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SHORT COMMUNICATION

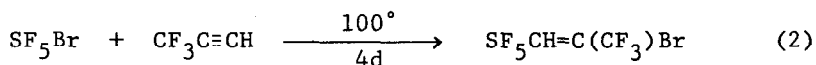
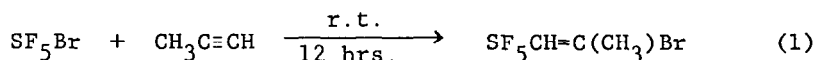
The Addition of SF<sub>5</sub>Br to Propyne and 3,3,3-Trifluoropropyne

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Roberts et al. [1] found that SF<sub>5</sub>Cl adds to the triple bond in acetylene and propyne to produce 2-chlorovinylsulfur pentafluoride (ClCH=CHSF<sub>5</sub>) and 2-chloropropenylsulfur pentafluoride [CH<sub>3</sub>C(Cl)=CHSF<sub>5</sub>]. Previously, we found in our studies of SF<sub>5</sub>Br that addition to fluoroolefins occurs more readily and directly than does addition of SF<sub>5</sub>Cl or S<sub>2</sub>F<sub>10</sub> and that the SF<sub>5</sub> group bonds to the carbon of the fluoroolefins with the most hydrogen [2]. It was of interest to determine whether similar results would be found by adding SF<sub>5</sub>Br to acetylene derivatives.

We have found that SF<sub>5</sub>Br reacts with CH<sub>3</sub>C≡CH and CF<sub>3</sub>C≡CH according to the following equations:

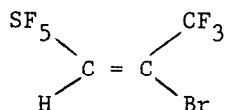


The products are clear, colorless, hydrolytically stable liquids. The product found in equation (2) is a mixture of two isomers that have been separated by gas chromatography (g.c.) and identified via their mass, infrared and NMR spectra.

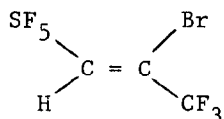
The structure of the addition products were determined from their respective nuclear magnetic resonance (NMR) spectra.

The proton spectra for both isomers of SF<sub>5</sub>CH=C(CF<sub>3</sub>)Br gave a basic five line pattern clearly demonstrating that the SF<sub>5</sub> group

added to the olefinic carbon with the hydrogen. Furthermore, the observed coupling constants for both isomers are in the range expected for gem coupling. In  $\text{SF}_5\text{CH}=\text{CH}_2$ , the  $J_{\text{SF}_5-\text{CH}}$  gem coupling constant was 6.1 Hz while the trans and cis values were respectively 2.3 and  $\approx 0$  Hz [3]. Integration of the areas for the CH peaks in the mixture indicates that the concentration of the two isomers are approximately equal. In order to differentiate between the two isomers, the coupling between  $\text{CF}_3$  and CH groups was examined. For the first g.c. isomer, the  $J_{\text{CF}_3-\text{CH}}$  was 1.0 Hz, while for the second g.c. isomer, the  $J_{\text{CF}_3-\text{CH}}$  was too small to be resolved. Finnegan and Norris [4] found that for trans-1,2-dichloro-3,3,3-trifluoropropene the proton chemical shift was 7.11 ppm and  $J_{\text{CF}_3-\text{CH}} = 1.1$  Hz, while for the cis isomer the proton chemical shift was 6.64 ppm and  $J_{\text{CF}_3-\text{CH}} < 0.2$  Hz. Therefore, based on both proton chemical shift and  $J_{\text{CF}_3-\text{CH}}$  coupling constants, the first g.c. isomer is assigned a structure in which the  $\text{CF}_3$  and H are trans to each other, while for the second g.c. isomer these groups are cis to one another.



First g.c. isomer



Second g.c. isomer

The  $^{19}\text{F}$ -NMR spectrum clearly showed separate  $\text{AB}_4$  patterns for the  $\text{SF}_5$  group as well as two distinct  $\text{CF}_3$  resonances. The chemical shifts for these resonances are in the region found for other  $\text{SF}_5$  and  $\text{CF}_3$  compounds.

