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THE ADDITION OF PENTAFLUOROSULFUR BROMIDE TO FLUOROOLEFINS II

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SUMMARY

This paper reports the preparation, properties, and structure of new SF_5Br-fluoroolefin adducts. The extent and direction of SF_5Br addition to fluoroolefins have been studied with seven fluoroolefins. Steric factors appear to be important for this addition.

INTRODUCTION

Pentafluorosulfur bromide (SF_5Br) has been found to be a useful reagent for introducing SF_5 groups into carbon compounds [1-3]. Recent work by Fox and Berry [4] has provided some insight into the mechanism of addition of SF_5Br to olefins. They found that when SF_5Br adds to cis- and trans-1,2-difluoroethylene, the erythro and threo diastereoisomers of $SF_5CHFCHFBr$ are obtained in similar quantities for each olefin, both in the presence and absence of light. Their work suggests that the reaction proceeds via a free radical mechanism in which a SF_5 radical adds to the double bond of the fluoroolefin.

In order to determine the scope and direction for this addition seven fluoroolefin-SF_5Br systems have been studied.

RESULTS AND DISCUSSION

We have found that SF_5Br will successfully add to $CH_2{=}CFCl$, $CF_2{=}CClH$, $CHF{=}CFCl$, $CHF{=}CHCl$, and $CH_2{=}CHCF_3$ according to equations 1-5·

$$SF_5Br + CH_2{=}CFCl \xrightarrow{r.t.} SF_5CH_2CFClBr \quad (1)$$

$$+ CH_2{=}CHCF_3 \xrightarrow{r.t.} SF_5CH_2CH(CF_3)Br \quad (2)$$

$$+ CHF{=}CHCl \xrightarrow{80^{\circ}} SF_5CHFCHClBr \quad (3)$$

$$+ CHF{=}CFCl \xrightarrow{80^{\circ}} SF_5CHFCFClBr \quad (4)$$

$$+ CF_2{=}CClH \xrightarrow{100^{\circ}} SF_5CF_2CClHBr \quad (5)$$

With the compounds $CFCl{=}CHCl$ and $CF_2{=}CFCOF$, a small amount of product was formed only with the former olefin. The new products, eq. 1-5, are clear, colorless, and distillable liquids.

The common feature of these new compounds is the presence of the SF_5 group showing infrared absorptions near 870 cm^{-1}. Cross and co-workers [5] reported that in compounds containing the SF_5 group the most intense bands should occur in the region 850-920 cm^{-1} (S-F stretching modes), and in the region of 600 cm^{-1} (S-F deformation modes). For the new compounds reported in this paper, absorption bands in 845-927 cm^{-1} region are assigned to S-F stretching vibrations. The S-F deformation modes are found near or at 600 cm^{-1}. For compounds containing a C-F group, the C-F stretching vibration is usually located in the 1000-1100 cm^{-1} region; for a CF_2 group the C-F stretching vibration is located in the 1050-1250 cm^{-1} range. Therefore, with $SF_5CH_2CFClBr$, $SF_5CFHCHClBr$, and $SF_5CFHCFClBr$, the absorption bands at 1020, 1100, and 1065 cm^{-1} respectively, are assigned to the C-F stretching mode. In $SF_5CF_2CHClBr$, the C-F absorption bands are located in the 1145-1288 cm^{-1} region, while in $SF_5CH_2CH(CF_3)Br$, the C-F stretch is assigned to bands in the 1115-1280 cm^{-1} region.

The major mass spectra peaks for these adducts are listed in Table I. In all compounds, the mass spectra contained prominent peaks at m/e = 89, the SF_3^+ peak, and m/e = 127, the SF_5^+ peak. The compounds $SF_5CF_2CHClBr$ and $SF_5CFHCHClBr$ showed parent ions.

Gas chromatographic data revealed essentially one peak for all adducts.

The structures of these new addition products and the previously reported compound $SF_5CF_2CFClBr$ [1], formed from the addition of SF_5Br to $CFCl{=}CF_2$, were determined from their nuclear magnetic resonance spectra. The various resonances were resolved into their respective spin-spin components; interacting components facilitated the assignment of coupling nuclei to yield the appropriate molecular geometry [1]. The nmr spectra (see Table II for chemical shift values) generally consist of complex multiplets; however, with most compounds first-order coupling constants could be determined, and these are listed in Table III. Since isomers could be formed by SF_5Br adding nonselectivity to the olefin group, careful analyses of the first-order coupling interactions and chemical shift values were made to ensure correct geometry assignment. The molecular geometries given in Table II and Figure I are consistent with the observed resonance patterns, coupling constants, and SF_5 chemical shift values.

