Measurements.—Aqueous 0.1 N thiosulfate solution (20 ml.) at 30° was pipetted into a stoppered volumetric flask. About 29 ml. of diglyme was added, and the mixture was allowed to attain thermal equilibrium in a bath at 30.00 ± 0.01°. To the mixture was added 1 ml. of a freshly prepared solution of the halogen compound in diglyme, and diglyme was added to bring the total volume to 50 ml. The first 5-ml. sample was transferred 10 minutes later (t = 0) into cold water and titrated with 0.02 N iodine solution. The reaction was followed to 60–80% completion. Infinite time titrations were made 24 hours later, and were unchanged at the end of 48 hours. The reactions between many organic halides and thiosulfate are known to be nearly quantitative.[6,15] An acetate buffer at a concentration 20% of the initial thiosulfate concentration was used to prevent decomposition of the latter by any acid formed by (slow) solvolysis.[16]

Acknowledgment.—This work was aided by grants from the Research Corporation and The University of Texas Research Institute.

[15] F. J. Crowell and L. P. Hammett, This Journal, **70**, 3444 (1948).

[16] P. M. Dunbar and L. P. Hammett, *ibid.*, **72**, 109 (1950).

Austin, Texas

[Contribution from the Department of Chemistry, University of Florida]

The Preparation and Properties of Some Vinyl and Glycidyl Fluoroethers

By Mary L. Brey and Paul Tarrant

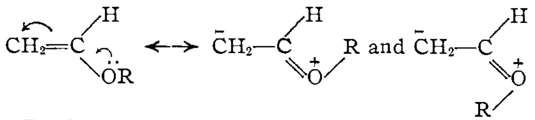
Received May 13, 1957

A series of vinyl fluoroalkyl and glycidyl fluoroalkyl ethers have been synthesized. A study of the infrared spectra of vinyl ethers was made and an explanation is offered for the presence of two bands in the carbon–carbon double bond stretching regions in non-fluorine-containing ethers. The spectra of the glycidyl ethers containing fluorine are similar to their unhalogenated analogs.

The chemical reactivity of vinyl and glycidyl ethers makes them useful in organic synthesis. Their ease of polymerization also makes them valuable for industrial purposes. In the present study, the preparation of vinyl and glycidyl ethers containing fluorine and a study of the effect of the fluorine substitution on their infrared spectra were undertaken.

Vinyl ethers exhibit a reactivity which is too great to be attributed solely to the separate functional groups which are present. Their vibration spectra also have characteristics which are different from those of either functional group alone. Instead of the usual single band for the carbon–carbon double bond stretch near 6.00 μ, two bands occur in their infrared spectra,[1,2] and a third has been reported for vinyl n-butyl ether.[3] Triplet lines are present in the Raman spectra of vinyl ethers in this region.[4] Also, a band probably associated with the carbon–oxygen stretch, usually found at about 9.0 μ in the infrared spectra of saturated ethers,[5] occurs at about 8.3 μ in the spectra of vinyl ethers and is very intense.

Batuev, *et al.*,[4] have proposed that the triplet carbon–carbon double bond stretching vibration in the Raman spectra is due to the existence of vinyl ethers as rotational isomers. The isomerism is explained as resulting from restricted rotation of the alkyl group about the carbon–oxygen bond because of conjugation of the unshared pair of electrons of the oxygen atom with the double bond



$$\mathrm{CH_2{=}C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \ddot{\mathrm{O}}\mathrm{R}\end{smallmatrix} \longleftrightarrow \bar{\mathrm{C}}\mathrm{H_2{-}C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown\!\!\diagdown \overset{+}{\mathrm{O}}\diagup\end{smallmatrix}\mathrm{R}\ \text{and}\ \bar{\mathrm{C}}\mathrm{H_2{-}C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown\!\!\diagdown \overset{+}{\mathrm{O}}\\ \mathrm{R}\diagup\end{smallmatrix}$$

The low wave length for the carbon–oxygen stretch in the infrared spectra, occurring at 8.3 μ, is consistent with the conjugation effect, which would result in a shorter, higher-energy carbon–oxygen bond. Shostakovskii[6] has postulated such a resonance effect to explain the unusual chemical reactivity of vinyl ethers. Heat of hydrogenation measurements[7] indicate that vinyl ethyl ether has a resonance energy of about 3.6 kcal. per mole. However, no direct proof of the nature of the resonance has been reported.

