interest, however, to check the rule using the data of Table III, particularly since few series of complexes have been studied for which there are as many data as in the present one. On this basis the expected positions of band maxima would be $n = 1$, 585 and 410 mμ; $n = 2$, 597 and 416 mμ; $n = 3$, 610 and 423 mμ; and $n = 4$, 623 and 430 mμ. The agreement is not quantitative, but it could be improved by use of an extrapolated value of 462 mμ for the position of the high-energy band in hexa(pyridine N-oxide)chromium(III) ion in aqueous solution. (Perhaps the position of this band maximum is sensitive to solvent.)

The Preparation and Characterization of Some New Pentafluorosulfuroxyalkanes and -alkenes[1]

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Abstract: By means of the addition reaction of pentafluorosulfur hypofluorite, SF_5OF, with alkenes, three new pentafluorosulfuroxyalkanes have been prepared: $SF_5OCHClCHClF$, $SF_5OCH_2CCl_2F$, and $SF_5OCHBrCHBrF$. A qualitative radical reaction mechanism is presented which is a possible explanation for all the experimental observations associated with these addition reaction systems. The new chloro-substituted alkanes were starting materials for dehydrohalogenation reactions which yielded four new pentafluorosulfoxyalkenes: $SF_5OCCl{=}CHF$ and $SF_5OCH{=}CClF$ in both their *cis* and *trans* isomers. One of these alkenes further reacted with SF_5OF to yield a bis(pentafluorosulfuroxy)alkane. Most of the new compounds are reasonably stable, noncorrosive liquids with moderate vapor pressures at room temperature. Molecular structures were established by nmr with other physical measurements supporting the assigned structures. Special attention is given to the complex nmr spectra of $SF_5OCHClCHClF$ which contains two magnetically distinguishable species resulting from the asymmetry associated with the two carbon atoms in this substituted alkane.

After considering the potential usefulness of alkenes that contain the elements of SF_5OF for subsequent studies on the stability of the SF_5O group and of its effect on double-bond reactivity, a convenient preparative route was proposed that would utilize either a dehalogenation or dehydrohalogenation reaction on the corresponding alkane. It had been previously observed that the alkanes could be produced by addition of SF_5OF to certain alkenes[3] in which the SF_5O group and the F atom are the two adding groups to the carbon atoms of the double bond.

Zinc dust could not be used to remove chlorine from the alkanes since it reduced the SF_5O group, so a solid–liquid heterogeneous dehydrohalogenation reaction between KOH and the substituted alkane was used to give good yields of the substituted alkene.

The 1,1- and 1,2-dichloroethylenes were used as starting materials in this study.

Experimental Section

General Procedures. Since most of the compounds investigated in this research had conveniently high volatilities, a general-purpose Pyrex glass vacuum system with the usual stopcocks, joints, and manometer was satisfactory for compound manipulation. Reaction vessels of Pyrex glass or metal were used depending on particular reaction conditions.

Reactions between SF_5OF and alkenes can be regarded as potentially dangerous. Therefore, these reactions were initially investigated in metal vessels that could withstand any possible explosion. A prefluorinated 5-cm o.d. copper tube sealed with copper plates (approximate volume, 200 ml) and fitted with a No. 327 Hoke valve was used for large-scale preparative reactions while a prefluorinated 1-cm o.d. closed-end nickel tube fitted with a No. 327 Hoke valve had particular value as a high-pressure reaction vessel. A 1-l. Pyrex glass vessel equipped with a cold finger was also used for addition reactions which were found to proceed slowly. Dehydrohalogenation reactions were carried out in a 50-ml flask equipped with a reflux condenser and mercury bubbler.

Low-boiling products were removed and purified by fractional codistillation[4] while higher boiling compounds could be separated using a Perkin-Elmer vapor fractometer (Model 154-L) equipped with a detector by-pass and a standard 3-m preparative column of 1-in. aluminum tubing packed with Celite 545 support and Dow Corning silicone grease (0) liquid phase. Relative retention times provided an excellent means for identification of the reaction products.

The infrared spectra of gaseous samples were obtained on a Perkin-Elmer 421 grating spectrophotometer using a 9-cm path-length cell equipped with NaCl windows. Nuclear magnetic resonance spectra were measured on Varian Associates equipment. The A-60 and HA-100 instruments were used for proton spectra, and an A-56.4/60.0 instrument provided the fluorine spectra. Internal standards of trichlorofluoromethane and tetramethylsilane calibrated the spectra. Mass spectra were obtained on Consolidated Electrodynamics Corp. Model 21-103-C and Varian Associates Model M-66 instruments. All mass spectra were taken with ionizing potentials of 70 V.

By using an apparatus similar to that described by Kellogg and Cady,[5] equilibrium boiling points could be determined for a liquid

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(1) This report is taken from the Ph.D. thesis of R. D. Place and was presented in part at the Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967.

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(3) S. M. Williamson and G. H. Cady, *Inorg. Chem.*, 1, 673 (1962).

(4) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, 31, 618 (1959).