Interestingly, we have found that the products obtained using $CHF{=}CHCl$ and $CHF{=}CFCl$ contained diastereoisomers (see Figure I). In the $CH_2{=}CHCF_3$ product a second CF_3 resonance was found at 72.2 ppm from $CFCl_3$ in addition to the primary CF_3 resonance at 73.9 ppm from $CFCl_3$; this additional resonance represents 10% of the total CF_3 peak height intensity and could be ascribed to a diastereoisomer. There is no additional evidence from our data to support the existence of a diastereoisomer. Previously, we reported that when SF_5Br adds to alkenes [1] or alkynes [6], the SF_5 group adds exclusively to the carbon carrying the most hydrogens. In this work we report the first exception to this rule. When SF_5Br adds to $CF_2{=}CHCl$, the major isomer formed is $SF_5CF_2CHClBr$ (83%) and not $SF_5CHClCF_2Br$ (17%).

Table I

Mass Spectra Data

$SF_5CH_2CFClBr$	CS^+ (13), $C_2H_2F^+$ (24), CCl^+ (10), $SFCH^+$ (13), SF_2^+ (13), $CHCFCl^+$ (30), $C_2H_2ClF^+$ (57), $CHCFCl^+$ (10), $C_2H_2ClF^+$ (19), SF_3^+ (100), BrF^+ (13), $C_2H_2F_2Cl^+$ (83), SF_3C^+, $C_2H_2F_2Cl^+$ (43), SF_5^+ (50), SC_2HBr^+ (17), SF_5CH^+, SC_2HBr^+ (23), $SFCBr^+$ (30), SF_5CF^+ (40), $SF_5CH_2F^+$ (55), $SF_5CH_2CFCl^+$ (35).
$SF_5CF_2CHClBr$	CS^+ (15), CCl^+ (15), $CHCl^+$ (35), SCF^+ (37), $CHCFCl^+$, Br^+ (22), SF_3^+ (39), CF_2CHCl^+, BrF^+, $SFCCl^+$ (100), SF_2CCl^+ (94), SF_2CCl^+ (31), SF_5^+ (83), $SF_2C_2Cl^+$ (39), $CHCF_2ClBr$ (56), $C_2F_3HClBr^+$ (56), $SF_5CF_2CHClBr^+$ (6).
$SF_5CFHCHClBr$	CFH^+ (29), CS^+ (17), $C_2H_2F^+$ (41), SF_2^+ (10), $CHFCCl^+$, Br^+ (24), $C_2H_2ClF^+$ (55), SF_3^+ (57), $C_2H_2F_2Cl^+$ (100), SF_3C^+, $C_2H_2F_2Cl^+$ (33), SF_5^+ (36), SF_5CH^+, SC_2HBr^+ (11), SF_5CF^+ (27), $SF_5CH_2F^+$ (34), $SF_5C_2H_2FClBr^+$ (3).
$SF_5CFHCFClBr$	CF^+ (11), CFH^+ (22), SF^+ (21), SF_2^+ (33), $CHCFCl^+$, Br^+ (18), SF_3^+ (100), $CHFCFCl^+$ (42), SF_5^+ (100), $CHFCFCl^+$ (12), $CHFCFClBr^+$ (15).
$SF_5CH_2CH(CF_3)Br$	$C_2H_2^+$ (28), $C_2H_3^+$ (15), CF_2^+ (22), CF_3^+ (35), SF_2^+ (14), $CH_2CHCF_2^+$ (17), SF_3^+ (56), $CH_2CHCF_3^+$ (36), $SF_3C_2^+$ (21), SF_5^+ (100), $CHC(CF_3)Br^+$ (64), $CH_2CHCF_3Br^+$ (63).

