The Syntheses of Ethers Containing a Chlorofluorovinyl Group

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In a previous paper,[1] the radiation-induced addition reaction of ethers to chlorofluoroethylenes was described as giving the corresponding 1 : 1 adduct, ethers with a chlorofluoroethyl group. The present paper will be concerned with the preparation of some ethers containing a chlorofluorovinyl group from these adducts by dehydrochlorination with potassium hydroxide or by dechlorination with zinc dust. The reaction is expressed by the following equation:

$$RCFXCHX_2 \xrightarrow{KOH} RCF{=}CX_2$$
$$RCFXCHX_2 \xrightarrow{Zn} RCF{=}CHX$$

R:  , $C_2H_5OCHCH_3$, or $(CH_3CH\text{-})_2O$

X: F or Cl.

The yields and physical properties of the ethers thus prepared are summarized in Table 1. Their infrared spectra showed absorption bands due to the double bond at 1650—1658 cm^{-1} for RCF=CCl_2, at 1661—1684 cm^{-1} for RCF=CHCl, at 1710—1718 cm^{-1} for RCF=CFCl, and at 1711—1725 cm^{-1} for RCF=CHF, showing the shift resulting from the inductive effect of the fluorines substituted on the double bond.[2]

The separation of the geometrical isomers was undertaken by means of a gas chromatograph as far as possible. The geometrical configuration of the isomers was assigned on the basis of the proton and fluorine NMR spectra of pure isomers, or of the mixture of isomers when their separation was difficult. All the cis isomers isolated were found to have a higher boiling point, density, and refractive index than the corresponding trans isomers, as the dipole rule had predicted.[3]

While the fluorine NMR spectra of the ethers with a $-CF{=}CCl_2$ group showed only a doublet due to coupling with a hydrogen on the tertiary carbon atom to which the halovinyl group is attached, those of the ethers with a $-CF{=}CFCl$ group consisted of four sets of lines, indicating the presence of the geometrical isomers (trans and cis). Each line was broken down into two doublets caused

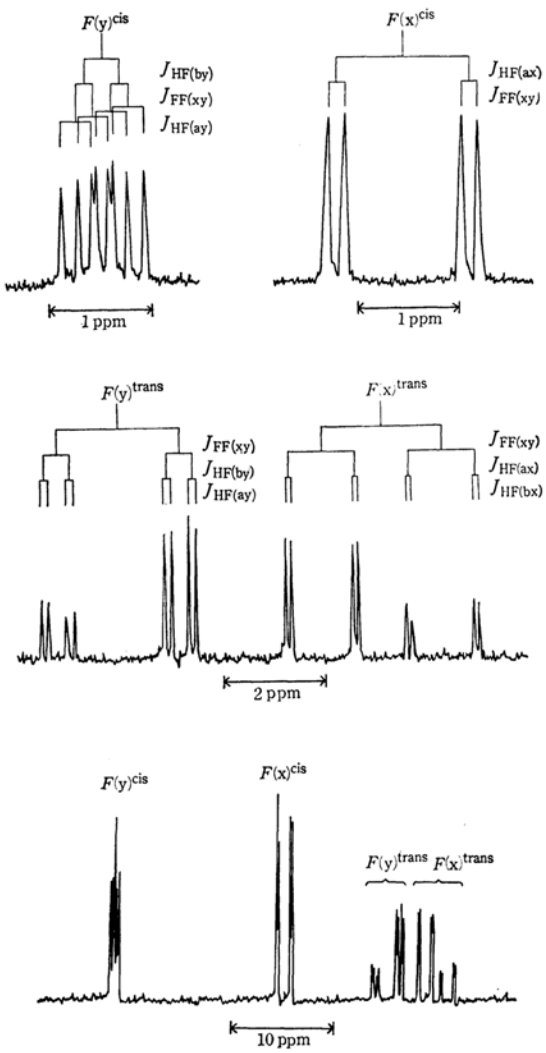


Fig. 1. Fluorine NMR spectrum of α-(1, 2-difluorovinyl)diethyl ether. The field increases from left to right.

1) H. Muramatsu, K. Inukai and T. Ueda, *J. Org. Chem.*, **29**, 2220 (1964).
2) D. G. Weiblen, "Fluorine Chemistry," Vol. II, Academic Press, New York (1954), p. 449.
3) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York (1962), p. 327.

