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MONO- AND DIHYDRYL-PENTAFLUOROSULFUR-F-ALKANES [1]

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SUMMARY

The systematic preparation of partially fluorinated pentafluorosulfur alkanes containing no additional halogens is reported. Thus, the indirect addition of "HF" (via KF/formamide) to $SF_5CH{=}CF_2$, $SF_5CF{=}CF_2$, and $SF_5C(CF_3){=}CF_2$ produces $SF_5CH_2CF_3$, SF_5CHFCF_3, and $SF_5C(CF_3)_2H$ respectively. The monohydryl-pentafluorosulfur-F-alkanes react readily with $S_2O_6F_2$ to form the corresponding fluorosulfates by oxidative displacement of hydrogen, while the dihydryl derivative undergoes cleavage to produce F-acetyl fluoride. Efforts to convert some of the new materials to the important but unknown pentafluorosulfur "ketone," $SF_5C(O)CF_3$, were unsuccessful.

INTRODUCTION

The preparation of organic derivatives containing the pentafluorosulfur group has recently become a matter of interest in this Laboratory and elsewhere. Most of the recently prepared SF_5-containing compounds result from the addition of SF_5Cl or SF_5Br [2,3] to unsaturated compounds, although some attempts have been made to incorporate the SF_5 moiety into molecules with other functional groups [4,5,6a,6b] or, conversely, to incorporate functional groups in SF_5-containing molecules [3,7-11]. The formation of SF_5-derivatives by addition of SF_5Cl and SF_5Br to unsaturated compounds necessarily results in concomitant production of a weak C-Cl or C-Br bond; although such materials are useful in preparing SF_5-

containing olefins through dehydrohalogenation, little work has been directed to converting the relatively weak carbon-halogen linkages to stronger C-F bonds. The systematic evaluation of the SF_5 group as a stabilizing function in fluorocarbons has therefore been limited by the presence of inherently weak C-Cl or C-Br bonds in available compounds. We have developed a general synthesis of mono- and dihydryl-pentafluorosulfur-*F*-alkanes to circumvent this problem, while maintaining a reactive proton site for further derivatization. Previously, only two examples of this class of compounds, SF_5CH_2F [12] and SF_5CF_2H [13] had been reported, and these were obtained only as minor by-products of fluorination reactions and not thoroughly characterized.

RESULTS AND DISCUSSION

The formation of the various hydryl-pentafluorosulfur-*F*-alkanes involves a sequence of three reasonably high yield reactions. In the first step, the SF_5 group is incorporated by the addition of SF_5Cl to a fluoroolefin:

$$HCX = CF_2 + SF_5Cl \rightarrow SF_5CH(X)CF_3Cl \qquad (1)$$

$$X = H,\ F,\ CF_3$$

The previously reported addition of SF_5Cl to $HCF{=}CF_2$ [14,15,16] and the unreported addition to $CH_2{=}CF_2$ were accomplished at 120° using an azo initiator. However, attempts to thermally add SF_5Cl to $CF_3CH{=}CF_2$ using azo or peroxide initiators were unsuccessful, a result which parallels previous failures to add SF_5Cl to *F*-propene [14]. The addition of SF_5Cl to $CF_3CH{=}CF_2$ was therefore completed by photolysis, although this method resulted in much lower yields (30%) than the thermal reactions (>85%) used in the other cases. (The lower photochemical yields presumably resulted from secondary photodecomposition of the SF_5 group and photochlorination of the olefin; the thermal reactions, on the other hand, were essentially unidirectional, with only minimal formation of less volatile telomer products.)

