[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XVII. Preparation and Properties of the 1,3-Dichloro-2-fluoropropenes[1]

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The two geometrical isomers of 1,3-dichloro-2-fluoropropene have been prepared and characterized. The assignment of configuration was made by a comparison of the relative reactivity of the two isomers toward potassium iodide in acetone. In addition to the 1,3-dichloro-2-fluoropropenes the following compounds were prepared and characterized: the 3-bromo-1-chloro-2-fluoro-1-propenes and the 3-chloro-2-fluoro-2-propen-1-ols. Configuration has also been assigned to the previously reported 1-chloro-2-fluoro-1-propenes and an average value of 0.95 for the atomic refraction of fluorine has been determined for compounds of this type.

The 1,3-dichloro-2-fluoropropenes and several closely related compounds have been prepared from the 1-chloro-2-fluoro-1-propenes in a manner similar to that used for the preparation of the 1,2,3-trichloropropenes from the 1,2-dichloro-1-propenes.[3]

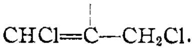
$$\mathrm{CHCl{=}CFCH_3 + N\text{-}bromosuccinimide \longrightarrow CHCl{=}CFCH_2Br} \quad \text{(I)}$$

$$\mathrm{CHCl{=}CFCH_2Br + H_2O \xrightarrow{Na_2CO_3} CHCl{=}CFCH_2OH} \quad \text{(II)}$$

$$\mathrm{CHCl{=}CFCH_2OH + PCl_3 \xrightarrow{C_5H_5N} CHCl{=}CFCH_2Cl} \quad \text{(III)}$$

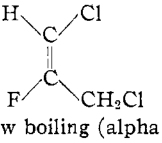
$$\mathrm{CHCl{=}CFCH_2Cl + LiAlH_4 \longrightarrow CHCl{=}CFCH_3} \quad \text{(IV)}$$

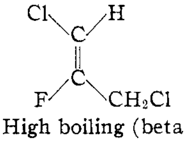
In reaction I, both geometrical isomers were treated separately with N-bromosuccinimide. However, both isomers of the allylic bromide, 3-bromo-1-chloro-2-fluoro-1-propene, were obtained from the reaction of each isomer of 1-chloro-2-fluoro-1-propene. The two isomeric bromides could be separated by distillation, but on standing at room temperature they rapidly isomerized into a mixture containing both isomers. At −70° each isomer could be kept without any detectable isomerization. The geometrical isomers of both 3-chloro-2-fluoro-2-propen-1-ol and the corresponding dichloride, 1,3-dichloro-2-fluoropropene, showed no isomerization at room temperature. Each isomer of the alcohol gave only the corresponding isomer of the dichloride when treated with phosphorus trichloride (III) and each isomer of the dichloride when reduced by means of lithium aluminum hydride (IV) gave only the corresponding isomer of 1-chloro-2-fluoro-1-propene.

The geometrical isomers of 1,3-dichloro-2-fluoropropene were prepared to extend the study of the relative reactivities of allylic chlorides of the series  $\mathrm{CHCl{=}\overset{\overset{\large Y}{|}}{C}{-}CH_2Cl}$. This series is of particular interest because these compounds have their reactivity influenced not only by the nature of Y but also by the geometrical configuration of the molecule. Previous investigations in this series[3] have included pairs of isomers where the substituent Y on the number 2 carbon atom was either H, $\mathrm{CH_3}$ or Cl. A pair of isomers wherein Y is F was chosen to obtain further information not only on the effect of geometrical configuration but also on the influence of a strongly electron attracting group on the number 2 carbon atom.

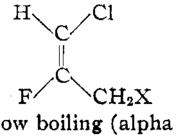
The data obtained for the 1,3-dichloro-2-fluoropropenes confirm the observation previously made that the relative reactivities of geometrical isomers in the reaction with sodium ethoxide in ethanol show no correlation between configuration and relative reactivity. The isomers of 1,3-dichloro-2-fluoropropene also show essentially the same relative reactivities as the other pairs of isomers.

