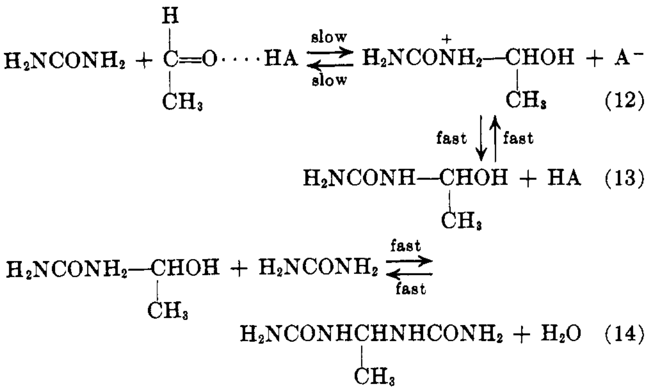
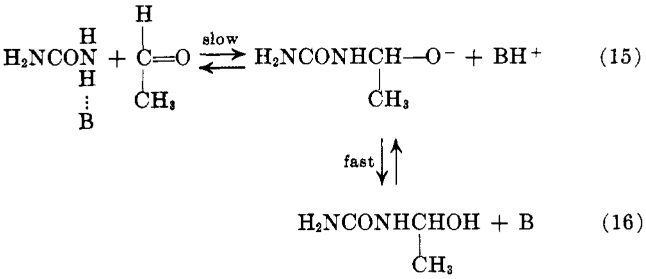
gous to amide–formaldehyde[1,2] and ammonia–aldehyde[7] reactions.


$$H_2NCONH_2 + \overset{H}{\underset{CH_3}{C}}{=}O\cdots HA \underset{slow}{\overset{slow}{\rightleftharpoons}} H_2NCO\overset{+}{N}H_2\!-\!\underset{CH_3}{CHOH} + A^- \quad (12)$$
$$\Big\downarrow\!\!\Big\uparrow \text{ fast}$$
$$H_2NCONH\!-\!\underset{CH_3}{CHOH} + HA \quad (13)$$
$$H_2NCONH_2\!-\!\underset{CH_3}{CHOH} + H_2NCONH_2 \underset{fast}{\overset{fast}{\rightleftharpoons}} H_2NCONH\underset{CH_3}{C}HNHCONH_2 + H_2O \quad (14)$$

Similarly, the following mechanism may be suggested for the base catalysis.


$$H_2NCO\overset{H}{\underset{\underset{B}{\overset{H}{\vdots}}}{N}} + \overset{H}{\underset{CH_3}{C}}{=}O \overset{slow}{\rightleftharpoons} H_2NCONH\underset{CH_3}{CH}\!-\!O^- + BH^+ \quad (15)$$
$$\text{fast}\ \Big\downarrow\!\!\Big\uparrow$$
$$H_2NCONH\underset{CH_3}{C}HOH + B \quad (16)$$

However, the possibility of the specific oxonium ion and the specific hydroxide ion catalysis is not ruled out on the basis of the present data.

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(7) Y. Ogata and A. Kawasaki, *Tetrahedron*, **20**, 855, 1573 (1964).

The Chemistry of Carbonyl Chloride Fluoride. I.
The Ring Opening of Cyclic Ethers with Carbonyl Chloride Fluoride

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Ring opening of cyclic ethers by carbonyl chloride fluoride yielded ω-chloroalkyl fluoroformates. The reactivity of carbonyl chloride fluoride with cyclic ethers was found to decrease in the order ethylene oxide > trimethylene oxide > tetrahydrofuran > tetrahydropyran. In addition, its reaction with substituted ethylene oxides and butadiene dioxide was investigated. The ω-chloroalkyl fluoroformates, a new class of compounds, are useful for the preparation of ω-chloroalkyl fluorides or ω-fluoroalkenes. Vinyl fluoride has been prepared from ethylene oxide and carbonyl chloride fluoride in an over-all yield of about 70%. A new method for the preparation of carbonyl chloride fluoride is described. The ring opening of tetrahydrofuran with phosgene resulted in a mixture of 1,3- and 1,4-dichlorobutane. Attempts to replace the carbonyl chloride fluoride by thionyl or sulfuryl fluoride were not successful.