(5) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, 70, 3986 (1948).

sample at a series of fixed pressures. From these data, molar heats of vaporization, Trouton constants, and normal boiling points could be determined for all of the new compounds. Molecular weights could be calculated from experimental vapor density measurements. Also, elemental analyses were carried out on most of these compounds, making use of standard microchemical techniques.[6]

Chemicals used in this study were reagent grade and did not require further purification. The SF_5OF was prepared according to the procedure reported by Dudley,[7] and it could be obtained in high purity by fractional codistillation of the reaction mixture.[4]

Preparation of $SF_5OCHClCHClF$ (I). A 20.0-mmole sample of *cis*-dichloroethylene was condensed at −183° near the bottom of the copper reactor, and an equimolar amount of SF_5OF was then condensed above it. The reactor was thoroughly cooled before the coolant was removed. The vessel then warmed slowly and uniformly to room temperature. The reaction proceeded smoothly and as much as 81% of the initial alkene was converted into I. The remaining material was found to be primarily the fluorination products, CHClFCHClF and SF_4O. The reaction between SF_5OF and *trans*-1,2-dichloroethylene was found to also produce I as the only addition compound containing the elements of SF_5OF. *Anal.* Calcd for $C_2H_2Cl_2SOF_6$: C, 9.28; H, 0.78; Cl, 27.38; mol wt, 259.1. Found: C, 9.42; H, 0.92; Cl, 27.62; mol wt (per gram molecular volume (gmv^{-1})), 260.00. The gas-phase infrared spectrum consists of absorptions at 3021 (w), 1342 (m), 1081 (s), 998 (m), 902 (vs), 884 (vs), 808 (s), and 744 (s) cm^{-1}. Most prominent mass spectral fragments correspond to SF_5^+, SF_5OCHCl^+, $SF_5OC_2H_2ClF^+$, and $C_2H_2Cl_2F^+$. The vapor pressure is represented by $\log P_{mm} = 8.2902 - 2025.6/T(°K)$, which gives a normal boiling point of 101.3°.

Preparation of $SF_5OCH_2CCl_2F$ (II). The reaction between SF_5OF and 1,1-dichloroethylene was much more energetic than those involving the 1,2-dichloroethylenes. An upper limit of 15.0-mmole quantities of each reactant was condensed into the copper reactor. After the entire reactor, to the bottom of the Hoke valve, was cooled to −183°, the coolant could be removed and the reaction proceeded smoothly. Up to 71% yields of II were recovered, and most of the remaining material was found to be the fluorination products, CH_2FCCl_2F and SF_4O. *Anal.* Calcd for $C_2H_2Cl_2SOF_6$: C, 9.28; H, 0.78; Cl, 27.38; mol wt, 259.1. Found: C, 9.37, H, 0.90; Cl, 27.56; mol wt (gmv^{-1}), 260.0. The gas-phase infrared spectrum consists of absorptions at 2977 (m), 1263 (m), 1161 (m), 1055 (s), 938 (m), 888 (vs), 766 (m), and 732 (m) cm^{-1}. Most prominent mass spectral fragments corresponded to SF_5^+, $SF_5OCH_2^+$, CCl_2F^+, and $C_2H_2Cl_2F^+$. The vapor pressure is represented by $\log P_{mm} = 8.3128 - 2012.5/T(°K)$, which gives a normal boiling point of 97.3°.

Preparation of $SF_5OCHBrCHBrF$ (III). This reaction was investigated because the elements of SF_5OF had not been added to alkenes containing bromine atoms. Also, the addition product was expected to give nmr spectra similar to those obtained from I. The reaction proceeded quite slowly, and it could be safely handled in a 1-l. Pyrex glass flask. Equimolar 11.0-mmole quantities of SF_5OF and 1,2-dibromoethylene were condensed into the flask, which was allowed to stand for 22 hr at 23°. The addition product was obtained in 15% yield with most of the remaining material accounted for as fluorination products, CHBrFCHBrF and SF_4O. The addition compound could be obtained in only 45% purity for its characterizations. Approximately the same product mixture was obtained from either the *cis*- or the *trans*-alkene. The gas-phase infrared spectrum was satisfactory for the addition compound with absorptions at 3010 (w), 1330 (w), 1085 (s), 1052 (s), 910 (vs), 882 (vs), and 801 (m) cm^{-1}. Most prominent mass spectral fragments correspond to SF_5^+, $SF_5OC_2H_2BrF^+$, $SF_5OC_2H_2Br_2F^+$, and $C_2H_2Br_2F^+$. Because of its impure state, no other analytical measurements were attempted.

Preparation of *cis*- and *trans*-$SF_5OCCl{=}CHF$ (IV and V). A 15.0-mmole quantity of I was condensed onto 0.18 mole of powdered KOH in a 50-ml Pyrex glass flask. Heating for 5 min at 85° produced a liquid mixture containing up to 80% of IV and V. These two products were isolated in approximately equimolar quantities. After characterization, the more volatile alkene was labeled IV and the less volatile one, V. No definite assignment could be made as to which *cis* or *trans* structure corresponded to IV and V because of subsequent decomposition into compound VI. Compound IV was obtained pure and possesses the following properties. *Anal.* Calcd for $C_2HClFSOF_6$: C, 10.80; H, 0.45; Cl, 15.93; mol wt, 222.6. Found: C, 10.92; H, 0.81; Cl, 16.13; mol wt (gmv^{-1}), 222.8. The gas-phase infrared spectrum consists of absorptions at 3108 (m), 1673 (m), 1614 (w), 1285 (m), 1176 (vs), 1129 (s), 904 (vs), 871 (vs), 810 (m), and 749 (m) cm^{-1}. Most prominent mass spectral fragments correspond to SF_5^+, $SF_5OC_2HF^+$, C_2HClF^+, $CHClF^+$, and C_2HF^+. The vapor pressure is represented by $\log P_{mm} = 8.1908 - 1783.4/T(°K)$, which gives a normal boiling point of 62.7°, and the sample of IV contained 2% acetone to prevent decomposition.