TABLE 1. YIELDS AND PHYSICAL PROPERTIES OF ETHERS WITH CHLOROFLUOROVINYL GROUP

R	Isomer*	Yield %	Bp °C(mmHg)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calcd	F, % Found	F, % Calcd	Cl, % Found	Cl, % Calcd	$\nu_{C=C}$ cm^{-1}
												
$-CF=CCl_2$		65	111(15)	1.4751	1.345	38.74	38.70	10.2	10.3	37.7	38.3	1655
$-CF=CFCl$**		71	154	1.4325	1.293	33.83	33.91	22.3	22.6	20.7	21.0	1715
$-CF=CHCl$**		75	174	1.4582	1.217	33.80	33.83	12.1	12.6	23.0	23.5	1683
$-CF=CHF$	trans	55	125	1.4110	1.163	28.65	29.04	28.0	28.3			1711
	cis		65(50)	1.4127	1.170	28.57	29.04	28.0	28.3			1723
												
$-CF=CCl_2$		86	76(7)***					9.1	9.5	34.9	35.3	1658
$-CF=CFCl$**		48	98(60)	1.4387	1.367	35.49	35.55	19.4	20.6	18.7	19.2	1718
$-CF=CHCl$	trans	62	179	1.4563	1.263	35.87	35.47	11.1	11.4	20.9	21.3	1677
	cis		187	1.4622	1.294	35.40	35.47	11.1	11.4	20.8	21.3	1684
$-CF=CHF$	trans	26	152	1.4200	1.254	30.31	30.69	25.0	25.3			1724
	cis		161	1.4210	1.265	30.10	30.69	24.9	25.3			1725
					$CH_3CH(R)OCH_2CH_3$							
$-CF=CCl_2$		71	92(137)	1.4361	1.199	40.78	40.90	10.0	10.2	37.1	37.9	1650
$-CF=CFCl$**		43	70(153)	1.3958	1.134	36.12	36.11	20.9	22.3	20.3	20.8	1710
$-CF=CHCl$	trans	74	127	1.4138	1.074	35.51	36.03	12.1	12.4	22.8	23.2	1661
	cis		140	1.4200	1.075	35.93	36.03	11.9	12.4	22.8	23.2	1678
$-CF=CHF$**		33	52(132)	1.3788	1.017	30.92	31.24	27.8	27.9			1721
					$CH_3CH(R)OCH(R)CH_3$							
$-CF=CCl_2$		56	214	1.4690	1.409	59.11	59.42	12.6	12.7	47.1	47.4	1650
$-CF=CFCl$**		36	169	1.4151	1.343	49.80	49.91	28.8	28.5	25.7	26.6	1710

* The trans and cis refer to the spatial relation of the fluorine-fluorine or fluorine-chlorine.
** A mixture of the trans and cis isomers.
*** Mp 38—39°C.

TABLE 2. THE PARAMETERS OF NMR SPECTRA OF ETHERS WITH CHLOROFLUOROVINYL GROUP AND THE RATIOS OF GEOMETRICAL ISOMERS

R*1	Isomer*2	Chemical shift of fluorine,*3 ppm		Coupling constant, *4 cps					Ratio of cis/trans
		δ_x	δ_y	$J_{FF(xy)}$	$J_{HF(ax)}$	$J_{HF(ay)}$	$J_{HF(bx)}$	$J_{HF(by)}$	
				R-CF=CCl$_2$					
R_T			41					26	
R_D			47					23	
R_E			40					25	
				R-CF=CFCl					
R_T	trans	44	79	138			5	29	1.2
	cis	25	69	14			3	28	
R_D	trans	41	76	139			4	25	0.9
	cis	24	66	16			2	25	
R_E	trans	44	79	138			5	29	1.1
	cis	26	69	14			3	28	
				R-CF=CHCl					
R_T	trans		48			11		27	4.3
	cis		41			25		13	
R_D	trans		47			11		23	5.5
	cis		41			25		13	
R_E	trans		48			11		27	6.8
	cis		41			25		15	
				R-CF=CHF					
R_T	trans	99	94	135	73	7	5	28	2.5
	cis	86	70	10	76	15		20	
R_D	trans	96	92	137	71	8	6	25	3.7
	cis	84	68	11	74	18	4	13	
R_E	trans	103	98	135	74	8	6	28	4.5
	cis	87	71	9	73	17	20	20	

*1 R_T:  , R_D:  , R_E: $C_2H_5OCHCH_3$.

*2 The trans and cis refer to the spatial relation of the fluorine-fluorine for the ether with -CF=CFCl or -CF=CHF group, and that of the fluorine-chlorine for the ether with -CF=CHCl group.

*3 The chemical shifts of fluorine are with respect to external trifluoroacetic acid increasing to upfield.

*4 -CH(b)-CF(y)=CF(x)X(a) X: H or Cl.

by the coupling of a fluorine with a vicinal fluorine and with a hydrogen on the tertiary carbon atom. The coupling constants between two vicinal fluorines across the double bond have been reported to be 115—124 cps for the trans form and 33—58 cps for the cis form of polyfluoroethylenes,[4] and 114—118 cps for the trans form and 36—39 cps for the cis form of polyfluoropropylenes.[5] In the spectra of the ethers with a -CF=CFCl group, the coupling constants between two vicinal fluorines of one isomer were 138—139 cps, while those of another isomer were 14—16 cps, showing the former to be the trans form and the latter, the cis form. The NMR spectral data for each isomer are tabulated in Table 2. The ratios of the trans forms to the cis forms were calculated from the peak areas of the fluorine NMR spectra; they are listed in the last column in Table 2.

