the refractive index of many of the ethers prepared was not taken.

In general, the α-fluoroethers have the same chemical properties as their chlorine analogs, although they are more unstable, polymerizing more easily on standing at room temperature.

Barr, et al.,[4] have reported that the stability of trifluorochloroethers is increased by passing them through a column containing six inches of activated silica gel over $1/8$ inch Norite. This is also the experience of the present authors with the α-fluoroethers. The HF can also be removed by stirring activated silica gel with the distilled ether and filtering.

The α-fluoroethers seem slightly more reactive, but follow closely the reactions of their chlorine analogs with water, alcohol and sodium alkoxide. Both CCl_3CHFOR and $CCl_3CHClOR$ react with sodium alkoxide to give the same 2,2-dichloroketene acetal.

Experimental

Chloromethyl Alkyl Ethers.—Hydrochloric acid, trioxymethylene and alcohol were used to prepare CH_2ClOR after the method of Henry (ref. 3). Before the final distillation they were stirred with activated silica gel grade 992 (Davidson Chemical Co.) filtered, distilled and used immediately. $CH_3CHClOR$ was prepared from paraldehyde. All constants agreed with those found in the literature.

1-Alkoxy-1,2,2,2-tetrachloroethane.—The method of McElvain and Curry[5] was used. Physical properties are given in Table III.

TABLE III

$CCl_3CHClOR$

R	B.p. °C.	Mm.	Yield, %	$n^{20}D$	d^{20}_4	Chlorine, % Calcd.	Found
CH_3	72–75	22	66	1.4840	1.5154	71.7	71.4
C_2H_5	188	740	42	1.4755	1.4168	66.9	66.7
	57	10					
C_3H_7	85	6	46	1.4687	1.3250	62.7	62.7
C_4H_7	106–107	8	42	1.4655	1.2626	59.1	58.8
$CH_2CH:CH_2$	98–99	17	42	1.4892	1.4001	63.3	62.9

1,2,2-Trichloro-1-ethoxyethane and 1,2-Dichloro-1-ethoxyethane.—Following the procedure of Shostakovskii and

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(4) J. T. Barr, K. E. Rapp, R. L. Pruett, J. D. Gibson and R. H. Lafferty, THIS JOURNAL, **72**, 4480 (1950).

(5) S. M. McElvain and M. J. Curry, J. Chem. Soc., **70**, 3781 (1948).

Sidel'kooskaya,[6] chlorine was passed into 72 g. (1 mole) of ethyl vinyl ether cooled by an ice–salt-bath, the product mixed with silica gel, filtered and fractionated to give 5 g. (2%) of 1,2,2-trichloro-1-ethoxyethane, b.p. 56–58° (6 mm.), d^{20}_4 1.3195; and 92 g. (64%) of 1,2-dichloro-1-ethoxyethane, b.p. 46–50° (16 mm.), d^{20}_4 1.1342.

Anal. Calcd. for $C_4H_7Cl_3O$: Cl, 60.0. Found: Cl, 59.7.

1-Alkoxy-2,2,2-trichloro-1-fluoroethane.—To one mole of HgF_2 was slowly added two moles of 1-alkoxy-1,2,2,2-tetrachloroethane. During the addition the mixture was stirred vigorously and the temperature kept around 10°. After addition of the tetrachloroether stirring was continued and the mixture was allowed to come to room temperature, filtered, and the filtrate fractionated. The distillate was mixed with a few grams of silica gel and again filtered before storage or use.

1-Alkoxy-1-fluoromethane.—With the exception of the methoxy compound, these fluoromethyl ethers were prepared in the same manner as were the fluorotrichloroethyl ethers, except that the reaction temperature was not allowed to go above 40°. While little difficulty was experienced in the preparation of the isopropoxy compound, all attempts to prepare the isobutoxy homolog were unsuccessful.

1-Methoxy-1-fluoromethane.—To one mole of CH_2ClOMe in a flask equipped with a stirrer and an outlet tube leading to a receiver immersed in a Dry Ice–acetone-bath, was added 0.5 mole of HgF_2 at such a rate as to allow a steady collection of CH_2FOMe in the receiving flask. The distillate was again distilled from a second flask as it was allowed to warm up, and the product collected in a receiver immersed in a Dry Ice-bath.

2,2-Dichloro-1-ethoxy-1-fluoroethane.—Mercuric fluoride (3.6 g., 0.015 mole) was added to 5 g. (0.03 mole) of 1,2,2-trichloro-1-ethoxyethane, the mixture stirred one-half hour, filtered and fractionated to give 2 g. (44.5%) of 2,2-dichloro-1-ethoxy-1-fluoroethane, b.p. 52° (80 mm.), d^{20}_4 1.2148.

Anal. Calcd. for $C_4H_7Cl_2FO$: F, 11.8; Cl, 44.0. Found: F, 11.4; Cl, 43.7.

Reaction of 1-Chloro-1-methoxyethane and of 1,2-Dichloro-1-ethoxyethane with Mercuric Fluoride.—Mercuric fluoride added to either of the above compounds at 0° seemed to give an exchange reaction, but on coming to room temperature the mixture rapidly polymerized, and no identifiable products of the reaction could be isolated. Potassium fluoride reacted similarly to HgF_2.

Action of 1-Allyloxy-1-chloromethane with HgF_2 or with KF.—When either HgF_2 or KF was added to $CH_2ClOCH_2CH{=}CH_2$, there seemed to be a halogen interchange, but the reaction mixture, even at room temperature, polymerized rapidly, and unidentifiable products were produced.

Fluorine.—The fluorine in the α-fluoroethers was unstable enough so that the compounds could be decomposed in a Parr bomb. After decomposition analysis was accomplished by a thorium nitrate titration procedure suggested by Dr. D. G. Weiblen of Minnesota Mining and Manufacturing Co.

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(6) M. F. Shostakovskii and F. P. Sidel'kooskaya, C. A., **46**, 4991b (1952).