In the present study, two methods for testing the existence of the proposed resonance effect and resulting isomerism were undertaken. First, it was desired to ascertain whether the conjugation could be overcome by the presence of a strongly electronegative substituent in the alkyl group of the vinyl ether. Because no infrared spectra of vinyl ethers substituted in this manner could be found in the literature, the synthesis of a series of vinyl fluoroethers was attempted, and infrared spectra were obtained for those ethers which were successfully prepared. Secondly, a study of the effect of a change in temperature on the relative intensities of the double-bond bands of an unfluorinated vinyl ether, in this case vinyl 2-ethylhexyl ether, was made in order to determine whether or not the split in the stretching frequency was due to the existence of rotational isomers. If the bands were due to rotational isomers, an increase in temperature would cause an increase in the concentration of higher energy isomer, shown by an increase in intensity of its band, and corresponding decrease in concentration of isomer of lower energy, with decrease in intensity of its band. This method has been used effectively by Mizushima and coworkers[8] to prove the existence of rotational isomerism in other types of compounds.

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[1] W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).

[2] A. Kirrmann and P. Chancel, *Bull. soc. chim. France*, 1338 (1954).

[3] G. D. Meakins, *J. Chem. Soc.*, 4170 (1953).

[4] M. I. Batuev, E. N. Prilezhaeva and M. F. Shostakovskii, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 123 (1947).

[5] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1938).

[6] M. R. Shostakovskii, *Zhur. Obshchei Khim.*, **20**, 608 (1950).

[7] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, This Journal, **60**, 440 (1938).

[8] S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).

