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Registry No.-12, 55759-61-0; 13, 19289-04-4; 14, 1945-92-2; KOC(CH₃)₃, 865-47-4; N-acetylethanolamine, 142-26-7; 2,4-dinitrofluorobenzene, 70-34-8.

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Cleavage Reaction of Cyclic Ethers by Alkyl Chlorosulfinates

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The reaction of alkyl chlorosulfinates with tetrahydrofuran (THF) produced predominantly 4-chlorobutylalkyl ethers, but with ethylene oxide β -chloroethylalkyl sulfites were the main product. The kinetic study on the formation of 4-chlorobutylalkyl ethers revealed that the nucleophilic attack of THF on the carbon atom of alkyl chlorosulfinates is the rate-determining step, followed by simultaneous fission of C-O and S-Cl bonds of alkyl chlorosulfinates.

Of the various classes of organic reactions, nucleophilic substitution reactions on carbon have, to date, been studied most intensively. On the formation of alkyl chlorides from the reactions of the corresponding alcohols with thionyl chloride, Hughes and Ingold¹ proposed a mechanism involving the formation of intermediate alkyl chlorosulfinates, followed by the loss of sulfur dioxide, and simultaneously with it formed the carbon-chlorine bond, presumably by way of a cyclic transition state due to their stereochemical reasons. They called this reaction the SNi mechanism. Since then, Boozer and Lewis² showed by the study dealing with the decomposition of alkyl chlorosulfinates that intermediates in the formation of alkyl chlorides must have much ionic character. Cram³ concluded that the SNi reaction proposed by Hughes and Ingold for the decomposition of alkyl chlorosulfinates differs from the SN1 reaction only in the sense that the leaving group is complex, and that the anion of the first ion pair can decompose internally under some conditions faster than a potential anion can react at the carbon undergoing substitution. However, the study on the reactions employing the alkyl chlorosulfinates as the substrate is lacking compared with those of the alkyl chloroformates⁴ except for the studies on the interactions of alkyl chlorosulfinates and pyridine by Gerrard.^{5,6} We will report the cleavage reaction of cyclic ethers by alkyl chlorosulfinates.

Results

The reaction of ethylene oxide with methyl chlorosulfinate in benzene at 0° gave 70.8% of β -chloroethylmethyl sulfite⁷ for 20 min. The results obtained from a variety of epoxides are shown in Table I; the preferential attack of the sulfinyl sulfur of methyl chlorosulfinate by epoxides seems to be predictable from the fact that methanesulfinyl chloride is known to react with ethylene oxide yielding the

corresponding sulfinate ester.⁸ However, from the fivemembered ether, tetrahydrofuran (THF), 4-chlorobutylmethyl ether is obtained as the main reaction product. As shown in Figure 1 this reaction proceeded with an exceedingly slow rate at 30°. At this temperature, the yield of methyl chloride formed by a side reaction is less than about 5% of that of 4-chlorobutylmethyl ether.

These interesting results by the use of THF caused us to elucidate the mechanism of the reaction of THF with alkyl chlorosulfinates yielding 4-chlorobutylalkyl ethers. As shown in Scheme I it is possible to consider two mechanisms containing different modes of attack: (1) THF as the nucleophilic reagent attacks the carbon atom of alkyl chlorosulfinates (C-attack) forming both O-alkyl tetrahydrofuranium ion and chlorosulfinate anion (I), followed by the loss of SO_2 to produce the chloride anion. On the other hand, (2) the nucleophilic attack of THF on the sulfur atom of alkyl chlorosulfinates (S-attack) may lead to the formation of an intermediate O-alkoxysulfinyl tetrahydrofuranium ion (II), followed by the formation of O-alkyl tetrahydrofuranium ion⁹ by way of a cyclic transition state.

It is conceivable that the intramolecular reaction of an intermediate (II) may proceed more rapidly than the attack of the chloride ion on an intermediate oxonium ion (II) because of the high stability of such an oxonium ion compared with that of the three-membered oxonium ions. Thus, we elucidate at first the distinction between the Cattack and S-attack of THF and then the feature of this reaction. The reaction rate of methyl chlorosulfinate with THF was followed by gas-liquid partition chromatography (GLC) determining the concentration of methyl 4-chlorobutyl ether formed by the use of *p*-cymene as an internal reference. The reactions were carried out at the temperatures below 50° in order to avoid the side reactions probably due to thermal instability of alkyl chlorosulfinates.