The chlorofluoroalkanes were readily dehydrochlorinated with KOH to the corresponding pentafluorosulfur olefins (2) and the latter were subjected to indirect "HF" addition:

$$SF_5CH(X)CF_2Cl + KOH \rightarrow SF_5CX = CF_2 \qquad (2)$$

$$SF_5CX{=}CF_2 + \text{"HF"} \rightarrow SF_5CH(X)CF_3 \qquad (3)$$

$$X = H, F, CF_3$$

The previously reported olefin $SF_5CF{=}CF_2$ [14] was isolated in >85% yield, and the new olefins $SF_5CH{=}CF_2$ and $SF_5C(CF_3){=}CF_2$ were isolated in 60-65% yields. The use of a solvent was not necessary with small-scale reactions and short contact times. We occasionally observed erratic reaction behavior which resulted in reduced yields or total degradation of the chlorofluoroalkane. The condition of the KOH appears most responsible for this inconsistency; bottles of KOH which were previously opened and left on the reagent shelf gave the least consistent results, while fresh bottles afforded smooth, high-yield reactions.

Reaction (3), if done by the direct addition of HF [17], usually requires high temperatures and catalysts, but Miller and coworkers [18] have developed an indirect but facile method involving nucleophilic addition of the elements of "HF" to fluoroolefins using a mixture of readily available KF and formamide; use of this method provided a rapid (<1 hr), high-yield (>80%) synthesis of the title compounds. The HF addition was found to be unidirectional and without evidence of SF_5 cleavage.

The mono- and dihydryl-pentafluorosulfur-F-alkanes are colorless liquids which boil above room temperature; vapor pressure data for these and the new chlorofluoroalkanes and SF_5-olefins are found in Table I. Trouton constants for these derivatives do not indicate any significant intermolecular association, and the compounds also demonstrated reasonable thermal stability, being recovered unchanged after three days at 170° in Pyrex glass.

The synthesis of $SF_5CH{=}CF_2$ seemed to present an opportunity to prepare bis(pentafluorosulfur) alkanes and alkenes by further SF_5X addition. Unfortunately, the SF_5 group apparently deactivated the double bond sufficiently to prevent addition of either SF_5Cl

TABLE I

Vapor pressure data

	Log P(mm) = a - $\frac{b}{T}$		Bp	ΔH_{vap}	ΔS_{vap}
	a	b	(°C)	(kcal/mole)	(eu)
$SF_5CH_2CF_2Cl$	7.88	1719.9	70.9	7.87	22.9
$SF_5CH(CF_3)CF_2Cl$	7.51	1628.5	78.8	7.45	21.2
$SF_5CH{=}CF_2$	7.69	1447.6	28.1	6.62	22.0
$SF_5C(CF_3){=}CF_2$	7.76	1561.5	47.0	7.17	22.3
$SF_5CH_2CF_3$	7.77	1530.8	40.0	7.00	22.4
SF_5CHFCF_3	7.76	1463.0	26.9	6.70	22.3
$SF_5C(CF_3)_2H$	7.71	1571.5	52.2	7.19	22.1
$SF_5CF(CF_3)OSO_2F$	7.98	1819.0	83.4	8.32	23.4
$SF_5C(CF_3)_2OSO_2F$	8.02	1942.5	105.1	8.89	23.5

or SF_5Br, using the azo compound or benzoyl peroxide as initiators. Although the photolysis of SF_5Cl with $SF_5CH{=}CF_2$ (300 nm) did afford a very low yield (<1%) of a material which, by infrared and mass spectral analysis, may have been the bis(pentafluorosulfur) compound $ClC_2HF_2(SF_5)_2$, we were unable to isolate a sufficient amount of the derivative for further characterization.

The presence of the hydrogens in the pentafluorosulfur-F-alkanes offered the opportunity to introduce additional functional groups, particularly in view of recent work by Merrill [19] and Kirchneier and Shreeve [20] which demonstrated that $S_2O_6F_2$ participates in facile hydrogen abstraction reactions to produce fluorosulfates (i.e., $RH + S_2O_6F_2 \rightarrow RSO_3F + HSO_3F$). We found the hydryl-pentafluorosulfur-F-alkanes reacted in an analogous manner:

$$SF_5CX(H)CF_3 + S_2O_6F_2 \rightarrow SF_5CX(OSO_2F)CF_3 + HOSO_3F \qquad (5)$$

$$X = F,\ CF_3$$

The yields for these mono-fluorosulfates were ~70%, but we were unable to isolate the bis(fluorosulfate) derivative from $SF_5CH_2CF_3$; mixtures of $S_2O_6F_2$ and $SF_5CH_2CF_3$ gave no evidence of reaction at room temperature, though slow decomposition at 50° and consumption of the reactants after 4 hr at 90° yielded $CF_3C(O)F$, O_2, $S_2O_5F_2$ and SF_4 as volatile products.