Compound V was not obtained pure, but the following absorptions in the infrared spectrum were assigned to it: 3114 (w), 1669 (m), 1622 (w), 1302 (m), 1150 (s), 1073 (vs), 899 (vs), 830 (vs), and 763 (m) cm^{-1}. The same mass spectral fragments were obtained as those from VI.

Preparation of *trans*-$SF_5OCH{=}CClF$ (VI). It was found that if either IV or V were allowed to warm to 25° in the liquid phase, an exothermic spontaneous rearrangement occurred and a new alkene was formed. Conversion was 80% complete after 1 hr. The new alkene has the hydrogen and fluorine atoms *trans* across the double bond. Since this rearrangement took place very slowly in the gas phase, purification of IV and V could be accomplished on a cool chromatographic column. The nmr spectra of IV and V had to be taken with a low-temperature probe to prevent decomposition. *Anal.* Calcd for $C_2HClSOF_6$: C, 10.80; H, 0.45; Cl, 15.93; mol wt, 222.6. Found: C, 10.90; H, 0.61; Cl, 16.08; mol wt (gmv^{-1}), 223.0. The gas-phase infrared spectrum consists of absorptions at 3079 (w), 1786 (s), 1551 (w), 1150 (m), 1067 (m), 974 (m), 875 (vs), 817 (m), and 739 (w) cm^{-1}. Most prominent mass spectral fragments correspond to SF_5^+, $SF_5OC_2HF^+$, C_2HClF^+, $CHClF^+$, and C_2HF^+. The vapor pressure is represented by $\log P_{mm} = 8.3103 - 1920.5/T(°K)$ which gives a normal boiling point of 80.6°.

Preparation of *cis*-$SF_5OCH{=}CClF$ (VII). A 15.0-mmole quantity of II was condensed onto 0.18 mole of powdered KOH in the 50-ml Pyrex glass flask. Heating for 15 min at 110° produced a liquid mixture containing up to 50% of VII. A second treatment with a fresh batch of KOH could produce an 80% conversion of II to VII. Compound VII was assigned the *cis* structure with respect to the hydrogen and fluorine atoms. *Anal.* Calcd for $C_2HClSOF_6$: C, 10.80; H, 0.45; Cl, 15.93; mol wt, 222.6. Found: C, 11.04; H, 0.69; Cl, 16.08; mol wt (gmv^{-1}), 223.2. The gas-phase infrared spectrum consists of absorptions at 3128 (m), 1683 (m), 1586 (w), 1322 (m), 1148 (s), 1101 (vs), 903 (vs), 870 (vs), and 788 (m) cm^{-1}. Most prominent mass spectral fragments correspond to SF_5^+, $SF_5OC_2HClF^+$, C_2HClFO^+, and $CHClF^+$. The vapor pressure is represented by $\log P_{mm} = 8.1935 - 1789.7/T(°K)$, which gives a normal boiling point of 63.7°.

Reaction of $SF_5OCCl{=}CHF$ (IV) with SF_5OF. The small-volume nickel reactor was loaded with 2.94 mmoles of each reactant. An infrared spectrum after 5 min indicated that IV had completely rearranged to VI. The mixture was allowed to stand at 23° for 18 hr, but essentially all the SF_5OF and VI were recovered unchanged. There was a small amount of chlorine gas present, but no fluorination or addition products were isolated.

Reaction of *cis*-$SF_5OCH{=}CClF$ (VII) with SF_5OF. At −50°, equimolar 3.04-mmole quantities of SF_5OF and VII exploded inside the nickel reactor and produced only low molecular weight gases. When 2.0 mmoles of VII and 2.2 mmoles of SF_5OF were combined in a 1-l. Pyrex glass flask, reaction was evident because smoke swirls were seen above the liquid alkene 1.5 min after the coolant was removed. The reaction temperature was not known, but was estimated to be $\sim -100°$. The products of this reaction contained alkanes representing both addition and fluorination by the SF_5OF. The ratio of addition to fluorination was 3:1, and the products were $(SF_5O)_2CHCClF_2$ (VIII) and $SF_5OCHFCClF_2$ (IX). It was found that the reaction mixture should stand for 30 min before further handling is attempted. This precaution ensures that the reaction is complete. *Anal.* Calcd for $C_2HClS_2O_2F_{12}$ (VIII): C, 6.25; H, 0.26; Cl, 9.22; mol wt, 385.6. Found: C, 6.50; H, 0.61; Cl, 9.48; mol wt (gmv^{-1}), 391.3. The gas-phase infrared spectrum consists of absorptions at 3039 (m), 1776 (w), 1337 (m), 1227 (m), 1162 (s), 1113 (s), 1090 (m), 1045 (m), 991 (m), 911 (vs), 852 (vs), and 798 (m) cm^{-1}. Most prominent mass spectral fragments correspond to SF_5^+, $S_2O_2F_{10}CH^+$, $SF_5OC_2HClF_2^+$, and $CClF_2^+$. The vapor pressure is represented by $\log P_{mm} = 8.2381 - 2034.8/T(°K)$, which gives a normal boiling point of 106.7°. *Anal.* Calcd for

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(7) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956).