The proton spectrum for  $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$  gave a basic five line pattern centered at 6.64 ppm which shows that the  $\text{SF}_5$  group is attached to the olefinic carbon containing the hydrogen. The five line pattern showed additional splitting due to coupling between  $\text{SF}_5$  and F of the  $\text{SF}_5$  group. The methyl protons exhibited a six line pattern caused by the splitting of the  $\text{SF}_4$  and CH groups for which  $J_{\text{CH}_3-\text{SF}_4} = J_{\text{CH}_3-\text{CH}}$ . The  $^{19}\text{F}$ -NMR spectrum showed the expected  $\text{AB}_4$

pattern for the SF<sub>5</sub> group. Integration of the areas for the CH and CH<sub>3</sub> peaks gave the expected ratio of 1:3. In an attempt to prepare its isomer, SF<sub>5</sub>CH=C(CH<sub>3</sub>)Br was heated to 125° for 20.7 hrs. Gas chromatographic and NMR analyses indicated only starting material.

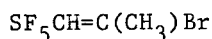
The infrared spectrum for SF<sub>5</sub>CH=C(CH<sub>3</sub>)Br contains the C=C stretch at 1643 cm<sup>-1</sup>. The absorption bands at 883 and 863 cm<sup>-1</sup> represent the S-F stretching frequency. The S-F deformation mode is located at 598 cm<sup>-1</sup>. The absorption band at 3100 cm<sup>-1</sup> is assigned to the C-H stretching mode. The symmetric and asymmetric bending vibration for the CH<sub>3</sub> group are tentatively assigned to the 1383 and 1435 cm<sup>-1</sup> absorption bands respectively.

The C=C stretching frequencies for the E and Z isomers of SF<sub>5</sub>CH=C(CF<sub>3</sub>)Br are located at 1637 and 1630 cm<sup>-1</sup> respectively. The shift to lower frequency for Z isomer is probably best explained by a mass effect and is consistent with the NMR assignment. The S-F stretching frequencies for the E and Z isomers are located in the very intense broad band centered on or about 882 cm<sup>-1</sup>. The S-F deformation mode for both isomers is located at 604 cm<sup>-1</sup>. The absorption band at 3100 cm<sup>-1</sup> for both isomers is assigned to the C-H stretching mode. These assignments are in good agreement with those reported for other SF<sub>5</sub> containing compounds [5]. Bands in 1340-1100 cm<sup>-1</sup> region are probably associated with the CF stretching modes.

The major mass spectra peaks for these new SF<sub>5</sub> olefins and SF<sub>5</sub>CH=CH<sub>2</sub> are listed in Table I. For both isomers of SF<sub>5</sub>CH=C(CF<sub>3</sub>)Br strong parent peaks were observed; SF<sub>5</sub>CH=CH<sub>2</sub> only showed a weak parent peak. The major peaks for both the E and Z isomers were essentially the same with the exception that the E isomer had a relatively higher tendency to lose a fluorine atom as indicated by the relative intensity of peaks at m/e = 281 and 283, the SF<sub>4</sub>C<sub>2</sub>HCF<sub>3</sub>Br<sup>+</sup> peaks. It is thought that the loss of a fluorine atom is from the SF<sub>5</sub> group rather than a CF<sub>3</sub> group. The mass spectrum of SF<sub>5</sub>CH=CH<sub>2</sub> contains a peak, attributable to SF<sub>4</sub>C<sub>2</sub>H<sub>3</sub><sup>+</sup>, in which the SF<sub>5</sub> group has lost a fluorine.

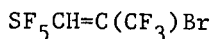
TABLE I

## MASS SPECTRAL DATA\*



$\text{C}_2\text{H}_4^+$  (19),  $\text{C}_3\text{H}^+$  (13),  $\text{C}_3\text{H}_2^+$  (19),  $\text{C}_3\text{H}_3^+$  (100),  
 $\text{C}_3\text{H}_4^+$  (13),  $\text{C}_3\text{H}_4\text{F}^+$  (19),  $\text{SF}_3^+$  (50),  $\text{C}_2\text{H}_3\text{Br}^{79+}$  (6),  
 $\text{C}_2\text{H}_3\text{Br}^{81+}$  (6),  $\text{C}_3\text{H}_4\text{Br}^{79+}$  (19),  $\text{C}_3\text{H}_4\text{Br}^{81+}$  (19),  $\text{SF}_5^+$  (19)  
 $\text{C}_3\text{H}_3\text{FBr}^{79+}$  (19),  $\text{C}_3\text{H}_3\text{FBr}^{81+}$  (19),  $\text{SF}_5\text{C}_3\text{H}_4^+$  (25).