The fluorosulfates are colorless liquids at room temperature (Table I) and demonstrated both thermal and photolytic stability. No evidence of decomposition was observed after heating the fluorosulfates in Pyrex at 170° for 3 days, and attempts to photolytically decompose $SF_5C(CF_3)_2OSO_2F$ in quartz vessels using 254, 300 or 354 nm lamps for 24-hr periods were also unsuccessful.

The fluorosulfates were expected to be useful as precursors of the important new compound $SF_5C(O)CF_3$, since Lustig and Ruff [21] have demonstrated that fluorocarbon fluorosulfates are readily converted to carbonyl compounds by elimination of SO_2F_2 upon treatment with alkali metal fluorides. Unfortunately, however, the reaction of $SF_5CF(OSO_2F)CF_3$ with KF or CsF resulted in cleavage of the SF_5-group and did not produce the desired ketone:

$$SF_5CF(OSO_2F)CF_3 \xrightarrow[MF]{} \begin{cases} \xrightarrow{X} SF_5C(O)CF_3 + SO_2F_2 \\ \longrightarrow CF_3C(O)F + SF_4 + SO_2F_2 \end{cases} \tag{6}$$

Although $SF_5C(O)CF_3$ has been proposed by Russian workers [6a] as an intermediate which decomposes to $CF_3C(O)F$ and SF_4, no direct evidence for its existence was demonstrated. The presence of metal fluorides, in both the Russian work and in our study, and their possible attack on the ketone would account for the formation of the observed products. A second consideration in our system is that the cleavage of the weaker C-S bond, rather than the C-F bond, may have occurred during the formation of the carbonyl function. This reaction mode would also give the observed products from decomposition of the SF_5^- ion to SF_4 and F^-.

Similar results were obtained in attempting to prepare an alkoxide salt from $SF_5C(CF_3)_2OSO_2F$. We observed a slight reaction with KF after 2 hr at 45° and extensive formation of $(CF_3)_2CO$, SF_4, and SO_2F_2 at 65°. The use of CsF to stabilize the alkoxide ion also proved unsuccessful; the fluorosulfate was recovered when treated with CsF at -80 and -23° but decomposed as before at 0°. Volatile components were removed and the solid

TABLE II

Infrared Spectra* (cm^{-1})

$SF_5CH_2CF_2Cl$	3056(vw), 3007(vw), 1420(mw), 1330(m), 1277(sh), 1267(m), 1229(ms), 1200(m), 1126(s), 1107(shm,), 1052(ms), 976(vs), 917(sh,ms), 895(vs), 876(vs), 857(vs), 808(ms), 751(m), 710(mw), 670(w), 614(ms) 573(mw)
$SF_5CH(CF_3)CF_2Cl$	3006(vvw), 2984(vvw), 1334(m), 1292(m), 1262(s), 1221(s), 1170(ms), 1149(ms), 1114(m), 1048(m), 982(m), 925(m), 911(sh,w), 890(vs), 873(sh,s), 855(sh,w), 834(m), 795(m), 779(sh,w), 742(m), 718(m), 682(m), 634(vw), 596(m), 562(mw), 524(w)
$SF_5CH{=}CF_2$	3138(w), 1787(w), 1748(s), 1348(ms), 1208(m), 1008(m), 892(vs), 782(ms), 680(m), 605(m), 564(w)
$SF_5C(CF_3){=}CF_2$	1722(s), 1361(vs), 1279(ms), 1201(ms), 1174(s), 1088(m), 1008(m), 897(vs), 845(vs), 738(mw), 692(mw), 612(m), 576(w)
SF_5CHFCF_3	3005(vw), 1377(m), 1293(s), 1221(s), 1167(s), 937(s), 887(vs), 857(sh,s), 768(s), 710(m), 678(ms) 605(m), 563(w), 517(w)
$SF_5CH_2CF_3$	3047(vvw), 3005(vvw), 1424(mw), 1353(ms), 1300(ms) 1272(ms), 1150(s), 918(s), 881(s), 860(s), 740(m), 686(mw), 656(m), 605(m), 562(mw), 529(sh,vw), 513(w)
$SF_5C(CF_3)_2H$	3008(vw), 1345(s), 1311(s), 1288(vs), 1254(s),1238 1185(vs), 1170(sh), 1148(w), 1112(m), 934(m), 893(vs), 857(vw), 795(vs), 740(m), 706(m), 694(m) 616(m), 581(w), 549(vw), 533(vw)
$SF_5CF(OSO_2F)CF_3$	1502(s), 1313(m), 1263(vs), 1234(s), 1185(m), 1102(m), 989(w), 905(vs), 864(vs), 847(sh,s), 826(sh,ms), 741(m), 705(w), 691(w), 600(sh,m), 590(ms), 557(m), 527(m)