TABLE I

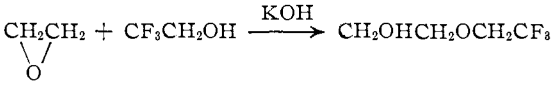
Ether	Yield, %	B.p., °C.	B.p., Mm.	$n^{25}\text{D}$	d^{25}_4	$MR\text{D}$[e] Calcd.	$MR\text{D}$[e] Found	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
$CH_2OHCH_2OCF_2CHFCl$[a]	54	114–118	100	1.3795[j]							
$CH_2OHCH_2OCF_2CHCl_2$	30	62–63	2	1.4245	1.4905	33.57	33.42	36.36[k]		36.04[k]	
$CH_2OHCH_2OCF_2CHFCF_3$	25	72–74	40	1.3192	1.5227	28.45	27.57	28.31	2.85	28.27	2.89
$CH_2OHCH_2OCH_2CF_3$	50	84	80	1.3502	1.2902	23.84	24.04	33.34	4.90	33.10	4.86
$CH_2OHCH_2OCH_2C_2F_5$	32	87	84	1.3370	1.3806	28.46	29.24	30.94	3.63	30.66	3.77
$CH_2OHCH_2OCH_2C_3F_7$	62	91–92	54	1.3300[f]	1.4965[f]	33.08	33.90	29.51	2.89	29.24	2.87
$CH_2OHCH_2OC(CH_3)_2CF_3$	35	92	77	1.3749[g]	1.1931[g]	33.08	33.02	41.86	6.44	42.05	6.81
$CH_2ClCH_2OCF_2CHFCl$[b]	27	85	100	1.3882	1.4471						
$CH_2ClCH_2OCF_2CHCl_2$	27	86–87	33	1.4270	1.4833	36.92	36.95	49.83[k]		50.94[k]	
$CH_2ClCH_2OCF_2CHFCF_3$	27	46	37	1.3349	1.4749	31.80	32.33	15.38[k]		14.53[k]	
$CH_2ClCH_2OCH_2CF_3$	53	114–115	760	1.3590[h]	1.3034[h]	27.18	27.46	29.56	3.72	29.41	3.68
								21.81[k]		22.08[k]	
$CH_2ClCH_2OCH_2C_2F_5$	49	120–121	760	1.3448[i]	1.3792[i]	31.80	32.72	28.25	2.85	27.61	2.93
$CH_2ClCH_2OCH_2C_3F_7$	67	75	80	1.3381	1.4673	36.42	37.32	13.50[k]		13.04[k]	
$CH_2ClCH_2OC(CH_3)_2CF_3$	45	135	760	1.3784	1.2102	36.42	36.34	37.81	5.29	37.74	5.02
$CH_2{=}CHOCF_2CHFCl$[c]	52	71–73	760	1.3531	1.2408						
$CH_2{=}CHOCH_2CF_3$[d]	32	42–48	760	1.3180[h]	1.118[h]						
$CH_2{=}CHOCH_2C_2F_5$	21	54–60	760	1.3131[h]	1.227[h]	26.47	27.92	34.10	2.86	34.51	3.22
$CH_2{=}CHOCH_2C_3F_7$	18	78–82	760	1.3111[i]	1.343[i]	32.56	31.08	31.87	2.23	32.01	2.49
$CF_3CH_2OCH_2CHOHCH_2Cl$	50	85–86	19	1.3951	1.3716	33.33	33.67	18.41[k]		18.91[k]	
$CF_3CH_2OCH_2\underset{\llcorner O \lrcorner}{CHCH_2}$	31	132-135	760	1.3560	1.2666	26.62	26.93	38.47	4.52	38.98	4.51
$(CF_3CH_2OCH_2)_2CHOH$	19	86	16	1.3528	1.3890	40.44	39.97	32.82	3.93	31.87	3.53
$C_2F_5CH_2OCH_2\underset{\llcorner O \lrcorner}{CHCH_2}$	19	81-79	86-84	1.3419	1.3534	31.24	32.08	34.96	3.42	35.15	3.36
$C_3F_7CH_2OCH_2\underset{\llcorner O \lrcorner}{CHCH_2}$	23	79	49	1.3350	1.4429	36.96	36.71	32.82	2.76	32.10	2.81
$(C_3F_7CH_2OCH_2)_2CHOH$	24	112-115	15	1.3338	1.5569	57.81	60.40	28.96	2.21	28.81	1.91

[a] Lawson[10] reported $n^{25}\text{D}$ 1.3808, d^{25}_{20} 1.456; Park, *et al.*,[11] b.p. 40° (1 mm.). [b] Prepared by Park, *et al.*,[11] who reported b.p. 80° (100 mm.), $n^{20}\text{D}$ 1.3929. [c] Lawson[10] prepared this ether, b.p. 71.4°. [d] A sample of this ether was also supplied by Air Reduction Co., Inc., which reports the constants: b.p. 42.7° (753 mm.), $n^{20}\text{D}$ 1.3193; Krantz, *et al.*,[12] report a specific gravity of 1.13 at 25° but no synthetic procedure. [e] *MR*D's calculated from Lange's "Handbook of Chemistry," Eighth Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1952. [f] 28°. [g] 22°. [h] 27°. [i] 26°. [j] 21°. [k] Chlorine, %.

The preparation of the vinyl fluoroethers was attempted by a three-step procedure: (1) synthesis of the corresponding hydroxyethyl ether, (2) substitution of the hydroxyl group by chlorine, and (3) dehydrochlorination of the chloroethyl ether. Two methods were used for preparing the hydroxyethyl ethers: (a) the base-catalyzed addition of ethylene glycol to a 1,1-difluoroölefin, for example

$$CH_2OHCH_2OH + CF_2{=}CFCl \xrightarrow{KOH} CH_2OHCH_2OCF_2CHFCl$$

a type of reaction first reported by Hanford and Rigby[9]; and (b) by the addition of a fluoroalcohol to ethylene oxide



$$\underset{\diagdown O \diagup}{CH_2CH_2} + CF_3CH_2OH \xrightarrow{KOH} CH_2OHCH_2OCH_2CF_3$$

Substitution of the hydroxyl group with chlorine was effected by treatment with phosphorus pentachloride, and dehydrochlorination of the resulting chloroether was carried out with alcoholic potassium hydroxide. The compounds which were prepared are listed in Table I.

