tography. The crystalline material was dissolved in a small amount of hot chloroform and adsorbed on a small amount of silica gel, after which the solvent was evaporated (air stream). The silica gel was then added to the top of a 20-cm column of dry silica gel and covered with an additional 3 cm of fresh dry silica gel. The column was packed tightly with glass wool and inverted into a 250 ml graduate cylinder containing chloroform. After 2 hr the solvent level had reached the top of the inverted column. The column was removed and again inverted, and two fractions (already partially separated) were eluted with further addition of solvent. This procedure allowed efficient separation of two materials with very similar retention times. The first fraction from this separation was identified as unreacted **1**. The second fraction gave yellow crystals of the **imino ethyl ether of 2-nitro-3,4,5,6-tetramethylacetanilide** (**3**): mp 79.5–81.0°; ir (CCl_4) 1660 ($\nu_{C=N}$) and 1520 and 1380 cm^{-1} (ν_{NO_2}); uv λ_{max}^{MeOH} 208 mμ (log ϵ 4.42); nmr (CCl_4) τ 8.68 (t, 3 H, J = 7 Hz), 8.27, 8.00, and 7.86 (s, 3 H each), 7.76 (6 H, br s), and 5.85 (q, 2 H, J = 7 Hz).

Anal. Calcd for $C_{14}H_{20}N_2O_3$: C, 63.62; H, 7.63; N, 10.60. Found: C, 63.46; H, 7.53; N, 10.57.

The yields were not determined precisely, but for purified, sublimed material were about 25% for **2** and 5% for **3**. Initial yields before purification were probably appreciably higher, but some tars were produced.

Irradiation of **1** in ethanol gave a fair yield of **2** but no **3**.

Diaminoprehnitene. From 1.—Catalytic hydrogenation of a solution of 0.2 g (0.894 mmol) of **1** in 10 ml of absolute ethanol over 5% Pd/C catalyst (25 mg) at 20 psig and room temperature for 2.5 hr afforded, after filtration and evaporation of the solvent, an essentially quantitative yield of diaminoprehnitene as white crystals: mp 142–144° (lit.[8] mp 144°); nmr (CCl_4) τ 7.86 and 7.92 (s, 6 H each) and 6.83 (br, 4 H). The compound darkened on standing in air.

From 2.—Hydrogenation of **2** as described for **1** gave the same product (melting point, mixture melting point, and nmr).

Registry No.—**1**, 18801-63-3; **2**, 18801-64-4; **3**, 18801-65-5.

The Reaction of SF_5Br with Fluoro Olefins

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SF_5Cl will add to fluoro olefins[3] at elevated temperatures and in the presence of free radicals to produce 2-chloropolyfluoroalkylsulfur pentafluorides.

Also, S_2F_{10} will react with olefins and fluoro olefins under pressure and elevated temperatures to give small amounts of SF_5 addition products.[4,5]

No report has appeared in the literature dealing with the SF_5Br addition to fluoro olefins.[6]

We have found that SF_5Br, produced from the reaction of S_2F_{10} and Br_2 at elevated temperatures (eq 1),

$$S_2F_{10} + Br_2 \xrightarrow{\Delta} 2SF_5Br \qquad (1)$$

Table I

2-Bromopolyfluoroalkylsulfur Pentafluorides

Compd	Bp,[a] °C	Mol wt Calcd	Mol wt Found	Yield,[b] %	Calcd, % C	H	Br	Cl	S	Found, % C	H	Br	Cl	S
SF_5CH_2CHFBr	99.5–100.5	253	255	70	9.49	1.20	31.58	0.00	12.67	9.88	1.31			12.41
$SF_5CH_2CF_2Br$	86–87	271	270	70	8.86	0.74	29.49	0.00	11.83	9.15	0.76			11.01
SF_5CHFCF_2Br	74–75	289	288	46	8.31	0.35	27.65	0.00	11.10	8.25	0.38			10.88
$SF_5C_2F_3ClBr$	94–95	323.4	323	60	7.43	0.00	24.71	10.96	9.91	7.45	0.00	25.29	11.94	9.53

[a] Boiling points were recorded at 766 ± 1 mm of Hg. [b] The yield was based on the assumption that only SF_5Br was added. However, we have found that SF_6, SF_4, and S_2F_{10} transferred over with the SF_5Br. Therefore, the actual yields are higher than the ones given here. Note: The boiling point of $SF_5CH_2CH_2Br$ is 109.5° at 760 mm of Hg. Thus, replacing the hydrogens with fluorines in $SF_5CH_2CH_2Br$ causes the boiling point to drop approximately 10° per hydrogen atom.