$SF_5C(CF_3)_2OSO_2F$	1495(s), 1310(sh), 1285(s), 1262(s), 1249(s), 1209(mw), 1177(w), 1162(w), 1102(s), 977(m), 936(w), 907(s), 852(s), 831(ms), 754(m), 737(m), 701(mw), 627(mw), 606(ms), 589(mw), 559(w), 537(mw)

* Corrected to calibrated polystyrene film

residue heated to decompose any SF_5-containing adduct, but only $(CF_3)_2CO$ was detected.

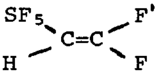
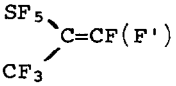
Additional attempts were made to synthesize $SF_5C(O)CF_3$ through oxidation reactions. A sample of $SF_5CH_2CF_3$ was treated with aqueous acidified permanganate but no reaction was detected. The mixture was heated to 105° for 1-1/2 hr, resulting in decomposition of the permanganate and nearly quantitative recovery of the $SF_5CH_2CF_3$. A homogeneous system was formed when the $SF_5CH_2CF_3$ was condensed onto an acetone/permanganate solution [22], but no reaction was detected to 50° where the permanganate decomposed. In contrast, $SF_5C(CF_3)=CF_2$ underwent immediate reaction in an acetone/permanganate solution on slowly warming to ambient temperature, but analysis of the volatile gases showed quantitative formation of SO_2F_2, indicating cleavage of the SF_5 group rather than the desired oxidation of the olefin linkage. The attempted oxidation of $SF_5CH_2CF_3$ with t-BuOOH/O_2 (18 hr, 120°) and $SF_5C(CF_3)=CF_2$ with O_2 (65 atm, 115°) were also unsuccessful and resulted in quantitative recovery of the SF_5 derivatives.

The infrared spectra for these derivatives are found in Table II. The characteristically strong bands between 850 and 900 cm^{-1} are assigned to the SF_5 group stretch, while the moderate band between 590 and 615 cm^{-1} is attributed to the SF_5 deformation [23]. The other functional groups also exhibit characteristic infrared bands. The fluorosulfates show the typically strong asymmetric FSO_3 stretch at ~1500 cm^{-1} while the symmetric stretch is buried in the CF_3 region. The olefinic stretch at 1748 cm^{-1} for $SF_5CH=CF_2$ correlates well with other $-CH=CF_2$ derivatives containing the olefinic stretch at ~1755 cm^{-1} [23]. A comparison of the difference in C=C stretching frequencies between $SF_5C(CF_3)=CF_2$ (1722 cm^{-1}) and $CF_3C(CF_3)=CF_2$ (1755 cm^{-1}) [23] correlates reasonably well with the approximate 20 cm^{-1} difference found in $SF_5CF=CF_2$ [24] and $CF_3CF=CF_2$ [23].

