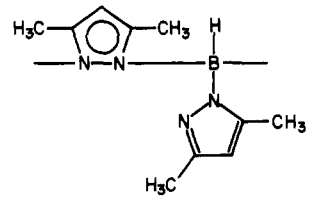

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fications and, of course, would influence the reactivity of the B–H bonds. The latter appear to be more reactive (in a condensation process) in the polymer. The identity of the NMR spectra of both modifications suggests that, once in solution, the macromolecule breaks down to the normal pyrazabole structure. (Note: indeed, the polymer is considerably less readily soluble in $CHCl_3$ as compared to the normal modification of the compound.)

In a previous study it has been shown that the condensation of pyrazabole with pyrazoles at high temperatures must involve at least partial cleavage of the central B_2N_4 ring of the pyrazabole.[5] The present findings seem to be in consonance with that observation. Apparently, 4,8-disubstitution at BH_2 sites of pyrazaboles occurs quite readily in a condensation process; however, a second such step may more readily proceed through polymeric intermediates formed by ring opening, although these have not been observed previously. This interpretation would readily account for the product mixture that was obtained on reacting $H_2B(\mu\text{-}pz)_2BH_2$ with C-substituted pyrazoles.[5]

In this connection it is of interest to note that the boat conformation of the central B_2N_4 ring seems to be the preferred structural arrangement of pyrazaboles.[4] It seems possible that, even in low-temperature electrophilically induced substitution processes, the arrangement of terminal substituents at the boron sites of pyrazaboles governs the reactivity to a major extent. This is already suggested by the pattern of B-disubstitution of a preformed pyrazabole, which always leads to a 4,8-disubstituted product rather than a geminal species. Furthermore, it is apparent that C-substitution at bridging pyrazolyl groups of pyrazaboles also induces specific features. For example, the parent pyrazabole reacts readily with an excess of either BBr_3 or Br_2 to form $Br_2B(\mu\text{-}pz)_2BBr_2$.[8] In contrast, 1,3,5,7-tetramethylpyrazabole reacts with excess BBr_3 to form only the corresponding 4,8-dibromo derivative. The latter exists as a mixture of cis and trans isomers, as was the case with the corresponding derivative of the parent compound, i.e., $HBrB(\mu\text{-}pz)_2BHBr$.[14] On the other hand, reaction of 1,3,5,7-tetramethylpyrazabole with excess Br_2 affords the 4,4,8,8-tetrabromo derivative, $Br_2B(\mu\text{-}pz')_2BBr_2$, in essentially quantitative yield.

In another experiment, K[pz] was reacted with $Br_2(B(\mu\text{-}pz')_2BBr_2$ in refluxing toluene to yield $(pz)_2B(\mu\text{-}pz')_2B(pz)_2$. This compound is the first example of an isolated and characterized pyrazolylpyrazabole where a boron atom is bonded to two chemically different pyrazole moieties. Remarkably, mass spectral data on the crude reaction product indicated the formation of the pyrazaboles of the compositions $B_2(pz)_3(pz')_3$ and $B_2(pz)_2(pz')_4$ as minor byproducts. Their formation again suggests opening of the central B_2N_4 ring of the starting material during the course of the reaction. Even though this seems to occur only to a small extent, it is apparent that such pyrazabole-ring opening may be much more common than heretofore assumed. This is in consonance with the various observations described above.

The observed $\delta(^1H)/\delta(^{13}C)$ data of $(pz)_2B(\mu\text{-}pz')_2B(pz)_2$ are readily assigned on comparison with those of $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$:[6] The shifts 7.63/142.6, 6.04/105.8, and 6.65/133.9 of the former belongs to the 3-, 4-, and 5-positions, respectively, of the terminal pyrazolyl groups. They are essentially identical with those of the terminal pyrazolyl groups in $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ with shifts 7.70/142.6, 6.16/105.7, and 6.81/133.6, respectively. Also, the values for the 2,6-positions of the pyrazabole skeleton of $(pz)_2B(\mu\text{-}pz')_2B(pz)_2$ with shifts 6.10/112.2 compare well with the corresponding data[5] of $(pz')_2B(\mu\text{-}pz')_2B(pz')_2\cdot H_2O$ with shifts 5.91/111.7 (and 5.88/111.1 in the anhydrous compound).

The compound $(pz')_2B(\mu\text{-}pz')_2B(pz')_2\cdot H_2O$ can be dehydrated, though with some difficulty.[5] The anhydrous material is readily reconverted to the monohydrate by stirring the compound with water for a few minutes. However, anhydrous $(pz')_2B(\mu\text{-}pz')_2B(pz')_2$ does not interact with liquid anhydrous ammonia, not even at room temperature in a sealed tube. Also, no reaction occurred when a solution of the anhydrous compound in $CHCl_3$ was mixed with a saturated solution of NH_3 in the same solvent and the mixture was subsequently evaporated. The starting material was recovered unchanged in all cases.

