and 1 mL of triethylamine. The mixture was heated, with stirring, at reflux for 31 h. After cooling, the solvent was allowed to evaporate at ambient temperature. The residue was extracted with cyclohexane, and the extract was placed on a column of neutral alumina. The column was eluted with toluene to remove a green band which contained a single component, as found by TLC (SiO_2, $CHCl_3$). Evaporation of the solvent yielded 35 mg (22%) of dark green microcrystalline powder.

Anal. Calcd for $C_{92}H_{102}N_{20}Ru$: C, 69.54; H, 6.47; N, 17.63. Found: C, 69.65; H, 6.4; N, 17.55.

Preparation of (4′-MeL)RuL–LRuL–LRu(4′-MeL) (14). To 70 mg (0.044 mmol) of HL–LRuL–LH and 52 mg (0.11 mmol) of (4′-MeLH)$RuCl_3{\cdot}C_2H_5OH$ was added 10 mL of dioxane and 1 mL of triethylamine; the mixture was heated at reflux with stirring for 24 h. The solvent was allowed to evaporate at ambient temperature, and the residue was extracted with cyclohexane and with toluene. The combined extracts were chromatographed over neutral alumina. A green band was eluted with toluene that produced a single spot on TLC (SiO_2, $CHCl_3$). A 70% yield of dark green microcrystals was obtained from cyclohexane–diethyl ether.

Anal. Calcd for $C_{132}H_{134}N_{30}Ru_3$: C, 64.87; H, 5.53; N, 17.20. Found: C, 64.55; H, 5.2; N, 17.2. Molecular weight: calculated, 2444; found, 2450 ± 70 (50 °C, toluene).

Physical Measurements. Procedures for making electrochemical measurements have been described previously.[2] Cyclic voltammograms and differential pulse voltammograms were obtained on millimolar solutions of the compound of interest. Potentials for the complexes were measured vs. that of ferrocene.[14] The formal potentials were then adjusted to potentials vs. NHE with assumption of a value of 0.400 V for the ferrocene/ferrocenium couple. When ferrocene overlapped with the wave under investigation, the cobaltocene/cobaltocenium couple, −0.936 V vs. NHE, was used as an internal standard. Magnetic susceptibility measurements were obtained on samples at ambient temperature with use of a Cahn Instruments Faraday balance, with $HgCo(SCN)_4$ as a calibrant. Diamagnetic corrections were made with use of Pascal's constants. Proton NMR spectra were obtained on a Varian EM-390 NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as a reference. Electronic spectra were recorded on a Cary 14 spectrophotometer. Solution spectra were obtained with use of 1-cm matched quartz cells. Elemental analyses were performed by the California Institute of Technology analytical facility and by Galbraith Laboratories, Knoxville, TN. Molecular weight determinations by vapor osmometry were made with a Wescan/Corona molecular weight apparatus.

Acknowledgment. We appreciate financial assistance from National Science Foundation Grant No. CHE80-24831 and a Sloan Fellowship to R.R.G.

Registry No. **3**, 82056-43-7; **4**, 82044-84-6; **5**, 82044-85-7; **6**, 82044-86-8; **8**, 82044-87-9; **9**, 82044-88-0; **10**, 82044-89-1; **11**, 82056-44-8; **12**, 82044-90-4; **13**, 82044-91-5; **14**, 82056-45-9; (5′-ClLH)$RuCl_3$, 82056-46-0; (4′-MeL)RuL–LRu(4′-MeL)$(ClO_4)_2$, 82044-93-7; Ru(4′-MeL)$_2$$PF_6$, 82044-94-8; $Ru(Me_2SO)_4Cl_2$, 11070-19-2; dichlorobis(benzonitrile)palladium(II), 14220-64-5.

Contribution from the Institut für Anorganische und Analytische Chemie,
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Ethylidenesulfur Tetrafluoride[1]

BRIGITTE PÖTTER and KONRAD SEPPELT*

Received February 12, 1982

In a multistep preparation $CH_3CH{=}SF_4$ is prepared starting from $CH_3C{\equiv}COR$ and $SClF_5$. It is a colorless liquid and undergoes slow decomposition at room temperature. Its structure is a trigonal-bipyramidal environment of sulfur with two axial and two equatorial fluorine atoms, and the ethylidene ligand is in an equatorial position also. The methyl group lies in the same plane with the axial fluoride atoms and sulfur. This is derived mainly from its NMR spectra and by comparison with the well-known structure of $CH_2{=}SF_4$, the only other known species of this type.