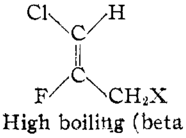
The relative reactivities in the reaction with potassium iodide in acetone show a definite and consistent correlation between geometrical configuration and relative reactivity. The data for the isomeric pairs of known configuration ($\mathrm{CHCl{=}CHCH_2Cl}$,[4] $\mathrm{CHCl{=}C(CH_3)CH_2Cl}$[4] and $\mathrm{CHCl{=}CClCH_2Cl}$[3]) show that in each case the isomer having the chlorine atom on the number 1 carbon atom and the chloromethyl group *cis* to each other is considerably more reactive than the other isomer. With the 1,3-dichloro-2-fluoropropenes there is also a marked difference in reactivity between the two isomers. The configurations of the 1,3-dichloro-2-fluoropropenes have, therefore, been assigned on the basis of this difference in reactivity. The low boiling isomer (alpha) is the more reactive and thus is assumed to have the chlorine atom and chloromethyl group in the *cis*-position. The high boiling isomer (beta) has these groups *trans* to each other.


Low boiling (alpha)


High boiling (beta)

Since each isomer of 1,3-dichloro-2-fluoropropene is related to the corresponding isomer of the olefin, bromide and alcohol, the configuration of the isomers of these compounds may be assigned by relating them to the corresponding chloride. These configurations are


Low boiling (alpha)


High boiling (beta)

where X is either H, Br or OH.

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[1] For Number XVI of this series see L. F. Hatch, L. O. Morgan and V. L. Tweedie, THIS JOURNAL, **74**, 1826 (1952).

[2] Research Corporation Fellow 1949–1950, Monsanto Fellow 1950–1951.

[3] L. F. Hatch, J. J. D'Amico and E. V. Ruhnke, THIS JOURNAL, **74**, 123 (1952).

[4] L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).

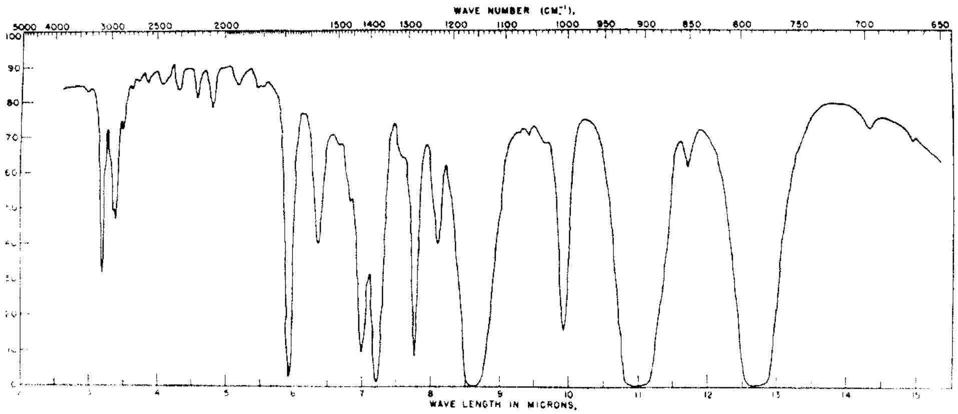

Fig. 1 (a).—Low Boiling 1-chloro-2-fluoro-1-propene.

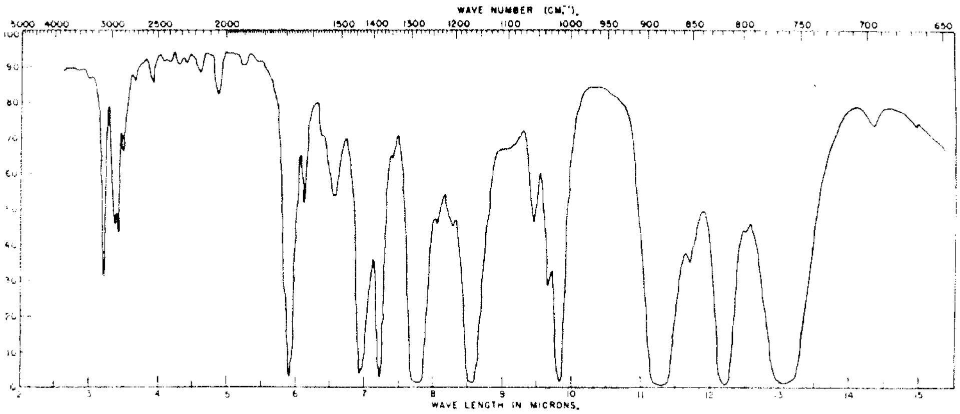

Fig. 1 (b).—High boiling 1-chloro-2-fluoro-1-propene.