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Syntheses of CF_3SF_4-Substituted Compounds

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The new olefins $CF_3SF_4CF{=}CF_2$ and $CF_3SF_4CH{=}CF_2$ resulted from the dehydrochlorination of $CF_3SF_4CHFCF_2Cl$ and $CF_3SF_4CH_2CF_2Cl$, respectively. Tetrafluoro(trifluoromethyl)(trifluorovinyl)sulfur(VI), $CF_3SF_4CF{=}CF_2$, when reacted with SO_2F_2, SF_4 or SOF_2, $S_2O_6F_2$, and ClF gave $(CF_3SF_4CFCF_3)_2SO_2$, $CF_3SF_4CF[S(O)F]CF_3$, $CF_3SF_4CF(SO_3F)CF_2(SO_3F)$, and $CF_3SF_4CFClCF_3$, respectively. With highly hindered olefins, such as $FSO_2C(CF_3)FCF_2OCF_2CF{=}CF_2$ and $CF_3SF_4CF{=}CF_2$, CF_3SF_4Cl behaved as a chlorofluorinating agent. However, $CF_3C{\equiv}CH$ with CF_3SF_4Cl gave equimolar amounts of $CF_3SF_4C(CF_3){=}CHCl$ and $CF_3C(Cl){=}C(SF_4CF_3)H$. The presence of chiral centers in several of the new compounds gave rise to ^{19}F NMR spectra typical of mixtures of diastereoisomers.

Introduction

Compounds that are formal derivatives of sulfur hexafluoride, e.g., SF_5X, SF_4X_2 (X = R_f, halogen), or CF_3SF_4X (X = Cl, R_f) have attracted considerable interest because of the likelihood that they may exhibit chemical inertness similar to that of the parent SF_6 but will have higher boiling points. Although the chemistry of SF_5-substituted olefins has been investigated extensively,[1] prior to this work, CF_3SF_4-substituted olefins were unknown.

trans-CF_3SF_4Cl is a useful reagent for the introduction of the CF_3SF_4 moiety into molecules. Its addition reactions with a variety of olefins[2] and nitriles[3] and with acetylene[2] gave the expected products. With silylated amines, reduction with concomitant defluorination occurs to give sulfuranes, such as $CF_3S(NR_2)_2Cl$.[4]

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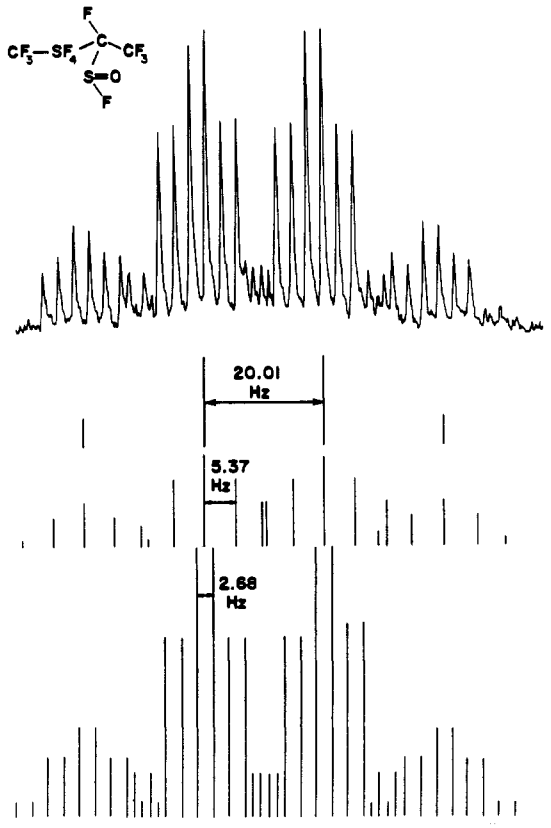


Figure 1. Expanded ^{19}F NMR spectrum for the $-S(O)F$ group in $CF_3SF_4CF[S(O)F]CF_3$.

However, $(CH_3)_3SiCN$ reacts with CF_3SF_4Cl to form the marginally stable $CF_3SF_2(CN)_2Cl$.[5]

In this paper, we wish to report the first syntheses and some reactions of CF_3SF_4-containing olefins that are obtained either via dehydrochlorination reactions with fluoroalkanes or from addition of CF_3SF_4Cl to trifluoropropyne under photolytic conditions. In some cases, CF_3SF_4Cl has a tendency to behave as a chlorofluorinating reagent with olefins.