Introduction

Sulfur ylides do not have the importance of phosphorus ylides, mainly because of their more limited use in organic preparations. They are well documented, however,[2] and are derivatives of either $(CH_3)_2S^{\delta+}CH_2^{\delta-}$ or $(CH_3)_2SO^{\delta+}CH_2$.[3] The preparation[4] and structural investigations[5–8] of $CH_2{=}SF_4$ opened a new area of sulfur ylide chemistry. This compound is remarkable for its high stability and having a sulfur–carbon double bond with little ylidic character. These features seemed to be so unique that we undertook a long search to determine if any other related species of $CH_2{=}SF_4$ could be made. The only successful result so far is the preparation of $CH_3CH{=}SF_4$, which is described here in detail.

Experimental Section

General Data. ^1H and ^{19}F NMR spectra were recorded on a Varian EM 360 instrument; IR spectra were taken on a Beckman IR 12 and mass spectra on a Varian MAT CH 4.

Reagents. Sulfur chloride pentafluoride was either prepared from ClF and SF_4[9] or purchased from PCR Inc., Gainsville, FL. 1-Methoxy-2-methylacetylene and 1-ethoxy-2-methylacetylene were prepared according to literature methods.[10,11]

1-Methyl-1-(pentafluorosulfonyl)-2-chloro-2-methoxyethene. A 1-mol sample of sulfur chloride pentafluoride and 200 mL of dry $CFCl_3$ (Freon 11) as solvent are condensed into a 500-mL glass vessel using a glass vacuum line. After addition of 1 atm of dry argon, the glass vessel was equipped with a −50 °C reflux cooler, magnetic stirrer, and a dropping funnel. A 1-mol sample of 1-methoxy-2-methylacetylene in 50 mL of $CFCl_3$ is added slowly, and the liquid mixture is irradiated by a focusable 500-W mercury high-pressure lamp. The reaction temperature is allowed to rise from −20 °C (boiling point bp of $SClF_5$) to +23 °C boiling point of solvent) over a period of several

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[1] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

[2] B. U. Trost and L. S. Melvin, Jr., in "Organic Chemistry", Vol. 31, Academic Press, New York, 1975.

[3] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

[4] G. Kleemann and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **17**, 516 (1978).

[5] H. Bock, J. E. Boggs, G. Kleemann, D. Lentz, H. Oberhammer, E. M. Peters, K. Seppelt, A. Simon, and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, **18**, 944 (1979).

[6] A. Simon, E. M. Peters, D. Lentz, and K. Seppelt, *Z. Anorg. Allg. Chem.*, **468**, (1980).

[7] H. Oberhammer and J. E. Boggs, *J. Mol. Struct.*, **56**, 107 (1979).

[8] S. Sunder, H. H. Eysel, G. Kleemann, and K. Seppelt, *Inorg. Chem.*, **18**, 3208 (1979).

[9] F. Nyman, H. L. Roberts, and T. Seaton, *Inorg. Synth.*, **8**, 160–5.

[10] J. R. Nori and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **74**, 284 (1959).

[11] H. J. Alkema and J. F. Arens, *Recl. Trav. Chim. Pays*-Bas, **79**, 1257–81 (1960).

hours and the reaction is then complete.

The total mixture is distilled through a 1-m spinning-band column, beginning at atmospheric pressure and ending at 20 mbar. The product distills at 40–45 °C (20 mbar) as a colorless, stable liquid (yield 197 g, 85%): ^{1}H NMR δ_{OCH_3} 3.79, δ_{CH_3} 217 ($J_{CH_3\text{-}F}$ = 0.8 Hz); ^{19}F NMR, AB$_4$ pattern, δ_A −83.83, δ_B −63.25 (J_{AB} = 151.3 Hz).