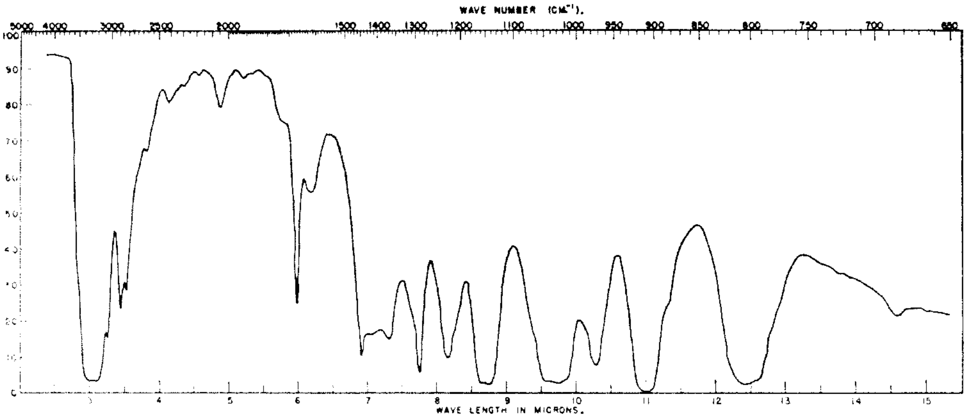

Fig. 1 (c).—Low boiling 3-chloro-2-fluoro-2-propen-1-ol.

There appears to be no relationship between the electronegativity of the substituent on the number 2 carbon atom and the reactivity of the allylic chlorine atom toward either sodium ethoxide or potassium iodide.

A calculation of the atomic refraction of fluorine in the various chloro-fluoro compounds prepared during this investigation gave an average value of 0.95 cc. per mole which is in good agreement with the values of 0.82 to 0.96 obtained by Hoffman[5] for a series of difluoroalkanes. Weissberger[6] states that values for R_F have a range from 0.68 in $CCl_2=CClF$ to 1.60 in $CCl_2=CClCCl_2F$ and that the average value is around 1 cc. per mole.

Figure 1 gives the infrared spectra for all of the stable compounds prepared in these studies. These spectra show no characteristics which are not in agreement with the assignment of configuration. The spectra of the 3-bromo-1-chloro-2-fluoro-1-propenes were not obtained because these allylic bromides isomerized too fast at room temperature to permit the obtaining of a pure isomer.

Acknowledgment.—This research was supported in part by Task 2 funds of the Defense Research Laboratory, The University of Texas, operating under Contract NOrd-9195, Bureau of Ordnance,

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[5] F. W. Hoffman, *J. Org. Chem.*, **14**, 105 (1949).

[6] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 879.

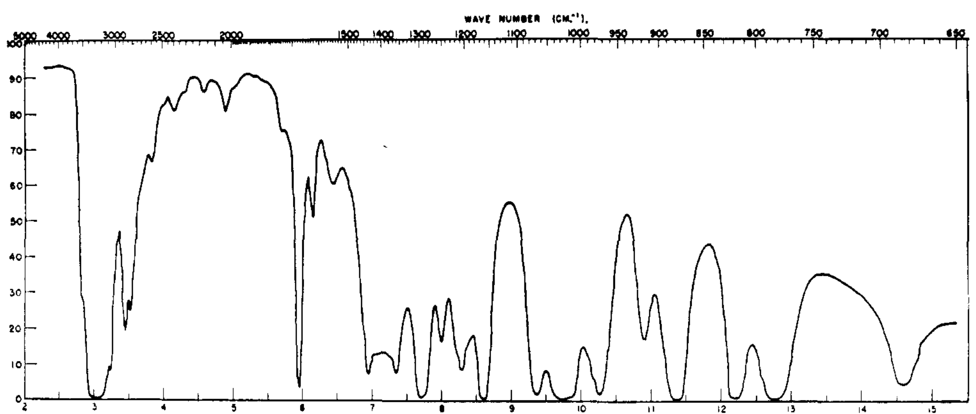

Fig. 1 (d).—High boiling 3-chloro-2-fluoro-2-propen-1-ol.