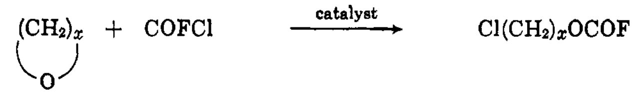
The chemistry of carbonyl chloride and carbonyl fluoride has been extensively investigated. Among many others, the reactions of carbonyl chloride with ethylene oxide and substituted ethylene oxides[1] forming ω-chloroalkyl chloroformates have been described. In the case of carbonyl fluoride and ethylene oxide[2] the unexpected $CF_3OCH_2CH_2OCOF$ has been obtained.

Ring-opening reactions of larger rings with phosgene or carbonyl fluoride have not been reported, but it is known[3] that the ring of tetrahydrofuran can be opened with hydrogen chloride, thionyl chloride, or phosphorous oxychloride, in the presence of catalysts such as zinc chloride, aluminum chloride, or aluminum oxide, yielding exclusively 1,4-dichlorobutane. In the case of carbonyl chloride fluoride, however, no other reactions with organic compounds except for ethanol and amines[4] have been described.

Since the organic fluoroformates proved in the course of our investigations to be very useful intermediates in the preparation of such compounds as fluorinated aromatics, 1,2-difluoroalkanes,[5] ω-chloroalkyl fluoride, etc., more systematic work was done in this field, part of which will be reported in this paper.

Preparation of Carbonyl Chloride Fluoride.—COFCl was first prepared from $COCl_2$ and SbF_3.[4] We found that it can be prepared more easily from $COCl_2$ and SiF_4[6] or on laboratory scale from $COCl_2$ and AsF_3. The purity of the COFCl used for the ring-opening reactions was not critical. Therefore, the crude reaction product consisting of 84 to 90% COFCl (the rest being COF_2 and $COCl_2$) could be used without further purification.

Ring Opening of Unsubstituted Cyclic Ethers with Carbonyl Chloride Fluoride.—ω-Chloroalkyl fluoroformates are formed when carbonyl chloride fluoride reacts with ethylene oxide, trimethylene oxide, tetrahydrofuran, or tetrahydropyran.


$$(CH_2)_x\text{-}O \text{ (ring)} + COFCl \xrightarrow{\text{catalyst}} Cl(CH_2)_xOCOF$$

Reaction conditions, physical and spectral properties, and analytical data of the new compounds are summarized in Tables I, II, and III.

The reactivity of carbonyl chloride fluoride with cyclic ethers was found to decrease in the order ethylene oxide > trimethylene oxide > tetrahydrofuran > tetrahydropyran. This order could be expected from the

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(1) J. I. Jones, *J. Chem. Soc.*, 2735 (1957).

(2) P. E. Aldrich and W. A. Sheppard, *J. Org. Chem.*, **29**, 12 (1964).

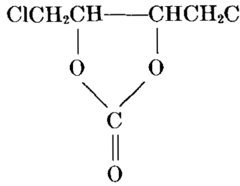
(3) French Patent 864,758; *Chem. Abstr.*, **43**, 1433d (1949); Italian Patent 424,590; *Chem. Abstr.*, **43**, 4284*a* (1949); V. I. Lutkova, *et al.*, *Zh. Obshch. Khim.*, **25**, 2102 (1955); N. I. Shuikin, I. F. Bel'skii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 747 (1956); German (East) Patent 10,675; *Chem. Abstr.*, **52**, 16373*h* (1958).

(4) H. J. Emeléus and J. F. Wood, *J. Chem. Soc.*, 2183 (1948).

(5) K. O. Christe and A. E. Pavlath, *J. Org. Chem.*, **30**, 1644 (1965).

(6) K. O. Christe and A. E. Pavlath, *ibid.*, **29**, 3007 (1964).