The nmr spectra (Table III) were generally complex, and cases where first-order coupling constants could be determined

TABLE III

NMR chemical shifts*

	CF	CF_2	CF_3	$SF_{(ax)}$	SF_4(eq)	X**
$SF_5CH_2CF_2Cl$		55.7		-77.4	-68.7	4.2
$SF_5CH(CF_3)CF_2Cl$		F_A 45.5 F_B 51.5	61.1	(-71.9)		4.5
		F' 67.0 F 85.8		-78.0	-72.0	5.73
		F' 58.9 F 67.6	57.0	(-72.3)		
SF_5CHFCF_3	172.1		76.3	-68.2	-51.6	5.41
$SF_5CH_2CF_3$			65.4	-75.5	-68.2	4.02
$SF_5C(CF_3)_2H$			62.8	(-70.8)		4.51
$SF_5CF(OSO_2F)CF_3$	110.3		79.9	-62.3	-45.3	-51.2
$SF_5C(CF_3)_2OSO_2F$			66.6	-65.8	-58.8	-51.0

* Fluorine chemical shifts in ppm from internal $CFCl_3$ and proton chemical shifts in ppm downfield from internal TMS

** X represents either H or FSO_3

TABLE IV

NMR coupling constants*

$FSF_4CH_2CF_2Cl$ 1 2 3 4	J_{1-2} = 139 J_{2-3} = 7.2	J_{2-4} = 11.6 J_{3-4} = 12.4	
$FSF_4CH_2CF_3$ 1 2 3 4	J_{1-2} = 138 J_{2-3} = 7.3	J_{2-4} = 10.1 J_{3-4} = 8.8	
$FSF_4CF(H)CF_3$ 1 2 3 4 5	J_{1-2} = 144.0 J_{1-3} = 2.5 J_{2-3} = 2.5	J_{2-4} = 5.0 J_{2-5} = 11.0 J_{3-4} = 43.5	J_{3-5} = 11.0 J_{4-5} = 5.4
$FSF_4CF(CF_3)OSO_2F$ 1 2 3 4 5	J_{1-2} = 142 J_{1-3} = 4.2 J_{2-3} = 12.0	J_{2-4} = 9.5 J_{2-5} = J_{3-4} = 2.8	J_{3-5} = 12.0 J_{4-5} = 2.8
$FSF_4C(CF_3)_2OSO_2F$ 1 2 3 4	J_{1-2} = 131 J_{2-3} = 12.4	J_{2-4} = 2.9 J_{3-4} = 3.0	

*Values given in Hz

are listed in Table IV. The axial S-F was not found to couple to protons on the α-carbon or to any group on the β-carbon in the aliphatic derivatives, but we do observe coupling with fluorine on the α-carbon in $SF_5CF(H)CF_3$ and $SF_5CF(OSO_2F)CF_3$. This coupling in the $SF_5CF(H)CF_3$ case was unusual and unexpected, in that the axial and equatorial S-F coupling constants to the CF are approximately equal. The C-F resonance appears as a hextet (SF_5) of quartets (CF_3) of doublets (H). Comparison of the assigned coupling constants from this resonance with those from the CF_3 and H resonances confirms this assignment. Although decoupling would have been desirable, the peak widths were sufficiently great that it was impossible to decouple the resonances successfully.

The equatorial sulfur-fluorine chemical shift shows the anticipated sensitivity to α-carbon substitution; however, a smaller shielding effect is also found when considering β-carbon substitution. Thus, when comparing the corresponding $SF_5CH(X)CF_3$ and $SF_5CH(X)CF_2Cl$ derivatives (X=H,F), enhanced shielding is found in the former case. Although the β-substitution effect is much smaller, it was interesting to note that the effect appears greater for the axial S-F than the equatorial fluorines.