Table I. Nuclear Magnetic Resonance Data[a]

I′ and I″
$FSF_4OCHClCHClF$
a b c d e
$J_{ab}' = 154.1$ $\delta_a' = 67.59$
$J_{ab}'' = 154.2$ $\delta_a'' = 67.90$
$J_{cd}' = 4.8$ $\delta_b' = 61.96$
$J_{cd}'' = 4.5$ $\delta_b'' = 61.54$
$J_{ce}' = 5.0$ $\delta_c' = 6.25$
$J_{ce}'' = 6.5$ $\delta_c'' = 6.26$
$J_{de}' = 49.6$ $\delta_d' = 6.03$
$J_{de}'' = 49.6$ $\delta_d'' = 6.06$
$X' = 0.484$ $\delta_e' = 143.58$
$X'' = 0.442$ $\delta_e'' = 145.23$

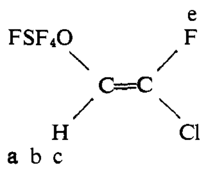
II
$FSF_4OCH_2CCl_2F$
a b c e
$J_{ab} = 153.2$ $\delta_a = 71.95$
$J_{ce} = 12.6$ $\delta_b = 60.35$
$\delta_c = 4.61$
$X = 0.234$ $\delta_e = 65.15$

III′ and III″
$FSF_4OCHBrCHBrF$
a b c d e
$J_{ab}' = 150.2$ $\delta_a' = 69.57$
$J_{ab}'' = 150.4$ $\delta_a'' = 69.45$
$J_{cd}' = \sim 5.5$ $\delta_b' = 63.80$
$J_{cd}'' = \sim 4.1$ $\delta_b'' = 62.99$
$J_{ce}' = \sim 4.2$
$J_{ce}'' = 10.5$
$J_{de}' = 49.9$
$J_{de}'' = 49.9$
$X' = 0.461$ $\delta_e' = 139.63$
$X'' = 0.413$ $\delta_e'' = 145.12$

IV
$FSF_4OCCl{=}CHF$
a b d e
$J_a' = 153.0$ $\delta_a = 64.11$
$J_{de} = 75$ $\delta_b = 60.19$
$\delta_d = 7.21$
$X = 0.691$ $\delta_e = 143.27$

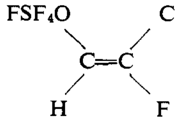
V
$FSF_4OCCl{=}CHF$
a b d e
$\delta_a = 64$
$J_{de} = 75$ $\delta_b = 63.12$
$\delta_d = 6.33$
$X > 1.5$ $\delta_e = 135.13$

VI



a b c
$J_{ab} = 150.4$ $\delta_a = 65.33$
$J_{ae} = 2.0$ $\delta_b = 50.84$
$J_{bc} = 4.5$ $\delta_c = 5.65$
$J_{be} = 4.3$ $\delta_e = 165.14$
$J_{ce} = 47.0$ $X = 0.184$

VII



a b c e
$J_{ab} = 151.6$ $\delta_a = 67.29$
$J_{ac} = 0.4$ $\delta_b = 59.61$
$J_{bc} = 1.1$ $\delta_c = 5.96$
$J_{be} = 2.4$ $\delta_e = 89.07$
$J_{ce} = 13.2$ $X = 0.350$

VIII
$(FSF_4O)_2CHCClF_2$
a b c e
$\delta_a = 61.99$
$\delta_b = 61.13$
$\delta_c = 6.27$
$\delta_e = 71.13$
$X > 1$

IX
$FSF_4OCHFCClF_2$
a b c f e
$J_{ab} = 150.5$ $\delta_a = 62.68$
$J_{af} = 2.0$ $\delta_b = 59.14$
$J_{bf} = 5.0$ $\delta_c = 6.32$
$J_{cf} = 54.0$ $\delta_f = 138.30$
$J_{ce} = 3.0$ $\delta_e = 71.31$
$J_{fe} = 9.0$ $X = 0.752$

[a] The lower case letters under each magnetic nucleus are used for purposes of identification of the coupling constants, J, given in cps, and the chemical shifts, δ, given in ppm downfield from the internal standards CCl_3F for fluorine and $Si(CH_3)_4$ for hydrogen. Chemical shifts for nuclei designated a and b are always upfield from the internal standards. Omission of some possible J and δ valves means that they were either too small to be measured or could not be resolved. $X = J_{ab}/|\delta_b - \delta_a|$), the ratio that determines the importance of second-order interaction as is described in ref 11.

$C_2HClSOF_8$ (IX): C, 9.22; H, 0.37; Cl, 13.61; mol wt, 259.6. Found: C, 9.40; H, 0.69; Cl, 13.82; mol wt (gmv^{-1}), 260.3. The gas-phase infrared spectrum consists of absorptions at 3015 (m), 1871 (w), 1380 (m), 1347 (m), 1242 (s), 1160 (vs), 1115 (vs), 998 (s), 916 (vs), 892 (vs), 849 (m), and 762 (m) cm^{-1}. Most prominent mass spectral fragments correspond to SF_5^+, SF_5OCHF^+, $C_2HClF_3^+$, and $CClF_2^+$. The vapor pressure is represented by $\log P_{mm} = 8.1644 - 1739.4/T(°K)$, which gives a normal boiling point of 56.1°.

Discussion

Identification of New Compounds. The identifications for the nine compounds reported here were made on the basis of consistent reaction stoichiometries, molecular weights, elemental analyses, and nmr, infrared, and mass spectra. They were further characterized by vapor-pressure curves. Clausius–Clapeyron plots of log P (mm) *vs.* $1/T$ allowed the calculation of normal boiling points, molar heats of vaporization, and Trouton constants. The nmr spectra were the most conclusive data for determination of the structures. The nmr parameters are presented in Table I, and a summary of the other important data appears above in the Experimental Section.