TABLE I. PHYSICAL PROPERTIES OF THE NEW COMPOUNDS[a,b]

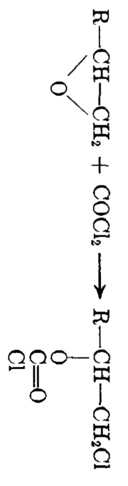
No.	Compd.	B.p. °C.	B.p. mm.	n_D (°C.)	Density, g./cc. (°C.)	Calcd., % C	Calcd., % H	Calcd., % Cl	Calcd., % F	Found, % C	Found, % H	Found, % Cl	Found, % F
I	$Cl(CH_2)_2OCOF$	122–124	760	1.3922 (22)	1.314 (23)	28.46	3.16	28.06	15.02	28.60	2.83	28.17	15.19
II	$Cl(CH_2)_3OCOF$	45	13	1.4028 (22)	1.241 (24.5)	34.18	4.30	25.23	13.52	34.08	4.42	25.38	13.81
III	$Cl(CH_2)_4OCOF$	62	11	1.4102 (30)	1.207 (26)	38.85	5.22	22.94	12.29	38.85	5.29	23.25	11.7
IV	$Cl(CH_2)_5OCOF$	38	2	1.4175 (22)	1.142 (24.5)	42.74	5.98	21.03	11.27	42.90	5.87	21.49	11.53
V	$CH_3CH(OCOF)CH_2Cl$,[c] 75%	30	12.5	1.3908 (29)	1.213 (24)	34.18	4.30	25.23	13.52	34.19	4.02	25.28	12.9
VI	$CH_3CHClCH_2(OCOF)$, 25%												
VII	$CH_2{=}CHCH(OCOF)CH_2Cl$,[c] 15%	39	11	1.4146 (29)	1.197 (24)	39.36	3.96	23.24	12.45	39.60	4.50	23.96	12.4
VIII	$CH_2{=}CHCHClCH_2(OCOF)$, 85%												
IX	$CH_2ClCH(OCOF)CH(OCOF)CH_2Cl$,[c,d] 35%	55–57	1	1.4300 (30)	1.494 (25)	28.71	2.41	28.25	15.14	28.96	2.67	28.63	14.9
X	$CH_2(OCOF)CHClCH(OCOF)CH_2Cl$, 26%												
XI	$CH_2(OCOF)CHClCHClCH_2(OCOF)$, 39%												
XII	$ClCH_2CH$—$CHCH_2Cl$[e]	...	...	...	...	32.46	3.27	38.33	...	32.75	3.21	37.76	...

[a] All compounds are colorless liquids of strong fluoroformate odor. [b] The infrared spectra of compounds I to XI, inclusive, show the typical absorptions for fluoroformate groups ($\nu_{C=O}$ at 1830 cm.$^{-1}$ and ν_{COC} at 1250 cm.$^{-1}$), CH_2 groups, and CCl groups (ν_{CCl} at 780 cm.$^{-1}$). [c] The boiling point of the isomers are similar, and therefore they could be isolated only as mixtures. [d] The mixture of IX, X, and XI was obtained as a colorless liquid, which solidified upon standing and showed m.p. 74–75°. [e] Colorless crystals, m.p. 80°, infrared shows absorptions characteristic for a cyclic carbonate and the absence of epoxide or CF groups.

general reactivity of the cyclic ethers, which increases with increasing ring tension. In the case of the low-membered rings (three and four) only one catalyst (tertiary amine) was used. The reaction proceeded also without a catalyst. For example, the conversion of ethylene oxide was always over 99%, but the yield of 2-chloroethyl fluoroformate was increased from 50 to 99% if a tertiary amine was added as catalyst.