1-Methyl-1-(pentafluorosulfonyl)-2-chloro-2-ethoxyethene. This preparation is analogous to that for 1-methyl-1-(pentafluorosulfonyl)-2-chloro-2-methoxyethene, starting from 1-ethoxy-2-methylacetylene. It is a colorless liquid and is obtained in 85% yield: ^{1}H NMR $\delta_{CH_3(-CH_2)}$ 1.37, $\delta_{CH_3(-C=)}$ 2.20, $\delta_{CH_2(-CH_3)}$ 4.16 ($J_{CH_2\text{-}CH_3}$ = 7.0 Hz); ^{19}F NMR, AB$_4$ pattern, δ_A −83.63, δ_B −63.33 (J_{AB} = 147.3 Hz); bp 45 °C (20 mbar).

1-(Pentafluorosulfonyl)propionyl Chloride. A 0.85-mol sample of 1-methyl-1-pentafluorosulfonyl-2-chloro-2-alkoxyacetylene is filled into a glass ampule, and on the glass vaccuum line a 3–5 molar excess of water-free hydrogen bromide is added under cooling with liquid nitrogen. After being sealed, the ampule is warmed to room temperature and then heated for about 0.5 h to 70 °C. The ampule is opened under cooling, and the contents are distilled on the spinning-band column. The propionyl chloride appears as colorless liquid: bp 50 °C (20 mbar), 90% yield; ^{1}H NMR δ_{CH_3} 1.76, δ_{CH} 4.96 ($J_{CH_3\text{-}CH}$ = 7.0 Hz, $J_{CH\text{-}F_6}$ = 2 Hz, $J_{CH\text{-}Fb}$ = 5,6 Hz); ^{19}F NMR, AB$_4$ pattern, δ_A −77.8, δ_B −62.9 (J_{AB} = 149.8 Hz). Any water contamination of the hydrogen bromide will give equivalent amounts of the ester SF$_5$CH(CH$_3$)C(O)OR, which could not be used further.

1-(Pentafluorosulfonyl)propionic Acid. A 0.7-mol sample of 1-(pentafluorosulfonyl)propionyl chloride is slowly added to 150 mL of water at 20 °C. A weak exothermic reaction is observed. The two reactants do not mix completely. After 3 h of stirring, the organic phase is extracted several times with methylene chloride, the solvent is distilled, and the free acid is sublimed at room temperature on to a −25 °C cold finger at 0.01 mbar. At the beginning of the sublimation, the ester SF$_5$CH(CH$_3$)(O)OR appears as colorless liquid, if the hydrogen bromide of the previous step was not absolutely free of water. 1-(Pentafluorosulfonyl)propionic acid is a colorless, crystalline solid: mp 43 °C; yield 95%; ^{1}H NMR (CFCl$_3$) δ_{CH_3} 1.73, δ_{CH} 4.53, δ_{OH} 12.03 ($J_{CH_3\text{-}CH_2}$ = 7.0 Hz, $J_{CH_3\text{-}F_b}$ = 2.0 Hz, $J_{CH\text{-}F_b}$ = 5.6 Hz); ^{19}F NMR, AB$_4$ pattern, δ_A −78.3, δ_B −60.1 (J_{AB} = 141.0 Hz); IR spectrum (solid in KBr) ν_{OH} 3120 (m, br), ν_{CH_3} CH 2995 (w), 2943 (w), 2900 (w), $\nu_{C=O}$ 1739 (st), ν_{SF} 878 (st), 843 (st) cm^{-1}; mass spectrum (70 eV) *m/e* 200 (parent peak C$_3$H$_5$O$_2$SF$_5^+$, 4.3%), 183 (C$_3$H$_4$OSF$_5^+$, 73.5%), 181 (C$_3$H$_5$O$_2$SF$_4^+$, 8.6%), 161 (C$_3$H$_4$O$_2$SF$_4^+$, 26.5%), 136 (C$_2$H$_4$SF$_4^+$, 45.3%), 127 (SF$_5^+$, 100%), 108 (SF$_4^+$, 48.2%), 89 (SF$_3^+$, 65%), 70 (SF$_2^+$, 63.3%). Anal. Calcd for C$_3$H$_5$O$_2$SF$_5$: C, 18.00; H, 2.50; S, 16.00; F, 47.5. Found: C, 18.18; H, 2.52; S, 16.23; F, 47.2.