In reactions involving the addition of SF_5OF to alkenes, the nmr spectra clearly show that the adding hypofluorite molecule cleaved at the O–F bond. The direction of addition to the 1,2-dichloro- and 1,2-dibromoethylenes is unambiguous, and the complex spectra of I and III will be discussed later in this section. The structure of II was found to be $SF_5OCH_2CCl_2F$ from the proton doublet and the fluorine triplet spectra. The J_{ce} value of 12.6 cps is considerably smaller than a coupling constant between hydrogen and fluorine atoms bound to the same saturated carbon atom. The structure for VIII was determined to be $(SF_5O)_2CHCClF_2$. The proton and fluorine spectra are single broad resonance lines having half-widths of 3.1 and 4.6 cps, respectively. The chemical shift for the two equivalent fluorine atoms of the $CClF_2$ group agrees very closely with the corresponding value in IX. The lack of a resolved J_{ce} value in VIII can be explained by the very large line widths which should conceal the small anticipated J value analogous to J_{ce} in IX. If the second SF_5O group had bound to the other possible carbon atom to give $SF_5OCHFC(SF_5O)ClF$, then a large J_{HF} value and two different fluorine resonances

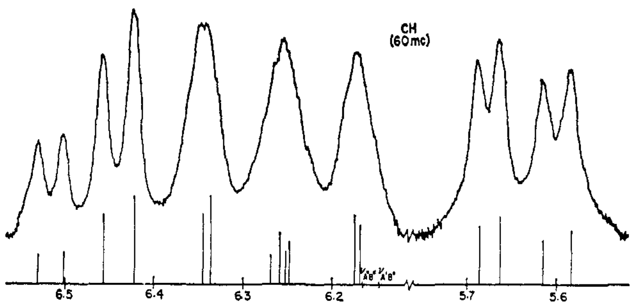


Figure 1. Proton nmr spectrum of $SF_5OCHClCHClF$ at 60 Mc.

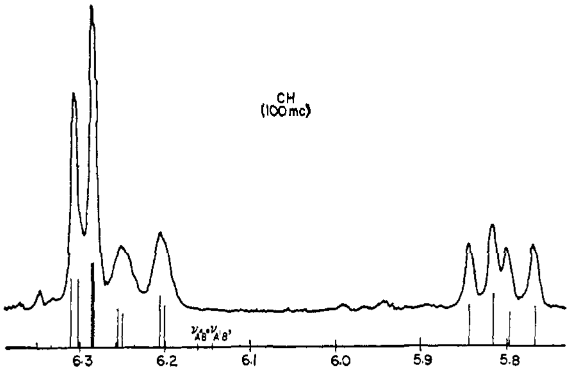


Figure 2. Proton nmr spectrum of $SF_5OCHClCHClF$ at 100 Mc.

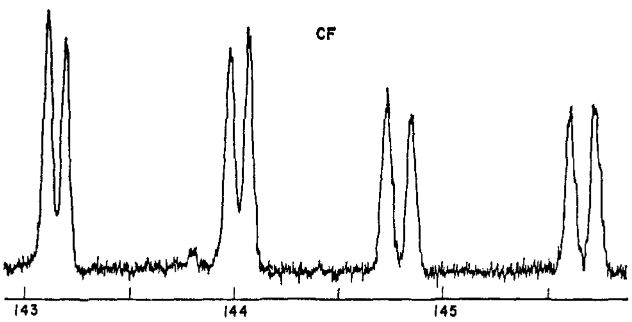


Figure 3. Fluorine nmr spectrum of $SF_5OCHClCHClF$ at 56.4 Mc.

analogous to IX should have been observed. The mass spectrum of VIII further substantiates the structural assignment. Peaks were observed at m/Q values corresponding to $(SF_5O)_2CH^+$ and $CClF_2^+$ but no peaks were found for SF_5OCHF^+ or SF_5OCClF^+. The structure for IX was shown to be $SF_5OCHFCClF_2$. This structure further helps to establish the structure of VII as $SF_5OCH{=}CClF$ since VII was used as the starting material to prepare IX.

All of the new alkenes containing the SF_5O substituent have the same empirical formula. Therefore, nmr spectra were the only effective means to determine the different structures. Compounds IV and V have proton and fluorine spectra which consist of doublets. The 75-cps J values indicate that the hydrogen and fluorine atoms are bound to the same carbon atom,[8] but no definite assignment can yet be made as to which isomeric structure corresponds to each of the two new compounds. The two isomers of $SF_5OCH{=}CClF$ were differentiated on the basis of their relative J_{HF} values. Reported data indicate that *trans* coupling constants are always greater than the corresponding *cis* values in similar compounds.[8] Compounds VI and VII have J_{HF} values which agree with the reported ranges for *trans* and *cis* hydrogen and fluorine atoms, respectively, so VI was designated as the *trans* compound and VII as the *cis* compound. All the vinyl hydrogen and fluorine atoms in these two compounds interact with the fluorine atoms of the SF_5O group, so the spectra are quite complex.

The nmr spectra for I and III are very complex. The discussion will be centered upon the spectra of I because its resonances were better resolved and the necessary parameters could be determined more precisely for I than for III. The general discussion and analytical procedure are applicable to either of the two compounds. Figures 1 and 2 for the 60- and 100-Mc proton nmr spectra show good agreement between the calculated and experimental energies and intensities. For an analysis of the spectra, the J_{AB} values could be determined from the two proton spectra and the J_{AX} and J_{BX} values from the fluorine nmr spectrum (Figure 3). The calculations were made using the procedure outlined by Pople[9] for the analysis of an ABX spectrum where A and B are the two hydrogen atoms and X is the fluorine atom bound to the carbon atom containing H_A.