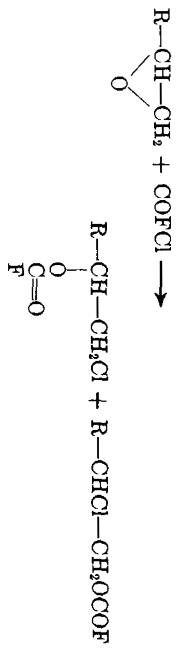
In the case of the higher membered rings, such as tetrahydrofuran and tetrahydropyran, however, the use of an additional catalyst (hydrogen chloride or hydrogen chloride donor) was necessary. Especially effective were catalysts, which released the HCl slowly during the reaction. Without the use of an HCl donor the yield of the corresponding fluoroformate was high; however, the conversion of the starting material was increased from 3 to 99% if ethylene glycol was added as a second catalyst. This indicates that each of the two catalysts fulfills different purposes. The tertiary amine is known to form complexes with compounds such as carbonyl halides. Therefore, it activates the COFCl and makes it more reactive. Hydrogen chloride, probably acting as a catalyst, is able to open the ring of tetrahydrofuran.[3] Consequently the catalytic effect on the reaction could be explained by the formation of an intermediate ω-chloroalkyl alcohol which reacts preferably with COFCl (activated by the presence of a tertiary amine) to form the corresponding ω-chloroalkyl fluoroformate. However, since the ω-chlorobutyl fluoroformate can also form without the presence of hydrogen chloride (but the conversion of the starting material is much lower), it must be assumed that the reaction between tetrahydrofuran and COFCl can proceed directly without the formation of an intermediate ω-chlorobutanol.

Ring Opening of Substituted Ethylene Oxides with Carbonyl Chloride Fluoride.—Jones[1] reported, that in the reaction of phosgene with substituted ethylene oxides, exclusively the 1-chloro-2-chloroformoxyalkane was formed. We investigated the reaction between



$$R\text{—}\underset{\diagdown O \diagup}{CH\text{—}CH_2} + COCl_2 \longrightarrow R\text{—}\underset{\substack{| \\ O \\ C{=}O \\ Cl}}{CH}\text{—}CH_2Cl$$

COFCl and propylene oxide, butadiene monoxide, and butadiene dioxide. In all reactions all theoretically possible isomers were found. In the case of the two



$$R\text{—}\underset{\diagdown O \diagup}{CH\text{—}CH_2} + COFCl \longrightarrow R\text{—}\underset{\substack{| \\ O \\ C{=}O \\ F}}{CH}\text{—}CH_2Cl + R\text{—}CHCl\text{—}CH_2OCOF$$

saturated epoxides, the formation of the fluoroformate group was favored at the secondary carbon atom. This must also be assumed for butadiene dioxide, since the formation of compound XII can be explained by elimination of 1 mole of carbonyl fluoride from compound IX. As compound XII was formed in 70% yield, compound IX was originally formed in 80.5% yield. In the case of butadiene monoxide, however, the direction of the ring opening reversed and the formation of the fluoroformate group was favored at the primary