Silver Salt of the 1-(Pentafluorosulfonyl)propionic Acid. A 0.6-mol sample of 1-(pentafluorosulfonyl)propionic acid, dissolved in 200 mL of water, is added slowly to 0.3 mol of freshly precipitated and alkali-free silver carbonate in 300 mL of water. The evolution of carbon dioxide causes foaming. After complete addition, the mixture is stirred for 1 h at room temperature, the undissolved silver carbonate is filtered off, and the resulting clear liquid is evaporated to dryness finally under a high vacuum at 50 °C. The dryness of the salt is essential for a good yield in the next step. The silver salt was used as such without further characterization.

1-Bromo-1-(pentafluorosulfonyl)ethane. A 0.6-mol sample of 1-(pentafluorosulfonyl)propionic acid is placed in a 200-mL stainless-steel autoclave, and on the glass vacuum line dry 100 mL of CFCl$_3$ (Freon 11) and 0.7–0.8 mol of dry bromine are condensed into it. After being warmed to 22 °C, the autoclave is vigorously shaken over night at 60 °C. The volatile materials are then removed at 22 °C and condensed in vacuo at −196 °C. The remaining solid (AgBr) in the autoclave is extracted twice with 50 mL of CFCl$_3$, and all liquids are combined and carefully distilled through a spinning-band column. At the beginning carbon dioxide evolves. 1-Bromo-1-(pentafluorosulfonyl)ethane distills at 99 °C under normal pressure as a colorless, stable liquid: yield 82%; ^{1}H NMR δ_{CH_3} 2.11, δ_{CH} 5.55 ($J_{CH_3\text{-}CH}$ = 6.6 Hz, $J_{CH_3\text{-}F_b}$ = 2.4 Hz, $J_{CH\text{-}F_b}$ = 5.0 Hz); ^{19}F NMR, AB$_4$ pattern, δ_A −77.5, δ_B −52.25 (J_{AB} = 143 Hz).

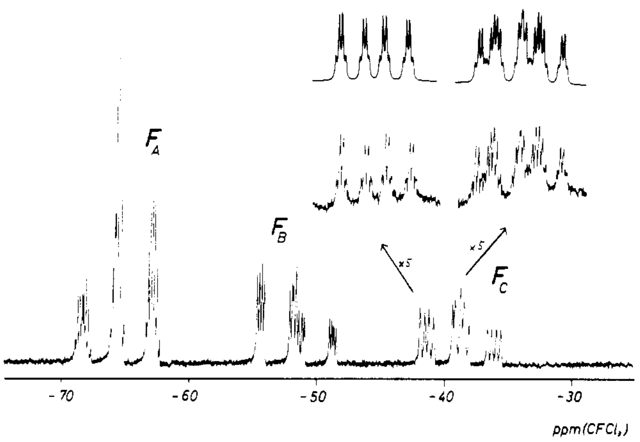


Figure 1. ^{19}F NMR spectrum of CH$_3$CH=SF$_4$, room temperature, neat liquid. The inserts show fine structure of some lines. The interpretation is straightforward, e.g., signal F$_C$: triplet by coupling to F$_A$ (149.9 Hz), doublet by coupling to F$_B$ (21.6 Hz), doublet by coupling to =CH– (39.48 Hz), and quartet by coupling to –CH$_3$ (1.6 Hz). The other fluorine resonances can be interpreted likewise. For comparison the computer simulations of the two expanded parts of the spectrum are shown (above).[14]