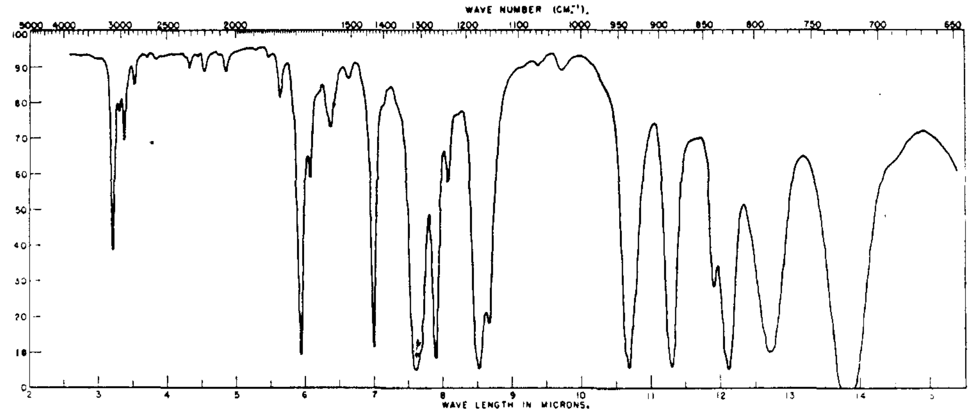

Fig. 1 (e).—High boiling 1,3-dichloro-2-fluoropropene.

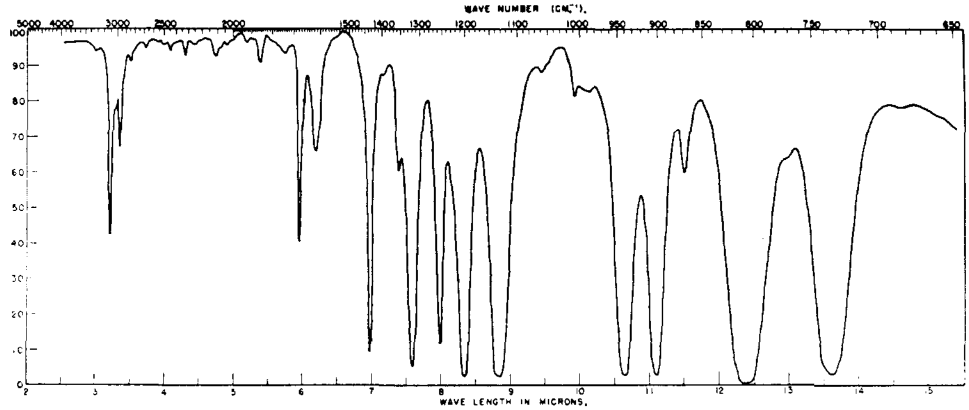

Fig. 1 (f).—Low boiling 1,3-dichloro-2-fluoropropene.

Department of the Navy. The authors are also grateful for the financial assistance given to this work by the Research Corporation and by the Monsanto Chemical Co.

Experimental

3-Bromo-1-chloro-2-fluoro-1-propene.—A mixture of low and high boiling 1-chloro-2-fluoro-1-propene (Halogen Chemicals, Inc., Columbia, South Carolina) was dried over anhyd. sodium sulfate and distilled through a three-foot vacuum-jacketed, glass-helix packed column to separate the isomers.

Low Boiling 1-Chloro-2-fluoro-1-propene.—B.p. 29.0° (747 mm.); $n^{20}\mathrm{D}$ 1.3770, $n^{25}\mathrm{D}$ 1.3740; d^{20}_{4} 1.0812, d^{25}_{4} 1.0760; *MR* 20.10, 20.06; R_F 0.74, 0.70.

High Boiling 1-Chloro-2-fluoro-1-propene.—B.p. 59.0° (747 mm.); $n^{20}\mathrm{D}$ 1.3920, $n^{25}\mathrm{D}$ 1.3894; d^{20}_{4} 1.1139, d^{25}_{4} 1.1058; *MR* 20.19, 20.23; R_F 0.83, 0.87.

Both high boiling and low boiling 1-chloro-2-fluoro-1-propene were brominated using N-bromosuccinimide in carbon tetrachloride in the presence of benzoyl peroxide.[7] Both isomers of 3-bromo-1-chloro-2-fluoro-1-propene were formed from either isomer of 1-chloro-2-fluoro-1-propene. The isomers were separated by distillation but each isomer underwent an isomerization at room temperature into a mixture of the isomers. The course of the isomerization was followed by changes in index of refraction. The best yield of 3-bromo-1-chloro-2-fluoro-1-propene was 45% from 3.06 moles of the high boiling isomer of 1-chloro-2-fluoro-1-propene and 2.00 moles of N-bromosuccinimide.