Table II
Reactions of Cyclic Ethers with Carbonyl Halides

Reactants, mole			Catalyst, % based on cyclic ether		Reaction temp., °C.	Reaction time, hr.	Conversion of the cyclic ether, %	Yield, %			
Cyclic ether	Carbonyl halide										
Ethylene oxide	COFCl							$Cl(CH_2)_2$-OCOF			
0.1	0.25		...		25	1.5	99	49.8			
0.1	0.25		...		0	12	99	49.8			
0.3	0.39		Tri-*n*-butylamine	1.5	25	12	100	99.8			
Trimethylene oxide	COFCl							$Cl(CH_2)_3$-OCOF			
0.3	0.345		Tri-*n*-butylamine	1.0	25	1	92.3	100			
Tetrahydrofuran	COFCl							$Cl(CH_2)_4$-OCOF			
0.1	0.5		...		100	3	<1	Trace			
0.1	0.3		Tri-*n*-butylamine	7.0	100	3	3	80			
0.1	0.13		Tri-*n*-butylamine	1.0	60	14	14.4	99			
			Ethylene glycol	2.0							
1.26	1.78		Tri-*n*-butylamine	2.0	100	14	99	78			
			Ethylene glycol	20.4							
Tetrahydropyran	COFCl							$Cl(CH_2)_5$-OCOF			
0.3	0.36		Tri-*n*-butylamine	2.0	130	14	43	55.4			
			Ethylene glycol	4.0							
Propylene oxide	COFCl							V	VI		
0.3	0.31		Tri-*n*-butylamine	1.2	0	0.5	99	75	25		
Butadiene monoxide	COFCl							VII	VIII	Carbonate	
0.3	0.46		Tri-*n*-butylamine	1.0	0	0.5	100	78	13.8	8	
Butadiene dioxide[a]	COFCl							XII	IX	X	XI
0.20	0.22		Tri-*n*-butylamine	1.2	10	12	100	70	10.5	7.8	11.7
Tetrahydrofuran	$COCl_2$	COFCl						1,3-Dichlorobutane	1,4-Dichlorobutane	$Cl(CH_2)_4$-OCOF	
0.1	0.2	...	HCl	4	100	0.5	10	47.1	52.9	...	
0.1	...	...	HCl	550	100	2	100	...	99.9	...	
0.1	...	...	HCl	460	100	1	100	...	99.9	...	
			Tri-*n*-butylamine	4							
0.1	0.09	0.2	Tri-*n*-butylamine	4	60	14	99	29.7	33	34	
			Ethylene glycol	4							
0.1	0.09	0.2	Tri-*n*-butylamine	4	100	12	100	50.6	34.5	14.9	
			CH_3OH	4							
0.1	0.1	0.2	Tri-*n*-butylamine	4	100	12	100	70.3	27.0	0.9	
			HCl	5							
0.1	0.12	0.37	HCl	4	100	12	100	65.6	34.3	Trace	

[a] 0.5 mole of benzene as solvent.

carbon atom. The isomer composition was determined by n.m.r. analysis, if separation by distillation or chromatography was impossible.

Attempts were made to dehydrochlorinate compound XII, which would result in an interesting monomer similar to vinylene carbonate,[7] but with two functional groups. However, all attempts were unsuccessful.

Preparation of ω-Fluoroalkenes by Decarboxylation and Dehydrohalogenation of ω-Chloroalkyl Fluoroformates.—The ω-chloroalkyl fluoroformates are a new class of compounds. They are very useful intermediates for the preparation of ω-chloroalkyl fluorides or ω-fluoroalkenes, which can be prepared according to the following equations. For this purpose the decarboxylation and dehydrohalogenation of ω-chloroethyl fluoroformate was investigated. The method, reported by Nakanishi, *et al.*,[8] using boron trifluoride etherate as a catalyst, was used for the decarboxylation. A 99% conversion of the starting material and yields of 51.7 and 20.6% of $ClCH_2CH_2F$ and $CHFClCH_3$, respectively, were obtained. Since both compounds can be used as starting materials for the subsequent dehydrohalogenation, no separation of the two is required. A high yield dehydrohalogenation can be done in the vapor phase using metal oxide catalysts.[9] Therefore, the over-all yield of vinyl fluoride from ethylene oxide and carbonyl chloride fluoride is about 70%, based on ethylene oxide.

$$\mathrm{ClCH_2{-}CH_2{-}(CH_2)_xOCOF} \xrightarrow{\mathrm{BF_3\cdot Et_2O}} \mathrm{ClCH_2{-}CH_2(CH_2)_xF + CO_2}$$

$$\mathrm{ClCH_2{-}CH_2{-}(CH_2)_xF} \xrightarrow{\text{metal oxide}} \mathrm{CH_2{=}CH{-}(CH_2)_xF + HCl}$$

Attempts to achieve the decarboxylation and dehydrohalogenation in a one-step vapor phase reaction, using platinum as a catalyst, exclusively produced vinyl chloride but not vinyl fluoride. The results of these reactions are given in Table IV.

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[7] M. S. Newmann and R. W. Addor, *J. Am. Chem. Soc.*, **77**, 3789 (1955).