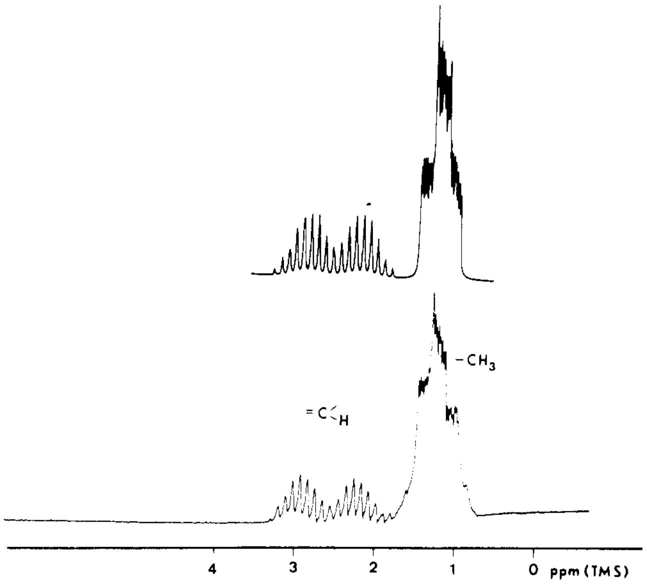


Figure 2. ^{1}H NMR spectrum of CH$_3$CH=SF$_4$, room temperature, neat liquid. The methine proton is strongly coupled to F$_C$, and the methyl protons are coupled strongly to F$_A$. The computer simulation is shown in the upper half.[14]

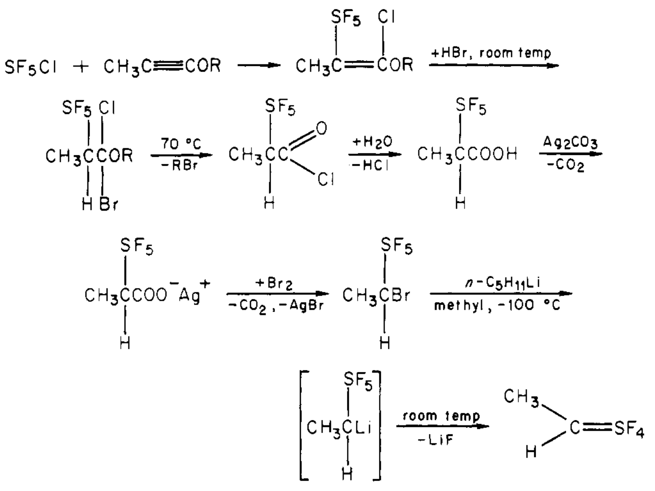
Ethylidenesulfur Tetrafluoride. A solution of 0.2 mol of 1-bromo-1-(pentafluorosulfonyl)ethane in dry methylcyclohexane is cooled to −100 °C. Under magnetic stirring, 0.2 mol of *n*-pentyllithium solution in methylcyclohexane is slowly added. The temperature should not rise above −100 °C. During the addition a white precipitate is formed, probably SF$_5$CH(CH$_3$)Li, which makes the stirring increasingly difficult. After 1 h of additional stirring at −100 °C, the mixture is allowed to warm to room temperature. At about −70 °C the precipitate disappears and LiF is formed. The mixture is cooled again to −40 °C, and in vacuo all volatiles are pumped into a −196 °C trap. Under these conditions the product contains mainly ethylidenesulfur tetrafluoride and a little pentane, methylcyclohexane, and *n*-pentyl bromide. A rapid distillation through a 10-cm spinning-band column affords 0.06 mol (30% yield) of colorless ethylylidenesulfur pentafluoride: bp 27 °C; mp below −120 °C (decomposes slowly at room temperature; (see below): ^{1}H NMR (see also Figure 1) δ_{CH_3} 1.16, δ_{CH} 2.53; ^{19}F NMR (see also Figure 2), A$_2$BC pattern, δ_A −65.3, δ_B 51.4, δ_C 38.6 (for coupling constants, see the detailed discussion); IR (gas) $\nu_{=CH}$ 3120 (w), ν_{CH_3} 2966 (m), 2880 (m), δ_{CH_3} 1446.5 (w), $\nu_{C=S}$ 1200 (m), 1081 (w), 1029 (vw), 932.5 (s) ν_{SF} 844.5 (m), 816.7 (vs), 723.8 (s), 715.8 (s), 595.2 (w), 555.5 (m) cm^{-1}; mass spectrum (70 eV) *m/e* 136 (C$_2$H$_4$SF$_4^+$, 86%), 89 (SF$_3^+$, 100%, 70 (SF$_2^+$, 26%), 47 (C$_2$H$_4$F$^+$, 17%).

Thermal Decomposition of Ethylidenesulfur Tetrafluoride. A 30-mL glass ampule is filled with a weighted amount (5 g) and sealed. After 1 week of standing at room temperature, the colorless liquid turns black. The ampule is opened, and all volatile materials are trapped at −196 °C, leaving a black tar behind. The very complex mixture of the volatiles has been analyzed with IR and NMR spectroscopy.