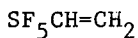
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(mixture of two  
isomers)

$\text{CF}^+$  (12),  $\text{SF}^+$  (25),  $\text{CF}_3^+$  (100),  $\text{SF}_2^+$  (14),  $\text{CHCCF}_2^+$  (30),  
 $\text{SF}_3^+$  (52),  $\text{C}_2\text{CF}_3^+$  (9),  $\text{C}_2\text{HCF}_3^+$  (9),  $\text{SF}_3\text{C}_2^+$  (27),  
 $\text{SF}_5^+$  (30),  $\text{CF}_3\text{CHCBr}^{79+}$  (49),  $\text{CF}_3\text{CHCBr}^{81+}$  (49),  
 $\text{CF}_3\text{CCHFBr}^{79+}$  (29),  $\text{CF}_3\text{CCHFBr}^{81+}$  (29),  
 $\text{SF}_4\text{C}_2\text{HCF}_3\text{Br}^{79+}$  (8),  $\text{SF}_4\text{C}_2\text{HCF}_3\text{Br}^{81+}$  (8),  
 $\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^{79+}$  (30),  $\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^{81+}$  (30).

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$\text{C}_2\text{H}_2^+$  (15),  $\text{C}_2\text{H}_3^+$  (100),  $\text{C}_2\text{H}_3\text{F}^+$  (17),  $\text{SF}_2^+$  (9),  
 $\text{SF}_3^+$  (100),  $\text{SF}_5^+$  (8),  $\text{SF}_4\text{C}_2\text{H}_3^+$  (9),  $\text{SF}_5\text{C}_2\text{H}_3^+$  (3).

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\*Relative peak intensities given in parenthesis.

## EXPERIMENTAL

SF<sub>5</sub>Br was prepared and handled as previously reported (2). Propyne was purchased from Air Products and Chemicals while 3,3,3-trifluoropropyne was purchased from PCR Research Chemicals; both chemicals were used as received. The infrared (IR) spectra of both compounds were taken and they agreed with the published spectra.

The IR spectra were recorded on a Perkin-Elmer 467 spectrometer. The IR gas cell was made of Monel metal and equipped with a Whitey-Brass valve. The cell windows were either AgCl or KRS-5 and the path length of the cell was 8.25 cm. The spectra were calibrated with a polystyrene film.

The purity of the new products was checked via gas chromatography using an Aerograph Autoprep (Model A-700) gas chromatograph. Separations were carried out with a 10' x 3/8" column containing 20% carbowax adsorbed on "Chromosorb W". The column temperature was 59 ±1° with a helium flow rate of 3 ml/sec.

The molecular weights were determined by the vapor density method.

The NMR spectra were recorded with a Varian Model EM 390 Analytical nmr spectrometer operating at 90.00 or 84.67 MHz with TMS (<sup>1</sup>H) or CCl<sub>3</sub>F(<sup>19</sup>F) as internal standards. The mass spectra were taken on a CEC 21-110 B double focus mass spectrometer equipped with a 6KV ion accelerator and operated at 70 volts. Perfluorokerosine (PFK) was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, West Germany.

#### Preparation of SF<sub>5</sub>CH=C(CH<sub>3</sub>)Br

In a 3-liter Pyrex-glass vessel equipped with a Kontes Teflon valve, 6.25 x 10<sup>-2</sup> mole of CH<sub>3</sub>C≡CH and 5.6 x 10<sup>-2</sup> mole of SF<sub>5</sub>Br were condensed at -196°. Upon warming to room temperature a clear colorless liquid and some dark residue were observed. The reaction was complete after 12 hours. Distillation of the mixture gave 1.7 x 10<sup>-2</sup> mole of product in 30% yield; b.p. 109 ±2° (n.c.). The gas chromatogram showed only one peak (retention time

of 12 minutes). Calcd. for  $C_3H_4SF_5Br$ : C, 14.58; H, 1.62; S, 12.96; F, 38.48; Br, 32.36; mol. wt., 246.9. Found: C, 15.37; H, 1.70; S, 12.40; F, 36.5; Br, 34.18; mol. wt. 245.3.