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[1] Taken from a M. S. thesis to be submitted to Portland State University.

[2] To whom inquiries should be addressed.

[3] J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 2070 (1961).

[4] M. Tremblay, *Can. J. Chem.*, **43**, 219 (1965).

[5] H. L. Roberts, *J. Chem. Soc.*, 3183 (1962).

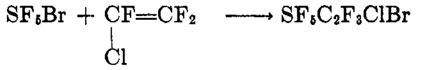
[6] C. Merrill found that SF_5Br added to ethylene giving $SF_5CH_2CH_2Br$. See C. Merrill, Ph.D. Thesis, University of Washington, Seattle, Wash., 1962.

reacted at room temperature in a Pyrex glass vessel with $CH_2{=}CHF$, $CH_2{=}CF_2$, $CHF{=}CF_2$, and $ClCF{=}CF_2$ according to eq 2–5.

$$SF_5Br + CH_2{=}CHF \longrightarrow SF_5CH_2CHFBr \quad (2)$$

$$SF_5Br + CH_2{=}CF_2 \longrightarrow SF_5CH_2CF_2Br \quad (3)$$

$$SF_5Br + CHF{=}CF_2 \longrightarrow SF_5CHFCF_2Br \quad (4)$$



$$SF_5Br + \underset{\displaystyle Cl}{\underset{|}{C}}F{=}CF_2 \longrightarrow SF_5C_2F_3ClBr \quad (5)$$

These reactions proceeded smoothly at room temperature and were essentially complete after 12 hr. However, reaction 2 showed signs of decomposition (darkening). The products when formed usually are clear, water-white, readily distillable liquids. In Table I are listed the boiling points along with the elemental analysis, molecular weight, and yield results for these new compounds. The infrared (ir) spectra were recorded for these compounds and a summary of the peaks together with their respective intensities is given in Table II.

TABLE II

INFRARED SPECTRA DATA[a]

	Cm^{-1}[a]
SF_5CH_2CHFBr	1416 (w),[a] 1364 (w), 1307 (w), 1196 (w), 1086 (s), 1042 (s), 900 (vs), 874 (vs), 847 (vs), 751 (w), 681 (w)
$SF_5CH_2CF_2Br$	1416 (w), 1323 (w), 1274 (w), 1224 (m), 1189 (w), 1124 (s), 1047 (m), 955 (vs), 914 (m), 891 (vs), 873 (vs), 855 (vs), 797 (m), 741 (w), 694 (w)
SF_5CHFCF_2Br	1324 (w), 1295 (w), 1232 (s), 1161 (vs), 1060 (m), 983 (vs), 968 (s), 883 (vs), 808 (m), 775 (m), 758 (w), 706 (s)
$SF_5C_2F_3ClBr$	1214 (s), 1175 (w), 1117 (s), 1055 (w), 1020 (w), 936 (vs), 894 (vs), 854 (m) 816 (m), 760 (m), 724 (s), 685 (m)

[a] w, weak; m, medium; s, strong; vs, very strong.

Cross and coworkers[7] reported that for compounds in which the SF_5 group is bound to an aliphatic hydrocarbon a very intense broad band centered on or about 870 cm^{-1} is found. They assigned this to the S–F stretching modes. We observed the same behavior with our compounds. For SF_5CH_2CHFBr the broad band is centered near 870 cm^{-1}. These bands may also be attributed to the S—F stretching modes.

Since isomers could be formed by SF_5Br adding nonselectively to the fluoro olefins, the vapor phase chromatography (vpc) of these compounds was studied.

TABLE III

GAS CHROMATOGRAPHY DATA[a]

Compd	Retention time, min
SF_5CH_2CHFBr	35
$SF_5CH_2CF_2Br$	15
SF_5CHFCF_2Br	5.6
$SF_5C_2F_3ClBr$	3.8
CCl_4	7.5

[a] The column temperature was 59 ± 1°. Helium flow rate was 2.5 ml/sec.

The results of this work are given in Table III. Only one major component was found for these compounds.