· · · · · · · · · · · · · · · · · · ·		Product				
Epoxide	Registry no.	Structure (mol %) (registry no.)		Bp, ^o C (mmHg)	Time, Tem min ^O C	
Ethylene oxide	75-21-8	CH ₃ OSO-(CH ₂ -) ₂ Cl (55913-34-3) $\ $ O	70.8	115–118 (46)	20	0
Cyclohexene oxide	286-20-4	$CH_{3}OSO C1 (55913-35-4) $ $(trans.isomer)$	68.2	130-135 (8)	100	25
Propylene oxide	75-56-9	$\begin{array}{c c} CH_{3}OSOCH_{2}CHCl & CH_{3}OSOCHCH_{2}Cl \\ \parallel & \parallel & \parallel & \parallel \\ O & CH_{3} & O & CH_{3} \\ (25,3) & (55913-36-5) & (74,7) & (55913-37-6) \end{array}$	85.6	105108 (58)	120	30
1, 2-Epoxy-3- methoxypropane	930-37-0	$\begin{array}{c c} CH_3OSOCH_2CHCH_2OCH_3 & CH_3OSOCHCH_2Cl \\ \ & \ & \ \\ O & Cl & 0 & CH_2OCH_3 \\ (11.7) & (55913-38-7) & (88.3) & (55913-39-8) \end{array}$	88.1	102 (11)	120	30
Epichlorohydrin 2	106-89-8	CH ₃ OSOCH ₂ CHCl CH ₃ OSOCHCH ₂ Cl O CH ₂ Cl O CH ₂ Cl (2.1) (55913-40-1) (97.9) (55913-41-2)	60.6	100 (8)	600	30
Concentration (M)	A A A					

 Table I

 Reaction Products of Methyl Chlorosulfinate with Various Epoxides in Benzene

Figure 1. Time dependence of products and methyl chlorosulfinate for the reaction of methyl chlorosulfinate with THF in carbon tetrachloride at 30°: $[CH_3OS(=O)Cl]_0 = [THF]_0 = 2.30 M$; \triangle , $CH_3OS(=O)Cl$; \bigcirc , $CH_3O(CH_2)_4Cl$; x, CH_3Cl .

600

(hr)

700

800

900

The reaction rates were followed up to 40-60% conversions; reactions obeyed good second-order kinetics, i.e., the rates of reaction were proportional to the concentrations of THF and methyl chlorosulfinate, respectively, as shown in Table II. The second-order rate constant (k_2) for these reactions was found to be $(2.86 \pm 0.25) \times 10^{-7} M^{-1} \text{ sec}^{-1}$ in benzene at 30°. Moreover, on the reaction of isobutyl chlorosulfinate with THF, only isobutyl 4-chlorobutyl ether was formed and not the other possible isomers, sec-butyl and *tert*-butyl 4-chlorobutyl ether, to which an intermediate isobutyl cation would isomerize¹⁰ if isobutyl chlorosulfinate might decompose according to the first-order reaction. Thus, these experimental results confirmed that the reac-

100

200

300

400

500

Reaction time

tion of the primary alkyl chlorosulfinates with THF proceeded by second-order reaction. The k_2 values derived from the reactions with various alkyl chlorosulfinates are given in Table III.

1000

1100

1200

The comparisons of relative reactivities among a series of alkyl chlorosulfinates studied and some bimolecular nucleophilic substitutions are informative. The results, relative rates (k_2 for the ethyl compounds in each series at unity) for some bimolecular nucleophilic substitutions of primary compounds containing a displaceable group, are given in Table IV; it is arranged in decreasing orders for the relative rates from methyl to isobutyl, suggesting that steric hindrance plays a dominant role. Thus, the resemb-

 Table II

 Second-Order Rate Constants for the Reaction of Methyl

 Chlorosulfinate with THF in Benzene at 30°

[CH308(0)C1],	[THF],	$k_2 \times 10^7$,
М	M	M ⁻¹ sec ⁻¹
2	3	2.56 ± 0.05
2	2.5	2.77 ± 0.23
2	2	2.94 ± 0.07
2	1.5	2.83 ± 0.11
2	1	2.92 ± 0.11
2	0.5	2.97 ± 0.20
1	2	2.92 ± 0.17
0.5	2	2.92 ± 0.25
1	3	3.03 ± 0.25
		av 2.86 ± 0.25