Table II

NMR Chemical Shifts[1]

$SF_5C_1X_1X_2C_2Y_1Y_2Br$		$SF_{(ax)}$	$SF_{4(eq)}$	C_1X_1	C_1X_2	C_2Y_1	C_2Y_2
I. $SF_5CH_2CHBr(CF_3)$		-79.9	-66.4	(4.4)[2]		4.9	(73.9)[2]
II. $SF_5CH_2CFClBr$		-77	-68	4.53	4.48	58	
III. $SF_5CHFCHClBr$	(a)	-71.4	-48.5	5.85	164	6.2	
	(b)	-71.6	-49.0	5.6	152	6.1	
IV. $SF_5CHFCFClBr$	(a)	-70.2	-53.5	5.68	152.5	71.1	
	(b)	-70.3	-54.2	5.50	149.1	73.0	
V. $SF_5CF_2CHClBr$	(a)	-66.0	-43.2	79.3†	88.5†	6.07	
$SF_5CHClCF_2Br$[3]	(b)	-71.9	-60.5	5.5		49.3†	58.2†
VI. $SF_5CF_2CFClBr$		-64.7	-48.7	86†	88†	76.4	

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†Average values of various AB multiplets.

[1] Fluorine chemical shifts in ppm from internal $CFCl_3$ and proton chemical shifts in ppm downfield from internal TMS.

[2] Insufficient resolution to determine the two C_1H resonance positions. C_2Y_2 value is for CF_3 group.

[3] Chemical shift values accurate to within 1 ppm because of low concentration (~17% of total sample).

Table III

NMR Coupling Constants (Hz)

		$J_{1,2}$	$J_{1,3}$	$J_{1,3'}$	$J_{1,4}$	$J_{2,3}$	$J_{2,3'}$	$J_{2,4}$	$J_{3,3'}$	$J_{3,4}$	$J_{3',4}$
I.	$\overset{1}{F}\overset{2}{S}F_4\overset{3}{C}HH'\overset{4}{C}HBr(\overset{5}{C}F_3)$ [i]	136.9	†	†	†	8.4	8.4		2	8.4	15.6
II.	$FSF_4CH_2CFClBr$	150	†	†	2	7.5	7.5	12	†	12	18
III.	$FSF_4CHF'CHClBr$ [Δ] (a)	145	†	2.8	†	4.9	5.6	*	48.0	1.2	21.2±1.4
	[Δ] (b)	145	†	2.8	†	4.2	5.6	*	56.4	3.6	17.4±2.4
IV.	$FSF_4CHF'CFClBr$ (a)	147	†	2.5	1.4	4.5	†	14.1	42.7	2.4	31.6
	(b)	147	†	2.8	1.4	4.5	1.4	12.7	42.9	4.5	26.0
V.	$FSF_4CFF'CHClBr$ (a)	145	5.7	5.7		16.2	14.0		188	5.5	12.8
	$FSF_4CHClCFF'Br$ [i] (b)	144								17	8
VI.	$FSF_4CFF'CFClBr$	149.9	4.23	4.23		5.95		*	195.6	25.4	

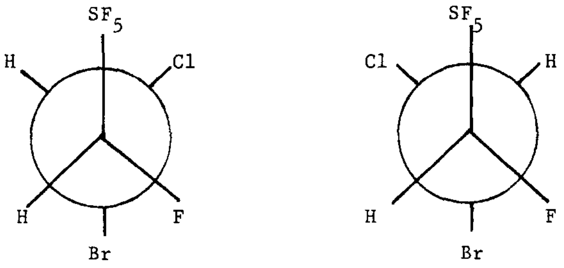
† Too small to measure, or not observed.

* Insufficient resolution.

[i] For $FSF_4CHClCFF'Br$ the $J_{4,4'}$ = 174Hz and for both diastereoisomers of $FSF_4CHH'CHBr(CF_3)$ $J_{4,5} = 6.5$

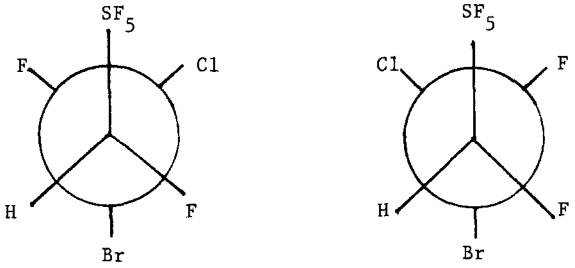
[Δ] Two values were obtained for each $J_{3'4}$ – one from the ^1H and one from the ^{19}F spectra. The reported values are the averages and the uncertainty represents the variation in measurement for the two determinations.

$SF_5CHFCHClBr$ (III)



(a) (b)

$SF_5CHFCFClBr$ (IV)



(a) (b)

Fig. I. Diastereoisomers for $SF_5CHFCHClBr$ (III) and $SF_5CHFCFClBr$ (IV)*.