The structures of the addition products were determined from their magnetic resonance spectra. The proton resonances were resolved into the various spin-spin components in order to identify the nearest neighbors. Coupling constants corresponding to the various interactions are listed in Table IV as are the chemical shift values.

The SF_5 group, as found by Muller, Lantebur, and Svatos,[8] contains four magnetically equivalent and one nonequivalent fluorine atoms (A_4M system). The equatorial, A_4, resonance is split into a doublet while the apex, M, resonance is grossly a pentet with "fine structure."

Where there is a magnetic difference between the equatorial and apex fluorines, it is reasonable to expect further splitting of the equatorial fluorine resonance by proton nuclei in adjacent alkyl groups. These splittings in turn can be used to identify the alkyl adjacent to the SF_5 group. With this basic assumption we have analyzed the proton and some of the fluorine resonance spectra of our compounds and found the spectra to be in good agreement with the proposed structures in Table IV.

In addition to the expected A_4M patterns, we have found additional splittings for SF_5CH_2CHFBr and SF_5CHFCF_2Br. In both cases an asymmetric carbon atom exists within the molecule to exert a nonequivalence on adjacent normally equivalent nuclei.[9] In the SF_5CH_2CHFBr spectrum, described as an ABKX spectrum for the non-SF_5 resonance, where the protons are designated as A, B, and K and the fluorine X, one finds a nonequivalence of two methylene protons with respect to the terminal proton, but not with respect to the adjacent SF_5 group.

The proton chemical-shift values reflect the variation in the molecule's electronegativity as exhibited by other halopropanes.[10] The methylene chemical shifts are in the range expected for the internal as opposed to the terminal positions.

The nmr resonance spectrum of the compound $SF_5C_2F_3ClBr$ has not been resolved. The SF_5 group again exhibits an A_4M pattern, and the $-CF_2-$ group can be differentiated from the $=CF-$ group but nothing further can be said at present.

The nmr analysis shows that the SF_5 group has attached itself to the carbon of the olefin carrying the most hydrogens. Further varification of this result has been accomplished by the dehydrobromination of SF_5CFHCF_2Br to $SF_5CF{=}CF_2$ in 83% yield as shown in eq 6.[11]

$$SF_5CFHCF_2Br + KOH \xrightarrow[\text{reflux}]{\text{petroleum ether}} SF_5CF{=}CF_2 \quad (6)$$

SF_5Br should be a useful reagent for introducing SF_5 groups into carbon compounds. It adds more readily and directly than either SF_5Cl or S_2F_{10}, and, like SF_5Cl,

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[7] L. H. Cross, G. Cushing, and H. L. Roberts, *Spectrochim. Acta*, **17**, 344 (1961).

[8] N. Muller, P. C. Lantebur, and G. F. Svatos, *J. Amer. Chem. Soc.*, **79**, 1044 (1957).

[9] P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4564 (1957).

[10] H. F. White, *Anal. Chem.*, **36**, 1291 (1964).

[11] This dehydrohalogenation procedure was used by J. R. Case, N. H. Ray, and H. C. Roberts, *J. Chem. Soc.*, 2070 (1961), in determining the orientation of the addition reaction between SF_5Cl and $CF_2{=}CFH$.

Table IV

Nmr Data

Proposed structure—skeletal atom number			Chemical shifts, band centers[a]						Coupling constants,[b]					
1	2	3	S-F	SF_4	CF	CF_2	CH_2	CH	$J_{1,2}^{H,F}$	$J_{2,3}^{H,F}$	$J_{2,2}^{H,H}$	$J_{2,3}^{H,H}$	$J_{2,3}^{H,H}$	$J_{3,3}^{H,F}$	$J_{2,2}^{H,F}$
SF_5	CH_2	CHFBr	−79.9	−66.4	139.2		4.27	6.95	8	24	*c*	*c*	*c*	50	
SF_5	CH_2	CF_2Br	−77.3	−70.5		51.5	4.46		7	14					
SF_5	CHF	CF_2Br	−70.0	−53.7	163.5	63.1		5.58	5		$J_{2,3}^{H,F} = 3; J_{2,3}^{H,F} = 13$				44
$SF_5C_2F_3ClBr$[d]			−65.4	−48.5	76.8	88.5									

[a] Chemical shifts in parts per million upfield from $CFCl_3$ internal standard or downfield from $Si(CH)_{34}$ internal standard. [b] Measured in cycles per second. [c] Data unavailable as a detailed analysis of this compound is incomplete; $J_{2,3}^{H,H} + J_{2,3}^{H,H} = 11$ cps. [d] Structure unknown.

the SF_5 group bonds to carbon of the fluoro olefins carrying the most hydrogens.