Table III Second-Order Rate Constants for the Reactions of Various Alkyl Chlorosulfinates with THF in Benzene

R	Temp, ^o C	$k_2 \times 10^7$, $M^{-1} \mathrm{sec}^{-1}$	Activation parameter
Ме	20	1.22 ± 0.09	$\Delta H^{*} = 17.8 \text{ kcal/mol}$
	20.5	1.39 ± 0.11	$\Delta S^* = -20.6 \text{ eu}$
	25	2.22 ± 0.19	
	30	2.86 ± 0.25	
	35	4.33 ± 0.31	
	40	7.28 ± 0.52	
Et	30	1.78 ± 0.04	$\Delta H^* = 19.0 \text{ kcal/mol}$
	40	4.71 ± 0.21	$\Delta S^{*} = -18.9 \text{ eu}$
	50	10.78 ± 0.54	
n-Pr	30	0.72 ± 0.01	
<i>i</i> -Bu	30	0.038 ± 0.003	
<i>i</i> -Pr	30	15.36 ± 1.50	

tion with the isopropyl chlorosulfinate proceeds with a faster rate than that with methyl compound as shown in Table III. It is reported in the literature² that secondary alkyl chlorosulfinates are more reactive than primary compounds for the thermal decomposition yielding the corresponding alkyl chlorides and sulfur dioxide.

The data of the influence of solvents on reaction rates are shown in Table V. The tendency of the increasing rate in more polar solvents implies that initially neutral reactants form a transition state which has some separation of charge in analogy with the Menschutkin reaction.

Discussion

The experimental results, having great resemblance of reactivity to the well-known other nucleophilic substitution reactions, predominantly to give inverted products, and the solvent effects make certain a mechanism that the nucleophilic attack of THF on the carbon atom of primary alkyl chlorosulfinates is a rate-determining step and then, as depicted in Scheme I, O-alkyl tetrahydrofuranium ion and chlorosulfinate anion would be formed, followed by the loss of sulfur dioxide forming chloride anion. When O-alkyl tetrahydrofuranium ion undergoes the nucleophilic attack of the chloride anion, we can consider two modes of reaction, that is, methylene-O and alkyl-O cleavage. It has been reported¹⁶ that methylene-O cleavage is greatly preferred in the cyclic oxonium intermediate, which can be ascribed to a decrease of steric hindrance and an increase in reactivity due to some eclipsing strain when the methylene-O carbon is constrained to a five-membered ring. From the structural analogy to alkyl chlorosulfates,¹⁷ we attempt in the reaction of alkyl chlorosulfinates with THF to distinguish between the typical SN2 reaction and the multiple bond fission (fragmentation SN2) reaction accompanied by simul-

Table IV
Relative Rates for Some Substitution Reactions Concerned with Primary Compounds

	Relative rate					
Reaction	Temp, ^o C	Me	Et	n - Pr	i-Bu	Ref
RBr + pyridine in MeOH	80	17.2	1.00	0.55	0.017	11
ROTs in EtOH	75	2.3	1.00		0.46	12
RBr in 50% aq EtOH	95	1.94	1.00		0.075	13
0 						
ROSC1 in 85.3% aq dioxane O	25	2.93	1.00	0.555	0.043	14
O 						
ROSPh in H_2O	60	1.05	1.00		0.235	15
ROSC1 + THF in benzene	30	1.61	1.00	0.40	0.022	This work

lances of reactivities among one another collected in Table IV provide strong evidence that alkyl chlorosulfinates react with THF by bimolecular substitution on carbon. Moreover, the reaction of optically active sec-butyl chlorosulfinate with THF gave a 64.3% inverted product, which was evaluated in comparison with the optically active material obtained by way of Williamson's method. This result, the low optical purity caused by the use of a secondary alkyl chlorosulfinate, may show that the reaction proceeds partially by a carbonium ion mechanism without participation of nucleophiles in the transition state. Actually, the reacTable V Solvent Effect on the Reaction Rate of Methyl Chlorosulfinate with THF at 30°

Solvent	$k_2 \times 10^7, M^{-1} sec^{-1}$	Dielectric constant (25 ⁰)	Registry no.
<i>n</i> -Hexane	0.86 ± 0.03	1.88	110-54-3
Benzene	2.86 ± 0.25	2.28	71-43-2
Dichloromethane	6.56 ± 0.27	8.93	75-09-2
1.2-Dichloroethane	8.06 ± 0.27	10.3	107-06-2
Nitrobenzene	10.83 ± 0.80	35.9	98-95-3





S-attack

taneous fission of C-O and S-Cl bonds. The effect of leaving groups on substitution reaction rates is shown in Table



VI; the order of the ease of the substitutions for leaving groups attached to the carbon atoms parallels the order of departing tendency¹⁸ of fragments attached to the sulfinyl sulfur atom.