[8] S. Nakanishi, T. C. Myers, and E. V. Jensen, *ibid.*, **77**, 5033 (1955).

[9] U. S. Patent 3,118,005 (1964).

TABLE III

N.M.R. DATA[a]

Compd.	F^{19} chemical shift, τ (J, c.p.s.)	F^{19} peak multiplicity[b]	Assignment	Proton chemical shift (J, c.p.s.)	Proton peak multiplicity[b]	Area	Assignment
I	18.6	s	pr. f.[c]	228	m	1	$-CH_2Cl$
				270	m	1	$-CH_2O-$
II	18.3 ($J_{F,H}$ = 2)	t[d]	pr. f.	129 ($J_{H,H}$ = 6) ($J_{H,F}$ = 2)	qui d	1	CCH_2C
				213 ($J_{H,H}$ = 6)	t	1	$-CH_2Cl$
				260 ($J_{H,H}$ = 6)	t	1	$-CH_2O-$
III	18.5	s	pr. f.	111	m	2	CCH_2C
				210	m	1	$-CH_2Cl$
				258	m	1	$-CH_2O-$
IV	18.3	s	pr. f.	100	m	3	CCH_2C
				205	t	1	$-CH_2Cl$
				250	t	1	$-CH_2O-$
V	16.9 ($J_{F,H}$ = 2)	d[d]	s.f.[c]	95 ($J_{H,H}$ = 6) ($J_{H,F}$ = 2)	dd	3	$-CH_3$
				215 ($J_{H,H}$ = 6)	dd	2	$-CH_2Cl$
				295 ($J_{H,H}$ = 6)	h	1	$>CHO-$
VI	18.4	s	pr. f.	95	dd	1	$-CH_3$
				255	m	1	$>CHCl, -CH_2O-$
VII	16.9	s	s.f.	255	m	1	$-CH_2Cl, >CHO-$
				320	m	1	$-CH=CH_2$
VIII	18.4	s	pr. f.	255	m	1	$>CHCl, -CH_2O-$
				320	m	1	$-CH=CH_2$
IX	17.7		s.f.[e]				
X	17.8		s.f.				
	18.8		pr. f.				
XI	18.8		pr. f.				
XII				225		2	$-CH_2Cl$
				285		1	$>CHCH<$

[a] All spectra were recorded on a Varian HR-60 spectrometer using 5% solutions in CCl_4 containing $CFCl_3$ as an internal reference. Chemical shifts are quoted as c.p.s. downfield from tetramethylsilane (TMS) and as p.p.m. upfield from $CFCl_3$. The coupling constants, J, are expressed in c.p.s. [b] s = singlet, d = doublet, dd = doublet of doublets, t = triplet, qui d = quintet of doublets, and m = multiplet. [c] pr. f. = primary fluoroformate group and s.f. = secondary fluoroformate group. [d] This splitting can be explained by free-space coupling between the fluorine atom and the β-hydrogen atoms. [e] This assignment was made on the basis of the known F^{19} spectra of $FOCOCH_2CH_2OCOF$ and compound I of this table, which show a F^{19} resonance at 18.5 and 18.6 p.p.m., respectively.

TABLE IV

COMBINED DECARBOXYLATION AND DEHYDROHALOGENATION OF $Cl(CH_2)_2OCOF$-ON-PLATINUM GAUZE CATALYST

Temp., °C.	Contact time, sec.	Conversion of starting material, %	Yield, %			
			CH_2FCH_2Cl	$CHFClCH_3$	$CH_2=CHCl$ (after bromination)	$CH_2=CHF$ (after bromination)
400	30	0	...	...	...	...
500	22	29	11.6	2.8	61.6	...
600	18	100	...	...	>70.0	...