The coupling constants between fluorine and hydrogen across the double bond have been found to be 12—34 cps for the trans form and 1—8 cps for the cis form of a number of fluoroethylenes.[6] An isomer of the ethers with a -CF=CHCl with a fluroine-hydrogen coupling constant of 25 cps was identified as the trans form, while another isomer

4) H.M. McConnel, C. A. Reilly and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956); G. V. D. Tiers and P. C. Lauterbur, *ibid.*, **36**, 1110 (1962); Soon Ng, J. Tang and C. H. Sederholm, *ibid.*, **42**, 79 (1965).

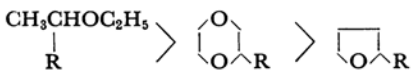
5) J. D. Swalen and C. A. Reilly, *ibid.*, **34**, 2122 (1961); K. C. Ramey and W. S. Brey, Jr., *ibid.*, **40**, 2349 (1964).

6) Ref. 4; C. A. Reilly, *ibid.*, **37**, 456 (1962); T. D. Coyle, S. L. Stafford and F. G. A. Stone, *Spectrochimica Acta*, **17**, 968 (1961); D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78, 232 (1962); A. D. Beveridge, H. C. Clark and J. T. Kwon, *Can. J. Chem.*, **44**, 179 (1966).

with an 11 cps coupling constant was identified as the cis form. Each isomer of the ethers with a –CF=CHF group was assigned in a similar way on the basis of the magnitude of the vicinal fluorine-fluorine and fluorine-hydrogen coupling constants. As an example, the fluorine NMR spectrum of α-(1, 2-difluorovinyl)diethyl ether is shown in Fig. 1.

It has been found[7] for the 1, 2-dihaloethylenes that the isomer containing the two most electronegative substituents cis to each other is the more stable one. This "electronegativity rule" has also been shown to apply to some trihaloethylenes, such as 1, 2-dibromo-1-fluoro- and 1-bromo-1, 2-difluoroethylenes.[8] The predominant formation of the cis isomer has been observed in the preparation of ethers with a perfluoropropenyl group.[9]

In ethers containing a –CF=CHCl or –CF=CHF group, the isomer with fluorine and chlorine or fluorine cis to each other (a bulky ethereal group and a halogen trans to each other) was found to be predominant, as is shown in the last column in Table 2; the ratios of the cis form to the trans form of the ethers increased in the following order:



R: –CF=CHCl or –CF=CHF

These distinct differences in the ratios of the cis form to the trans form between the dihaloethylenes with different ethereal groups indicate that the steric factor may also play a role in determining the relative stability of the configuration. In ethers containing a –CF=CFCl group, on the other band, the ratios of the cis form to the trans form were almost unity in all three cases.

7) A. Demiel, *J. Org. Chem.*, **27**, 3500 (1962).
8) A. Demiel, *ibid.*, **30**, 2121 (1965).
9) H. Muramatsu, K. Inukai and T. Ueda, This Bulletin, **40**, 903 (1967).

Experimental

All temperature readings are uncorrected.

Materials. The tetrahydrofurans, dioxanes, and diethyl ethers with 1-fluoro-1, 2, 2-trichloroethyl or 1, 2-dichloro-1, 2-difluoroethyl group were prepared as has been reported[1] previously.

The Dehydrochlorination of Ethers with a Haloethyl Group. To 50 g (0.23 mol) of 2-(1, 2, 2-trichloro-1-fluoroethyl)tetrahydrofuran, 20 g (0.35 mol) of potassium hydroxide in 105 m*l* of ethanol were added, drop by drop. The mixture was stirred for 30 min at room temperature and then poured into 500 m*l* of water. The organic layer was separated, dried, and distilled to give 28 g (0.15 mol, 65% yield) of 2-(1-fluoro-2, 2-dichlorovinyl)tetrahydrofuran.

Using the same procedure, other ethers with a haloethyl group were also dehydrochlorinated. Their yields and physical properties are listed in Table 1.

The Dechlorination of Ethers with a Haloethyl Group. To 17 g (0.26 g-atom) of zinc dust suspended in 70 m*l* of ethanol, 40 g (0.17 mol) of 2-(1, 2, 2-trichloro-1-fluoroethyl)dioxane were added, driop by drop. The reaction mixture was stirred at 80—100°C for 3.5 hr and then filtered. Dilute hydrochloric acid was added to the filtrate. The organic layer was separated and dried. Distillation gave 18.1 g (0.11 mol, 62% yield) of 2-(1-fluoro-2-chlorovinyl)dioxane, whose gas chromatogram showed two peaks, that of the trans isomer and that of the cis isomer (with respect to two halogens), in a ratio of 1 : 5.5. Each isomer was separated by means of a preparative gas chromatograph. The geometrical configurations of the isomers were determined from their NMR spectra.

The other ethers with a haloethyl group were dechlorinated in a similar way.

Spectral Measurements. The NMR spectra were obtained for a 25% solution in carbon tetrachloride, using a JNM-C-60 high-resolution NMR spectrometer (60 Mc for protons and 56.4 Mc for fluorines). Tetramethylsilane was used as the internal standard for proton, and trifluoroacetic acid, as the external standard for fluorine.