The carbon–carbon double bond infrared absorption wave lengths for the vinyl ethers which were obtained in a pure state are shown in Table II. Only one vinyl α-fluoroalkyl ether, $CH_2{=}CHOCF_2CHFCl$, was prepared successfully. It had been reported previously by Lawson[10] in a polymerization study, but the only physical constant which was given was the boiling point. The infrared spectrum of the ether possesses only a single double-bond band, at 6.05 μ, which is very sharp. In this case the inductive effect of the two α-fluorine atoms is strong enough to prevent resonance, thus allowing free rotation of the alkyl group about the carbon–oxygen bond. The three vinyl β-fluoroalkyl ethers which were prepared exhibit in their spectra the usual doublet. Evidently the intervening methylene group sufficiently insulates the oxygen electrons from the fluorine atoms to allow conjugation with the double bond to occur.

TABLE II

C=C INFRARED STRETCHING WAVE LENGTHS IN MICRONS

$CH_2{=}CHOCF_2CHFCl$	6.05
$CH_2{=}CHOCH_2CF_3$	6.08; 6.15
$CH_2{=}CHOCH_2C_2F_5$	6.06; 6.13
$CH_2{=}CHOCH_2C_3F_7$	6.06; 6.13

The temperature study demonstrated the existence of rotational isomers in the unfluorinated ether, vinyl 2-ethylhexyl ether. In the spectrum

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(9) W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274, Oct. 15, 1946.

(10) J. K. Lawson, Jr., U. S. Patent 2,631,975, Mar. 17, 1953.

(11) J. D. Park, D. M. Griffin and J. R. Lacher, THIS JOURNAL, **74**, 2292 (1952).

(12) J. C. Krantz, Jr., C. J. Carr, G. Lu and F. K. Bell, *J. Pharmacol. Exptl. Therapy*, **108**, 488 (1953).

of this vinyl ether three double-bond bands are present: band I, 6.06 μ; band II, 6.09 μ; and band III, 6.20 μ. Batuev, *et al.*,[4] reported the values 6.06, 6.10 and 6.20 μ for the vibrations of vinyl alkyl ethers occurring in their Raman spectra. They attributed the 6.06 and 6.10 μ lines to one rotational isomer, and they explained the split as the result of Fermi resonance due to the interaction of the vibration with an overtone at 12.2 μ. From Table III it may be seen that the ratio of the optical density of band I to band III remains constant with increasing temperature, within experimental error. The ratio of the optical density of band II to band III, however, increases noticeably with increasing temperature. This would indicate that bands I and III are due to one isomer, the more stable form, and band II results from the vibration of the isomer of higher energy.

TABLE III

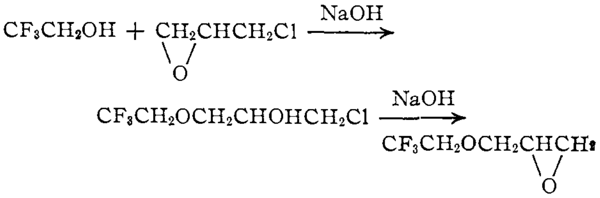
EFFECT OF TEMPERATURE CHANGE ON THE C═C ABSORPTION OF VINYL 2-ETHYLHEXYL ETHER

Ratios of optical densities of bands I and II to optical density of band III (6.20 μ)

	25°		45°		65°	
	I	II	I	II	I	II
	6.06	6.09	6.06	6.09	6.06	6.09
	0.470	0.482	0.478	0.525	0.462	0.542
	.481	.506	.468	.526	.505	.632
	.473	.477	.473	.507		
Av.	.475	.488	.473	.519	.483	.587

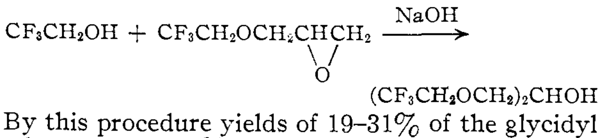
In addition to the study of vinyl fluoroethers, a series of glycidyl fluoroethers was prepared. This synthesis was performed by treating fluoroalcohols with epichlorohydrin.