Ring Opening of Tetrahydrofuran with Phosgene.—The ring opening of tetrahydrofuran with phosgene resulted in a mixture of 1,3- and 1,4-dichlorobutane. A small amount of HCl or HCl donors had to be used to catalyze the ring opening. Tertiary amines were not required as a second catalyst, as in the case of carbonyl chloride fluoride. Without using a tertiary amine as a catalyst the conversion of the starting material at 100° was between 10 and 100%, depending on the reaction time. The main products were (i) 1,3-dichlorobutane with a yield between 65 and 47%, respectively, and (ii) 1,4-dichlorobutane with a yield between 34 and 53%, respectively. The intermediately formed chloroformates could not be isolated owing to their low thermal stability. (The chloroformates generally show a much lower thermal stability than the corresponding fluoroformates.)

It could be shown by treating THF with HCl in the presence of tertiary amines that exclusively 1,4-dichlorobutane was formed. Therefore, the formation of 1,3-dichlorobutane is not caused by the presence of the tertiary amine.

The following explanation can be given for the different reaction products in the case of the ring opening of tetrahydrofuran with phosgene and hydrogen chloride. The formation of 1,3-dichlorobutane in addition to the expected 1,4-dichlorobutane must be due to a different reaction mechanism. In the case of the hydrogen chloride a second-order reaction is assumed, while in the case of phosgene the decomposition of the intermediately formed chloroformate is a reaction of first order. If reactions of tetrahydrofuran were done with mixtures of phosgene and carbonyl chloride fluoride in the presence of hydrogen chloride and tertiary amines as catalysts, both dichlorobutane and ω-chlorobutyl fluoroformate formed simultaneously. However, the formation of dichlorobutanes appears to be preferred. The results of these reactions are included in Table II.

Ring Opening of Cyclic Ethers with Thionyl Fluoride or Sulfuryl Fluoride.—Cyclic ethers can be expected to react with such compounds as thionyl or sulfuryl fluoride analogous to the above-described reactions with carbonyl halides.

Sulfuryl fluoride and ethylene oxide at temperatures up to 90° did not react with each other in the presence of tertiary amines as a catalyst.

Thionyl fluoride, prepared from thionyl chloride and arsenic trifluoride in 96% yield and high purity, reacted with ethylene oxide in the presence of tertiary amines as catalyst. The conversion of the tetrahydrofuran was 88% and the main product was obtained in yields as high as 72.5%. However, the results obtained by n.m.r., infrared, and elemental analysis for the compound were not conclusive.

This agrees well with the higher reactivity of thionyl fluoride compared with that of sulfuryl fluoride toward most reactants.

Experimental

Preparation of Carbonyl Chloride Fluoride.—In a typical experiment arsenic trifluoride (1.33 moles) was mixed with phosgene (5.50 moles) and antimony pentachloride (2.5 ml.) as a catalyst, in a 1-l. stainless steel lecture bottle. The mixture was kept at 130° for 10 hr. and a pressure of 800 p.s.i. developed. After cooling to 0°, 340 g. of volatile products was condensed at $-78°$. Gas chromatographic analysis of the reaction products showed the following composition: 89% COFCl, 7% $COCl_2$, and 4% COF_2.

Ring-Opening Reactions of the Cyclic Ethers with Carbonyl Halides.—All reactions were run in the same way varying only in the conditions that are listed in Table II for each reaction. The cyclic ether was placed together with the catalyst into a stainless steel lecture bottle, which was equipped with a pressure gauge and a stainless steel valve. Then, the lecture bottle was connected to a cylinder containing the carbonyl halide through a stainless steel pressure tubing and Swagelok fittings. The desired amount of carbonyl halide was carefully introduced into the reaction bottle. When the reaction was fast and exothermic, external cooling of the reaction vessel with ice–water was also desirable. After addition of the carbonyl halide, the reaction vessel was disconnected from the carbonyl halide container and agitated as a shaker for the time that is listed in Table II. If necessary, heating was applied by means of infrared lamps. The temperature was measured by a thermocouple taped to the cylinder. The reaction products were worked up by slow bleeding off of the volatile gases followed by vacuum distillation of the residue. The conversion of the cyclic ether and the yields of fluoroformates were determined by gas chromatography of the crude product. Infrared spectra of all new products were taken on a Beckman IR-9 in the range from 400 to 4000 cm.$^{-1}$.