From the analysis of spectra, it was found that the observed spectra were due to the two different stereochemical forms of I in which the J and δ values are only slightly different in each form. (In this work, no other physical or chemical measurement differentiated between the two forms.) The results of the calculations are given in Table II. The actual molar amounts of the two different species were not equal, so the calculated relative intensities for the species of larger concentration were multiplied by a factor of 1.2.

The high-resolution second-order fluorine nmr spectra of all the new compounds further confirmed both the presence of the SF_5O group and the model used for the calculation of the appropriate spectral parameters. In the SF_5O group, the fluorine atom *trans* to the oxygen atom is magnetically unique while the fluorine atoms which are *cis* can be treated as equivalent to each other. A_4B model can be used to determine the nmr parameters for the five fluorine atoms.[10] However, a graphical modification was found to be more convenient for determination of the parameters listed in Table I.[11] The A_4B fluorine spectrum for I further confirmed the presence of the two distinguishable magnetic isomers.

The Addition Reaction. It might be expected that the two spectra for I resulted from two energetically favored rotamers in a system exhibiting hindered rotation. However, a temperature study over the temperature range of -60 to $+160°$ showed that there was no change in chemical shifts or coupling constants. New-

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(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132.

(10) H. M. McConnell, A. D. McLean, and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

(11) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

Table II. Calculated ABX Spectra for $F_5SOCHCl–CHClF$[a]

	I′			I″		
Line	Calcd, cps	Obsd, cps	Calcd int	Calcd, cps	Obsd, cps	Calcd int
			60 Mc			
1	−21.22	−21.25	0.63	−21.95	−21.95	0.60
2	−6.63	−6.3 U	1.04	−5.05	−5.4 U	0.87
3	−16.32	−16.35	1.77	−17.45	−17.45	1.40
4	−1.83	−1.6 U	1.36	−0.55	−0.6 U	1.13
5	−11.02	−11.5 U	1.77	−10.75	−11.0 U	1.40
6	29.27	29.25	1.36	28.75	22.75	1.13
7	−6.22	−6.3 U	0.63	−6.25	−5.4	0.60
8	34.07	34.05	1.04	33.25	33.25	0.87
		$\nu_{A'B'}$ = 0 cps			$\nu_{A''B''}$ = 0 cps	
			100 Mc			
1	−18.59	−18.57	0.05	−19.03	−18.76	0.14
2	−10.73	−10.2 U	1.07	−8.60	−8.5 U	0.89
3	−13.79	−13.70	2.35	−14.53	−14.5 U	1.86
4	−5.93	−5.7 U	1.33	−4.10	−4.1 U	1.11
5	−13.65	−13.70	2.35	−13.67	−14.5 U	1.86
6	33.37	33.35	1.33	32.30	31.92	1.11
7	−8.92	−10.2 U	0.05	−9.17	−8.5 U	0.14
8	38.17	38.15	1.07	36.80	36.42	0.89
		$\nu_{A'B'}$ = 0 cps			$\nu_{A''B''}$ = 0 cps	

[a] Calcd = calculated line position; obsd = observed line position; calcd int = calculated relative intensity; $\nu_{AB} = (\nu_A + \nu_B)/2$; U = unresolved theoretical peak. Nearest experimental peak is listed.

mark found that 1,1,2-tribromo-1,2,2-trifluoroethane exhibited hindered rotation only up to −53°.[12] Therefore, I, which is less hindered, should be rotating rapidly with respect to the oscillating nmr field. It was decided that the reason for the two spectra for each hydrogen and fluorine atom instead of the one expected for a freely rotating molecule was that each of the carbon atoms in I is in an asymmetric environment. Gutowsky calculated that two different hydrogen atoms next to an asymmetric carbon atom should always give different chemical shifts and coupling constants.[13] The reason for this difference is that the chemical shifts and coupling constants are the populationally averaged sums of the contributions from the three possible staggered forms which the molecule can assume during rotation. Staggered forms are more probable than eclipsed forms because of activation energy considerations.[14] Since two distinct magnetic species are present in the spectra of I and III, the addition compounds must have been formed in two different configurations which can be referred to as the *erythro* and *threo* addition products. By reference to Figure 4, it can be seen that there are two different ways in which the individual groups can be oriented around each carbon atom. Equivalent rotational staggered forms are not included here for the sake of clarity. There are four different combinations of these two asymmetric carbon atoms.

It might be expected that four different nmr species should have been detected. However, there are two sets of mirror image pairs which result from the four illustrated configurations. The *dd′* and *ll′* forms are mirror images of each other, and the same holds for the *dl′* and *ld′* pair. There is an equivalent staggered form for each of the two configurations of a mirror image pair in which a particular substituent occupies the same position relative to all the other groups in the molecule. Therefore, the average magnetic environments should be equivalent and the nmr parameters should be identical. However, these parameters should be different for each set of mirror image configurations because there is no correspondence between any of the different staggered forms of the two unique sets. Hence, the requirement of two distinct nmr spectra for this molecule can be deduced from this model.