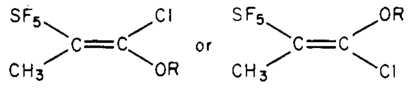
The following products were identified: SiF_4, SOF_2, CH_3CHF_2, $C_2H_5SF_5$,[12] and a very small amount of a compound that is probably $FSOCF_2CH_3$. If decomposition is allowed to take place in a poly(chlorotrifluoroethylene) vessel, the resulting mixture is the same, except HF is observed instead of SiF_4.

Results

Ethylidenesulfur tetrafluoride has been prepared according to the reaction scheme



The addition of SF_5Cl to the acetylene $CH_3C{\equiv}COR$ gives only one isomer. The formation of $CH_3(SF_5)C{=}C(Cl)OR$ is favored over $CH_3(Cl)C{=}C(SF_5)OR$, probably because of the radical nature of the reaction. However, there are still two geometrical isomers; a decision between them has not been possible. NMR findings indicate only that one isomer is present.



The reaction of the olefin with gaseous HBr involves two steps. The simple addition of HBr can clearly be observed by NMR methods, but no attempt was made to isolate this intermediate. The desired 1-(pentafluorosulfanyl)propionic acid chloride was obtained after heating, which causes the elimination of RBr.

Aqueous hydrogen bromide, however, addes to the olefin forming the ester $CH_3(SF_5)CHC(O)OR$, which could not be used further because all attempts of acidic or basic cleavage resulted in complete decomposition. The transformation of the acid via the bromide into the desired product $CH_3CH{=}SF_4$ is completely analogous to the preparation of $CH_2{=}SF_4$.[4]

All new compounds could be completely identified by NMR methods. While the SF_5-containing materials are easily detected by their typical AB_4 pattern in the ^{19}F NMR spectra, the novel ethylidenesulfur tetrafluoride exhibits very complex NMR spectra, whose interpretation was nevertheless straightforward (see Figures 1 and 2).

Basically, the ^{19}F NMR spectrum (Figure 1) is an A_2BC pattern with relatively large coupling constants between the different fluorine atoms (16.2–157.3 Hz). The J_{H-F} coupling constants are in the range of 3.0–39.5 Hz and are better taken from the ^{19}H NMR spectra (see inserts in Figure 1). The various coupling constants are shown in Figure 3, as calculated by computer simulation. The assignment is somewhat ambiguous because F_B and F_C can be exchanged. However, this would not affect the proof of the structure. The spectra remain unchanged on cooling, and because of the decomposition, no recording of high-temperature spectra was attempted.

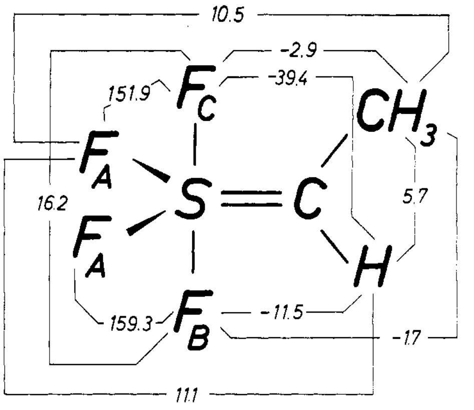


Figure 3. Structure of $CH_3CH{=}SF_4$, as derived from NMR findings and in analogy to $CH_2{=}SF_4$.[5-7] The figures indicate the NMR coupling constants in Hz, which were obtained by computer simulation.[14]

Discussion

The preparation of ethylidenesulfur tetrafluoride is the second example of this new class of compounds, the first being the unsubstituted species $CH_2{=}SF_4$.[4] The methods of preparation for both compounds are related. The first step is always the addition of SF_5Cl to a suitable multiple-bond system followed by further steps designed to produce the geminal bromo(pentafluorosulfonyl) compounds, here $CH_3CHBrSF_5$.