If the typical SN2 reaction occurs we cannot expect the remarkable retardation of the reaction rate by the change of the X in the leaving groups -OS(O)X.¹⁹ Further insight into the mechanism of the reaction of alkyl chlorosulfinates with THF may be gained by consideration of the actual magnitudes of the activation parameters. A discussion of activation parameters must consider their large dependence on both the medium and reaction mechanism. The

Table VI Effect of Leaving Groups on Substitution Reaction Rates of CH₃OS(O)X with THF in Benzene at 30°

X C1		oc(o)CH3	осн3	
$k_2, M^{-1} \sec^{-1}$	2.86 × 10 ⁻⁷	10 ⁻¹¹ -10 ⁻¹²	No reaction for 7 days	

comparison of the activation parameters for the reactions of alkyl chlorosulfinates with those for some Menschutkin reactions in the same reaction medium (benzene) is listed in Table VII. The actual magnitudes of the activation entropies should be considered in correlation with both the solvation and degrees of freedom of the initial and transition states. If the simultaneous fission of two bonds accompanied by formation of three fragments occurs in the transition state we can expect an increased ΔS^{\ddagger} owing to the gain of a degree of freedom, but contrary to this, increased solvation to the transition state results in a more negative ΔS^{\ddagger} . Although the balance of the two opposite effects is difficult to estimate, Buncel¹⁷ indicated that the increase of the activation entropy caused by the gain of a degree of freedom predominates over the solvation by 10-20 eu in the hydrolysis of alkyl chlorosulfates. Our result that the reaction of alkyl chlorosulfinates and THF proceeds with a more positive ΔS^{\ddagger} (10-20 eu) compared with the typical Menschutkin reactions may be due to simultaneous fission of two bonds. In addition to this, it is most likely that the remarkable retardation of the reaction by the change of the X in the leaving groups -OS(O)X is responsible for the fact that the reaction of alkyl chlorosulfinates with THF proceeds with a greater charge separation and also forms the incipient sulfur dioxide in this transition state. The generation of O-alkyl tetrahydrofuranium ions from the reactions



of alkyl chlorosulfinates with THF, for which the corresponding alkyl chlorides are unreactive without catalyst, is taken to indicate that the loss of sulfur dioxide provides a substantial driving force for the reactions.

Although it is possible to interpret the difference in the reaction products between epoxides and THF as a catalytic action of a small amount of hydrochloric acid which is difficult to remove by purification of alkyl chlorosulfinates, it can be ruled out by the following facts. As shown in Table I, the distribution of the isomers in products obtained from asymmetric epoxides such as propylene oxide and epichlorohydrin greatly differs from that which would be expected from the acid-catalyzed reaction²⁴ in which the chloride anion prefers to attack the methylene–O carbon, not the

 Table VII

 Comparison of Activation Parameters Obtained from Reactions of Alkyl Chlorosulfinates and THF with Those of Some Menschutkin Reactions in Benzene

Reaction	k ₂ , M ⁻¹ sec ⁻¹	Temp, ^o C	Δ H[‡], kcal/mol	Δ <i>5</i> *, εu	Ref
MeI + pyridine	7.1 × 10 ⁻⁵	50	15.7	54.0	20
$MeI + Et_3N$	1.85×10^{-3}	30	10.3	-42.9	21
EtBr + pyridine	$0.744 imes10^{-5}$	79	17.5	-34.5	22
$EtBr + PhNEt_{2}$	5.58×10^{-6}	70	9.05	-59.2	23
MeOSCl + THF	2.86 × 10-7	30	17.8	-20.6	This work
$ \begin{array}{c} \mathbf{O} \\ \mathbf{EtOSC1} + \mathbf{THF} \\ \ \\ \mathbf{O} \end{array} $	1.78×10^{-7}	30	19.0	-18.9	This work