The four different configurations which are postulated for I can be obtained from a reaction intermediate which contains only one of the adding segments of the SF_5OF initially. Rapid rotation of the intermediate and random addition of the other portion of the hypofluorite would then result in the formation of all possible configurations. A four-center reaction mechanism would produce only the *dd′* and *ll′* isomers from the *cis*-alkene and the *dl′* and *ld′* pair from the *trans*-alkene. However, the same nmr spectra were obtained from samples of the addition product from either the *cis*- or *trans*-dichloroethylenes.

Additional data to support this asymmetry phenomenon in the nmr are that the spectra of the addition products from the reaction of SF_5OF with the *cis*- and *trans*-dibromoethylenes are identical with each other and qualitatively very similar to the spectra obtained from the dichloroethylene addition products.

The sequence of steps listed below is being postulated as the mechanism by which SF_5OF adds to unsaturated carbon–carbon bonds. Reactions of SF_5OF with unsaturated inorganic molecules such as N_2F_4[15] and SF_4[16] have also been reported to proceed by radical mechanisms. In this mechanism the ΔH values have

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(12) R. Newmark, University of California Radiation Laboratory Report, UCRL-11649, Nov 1964.

(13) H. S. Gutowsky, *J. Chem. Phys.*, 37, 2196 (1962).

(14) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954.

(15) W. H. Hale, Jr., and S. M. Williamson, *Inorg. Chem.*, 4, 1342 (1965).

(16) G. Pass and H. L. Roberts, *ibid.*, 2, 1016 (1963).

been calculated from the average bond energies,[17] and no measurements have been made to establish the values of any of these steps. Therefore, the listed numbers are only approximate. However, a general consideration of their relative values is valuable in understanding the reaction. The notation used is that X = SF_5O and E = alkene.

Initiation

$$XF + E \longrightarrow X\cdot + EF\cdot \quad \Delta H = +2 \text{ kcal} \qquad (1)$$

Propagation

$$FE\cdot + XF \longrightarrow EF_2 + X\cdot \quad \Delta H = -61 \text{ kcal} \qquad (2)$$

$$X\cdot + E \longrightarrow XE\cdot \quad \Delta H = -21 \text{ kcal} \qquad (3)$$

$$XE\cdot + XF \longrightarrow XEF + X\cdot \quad \Delta H = -61 \text{ kcal} \qquad (4)$$

Propagation (competition)

$$X\cdot + E \longrightarrow FE\cdot + SF_4O \quad \Delta H = -9 \text{ kcal} \qquad (5)$$

$$XE\cdot + E \longrightarrow XE_2\cdot \quad \Delta H = -20 \text{ kcal} \qquad (6)$$

$$X\cdot + E \longrightarrow SF_4O + HF + E(-H)\cdot \quad \Delta H = -25 \text{ kcal} \qquad (7)$$

Termination

many radical recombinations (−33 to −83 kcal)

This radical mechanism is analogous to the kinetically established radical mechanism proposed by Miller and Dittman[18] for the addition of elemental fluorine to alkenes. The initiation step in the addition of SF_5OF is approximately thermal neutral, and the initiation step for fluorine addition should be only 7 kcal more exothermic from an average bond-energy calculation. This difference would be the variation between the F–F and O–F bond energies of 37 and 44 kcal, respectively.

It has been reported that the SF_5O group bonds preferentially to one of the two possible carbon atoms of an unsymmetrical alkene.[3,19] This requires a mechanism which introduces the SF_5O group into the product in one consistent manner. This characteristic seems to be present in the proposed mechanism where the thermally neutral initiation step is followed by very exothermic propagation addition steps which create very long chains. The addition products are formed by steps 3 and 4 in which the SF_5O radical adds to a molecule of alkene and the resulting intermediate abstracts a fluorine atom from a hypofluorite molecule. A radical mechanism involving long chains should be affected by small amounts of radical inhibitors. A small concentration of acetone did drastically reduce the reaction rate between SF_5OF and acetylene or ethylene.

In the addition reactions the relative amounts of SF_4O and EF_2 produced were always approximately equivalent. This would be predicted if the major portion of these products were produced by the sequence of steps 5 and 2. The presence of appreciable amounts of SF_4O indicated that step 5 should compete favorably with step 3 which yields the addition compound. Step 3 appears to be thermodynamically favored. However, its free energy is surely raised by an unfavorable entropy caused by going from two molecules to one. Since step 5 does not change the number of molecules, the free-energy difference between the two steps might be reduced to only a few kilocalories. The lower quantities of SF_4O which were produced when the addition reactions were carried out at pressures of several atmospheres further illustrated the competition between steps 3 and 5 because step 3 should be favored at these higher pressures.

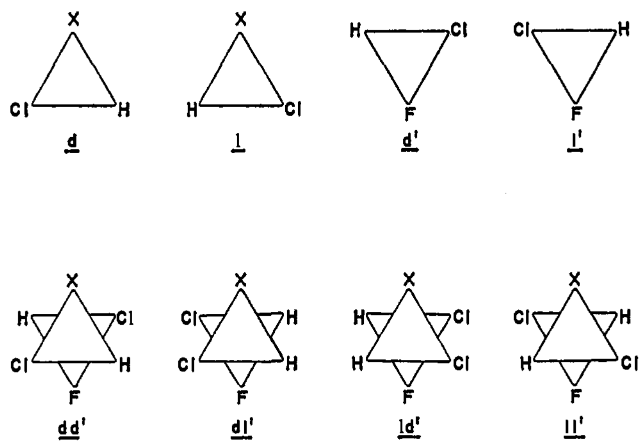

Figure 4. Schematic representation of the isomeric forms of $SF_5OCHClCHClF$. The *d* and *l* notation is for identification purposes only and does not imply direction of the rotation of polarized light.