Although unsubstituted alcohols add readily to the epoxy ring of epichlorohydrin when an acid catalyst is present,[13] the reaction, in the present study, of trifluoroethyl alcohol with epichlorohydrin under the same conditions was slight. However, addition occurred in fair yields when a basic catalyst was used. When excess sodium hydroxide was present, the glycidyl ether was obtained in one operation



$$CF_3CH_2OH + \underbrace{CH_2CH}_{O}CH_2Cl \xrightarrow{NaOH} CF_3CH_2OCH_2CHOHCH_2Cl \xrightarrow{NaOH} CF_3CH_2OCH_2\underbrace{CHCH_2}_{O}$$

This synthesis was complicated by the further reaction of alcohol with the glycidyl ether to form the diether



$$CF_3CH_2OH + CF_3CH_2OCH_2\underbrace{CHCH_2}_{O} \xrightarrow{NaOH} (CF_3CH_2OCH_2)_2CHOH$$

By this procedure yields of 19–31% of the glycidyl ether and 19–24% of the diether were obtained. By the use of a catalytic amount of pyridine, a 50% yield was obtained of the simple adduct, $CF_3CH_2OCH_2CHOHCH_2Cl$, from which the glycidyl ether could then be prepared by dehydrochlorination with sodium hydroxide.

The three primary fluoroalcohols CF_3CH_2OH, $C_2F_5CH_2OH$ and $C_3F_7CH_2OH$ reacted with epichlorohydrin to form the glycidyl ethers; however, the tertiary alcohol $CF_3C(CH_3)_2OH$ did not react appreciably under these conditions. The ethers prepared by this reaction are given in Table I.

In their need for a basic catalyst in order to add to the epoxy ring, the fluoroalcohols resemble the phenols. They are also much more acidic than unsubstituted alcohols, and this property probably accounts for the difference in chemical activity. The lack of reactivity of the tertiary alcohol with epichlorohydrin in the presence of base may be due to the lower acidity of the alcohol.

The infrared spectral characteristics of the epoxy ring of the glycidyl ethers containing fluorine were similar to those of unfluorinated glycidyl ethers. Bands which have been attributed to the epoxy group,[14] near 8.00 μ and near 11 and 12 μ, were present in the spectra of the glycidyl fluoroethers and are listed in Table IV.

TABLE IV

BANDS CHARACTERISTIC OF THE EPOXY GROUP

Glycidyl ether	Wave length in microns		
$CF_3CH_2OCH_2\underbrace{CHCH_2}_{O}$	7.98	11.08	11.78
$C_2F_5CH_2OCH_2\underbrace{CHCH_2}_{O}$	7.95	11.10	11.74
$C_3F_7CH_2OCH_2\underbrace{CHCH_2}_{O}$	Masked by C–F	11.00	11.76

Experimental

Addition of Ethylene Glycol to 1,1-Difluoroölefins.—A cooled solution of 94 g. (1.7 moles) of potassium hydroxide in 500 ml. of ethylene glycol was placed in an autoclave (capacity about 1300 ml.) which was chilled in a Dry Ice-acetone-bath. Approximately 2.5 moles of the olefin was added to the contents of the bomb, which was then sealed and rocked overnight at room temperature. The reaction mixture was poured into ice-water. The organic layer was separated from the lighter water layer, it was washed several times with water, dried over anhydrous sodium sulfate and distilled through a 65-cm. column packed with Berl saddles.

Addition to $CF_2{=}CFCl$, $CF_2{=}CCl_2$ and $CF_2{=}CFCF_3$ was accomplished by this procedure. Attempts to obtain the adduct of ethylene glycol with $CF_2{=}CH_2$ and $CF_2{=}CF_2$ were unsuccessful. It is believed that reaction occurred in the case of the former olefin, but that the product hydrolyzed to the ester, β-hydroxyethyl acetate. The tetrafluoroethylene was bubbled through the reaction mixture at atmospheric pressure because of its explosive nature when under pressure. However, no evident reaction occurred by this method.