The following physical constants were obtained immedi-

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[7] K. Ziegler, A. Spath, E. Schaaf, W. Shumann and E. Winklerman, *Ann.*, **551**, 80 (1942).

ately after distillation and may be considered as approximately correct.

Low Boiling 3-Bromo-1-chloro-2-fluoro-1-propene.—B.p. 39–40° (40 mm.); n^{20}_{D} 1.4917.

High Boiling 3-Bromo-1-chloro-2-fluoro-1-propene.—B.p. 61–62° (40 mm.); n^{20}_{D} 1.5040.

3-Chloro-2-fluoro-2-propen-1-ol.—A mixture of the isomers of 3-bromo-1-chloro-2-fluoro-1-propene (1.03 moles) was hydrolyzed using 1.03 moles of sodium carbonate in a 10% solution at 70° for 5.5 hours.

A 71% yield of 3-chloro-2-fluoro-2-propen-1-ol was obtained. The ratio of high-boiling isomer to low boiling isomer was 6 to 1. When the low boiling isomer of 3-bromo-1-chloro-2-fluoro-1-propene was added at −70° to the sodium carbonate solution at 70° the ratio of isomeric alcohols was 1 to 1. The isomeric alcohols were readily separated using an 18-inch, vacuum-jacketed column and they did not isomerize at room temperature.

Low Boiling 3-Chloro-2-fluoro-2-propen-1-ol.—B.p. 48–49° (15 mm.); n^{20}_{D} 1.4399; d^{20}_{4} 1.3472; *MR* 21.61; R_{F} 0.72.

Anal.[8] Calcd.: Cl, 32.09. Found: Cl, 31.99, 32.16.

High Boiling 3-Chloro-2-fluoro-2-propen-1-ol.—B.p. 65–66° (15 mm.); n^{20}_{D} 1.4480; d^{20}_{4} 1.3519; *MR* 21.88; R_{F} 0.99.

Anal.[8] Calcd.: 32.09. Found: Cl, 31.97, 32.14.

1,3-Dichloro-2-fluoropropene.—The two isomers of 1,3-dichloro-2-fluoropropene were prepared by the interaction of the corresponding isomers of 3-chloro-2-fluoro-2-propen-1-ol with phosphorus trichloride in pyridine.[9] The low boiling isomer of the alcohol gave a 38% yield of low boiling 1,3-dichloro-2-fluoropropene and high boiling alcohol gave a 31% yield of high boiling 1,3-dichloro-2-fluoropropene.

Low Boiling 1,3-Dichloro-2-fluoropropene.—B.p. 41.7° (100 mm.); n^{20}_{D} 1.4411, n^{25}_{D} 1.4386; d^{20}_{4} 1.3510, d^{25}_{4} 1.3427; *MR* 25.21, 25.23; R_{F} 0.99, 1.02.

Anal.[8] Calcd.: Cl, 54.99. Found: Cl, 54.65, 54.83.

High Boiling 1,3-Dichloro-2-fluoropropene.—B.p. 46° (44 mm.); n^{20}_{D} 1.4571, n^{25}_{D} 1.4543; d^{20}_{4} 1.3769, d^{25}_{4} 1.3691; *MR* 25.51, 25.52; R_{F} 1.29, 1.30.

Anal.[8] Calcd.: Cl, 54.99. Found: Cl, 54.38, 54.41.

1-Chloro-2-fluoro-1-propene.—In order to relate the structure of the isomeric 1,3-dichloro-2-fluoropropenes to the corresponding 1-chloro-2-fluoro-1-propenes the dichlorides were treated with lithium aluminum hydride to replace the allylic chlorine atom by a hydrogen atom.[10] Low boiling 1,3-dichloro-2-fluoropropene (0.04 mole) gave a 56% yield (65% conversion) of low boiling 1-chloro-2-fluoro-1-propene (b.p. 28–31°, n^{25}_{D} 1.3748) and no high boiling monochloride. Diethyl Cellosolve (Union Carbide and Carbon Corp., New York) was used as a solvent.