The last step involving the elimination of LiF may be a general procedure to prepare $R_2C{=}SF_4$ compounds, if the appropriate bromo compounds R_2BrCSF_5 are available. However, our experience with a few compounds R_2BrCSF_5 have shown that the reaction seems to be limited to R = alkyl. Species such as $CH_2{=}CBrSF_5$, Br_2HCSF_5, etc. have not produced any $>C{=}SF_4$ compounds thus far.

The structure of $CH_3CH{=}SF_4$ is schematically shown in Figure 3 and corresponds to the well-investigated structure of $CH_2{=}SF_4$.[5-7] The sulfur coordination is trigonal bipyramidal, the double-bonded carbon occupies an equatorial position, and the substituents on carbon are situated in the axial plane of the molecule. Furthermore the structure is rigid, as indicated by NMR measurements at different temperatures. The C=S stretching frequency at 1200 cm^{-1} indicates a strong double bond (1167 cm^{-1} in $CH_2{=}SF_4$[8]).

The overall geometry of the molecule may be rationalized, if it is assumed that the π-electron density of the double bond is indeed mostly located in the equatorial plane (rather than of cylindrical shape as assumed in $F_3P{=}O$ or $F_4S{=}O$). So the axial positioning of the carbon substituents is then a consequence of this.[13]

It is questionable if $CH_3CH{=}SF_4$ or any other possible alkylidenesulfur tetrafluoride are ylides in the original sense.

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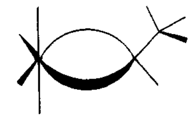
(12) G. Kleemann and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **20**, 1037 (1981).

(13) A simpler rationale for the structure is obtained if the double bond is represented by two bent single bonds. By linking an octahedron to a tetrahedron, the position of the carbon substituents in the axial plane becomes evident:



(14) We are indebted to H. Nies, Berlin, for the computer simulation of the NMR spectra of $CH_3CH{=}SF_4$.

The rigidity of the molecular array and the strong CS bond indicate that the double-bond formulation of the two canonical forms

$$R_2C{=}SF_4 \longleftrightarrow R_2\bar{C}{-}\overset{+}{S}F_4$$

certainly has major importance, quite in contrast to normal ylides. However, there are many examples where $CH_2{=}SF_4$ does react as polar species in addition reactions.[12]

The chemistry of $CH_3CH{=}SF_4$ has not been investigated so far, except for its thermal decomposition at ambient temperature. The formation of $CH_3CH_2SF_5$ is a clear indication that HF is among the decomposition products since $CH_3CH{=}SF_5$ is expected to add HF rapidly, as does $CH_2{=}SF_4$, forming CH_3SF_5. The presence of CH_3CHF_2 may indicate some intermediate formation of methylcarbene.

Conclusion

The method of lithiation of a 1-bromo-1-pentafluorosulfonyl compound and its LiF elimination may be a general procedure for preparing $>C{=}SF_4$ species, as long as the carbon atom is alkyl substituted. The structure of the alkylidenesulfur tetrafluorides are probably all alike, as indicated by two known cases.

Registry No. $CH_3CH{=}SF_4$, 81553-81-3; $CH_3C{\equiv}COCH_3$, 13169-01-2; $CH_3C(SF_5){=}C(Cl)OCH_2CH_3$, 81535-06-0; $CH_3C{\equiv}COCH_2CH_3$, 14273-06-4; $CH_3CH(SF_5)COCl$, 81535-07-1; $CH_3CH(SF_5)COOH$, 81535-08-2; $CH_3CH(SF_5)COO^-Ag^+$, 81553-82-4; $CH_3CH(SF_5)Br$, 81535-09-3; $CH_3C(SF_5){=}C(Cl)OCH_3$, 81535-10-6; $SClF_5$, 13780-57-9.

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Rate Study on the Rearrangement of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ Isomers and Mechanistic Implications

BAEK OH and THOMAS ONAK*

Received December 18, 1981

The rates of rearrangement of 5- and 3-CH_3-*closo*-2,4-$C_2B_5H_6$ at 295 °C to an equilibrium mixture of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers were measured and correlated to possible mechanisms. Of two possible mechanistic routes (diamond–square–diamond, DSD, and triangle face rotation, TFR) the DSD pathway is in much better accord with the observed rate patterns than the TFR route.