carbon having the substituent. The reaction of methyl chlorosulfinate with ethylene oxide proceeds more rapidly even in benzene than predicted from the acid-catalyzed hydrolysis of ethylene oxide in a more polar solvent, H₂O. Accordingly, the possibility of the action by hydrochloric acid can be ruled out in this reaction. The preferential attack on sulfinyl sulfur by ethylene oxide seems to be reasonable from the fact that the addition of β -chloroethyl chloroformate to ethylene oxide produces bis(2-chloroethyl) carbonate quantitatively and this is a violent exothermic reaction.²⁵ It is known that lone pair electrons on the oxygen atom of epoxides possess much more s character than those of THF because of its large ring strain. Thus, we assume that the difference in the mobilities of lone pair electrons located on the oxygen atoms of epoxides and THF is due to the difference in the contributions to the Coulombic repulsions in the transition state between the neutral nucleophile and the sulfur atom of alkyl chlorosulfinates having the positive charge.²⁶ The nucleophilic attack of THF on the sulfur atom of alkyl chlorosulfinates requires much more activation energy than that of epoxides to overcome the Coulombic repulsion in the transition state.

>0 + HCl \rightarrow HO \leftarrow CH₂ \rightarrow ₂Cl

 $CH_{3}OSCl + HO \leftarrow CH_{2} \xrightarrow{\rightarrow}{_{2}}Cl \longrightarrow CH_{3}OSO \leftarrow CH_{2} \xrightarrow{\rightarrow}{_{2}}Cl + HCl$

-

However, we cannot interpret clearly the reason for the more favorable attack of THF on the carbon atom of alkyl chlorosulfinates. The mechanism of the reaction of alkyl chlorosulfinates with epoxides is now under active study.

Experimental Section

Materials. All of the solvents were purified by the usual methods. Commercial THF was dehydrated over sodium wire and then purified by distillation. Cyclohexene oxide, propylene oxide, and epichlorohydrin, commercially available, were dried with calcium hydride and then purified by distillation. Ethylene oxide, prepared from ethylene chlorohydrin and sodium hydroxide pellets, was purified by low-temperature distillation from dried sodium hydroxide and finally by drying over barium oxide. 1,2-Epoxy-3-methoxypropane, obtained by the method of Gallardo and Pollard,²⁷ was purified by distillation, bp 53° (86 mmHg). Alkyl chlorosulfinates used in this study were prepared and purified by the method of Lewis.² Optically active (R)-sec-butyl chlorosulfinate was synthesized by the reaction of thionyl chloride with the corresponding alcohol prepared by a modification of the method of Prichard and Kenyon²⁸ and optically active (R)-sec-butyl 4-chlorobutyl ether was prepared by the reaction of (R)-sec-butyl alcoholate with 1,4dichlorobutane. Methyl acetoxysulfinate was obtained by the reaction of methyl chlorosulfinate with anhydrous sodium acetate as reported by Kobayashi²⁹ and purified by distillation, bp 40–45° (5 mmHg).

Anal. Calcd for C₃H₆O₄S: S, 23.19. Found: S, 21.17

The structure of methyl acetoxysulfinate was confirmed by the agreement with the ir spectrum shown in the literature. The purity was calculated to be 91% from sulfur content; thus only a rough estimate of the rate constant was done for this compound. Methyl sulfite was obtained as a by-product in the preparation of methyl chlorosulfinate and then purified by distillation.

Authentic Compounds for GLC. 4-Methoxybutyl acetate was prepared by the slow addition with stirring of acetyl chloride in anhydrous ether to a mixture of dry pyridine and 4-methoxybutyl alcohol, which was itself obtained by treating butane-1,4-diol with sodium and methyl iodide.^{16,30}

Kinetic Measurement. A flask was equipped with a needle valve and a neoprene rubber stopper. The appropriate solvent, THF, and sealed glass ampoule containing alkyl chlorosulfinate were placed in the flask, and then dry nitrogen was bubbled into the reaction flask immersed in cold methanol. The initial time for the reaction was taken when the glass ampoule in the flask immersed in a thermostat was broken. A small amount of the reaction mixture was taken out from the flask at a given time through the neoprene rubber stopper with a syringe and then treated with 50% aqueous sodium carbonate solution. The reaction rates were determined from the measurement of GLC peak areas. The concentration of the product in the reaction mixture was corrected using p-cymene as internal standard for difference in detector responses between products and internal standard. GLC was performed on a Yanaco Model 201 with flame ionization detector.