In the reaction of ethylene glycol with $CF_2{=}CCl_2$, the diether $(CHCl_2CF_2OCH_2-)_2$ was also formed in 18% yield, b.p. 90° (2.2 mm.), n^{25}_D 1.4194, d^{25}_4 1.5786, *MR*D calcd. 52.66, *MR*D found 52.50.

Anal. Calcd. for $C_5H_6Cl_4F_4O_2$: C, 21.97; H, 1.84. Found: C, 22.33; H, 2.08.

This material was hydrolyzed to the diester $(CHCl_2\overset{O}{\overset{\|}{C}}OCH_2-)_2$ in 31% yield by treatment with concentrated sulfuric acid according to the method of Young and Tarrant.[15] The ester had the properties: b.p. 148–150° (3 mm.), n^{25}_D 1.4840, d^{25}_4 1.5386; *MR*D calcd. 52.86, *MR*D found 52.79.

Anal. Calcd. for $C_6H_6Cl_4O_4$: Cl, 49.95. Found: Cl, 48.39.

The infrared spectrum of this material was identical with that of the esterification product of dichloroacetic acid and ethylene glycol.

The addition of ethylene chlorohydrin to $CF_2{=}CFCl$ was attempted, and a small amount of the adduct CH_2ClCH_2-

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(13) L. Blanchard, *Bull. soc. chim.*, **39**, 1263 (1926).

(14) W. A. Patterson, *Anal. Chem.*, **26**, 823 (1954).

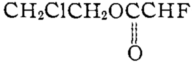
(15) J. A. Young and P. Tarrant, THIS JOURNAL, **71**, 2432 (1949).

OCF_2CHFCl was obtained. However, the basic catalyst potassium hydroxide reacts with the ethylene chlorohydrin to form ethylene oxide so rapidly that the yield of adduct is necessarily low.

Addition of Fluoroalcohols to Ethylene Oxide.—A cooled solution of 5 g. of potassium hydroxide in 1.5 moles of the fluoroalcohol was placed in an autoclave having a capacity of 300 ml., which was cooled in a Dry Ice–acetone-bath; 44 g. (1.0 mole) of ethylene oxide was added to the contents of the autoclave, which was rocked at 70° for four hours. The reaction mixture was distilled through the 65-cm. fractionating column.

CF_3CH_2OH, available commercially, $C_2F_5CH_2OH$ and $C_3F_7CH_2OH$, prepared by reduction of the appropriate perfluoroacids with lithium aluminum hydride, and $CF_3C(CH_3)_2OH$, were added successfully to ethylene oxide by this procedure.

Treatment of Hydroxyethyl Ethers with Phosphorus Pentachloride.—Sixty grams (0.29 mole) of phosphorus pentachloride was added gradually to approximately 0.25 mole of the hydroxy-ether, in a 500-ml., three-necked flask, while the mixture was stirred vigorously. Immediate reaction occurred, as shown by the evolution of hydrogen chloride and heating of the mixture. After addition was complete, the reaction mixture was refluxed 20 minutes; it was then cooled, poured into ice-water, washed with sodium bicarbonate solution, dried over anhydrous sodium sulfate, and fractionated. Yields of 27% were consistently obtained by this procedure. When the reaction mixture was diluted with about 100 ml. of chloroform, yields of 45–67% were obtained.



Hydrolysis of two of the chloroethers was performed. $CH_2ClCH_2O\underset{\underset{O}{\|}}{C}CHFCl$ was obtained from $CH_2ClCH_2OCF_2CHFCl$ in 34% yield, b.p. 106° (47 mm.) 105° (45 mm.), n^{23}_D 1.4369, d^{25}_4 1.4256; MR_D calcd. 32.06, MR_D found 32.20.

Anal. Calcd. for $C_4H_5Cl_2FO_2$: Cl, 40.52. Found: Cl, 40.09.