Introduction

It has been previously reported that 5-CH_3-*closo*-2,4-$C_2B_5H_6$ slowly equilibrates with a mixture of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers at 300 °C, with the *B*-methyl group showing a positional preference $3 > 1$, $7 > 5$, 6 based on enthalpy considerations alone.[1] A related set of equilibria and methyl group positional preferences were also established for B-polymethylated derivatives of 2,4-$C_2B_5H_7$. For the 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ rearrangement a rate study was found to be consistent with two viable mechanisms, diamond–square–diamond (DSD)[2-8] and triangle face rotation (TFR).[8-12] In an attempt to differentiate between these two possible mechanistic pathways, we conducted a rearrangement rate study on two isomers of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$.

Experimental Section

Materials and Handling of Chemicals. The parent *closo*-2,4-$C_2B_5H_7$ was obtained from Chemical Systems Inc., Irvine, CA. Methyl chloride (J. T. Baker) was used without further purification. Aluminum trichloride (Matheson Coleman and Bell) was freshly sublimed into the reaction vessel immediately prior to use. All materials were handled in conventional high-vacuum equipment or in a drybox under an atmosphere of dry nitrogen. Cold-column fractionation was effected with an apparatus similar to that described previously.[13]

Table I. ^1H NMR Data for 1-, 3-, and 5-CH_3-*closo*-2,4-$C_2B_5H_6$

compd	position	δ^a	$J(H-^{11}B)$/ Hz
1-CH_3-2,4-$C_2B_5H_6$	$CH_3B(1)$	−0.47	*b*
	HC(2,4)	5.58	
	HB(3)	4.94	190
	HB(5,6)	4.10	163
	HB(7)	−0.03	178
3-CH_3-2,4-$C_2B_5H_6$	HB(1,7)	0.18	176
	HC(2,4)	5.25	
	$CH_3B(3)$	1.02	
	HB(5,6)	4.03	168
5-CH_3-2,4-$C_2B_5H_6$	HB(1,7)	0.22	184
	HC(2)	5.36	
	HB(3)	4.87	190
	HC(4)	5.19	
	$CH_3B(5)$	0.75	*c*
	HB(6)	3.94	167

[a] Relative to internal $(CH_3)_4Si$. [b] An ill-defined pattern, $J \simeq 9$ Hz, was observed that may be due to $H_3CB(1)$ coupling. [c] An ill-defined pattern, $J \simeq 4$ Hz, was observed that is possibly due to $H_3CB(5)$ coupling.

Nuclear Magnetic Resonance. Proton NMR spectra, Table I, were recorded on a Bruker WM-500 instrument and on a FT-Bruker WP-60 equipped with a Fluke 6061 B frequency synthesizer operating at 19.255 MHz and a ENI-320 L amplifier. The boron-11 NMR spectra were obtained on a Varian HA-100 spectrometer operating at 32.1 MHz and on a Bruker WM-500 operating at 160.44 MHz. The proton-decoupled boron-11 NMR spectra at 32.1 MHz were obtained while irradiating at 100.08 MHz with a General Radio 1061 frequency synthesizer, an Electronic Navigation Industries 320 L power amplifier,

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(1) A. P. Fung and T. Onak, *J. Am. Chem. Soc.*, **99**, 5512 (1977); T. Onak, A. P. Fung, G. Siwapinyoyos, and J. B. Leach, *Inorg. Chem.*, **18**, 2878 (1979).

(2) W. N. Lipscomb, *Science (Washington, D.C.)*, **153**, 373 (1966).

(3) R. E. Williams, *Prog. Boron Chem.*, **2**, Chapter 2 (1970).

(4) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).

(5) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).

(6) E. L. Muetterties, *Rec. Chem. Prog.*, **31**, 51 (1970).

(7) E. L. Muetterties, "Boron Hydride Chemistry", Academic Press, New York, 1975, Chapter 1.

(8) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes", Marcel Dekker, New York, 1968, p 70.

(9) T. Onak, *Adv. Organomet. Chem.* **3**, 263 (1965); see p 334.

(10) H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4218 (1967).

(11) H. Hart and W. N. Lipscomb, *J. Am. Chem. Soc.*, **91**, 771 (1969).

(12) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **97**, 4213 (1975).

(13) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).

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