The addition of the $SF_5CH(CF_3)CF_2X$ derivatives (X=Cl,F) to this comparison would have been of value, but the nmr spectra of these compounds do not correspond to the typical AB_4 spectrum observed for the ethyl cases. The SF_5 group appears essentially as one complex resonance, undoubtedly due to a very small chemical shift difference ($\Delta\varphi$ ~10-20 Hz) between the highly coupled axial and equatorial fluorines. This effect has been observed recently [25], and although sufficient to explain the spectra, it does not offer a rationale for the departure from the "normal" AB_4 pattern of the other derivatives. The carbon-fluorine and proton resonances are very broad, complicated, and contain unsymmetrical multiplets suggestive of differing conformers. The wide resonances prevented simplication through decoupling experiments, and attempts to thermally (65°) eliminate potential conformers in $SF_5C(CF_3)_2H$ were unsuccessful. The conversion of $SF_5C(CF_3)_2H$ to the fluorosulfate results in the "normal" AB_4 pattern and simplification of the CF_3 resonance. Although it is tempting to suggest that the complex spectra resulted from a hydrogen interaction, we must also consider that this effect was not observed in the other hydryl derivatives and that the fluorosulfate conversion results in an α-carbon substitution which could produce the required $\Delta\varphi$ to give a "normal" AB_4 pattern.

EXPERIMENTAL

Starting materials and apparatus

The SF_5Cl, CF_3I, $CH_2{=}CF_2$, $CHF{=}CF_2$ (PCR, Inc.), KOH (J. T. Baker), $KMnO_4$, $(CH_3)_2CO$ (Fischer Scientific Co.), $[(CH_3)_2C(CN)N{=}]_2$ (Eastman) and $HC(O)NH_2$ (Eastman, <0.05% H_2O) were used as received;

the $KF\cdot 2H_2O$ (Baker & Adamson) was ground and dried at 300°, then stored at 180°. The $CF_3CH{=}CF_2$ was synthesized by the KOH dehydroiodination of $CF_3CH_2CF_2I$ [26] and identified from its infrared spectrum [27].

The gases and volatile liquids were measured by PVT relationships in a conventional Pyrex glass vacuum system equipped with Teflon stopcocks. The $HC(O)NH_2$ was syringed into the reaction vessels after addition of the preweighed dry KF. The photochemical reactions were carried out in quartz vessels with a Rayonet Model RPR-100 Photochemical Reactor using 16 300 nm lamps of approximately 21 watts power. Gas chromatographic separations were carried out on a GOW-MAC Model 69-550 chromatograph with an 8 ft. x 0.25 in. stainless steel column packed with 15% DCQF-1 on Chromosorb P. The thermal stabilities were carried out in an oil bath at ~170° using 0.2 to 0.5 mmole of sample in a 10 ml Pyrex tube equipped with a Teflon stopcock.

Infrared spectra were recorded on a Perkin-Elmer Model 567 Infrared Spectrometer using sample pressures of 3-5 mm Hg in an 8.0 cm Pyrex cell with KBr optics. The ^{19}F nmr spectra were recorded on a JEOL Model MH-100 NMR Spectrometer, and the ^{1}H spectra were recorded on a Varian HA-100 NMR Spectrometer. Elemental analyses, where possible, were obtained from PCR, Inc.

2-Chloro-1,1-dihydryl-1-pentafluorosulfur-*F*-ethane

Approximately 0.35g azobis[2-methylpropionitrile] was added to a 30 ml stainless steel Hoke cylinder and the cylinder evacuated before adding 38 mmole each of SF_5Cl and $CH_2{=}CF_2$. The cylinder was slowly warmed to room temperature, then heated in an oven at 120° for 24 hr. The N_2 generated was removed at -196° and the remaining volatile material fractionated using -45°, -80°, -96° and -196° traps. Final purification of the $SF_5CH_2CF_2Cl$ (-80°) was accomplished by gas chromatography. Yield 33.2 mmole (87.7%), MW 228.6, Theory 226.5. Elemental analysis: C 9.92, H 0.86, F 57.81, S 14.46; Theory C 10.60, H 0.89, F 58.7, S 14.15.

1-Chloro-2-hydryl-2-pentafluorosulfur-F-propane

SF_5Cl (22.0 mmole) and $CF_3CH=CF_2$ (22.0 mmole) were condensed into a 670 ml quartz vessel equipped with a Teflon stopcock. The bottom 10.0 cm of the photolysis bulb was then covered with blackened foil and the mixture photolyzed for 6 hr with 300 nm lamps. Initial fractionation of the reaction mixture using -80°, -110°, and -196° traps was followed by refractionation of the -80° trap with -45°, -63°, -80° and -196° traps. Final g.c. purification of the $SF_5CH(CF_3)CF_2Cl$ in the -63° trap yielded 6.67 mmole (29.5%) of product. MW 297.5; theory 294.4. Elemental analysis: C 12.31, H 0.30, Cl 11.8, F 64.49, S 10.91; theory 12.23, H 0.34, Cl 12.04, F 64.50, S 10.89.