$CH_2ClCH_2O\overset{\overset{O}{\|}}{C}CHCl_2$ was obtained from $CH_2ClCH_2OCF_2CHCl_2$ in 36% yield, b.p. 207–211° (atm. press.), n^{25}_D 1.4719, d^{25}_4 1.4544; MR_D calcd. 36.93, MR_D found 36.85.

Anal. Calcd. for $C_4H_5Cl_3O_2$: Cl, 55.56. Found: Cl, 54.85.

This compound is reported by Delacre[16] to have the constants b.p. 209–212° (767 mm.) and d^{15} 1.200. However, this density value appears to be unreasonably low.

Dehydrochlorination of the Chloroethyl Ethers.—A solution of 18 g. (0.32 mole) of potassium hydroxide in 120 ml. of *n*-propyl alcohol was added dropwise to about 0.20 mole of the chloroethyl ether in a 500-ml. flask, with heating and vigorous stirring. Salt formation began immediately. A distillate consisting of a mixture of vinyl ether and alcohol was collected. It was poured into ice-water, and the organic layer was separated, washed, dried and distilled.

Only four of the seven desired vinyl ethers were isolated. Other dehydrochlorinating agents, including tri-*n*-butylamine, powdered sodium hydroxide and aqueous potassium hydroxide, were ineffective.

Addition of Fluoroalcohols to Epichlorohydrin with Excess Sodium Hydroxide.—The fluoroalcohol (0.50 mole) and epichlorohydrin (46 g., 0.50 mole) were added to a cooled solution of 25 g. (0.62 mole) of sodium hydroxide in 300 ml. of water. The reactants were mixed thoroughly, and the mixture was allowed to stand at room temperature overnight. The organic layer was then separated and treated in the usual manner.

Addition of Trifluoroethyl Alcohol to Epichlorohydrin with a Catalytic Amount of Pyridine.—One hundred grams (1.0 mole) of trifluoroethyl alcohol, 185 g. (2.0 moles) of epichlorohydrin and 2 ml. of pyridine were heated to 80–90° with stirring for 12 hr. The mixture was then fractionated.

Infrared spectra were determined with a Perkin-Elmer model 21 double-beam infrared recording spectrophotometer equipped with sodium chloride optics. Approximately 0.2 *M* solutions of the freshly distilled vinyl ethers in Eastman Spectro Grade carbon tetrachloride were prepared and placed in a cell of 0.1 mm. thickness, with compensating cell of about the same thickness containing carbon tetrachloride only. The higher boiling points of the glycidyl fluoroethers made it possible to obtain spectra of the liquids, using a demountable cell.

The study of the effect of temperature on the intensity of the carbon–carbon double-bond stretching bands was performed with a demountable cell which was heated by wrapping with heating tape. Freshly distilled vinyl 2-ethylhexyl ether, b.p. 177° (atm. press.), was used because of its relatively high boiling point. Low temperature spectra could not be obtained with the equipment available because of interfering absorption of water which immediately condensed on the cold cell upon exposure to air.

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[16] M. Delacre, *Bull. soc. chim.*, **48**, 708 (1887).

[CONTRIBUTION FROM PENINSULAR CHEMRESEARCH, INC.]

The Preparation of Some Fluoroalkylmethyldichlorosilanes and their Hydrolysis Products[1]

BY PAUL TARRANT, G. W. DYCKES, ROBERT DUNMIRE AND G. B. BUTLER

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Methyldichlorosilane has been added to various fluorine-containing olefins to give fluoroalkylmethyldichlorosilanes. Explosions occurred in attempts to treat silanes with chlorotrifluoroethene and perfluoropropene. Cyclic siloxanes obtained by hydrolysis of the dichlorosilanes were characterized.

Silicone elastomers are useful because of the wide temperature range over which they retain elasticity. These materials have some disadvantages, particularly in their lack of resistance to swelling by fuels and similar organic materials. Several years ago samples of bis-(heptafluoropentyl)-diethoxysilane and heptafluoropentylmethyldiethoxysilane

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