General Method of Reaction of Methyl Chlorosulfinate with Epoxides in Benzene. To epoxide in benzene, methyl chlorosulfinate was added. After the reaction had continued for the prescribed time, the reaction mixture was immediately evaporated at reduced pressure to remove the solvent, and alkyl sulfites were isolated by distillation under reduced pressure and obtained in pure form by preparative GLC. The structure of the products was identified by its infrared and NMR spectra. Product yields were determined by the GLC method using an internal reference with corrections for differences in detector responses and measurement of peak areas. The isomer distributions of alkyl sulfites obtained from asymmetric epoxides were determined by the intensity of the NMR signals for the methine and methylene protons attached to the sulfite group. Yields and product distributions of the individual compounds are summarized in Table I.

2-Chloroethyl Methyl Sulfite. Gaseous ethylene oxide was bubbled into methyl chlorosulfinate in benzene. After the reaction was carried out for 20 min at 0°, 2-chloroethyl methyl sulfite was obtained by distillation: ir ν_{\max} S=O 1210, S=O 730 cm⁻¹.

Anal. Calcd for C₃H₇ClO₃S: C, 22.71; H, 4.42; S, 20.19. Found: C, 23.15; H, 4.56; S, 20.45.

2-Chlorocyclohexyl Methyl Sulfite. The reaction was carried out as described in the general procedure. Distillation of the crude product under reduced pressure afforded pure compound: ir ν_{max} S=0 1200, S=0 700, 740 cm⁻¹.

Anal. Calcd for $C_7H_{13}ClO_3S$: C, 39.52; H, 6.12; S, 15.06. Found: C, 39.73; H, 5.87; S, 15.37.

 Table VIII

 Reaction Product of Various Alkyl Chlorosulfinates with Tetrahydrofuran

R in		,			Elemental analysis, %		
ROS(0)C1	Registry no.	Product $RO+CH_2+4C1$	Registry no.	Bp, °C	.	с	Н
Me		Me-O-(CH ₂)-4Cl	17913-18-7	50 (40 mmHg)	Calcd	48.98	8.98
		L · *		-	Found	49.02	8.76
Et	6378-11-6	Et-O+CH ₂ + ₄ Cl	36865-43-7	149	Calcd	52.75	9.52
		2 . 4			Found	52.51	9,36
<i>n</i> -Pr	22598-38-5	$n-\Pr-O+CH_2+_4Cl$	14860-82-3	168	Calcd	55.8 1	9.97
					Found	55.69	9.71
<i>i-</i> Bu	13291-52-6	$i-Bu-O-(CH_2)4Cl^a$	55913-42-3	178	Calcd	58.36	10.33
		· / 4 · 16			Found	58.45	10.33
<i>i</i> -Pr	22598-56-7	i-Pr-O-(CH ₂)- ₄ Cl	55913-43-4	166-168	Calcd	55.81	9.97
		- •			Found	56.08	10.08
sec-Bu	55954-47-7	sec-Bu-O-(CH ₂)-4Cl	55913-44-5	165-168	Calcd	58.36	10.33
^a Seconda	rv and tertiarv ison	ners were not detected.			Found	57.99	10.01

2-Chloropropyl Methyl Sulfite and Isomer. The product was obtained according to the above procedure. To determine the isomer distribution, the reaction products were isolated by preparative GLC: ir ν_{max} S=O 1192, S=O 690, 735 cm⁻¹; NMR δ 4.69 (sextet, -OCH(CH₃)CH₂Cl), 4.04 (AA'X, -OCH₂CH(CH₃)Cl).

Anal. Calcd for C₄H₉ClO₃S: C, 27.83; H, 5.52; S, 18.52. Found: C, 27.55; H, 4.97; S, 18.72.

2-Chloro-3-methoxypropyl Methyl Sulfite and Isomer. The results of elementary analyses were satisfactorily consistent with calculated values without further preparative GLC: ir ν_{max} S=O 1200, S–O 710 cm⁻¹; NMR δ 4.58 [q, –O(CH₂Cl)CH(CH₂OCH₃], 4.10 [m, –OCH₂CH(Cl)–].

Anal. Calcd for C5H11ClO4S: C, 29.63; H, 5.43; S, 15.80. Found: C, 29.69; H, 5.59; S, 15.36.