1-Hydryl-1-pentafluorosulfur-F-ethylene

The $SF_5CH=CF_2$ was prepared in a 200 ml Pyrex reaction vessel by shaking 13.3 mmole $SF_5CH_2CF_2Cl$ with excess KOH for ~1 hr. Fractionation of the reaction mixture with -45°, -80° and -196° traps isolated the product in the -80° and -196° traps. Subsequent g.c. purification afforded 11.2 mmole (84.6%) $SF_5CH=CF_2$. MW 190.6; theory 190.1.

2-Pentafluorosulfur-F-propene

$SF_5C(CF_3)=CF_2$ was prepared in an analogous method using $SF_5CH(CF_3)CF_2Cl$ (10.1 mmole) and KOH. The volatile gases were fractionated with -80°, -95°, -110° and -196° traps and the -80° and -95° fractions recombined and refractionated with -45°, -63°, -80° and -196° traps. Final purification by g.c. resulted in isolation of 6.0 mmole (59.5%) $SF_5C(CF_3)=CF_2$. MW 262.0, theory 258.1.

1,1-Dihydryl-1-pentafluorosulfur-F-ethane

A 50 ml Pyrex reactor was charged with 1.03 g KF (19.8 mmole) and 22 ml $HC(O)NH_2$, then evacuated before condensing 9.5 mmole $SF_5CH=CF_2$ into the vessel. The mixture was carefully warmed to room temperature and placed on a wrist-action shaker for 45 minutes. The majority of the volatile gases were removed under static vacuum prior to removal by dynamic vacuum. Fractionation with -45°, -80°, -95°, and -196° traps afforded essentially pure $SF_5CH_2CF_3$ in the -80° and -95° traps. Further purification by gas chromatography gave 7.95 mmole (83.8%) $SF_5CH_2CF_3$. MW 210.1; theory 210.1.

1-Hydryl-1-pentafluorosulfur-F-ethane

In an analogous reaction, $SF_5CF{=}CF_2$ (12.2 mmole) was condensed into a mixture of KF (20.3 mmole) and $HC(O)NH_2$ (20 ml) and placed on a shaker for ~1 hr. Subsequent fractionation with -80°, -95°, -110° and -196° traps yielded SF_5CHFCF_3 in the -95° and -110° traps. Minor impurities were removed by g.c. purification resulting in 10.5 mmole (86.3%) of product. MW 228.6; theory 228.1.

2-Hydryl-2-pentafluorosulfur-F-propane

The preparation of $SF_5C(CF_3)_2H$ was achieved from 5.5 mmole $SF_5C(CF_3){=}CF_2$ and 12.3 mmole KF in 15 ml $HC(O)NH_2$ using a 50 ml reactor. The volatile gases were carefully removed and fractionation isolated the product at -80° and -95° traps. Purification by g.c. resulted in 5.0 mmole (90.9%) $SF_5C(CF_3)_2H$. MW 277.9; theory 278.1. Elemental analysis: C 12.95, H 0.54, F 75.45; theory C 12.96, H 0.36, F 75.15.

F-(1-pentafluorosulfur)ethyl-1-fluorosulfate

SF_5CHFCF_3 (5.0 mmole) and $S_2O_6F_2$ (6.0 mmole) were condensed into a 50 ml Pyrex reactor equipped with a Teflon stopcock. The reaction mixture was warmed to 60° for 4 hr, then cooled to -23° for static removal of the volatile gases. This material was placed on Hg to remove unreacted $S_2O_6F_2$ prior to fractionation with -45°, -80° and -196° traps. The -80° trap contained the $SF_5CF(OSO_2F)CF_3$ which was g.c.'ed to yield 3.85 mmole (76.9%) of product. MW 325.9; theory 326.1. Elemental analysis: C 7.45, F 57.54; theory C 7.37, F 58.25.