High boiling 1,3-dichloro-2-fluoropropene (0.05 mole) gave a 66% yield (50% conversion) of high boiling 1-chloro-2-fluoro-1-propene (b.p. 58.5°, n^{25}_{D} 1.3888) and no low boiling monochloride. Diethyl ether was used as the solvent.

Infrared Spectra.—The infrared spectra data were obtained through the courtesy of R. E. Kitson and the Chemical Division, Polychemicals Department, E. I. du Pont de Nemours and Company. The spectra were made in the liquid phase using a Perkin–Elmer Model 21 double-beam spectrophotometer. Sodium chloride optics were used with a cell thickness of 0.030 mm. for the two isomers of 1-chloro-2-fluoro-2-propen-1-ol, 0.031 mm. for the 1,3-dichloro-2-fluoropropenes and 0.035 mm. for the 1-chloro-2-fluoro-1 propenes.

Reaction with Potassium Iodide in Acetone at 20°.—The usual procedure was followed.[4] With modified second order equation $k = 1/4bt \log (5 - z)/5(1 - z)$, a plot of $\log (5 - z)/5(1 - z)$ *vs.* time gave a straight line between 53 and 77% reacted for the high boiling 1,3-dichloro-2-fluoropropene. The low boiling isomer reacted very rapidly at 20° with a resulting slight drift in the data between 69 and 90% reacted over a time period of 15 to 36 minutes. The data are in Table I.

TABLE I

RELATIVE REACTIVITIES OF LOW AND HIGH BOILING 1,3-DICHLORO-2-FLUOROPROPENE

Reaction with potassium iodide in acetone at 20°					
Low boiling 1,3-dichloro-2-fluoropropene					
Time, hr.	0.25	0.38	0.45	0.50	0.60
Reacted, %	69.2	80.4	84.6	87.0	90.0
k hr.$^{-1}$ mole^{-1} l.	11.4	10.8	10.4	10.3	9.8
Av. k			10.5 ± 0.4		
Relative reactivity[a]			48.2		
High boiling 1,3-dichloro-2-fluoropropene					
Time, hr.	2.00	2.50	3.00	3.50	4.00
Reacted, %	53.1	61.4	67.2	73.2	77.1
k hr.$^{-1}$ mole^{-1} l.	0.896	0.908	0.901	0.918	0.908
Av. k			0.906 ± 0.006		
Relative reactivity[a]			4.16		
Reaction with sodium ethoxide in ethanol at 50°					
Low boiling 1,3-dichloro-2-fluoropropene					
Time, hr.	2.75	3.50	5.50	7.00	9.00
Reacted, %	34.5	39.6	52.1	58.3	63.6
k hr.$^{-1}$ mole^{-1} l.	3.85	3.77	3.94	3.97	3.86
Av. k			3.88 ± 0.06		
Relative reactivity[b]			3.29		
High boiling 1,3-dichloro-2-fluoropropene					
Time, hr.	2.75	4.50	6.00	8.00	10.5
Reacted, %	24.1	34.4	41.3	48.7	56.0
k hr.$^{-1}$ mole^{-1} l.	2.31	2.32	2.30	2.37	2.41
Av. k			2.34 ± 0.04		
Relative reactivity[b]			1.97		

[a] Allyl chloride as 1.00 with $k = 0.218$. [b] Allyl chloride as 1.00 with $k = 1.19$.

Reaction with Sodium Ethoxide in Ethanol at 50°.—The procedure was the same as that previously described[11] and the data were calculated using the rate expression for a second-order reaction. The sodium ethoxide solution was 0.04966 molar for the reaction with both low boiling 1,3-dichloro-2-fluoropropene (0.05000 molar) and high boiling 1,3-dichloro-2-fluoropropene (0.05000 molar). A plot of $\log b(a - x)/a(b - x)$ *vs.* time gave a straight line for low boiling 1,3-dichloro-2-fluoropropene between 35 and 64% reacted, and between 24 and 56% reacted for the high boiling isomer. The data are given in Table I.

AUSTIN, TEXAS

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(8) E. Chablay, *Ann. chim.*, **1**, 510 (1914).

(9) A. Juvala, *Ber.*, **63B**, 1989 (1930); L. F. Hatch and S. S. Nesbitt, THIS JOURNAL, **72**, 727 (1950).

(10) L. F. Hatch and R. H. Perry, *ibid.*, **71**, 3262 (1949).

(11) L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1038 (1949).