The infrared spectrum gave the following absorption bands ( $cm^{-1}$ ): 3100 (vw), 1643 (m), 1435 (w-m), 1383 (m), 1296 (w), 1084 (m), 980 (s), 883 (vs), 863 (vs), 735 (m), 619 (m), 598 (s, with sh., at 575). The  $^{19}F$  nmr spectra: SF, -81.0 ppm (9 line pattern);  $SF_4$ , -64.6 ppm (complex doublet,  $J_{SF_4-SF} = 141$  Hz). The  $^1H$  nmr spectra: CH, 6.64 ppm (5 lines split into quartets and further split into doublets,  $J_{CH-SF_4} = 8.1$  Hz,  $J_{CH-SF} = 0.6$  Hz);  $CH_3$ , 2.41 ppm (6 lines,  $J_{CH_3-CH} = J_{CH_3-SF_4} = 1.2$  Hz).

### Preparation of $SF_5CH=C(CF_3)Br$

In a 200 ml Hoke stainless steel vessel equipped with a Whitey-Brass valve,  $5.3 \times 10^{-2}$  mole of  $CF_3C\equiv CH$  and  $6.1 \times 10^{-2}$  mole of  $SF_5Br$  were condensed together at  $-195^\circ$ . The mixture was heated at  $100^\circ$  for four days. Distillation of the mixture gave  $3.1 \times 10^{-2}$  mole of product in 58% yield; b.p.  $93 \pm 1^\circ$  (n.c.). Calc'd. for  $C_3HSF_8Br$ : C, 11.96; H, 0.33; S, 10.64; F, 50.52; Br, 26.55; mol. wt. 300.9. Found: C, 11.79; H, 0.40; S, 10.74; F, 50.2; Br, 26.71; mol. wt., 301.8.

The gas chromatogram showed that two compounds were present; the respective retention times were 3.7 min. (first g.c. isomer) and 6.5 min. (second g.c. isomer). The infrared spectrum of the first g.c. isomer gave the following absorption bands ( $cm^{-1}$ ): 3100 (m), 1637 (m), 1285 (w-m), 1262 (vs, b), 1191 (vs, b), 1120 (w-m), 960 (vs with sh. at 982), 882 (vs, b-with sh. at 832), 765 (m-s), 635 (m-s), 604 (m-s), 572 (w), 534 (w). The second g.c. isomer gave the following absorption bands ( $cm^{-1}$ ): 3100 (w), 1664 (w), 1630 (m), 1336 (s), 1285 (w), 1262 (m), 1226 (s), 1191 (vs, b), 1120 (w), 944 (vs), 882 (vs, b), 832 (w), 770 (m-w), 724 (m), 654 (m), 604 (m-s), 572 (w), 534 (w).

The  $^{19}F$  nmr spectra: First g.c. isomer - SF, -75.6 ppm (9 line pattern);  $SF_4$ , -64.1 ppm (complex doublet,  $J_{SF_4-SF} = 149$  Hz);  $CF_3$ , +68.3 ppm (6 line pattern,  $J_{CF_3-SF_4} = J_{CF_3-CH} = 1.0$  Hz). Second g.c. isomer - SF, -74.3 ppm (9 line pattern);  $SF_4$ , -66.5 ppm (complex doublet,  $J_{SF_4-SF} = 144$  Hz);  $CF_3$ , +62.6 ppm

(5 line pattern,  $J_{\text{CF}_3\text{-SF}_4} = 13.7$  Hz,  $J_{\text{CF}_3\text{-CH}} < 0.2$  Hz). The  $^1\text{H}$  nmr spectra: first g.c. isomer - CH, 7.61 ppm (5 line pattern,  $J_{\text{CH-SF}_5} = 7.10$  Hz,  $J_{\text{CH-CF}_3} = 1.0$  Hz). Second g.c. isomer - CH, 7.13 ppm (5 line pattern,  $J_{\text{CH-SF}_5} = 8.60$  Hz). Note: All proton chemical shifts are downfield from TMS.

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