Experimental Section

SF_5Br was prepared by the method of Cohen and MacDiarmid[12] in a 50-cc monel reactor equipped with an autoclave space-saver valve. No attempts were made to purify the SF_5Br (possible contaminants are SF_6, SF_4, S_2F_{10}, and Br_2) other than transferring it from the monel reactor at −60 to −70°. All transfers of SF_5Br and its adducts were performed with a Pyrex glass vacuum system equipped with Eck & Krebs stopcocks. In handling the adducts, Apiezon M and not Kel-F grease was used. Identification of the SF_5Br was made *via* its known ir spectrum.[6]

The fluoro olefins used in this study were purchased from the Peninsular Chemresearch Co. The ir spectrum of each one was taken and found to agree with their published spectrum.

The ir spectra were recorded on a Perkin-Elmer 137 Infracord spectrophotometer. The ir cell was made of monel metal and equipped with a Whitey-Brass valve. Path length of the cell was 8.25 cm.

Gas chromatographic separations were carried out with a preparative-scale 10-ft column containing 20% Carbowax absorbed on "Chromosorb W." An Aerograph Autoprep (Model A-700) was used.

The proton magnetic resonance (pmr) spectra were obtained with a Varian Model A-60 analytical nmr spectrometer. The fluorine spectra were obtained with a Varian Model HA-100 Analytical nmr spectrometer operating at 94.07 Mcps.

The vapor densities were determined using a Pyrex glass bulb having a calibrated volume of 200.7 cc.

Elemental analyses of these compounds were determined by the Huffman Laboratories.[13]

Reaction of SF_5Br with the Fluoro Olefins.—SF_5Br was transferred into a predried and weighed 1-l. Pyrex glass vessel equipped with an Eck & Krebs stopcock and lubricated with Kel-F grease. A weighed amount of olefin was then added and the temperature was slowly raised from −195° to room temperature. After the mixture was allowed to stand overnight, a liquid collected in the bottom of the reaction flask. The products were distilled in an all glass distillation set-up. This procedure was used in all cases and only modified in the reaction of SF_5Br with CH_2=CHF where some side reactions occurred.

In the particular case of CH_2=CHF, the olefin was slowly admitted into the 1-l. reaction vessel (the vessel contained SF_5Br at room temperature) over a period of approximately 2 hr and then the mixture was allowed to stand overnight. With this procedure, no side reactions were noticed.

Dehydrobromination of 2-Bromo-1,2,2-trifluoroethylsulfur Pentafluoride.—A 50-ml round-bottom flask was fitted with a reflux condenser, the top of which was connected to a trap cooled to −80°. Potassium hydroxide (1.0 g) was added to 20 ml of petroleum ether (bp 90–110°). This mixture was heated until a gentle reflux was obtained and then cold SF_5CFHCF_2Br was added. After 1 hr, 1.5 g of potassium hydroxide was added and the mixture was heated for an additional 0.5 hr. A colorless liquid collected in the −80° trap and was shown by ir and molecular weight analysis to be $SF_5CF{=}CF_2$ (its ir spectrum agreed with the published spectrum, and the molecular weight found was 207.0, theoretical was 208.2). The yield was 83%.

Registry No.—SF_5Br, 15607-89-3; SF_5CH_2CHFBr, 18801-66-6; $SF_5CH_2CF_2Br$, 18801-67-7; SF_5CHFCF_2Br, 18801-68-8.

Acknowledgments.—We wish to thank Dr. Felix Aubke of the University of British Columbia for obtaining the fluorine nmr spectra and Dr. A. Levinson for obtaining the proton spectra. We are indebted to the Research Corporation for funds supporting this work and to Dr. Dale of the Monsanto Co. for his gift of S_2F_{10}.

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(12) B. Cohen and A. G. MacDiarmid, *Inorg. Chem.*, **4**, 1782 (1965).

(13) Huffman Laboratories, Inc., Wheatridge, Colo.