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*For $SF_5CHFCHClBr$ (III) the ratio of the (a) isomer to (b) isomer was 3:1 and for $SF_5CHFCFClBr$ (IV) the ratio of the (a) isomer to (b) isomer was 2:1.

We have found, as have other workers [7] that the SF_5 chemical shift values are sensitive to the α-carbon substitution with the greatest sensitivity exhibited by the SF axial fluorine (enhanced shielding occurring in the hydrogen containing molecules). The axial S-F was not found to couple to protons on the α or β-carbons in these aliphatic derivatives; however, we do observe coupling with fluorine on the α-carbon and, interestingly, between the axial S-F and fluorines on the β-carbon for $SF_5CH_2CFClBr$ and $SF_5CHFCFClBr$. Fox and DeMarco did not find in their SF_5 aliphatic derivatives any SF(ax) coupling to H and F groups on the β-carbon [7].

A number of olefinic and SF_5Br systems have now been examined by our group [1] and others [2-4], and to a first order approximation these results demonstrate that the successful addition and direction of SF_5Br to fluroolefins is sterically influenced. This addition suggests that the SF_5 group attacks the less hinderd site of the olefin, supporting the proposed mechanism of Berry and Fox[4]. Additional preliminary experiments indicate that SF_5Br will add to CHCl=CFCl, if only slightly, and from the above results it is assumed that the SF_5 group attaches to the CHCl portion of the olefin.

EXPERIMENTAL

SF_5Br was prepared and handled as previously reported [1]. The Fluoroolefins used in this study were purchased from the PCR Research Chemicals and were used as received. The infrared spectra (IR) agreed with the published spectra.

The IR spectra were recorded on a Perkin-Elmer 476 spectrometer. Gas samples were contained in a Monel cell 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 by using an Aerograph Autoprep (Model A-700) gas chromatograph with a 10' x 3/8" column containing 20% carbowax absorbed on 'Chromosorb W.' The yield for all reactions was based on an equimolar amount of olefin reacting with SF_5Br present. Attempts to isolate the isomers as found in the NMR studies were unsuccessful.

The molecular weights were determined by the vapor density method.

The NMR spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.6 MHz for fluorine resonances. TMS and F-11 were used as internal standards. The mass spectra were taken on a CEC 21-110 B double focus mass spectrometer equipped with a 6 KV ion accelerator and operated at 70 volts. Perfluorokerosine (PFK) was used as an internal standard.

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

Preparation of $SF_5CH_2CFClBr$

In a 3-liter Pyrex vessel equipped with a Kontes Teflon valve, 62.5 mmol of $CH_2=CFCl$ and 73 mmol of SF_5Br were condensed at -196°. The product, $SF_5CH_2CFClBr$, was formed in a 28% yield after 1 day at room temperature; bp 119° (n.c.).

In a 75 ml stainless steel vessel equipped with a Whitey brass valve, 170 mmol of $CH_2=CFCl$ and 170 mmol of SF_5Br were condensed at -196°. The product, $SF_5CH_2CFClBr$, was formed after 6 days [room temperature (2d), 37° (2d), and 50° (2d)] in 51% yield.

Calcd. for $SF_5CH_2CFClBr$: C, 8.35; H, 0.70; S, 11.15; F, 39.66; Cl, 12.33; Br, 27.80. Found: C, 8.51; H, 0.72; S, 11.03; F, 38.8; Cl, 12.48; Br, 28.10. MW, Calcd. 287, found 286.

The gaseous infrared spectrum of the distilled product gave the following absorption bands (cm^{-1}): 1410 (w), 1149 (m-s), 1020 (s), 974 (w), 912 (vs), 870 (vs), 845 (vs), 790 (w), 720 (w), 664 (w), 618 (vw), 596 (s), 568 (m).

Preparation of $SF_5CF_2CHClBr$

In a 200 ml Hoke stainless steel vessel equipped with a Whitey brass valve, 34 mmol of $CF_2=CHCl$ and 82 mmol of SF_5Br were condensed at -196°. The product, $SF_5CF_2CHClBr$, was formed after 14 days at 100° in a 73% yield; bp 111° (n.c.).

Calcd. for $SF_5CF_2CHClBr$: C, 7.86; H, 0.33; S, 10.50; Cl, 11.61; Found: C, 8.10; H, 0.32; S, 9.35; Cl, 10.68. MW, Calcd. 305, found 297.