Preparation of Thionyl Fluoride.—Arsenic trifluoride (2.2 moles) and antimony pentafluoride (20 ml.) as a catalyst were placed into a three-necked flask, provided with a dropping funnel magnetic stirrer, thermometer, and water-cooled condenser. The outlet of the condenser was connected to a cold trap, kept at $-78°$. Thionyl chloride (3.3 moles) was added dropwise and the flask was kept at room temperature by using a water bath. The thionyl fluoride was collected in the cold trap, purified by fractionation, and transferred to a stainless steel lecture bottle. A 100% conversion of the thionyl chloride and a 96% yield of thionyl fluoride was obtained.

Reaction between Thionyl Fluoride and Ethylene Oxide.—Six reactions between ethylene oxide and thionyl fluoride were carried out in stainless steel lecture bottles using tertiary amines as catalysts. The reaction temperatures were varied from room temperature to 110°. Conversions of the ethylene oxide up to 88% and yields of the main reaction product up to 72.5% were obtained. The structure of this product, however, could not be determined definitely.

Reaction between Sulfuryl Fluoride and Ethylene Oxide.—Ethylene oxide (0.2 mole), *m*-dichlorobenzene (25 g.) as a solvent, tri-*n*-butylamine (0.2 ml.) as a catalyst, and sulfuryl fluoride (0.5 mole) were placed into a 100-ml. stainless steel lecture bottle and shaken for 12 hr. at 90°. Gas chromatographic analysis of the reaction product showed, however, that no reaction had occurred.

Decarboxylation of ω-Chloroethyl Fluoroformate.—Freshly prepared boron trifluoride–tetrahydrofuran complex (15 ml.) was placed into a 30-ml. flask, equipped with a magnetic stirrer, a dropping funnel, a gas inlet for dry nitrogen, and a condenser which was connected to two cold traps (-78 and $-196°$) and a mercury blowoff. The set up was purged with dry N_2 and the temperature was increased to 110–120°. Then $Cl(CH_2)_2OCOF$ (0.027 mole) was slowly added. After the reaction was completed, the contents of the flask and the cold traps was quantitatively analyzed by weighing and gas chromatographic analysis. The following results were obtained. Conversion of the starting material was 95%, yield of CH_2FCH_2Cl was 36% (b.p. 53°, characterized after separation on a preparative gas chromatographic column by infrared and n.m.r. spectroscopy), and of $CHFClCH_3$ was 15% (b.p. 16°, characterized as mentioned above).

The reaction was repeated using boron trifluoride diethyletherate as a catalyst. Otherwise, the reaction conditions were identical. A 99% conversion of the starting material and a 51.7 and 20.6% yield of CH_2FCH_2Cl and $CHFClCH_3$, respectively, were obtained. This gives a 72.3% over-all yield of vinyl fluoride precursor.

Combined Decarboxylation and Dehydrohalogenation of $Cl(CH_2)_2OCOF$.—Three reactions were carried out by passing vapors of $ClCH_2CH_2OCOF$ with a carrier stream of dry nitrogen (ratio of 1:10) through a platinum-lined Inconel tube (diameter 6 mm., length of heated zone 30 cm.) containing platinum gauze as a filling material. A tube furnace gave adequate temperature control. The gas inlet was heated by an infrared lamp in order to avoid condensation of the starting materials. The reaction products were collected in three cold traps (one at $-78°$ and two at $-196°$), weighed, and analyzed by gas chromatography. The results are given in Table III. The volatile products were bubbled through bromine and the vinyl chloride was identified after separation as $CH_2BrCHClBr$ by refractive index, infrared spectrum, and elemental analysis.

Attempted Dehydrohalogenation of XII.—The dehydrohalogenation of compound XII was attempted by refluxing it with triethylamine, tributylamine, and quinoline, respectively, for 24 hr., but in all cases no reaction occurred. If potassium hydroxide was used, potassium carbonate was formed.

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