F-(2-pentafluorosulfur)propyl-2-fluorosulfate

$SF_5C(CF_3)_2OSO_2F$ was prepared from $SF_5C(CF_3)_2H$ (3.67 mmole) and $S_2O_6F_2$ (4.3 mmole) in a 50 ml Pyrex reactor heated to 80° for 2.5 hr. Fractionation with -45°, -63°, -80° and -196° traps followed removal of the volatile liquids at 0° and Hg treatment. The contents of the -45° and -63° traps were combined and g.c.'ed to yield 2.42 mmole (65.8%) $SF_5C(CF_3)_2OSO_2F$. MW 381.7; theory 376.1. Elemental analysis: C 9.54, S 17.62; theory C 9.38, S 17.05.

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REFERENCES

1 The nomenclature in this paper follows the ACS Division of Fluorine Chemistry approved rules for naming highly fluorinated molecules.

2 R.D. Dresdner and T.R. Hooper, Fluorine Chem. Rev. 4 (1969) 1.

3 J. Steward, L. Kegley, H.F. White and G.L. Gard, J. Org. Chem. 34 (1969) 760.

4 R. Czerepinski and G.H. Cady, J. Amer. Chem. Soc. 90 (1968) 3954.

5 M.D. Vorob'ev, A.S. Filatov and M.A. Englin, J. Org. Chem. USSR 10 (1974) 1009.

6 M.D. Vorob'ev, A.S. Filatov and M.A. Englin, (a) J. Gen. Chem. USSR 43 (1973) 2371; (b) ibid 44 (1974) 2677.

7 R.A. Bekker, B.L. Dyatkin and I.L. Knunyants, Bull. Acad. Sci. USSR 12 (1970) 2575.

8 G.L. Gard and C. Woolf, J. Fluorine Chem. 1 (1971/72) 492.

9 R.E. Banks, M.G. Barlow, R.N. Haszeldine and W.D. Morton, J.C.S. Perkin I (1974) 1266.

10 M.D. Vorob'ev, A.S. Filatov and M.A. Englin, J. Org. Chem. USSR 9 (1974) 407.

11 G. Oates and J.M. Winfield, J. Fluorine Chem. 4 (1974) 235.

12 H.J. Emeleus and B.W. Tattershall, J. Inorg. Nucl. Chem. 28 (1966) 1823.

13 G.A. Silvey and G.H. Cady, J. Amer. Chem. Soc. 72 (1950) 3624.

14 J.R. Case, N.H. Ray and H.L. Roberts, J. Chem. Soc. (1961) 2070.

15 R.E. Banks, R.N. Haszeldine and W.D. Morton, J. Chem. Soc. (C) (1969) 1947.

16 H.W. Sidebottom, J.M. Tedder and J.C. Walton, J. Chem. Soc. (D) (1970) 253.

17 B.L. Dyatkin, E.P. Mochalina and I.L. Knunyants, Fluorine Chem. Rev. 3 (1969) 45.

18 W.T. Miller, J.H. Fried and H. Goldwhite, J. Amer. Chem. Soc. 82 (1960) 3091.

19 C.I. Merrill, 6th International Symposium on Fluorine Chemistry, Durham, England, July 1971.

20 R.L. Kirchmeier and J.M. Shreeve, Inorg. Chem. 12 (1973) 2886.

21 M. Lustig and J.K. Ruff, Inorg. Chem. 4 (1965) 1441.

22 J. Burdon and J.C. Tatlow, J. Appl. Chem. 8 (1958) 293.

23 J.K. Brown and K.J. Morgan, Adv. Fluorine Chem. 4 (1965) 253.

24 A.W. Marcellis and R.E. Eibeck, J. Fluorine Chem. 5 (1975) 71.

25 D.D. DesMarteau, private communication.

26 R.N. Haszeldine and B.R. Steele, J. Chem. Soc. (1954) 923.

27 L.H. Cross, G. Cushing and H.L. Roberts, Spectrochimica Acta 17 (1961) 344.