Polymerization and hydrogen-atom abstraction reactions indicated by steps 6 and 7, respectively, did not play significant roles in the addition reactions. Only trace amounts of polymeric material were produced in these reactions, and this lack of competition is probably a result of the large difference in the heats of reaction between steps 4 and 6. The competing allylic hydrogen-atom abstraction reaction should have taken place if only a comparison of the heats of reaction for steps 3 and 7 is considered. However, when 2-butene which has six allylic hydrogen atoms was studied, very little abstraction was detected. The abstraction reaction requires that two bonds be broken simultaneously, and the activation energy for this process may be too high to allow successful competition with step 3.

The Dehydrohalogenation Reaction. It is felt that the SF_5O-substituted alkenes, which are reported in this paper, were formed by an E2 elimination reaction mechanism in which the proton and halide ions are simultaneously removed from a *trans* configuration of the alkane. Polar solvents can stabilize intermediates formed in the unimolecular E1 or unimolecular conjugate base E1cB elimination reactions where either carbanion or carbonium ions are formed. However, the liquid phase in the elimination reactions reported here should be essentially nonpolar, thus favoring the E2 mechanism. No solvents were used in the reactions, and the SF_5O-substituted alkanes should not have a significant dipole moment. Also, a strong dependence upon the base concentration was found for the dehydrochlorination of I, and this is characteristic of E2 elimination reactions where the base removes the proton. A solvent system using KOH, I, and ethanol was not effective in producing good yields of alkenes, while K_2CO_3

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(17) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p 88.

(18) W. T. Miller, Jr., and A. L. Dittman, *J. Am. Chem. Soc.*, **78**, 2793 (1956).

(19) S. M. Williamson, *Inorg. Chem.*, **2**, 421 (1963).

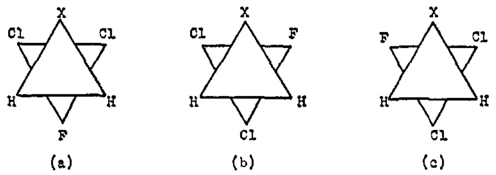

Figure 5. The three rotameric forms of $SF_5OCH_2CCl_2F$.

did not react at all with I. However, the heterogeneous reaction between solid KOH and the liquid alkane was very effective and produced good yields of products.

In the reaction of I and KOH, the only isolated products were IV and V where the removed proton had been bound to the carbon atom containing the SF_5O and Cl substituents. This is analogous to a reaction reported by Hoover and Coffman[20] where HBr was removed from $SF_5CHBrCHBrCl$ with K_2CO_3 and the two isomers of $SF_5CBr{=}CHCl$ were isolated. From a steric argument, it would seem unusual that the most hindered hydrogen atoms were removed from both I and $SF_5CHBrCHBrCl$. However, chlorine and bromine atoms tend to weaken neighboring bonds,[21] and if SF_5O and SF_5 substituents also weaken bonds, the combined substituent effects might make the hydrogen atoms which participated in the elimination reactions more acidic.

In the reaction of II and KOH, only one alkene (VII) was produced. The E2 elimination mechanism involves *trans* removal of the proton and halide ion. If this mechanism is in effect in this particular reaction, then elimination occurs from only one of the three possible rotamers of II. In Figure 5, the staggered configuration (a) with the SF_5O group between the chlorine atoms on the adjacent carbon atom would yield VII, the observed product, by elimination of either HCl *trans* pair. However, *trans* elimination from the other two possible rotamers (b and c) would yield only VI, the product observed in the rearrangement reaction but not found in even trace amounts from this reaction mixture. Random or *cis* elimination should yield both of the alkenes from all of the rotamers. It is not understood why elimination should occur from only one of the three rotamers to produce one alkene instead of two, but the observations strongly suggest that this is probably what is happening.

The Rearrangement of $SF_5OCCl{=}CHF$. The difference in properties of VI and VII was illustrated by the large variation in their relative reactivities with SF_5OF. The double bond in compound VI appeared to be blocked from attack by SF_5OF while the interchange of a chlorine atom for a fluorine atom in VI to give VII resulted in its very rapid reaction with the hypofluorite. Steric restrictions may be the answer, but no completely satisfactory explanation is proposed.

The formation of VI from IV or V is a very interesting reaction. The rearrangement did not occur initially in the KOH reaction vessel at 85°. However, the migration of the chlorine atom was spontaneous in the liquid phase at room temperature, and an appreciable amount of heat was evolved. Either SF_5OF or benzoyl peroxide greatly increased the rate of rearrangement, but a 3% concentration of acetone virtually stopped the formation of VI for at least 24 hr. These observations are consistent with a radical mechanism in this system, but the particular sequence of elementary steps is not known. The mechanism is surely intermolecular since other molecules can strongly affect the reaction rate. The large amount of steric hindrance produced by the SF_5O and Cl groups on the same carbon atom should also aid in the rearrangement. Whether the actual mechanism involves hydrogen-atom and/or chlorine-atom exchange between different molecules is not known at this time. However, the explanation for the lack of rearrangement in the 85° reaction flask might be that the products were primarily in the less reactive gas phase because of their high volatilities at this temperature, and the reaction time was not long enough to allow for rearrangement to occur. When the reaction time was extended to 15 min, significant amounts of VI could be isolated from the reaction mixture.

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