The gaseous infrared spectrum of the distilled product gave the following absorptions (cm^{-1}): 1288 (m), 1225 (s), 1189 (m), 1163 (s), 1145 (s), 1032 (w), 960 (m), 885 (vs), 863 (vs), 815 (m), 792 (m), 778 (w), 731 (s), 702 (w), 660 (s), 600 (s), 588 (m, with sh at 575).

Preparation of $SF_5CHFCFClBr$

In a 200 ml Hoke Monel vessel equipped with a Whitey brass valve, 39 mmol of CHF=CFCl and 54 mmol of SF_5Br were condensed at -196°. The product, $SF_5CHFCFClBr$, was formed after 5 days at 80° in a 70% yield; bp 111° (n.c.).

Calcd. for $SF_5CHFCFClBr$: C, 7.87; H, 0.33; S, 10.5; F, 43.6; Cl, 26.2; Br, 11.5. Found: C, 8.00; H, 0.33; S, 10.46; F, 43.9; Cl, 26.41; Br, 11.73.

The gaseous infrared spectrum of the distilled product gave the following absorptions (cm^{-1}): 1155 (m-s, sh. at 1195, 1255, 1280, 1330), 1120 (s), 1065 (m, sh. at 1035), 960 (m) 870 (vs, sh. at 905, 925), 815 (s), 755 (w), 645 (m, sh. at 665, 685, 705), 600 (s), 570 (m), 540 (m).

Preparation of $SF_5CHFCHClBr$

In a 200 ml Hoke Monel vessel equipped with a Whitey brass valve, 73 mmol of CHF=CHCl and 59 mmol of SF_5Br were condensed at -196°. The product, $SF_5CHFCHClBr$, was formed after 4.5 days at 80° in a 49.5% yield; bp 127.5 (n.c.).

Calcd. for $SF_5CHFCHClBr$: C, 8.36; H, 0.69; S, 11.1; F, 39.7; Cl, 27.92; Br, 12.2. Found: C, 9.04; H, 0.80; S, 10.84; F, 39.0; Cl, 28.53; Br, 12.57. MW, calcd. 287.4, found 290.1

The gaseous infrared spectrum of the distilled product gave the following absorptions (cm^{-1}): 1368 (m), 1345 (m), 1270 (w), 1150 (m, sh. at 1175), 1100 (m), 1050 (w), 932 (m), 900 (s), 872 (s), 817 (m), 717 (m-w), 700 (m-w), 630 (m), 600 (m), 567 (w).

Preparation of $SF_5CH_2CH(CF_3)Br$

In a 3-liter Pyrex vessel equipped with a Kontes Teflon stopcock, 58.3 mmol of $CF_3CH{=}CH_2$ and 54 mmol of SF_5Br were condensed at -196°. The product, $SF_5CH_2CH(CF_3)Br$, was formed after 18 days at room temperature in a 39% yield; bp 102.5° (n.c.).

Calcd. for $SF_5CH_2CH(CF_3)Br$: C, 11.9; H, 0.99; S, 10.6; F, 50.2; Cl, 26.4. Found: C, 11.88; H, 1.00; S, 10.44; F, 49.8; Cl, 26.2. MW, calcd. 303, found 299.1.

The gaseous infrared spectrum of the distilled product gave the following adsorptions (cm^{-1}): 1480 (w), 1410 (m,sh. at 1420, 1427), 1365 (w), 1280 (s), 1252 (s), 1165 (vs,sh. at 1190), 1115 (s), 927 (vs), 870 (vs,sh. at 895), 850 (s), 816 (s), 600 (m-s), 570 (m-s), 540 (s).

Reaction of $CFCl{=}CHCl$ and SF_5Br

In a 200 ml Hoke Monel vessel equipped with a Whitey brass valve, 39 mmol of $CHF{=}CFCl$ and 51.4 mmol of SF_5Br were condensed at -196°. Heating at 80° for 5 days produced little product; heating this mixture to 125° over 5 days resulted in a small amount of high boiling crude product. A mass spectrum of this sample showed the presence of SF_5^+ and $C_2HFCl_2Br^+$ groups. An infrared spectrum contained absorption bands attributable to SF_5 and C-F groups.

Reaction of $CF_2{=}CFC(O)F$ and SF_5Br

In a 200 ml Hoke Monel vessel equipped with a Whitey brass valve, 27 mmol of $CF_2{=}CFC(O)F$ and 36 mmol of SF_5Br were condensed at -196°. Heating at 80° for 6 days resulted in no product information.

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