2-Chloromethyl-2-chloroethyl Methyl Sulfite and Isomer. Methyl chlorosulfinate was added to epichlorohydrin as described in the general procedure. The reaction mixture slowly darkened in 10 hr at 30°. An appreciable by-product was isolated by the use of GLC at this stage. Crude product was purified by preparative GLC: ir ν_{max} S=0 1190, S=0 705, 730 cm⁻¹; NMR δ 4.73 [q, -OCH(CH₂Cl)₂], 4.20 [m, -OCH₂CH(CH₂Cl)Cl].

Anal. Calcd for C₄H₈Cl₂O₃S: C, 23.18; H, 3.86; S, 15.46. Found: C, 23.01; H, 4.33; S, 15.26.

Reaction of Alkyl Chlorosulfites with THF. To excess THF alkyl chlorosulfinates were added. After reflux had continued for 4-5 hr, the corresponding 4-chlorobutyl alkyl ethers were isolated by distillation at atmospheric pressure after treating the reaction mixture with 10% aqueous sodium hydroxide solution and dehydrating by anhydrous sodium sulfate. Boiling points and elementary analyses of individual products are summarized in Table VIII. The structures of all of the compounds were confirmed by infrared and NMR spectra: for CH₃CH(CH₃)CH₂O(CH₂)₄Cl ir ν_{max} ether bond 1112 cm⁻¹; NMR δ 0.89 [d, 6 H, (CH₃)₂CH₋], 3.12 (d, 2 H, -CHCH₂O-), 3.30-3.70 (m, 4 H, -OCH₂CH₂-, -CH₂Cl), 1.60-2.10 (m, 5 H, --CH₂CH₂--, -CHCH₂--)

Time Dependence of 4-Chlorobutyl Methyl Ether and Methyl Chlorosulfinate. An equimolar mixture of methyl chlorosulfinate and THF was allowed to react in carbon tetrachloride, and the progress of the reaction was followed by means of NMR spectroscopy. The amounts of the products and methyl chlorosulfinate were determined from the integrated values on NMR spectra by using dichloromethane as the internal standard: NMR δ 4.08 [CH₃OS(O)Cl], 3.28 [CH₃O(CH₂)₄Cl], 3.05 (CH₃Cl).

Registry No.-Methyl chlorosulfinate, 13165-72-5; 1,4-dichlorobutane, 110-56-5; methyl acetoxysulfinate, 5308-06-5.

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Fluoro Olefins. VI. Ring Size Effects in Cyclic Fluoro Olefins with Alkoxide Nucleophiles

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In contrast to 1,2-dichloro-3,3-difluorocyclobutene (I), which undergoes almost exclusive displacement of chloride ion when reacted with ethoxide, the five-membered analog, 1-chloro-5,5-dihydropentafluorocyclopentene (V), undergoes facile allylic rearrangement. Similarly, the six-membered analog undergoes facile dehydrohalogenation. These results show that the conformational changes, as the ring size changes, dominate the reactions of these cyclic fluoro olefins containing *gem*-dihydro groups, and that the "carbanion stabilization" theory of Park cannot be applied indiscrimately to the larger ring system.

The susceptibility of fluorinated olefins to nucleophilic attack is well documented.² Park and coworkers theorized the kinetic control of intermediate carbanion formation by α - and β -position substituents.³ However, a report by Burton and Johnson suggested that the carbanion stabilization theory did not completely explain the reactions of metal hydrides with cyclic polyfluoro olefins.⁴ They suggested that steric effects (between entering nucleophile and the leaving group) might be contributing to the different mixtures of products obtained from the reactions of sodium borohydride or lithium aluminum hydride with cyclic fluoro olefins. In addition to this apparent discrepancy between alkoxides and complex metal hydrides, both Burton and Park have observed that the ring size of the cyclic fluoro olefins can have an effect upon product ratios.^{4,5} Since most of Park's kinetic control theory has been obtained with cyclobutene systems, it suggested to us that these discrepancies between alkoxides and hydrides might be another example of ring size effects. Accordingly, this paper presents the results of our study into this problem with respect to alkoxides. A later paper will report results obtained with these substrates and their reaction with complex metal hydrides.

The experimentally determined order of α -stabilization was reported to be I > Br > Cl > H > OR > F.⁶ To a lesser extent, these intermediates are stabilized by substituents