Results and Discussion

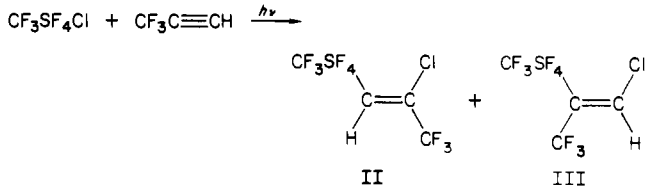
Photolysis of CF_3SF_4Cl with $CHF{=}CF_2$ and $CH_2{=}CF_2$ gave rise to anti-Markovnikov-type addition products $CF_3SF_4CHFCF_2Cl$ and $CF_3SF_4CH_2CF_2Cl$.[2] These alkanes were readily dehydrochlorinated with powdered, anhydrous potassium hydroxide to form the new olefins $CF_3SF_4CF{=}CF_2$ (I) and $CF_3SF_4CH{=}CF_2$. While we have not examined the reactions of the latter, I has been found to undergo reactions with nucleophiles, such as SF_4 or SOF_2, and SO_2F_2 in the presence of fluroide ion to form $CF_3SF_4CF[S(O)F]CF_3$ and the sulfone $[CF_3SF_4CF(CF_3)]_2SO_2$, under milder conditions than when unsubstituted fluoro olefins were used.[6,7] Moreover, above 100 °C, I behaved as a fluorinating agent toward SF_4 and SOF_2 and was itself reduced to a CF_3S^{II}-containing species.

It is likely that, in the fluoride ion catalyzed reaction of I with SF_4, $CF_3SF_4CF(SF_3)CF_3$ was formed initially but, because of hydrolytic sensitivity or glass attack, only $CF_3SF_4CF[S(O)F]CF_3$ was isolated and characterized. (See Figure 1 for the ^{19}F NMR spectrum of the S(O)F group.) While this sulfinyl fluoride was formed readily from I with SOF_2 in the presence of fluoride ion, it was not possible to form the sulfoxide under any conditions tried. This is an interesting contrast with the reaction of I with SO_2F_2 under similar conditions, for in this case, only the disubstituted sulfone $[CF_3SF_4CF(CF_3)]_2SO_2$ was obtained essentially quantitatively while it was impossible to prepare the sulfuryl fluoride.

It should be noted that $SF_5CF{=}CF_2$ did not react with SO_2F_2 under any conditions attempted to form either the sulfuryl fluoride or sulfone.[8] In an easy free-radical addition, peroxydisulfuryl difluoride reacted quantitatively to saturate the olefinic link in I. The exothermic gas-phase reaction was moderated with equimolar amounts of anhydrous nitrogen.

Although chlorine monofluoride added with ease to I at 25 °C or below, CF_3SF_4Cl did not react with I under photolytic conditions (through Pyrex). When CF_3SF_4Cl and I were reacted at 60 °C in the presence of fluoride ion, chlorofluorination of I occurred to give the product that was obtained with ClF. Similarly, CF_3SF_4Cl did not react with $FSO_2CF(CF_3)CF_2OCF_2CF{=}CF_2$ when photolyzed through Pyrex, but chlorofluorination occurred when it was photolyzed through quartz. Reaction of this olefin with ClF produced the identical compound.

Olefins that contain CF_3SF_4- also were obtained when CF_3SF_4Cl and $CF_3C{\equiv}CH$ were photolyzed through Pyrex to give an equimolar mixture of two of the four possible isomers. These isomers were separated by using gas chromatography and were tentatively identified as *Z* isomers with structures based on their respective ^{19}F and ^1H NMR spectra. For II, CF_3C is a pentet



($J_{CF_3C-SF_4}$ = 13.2 Hz), CF_3S is a pentet ($J_{CF_3S-SF_4}$ = 23.4 Hz), and SF_4 is a complex multipet with J_{H-SF_4} = 9.28 Hz; for III, CF_3C is a singlet, SF_4 is a quartet ($J_{SF_4-CF_3S}$ = 24.2 Hz) of doublets (J_{SF_4-H} = 7.57 Hz), and CF_3S is a pentet. No coupling is observed between the fluorine atoms of CF_3C and H in either case, which suggests that the two groups are most likely cis to each other in both isomers. In II, coupling between the fluorine atoms of $-SF_4-$ and those of CF_3C suggests that these groups are trans. The ^1H chemical shift in III is farther downfield than that in II, which supports the assignment of III as the isomer where H and Cl are geminal. Unfortunately there were no useful skeletal fragments in the mass spectrum that did not contain C_2 and that would have aided firm structure assignments.

The presence of asymmetric centers as well as the fact that nearly all chemically nonequivalent fluorine atoms in the molecules undergo spin–spin interactions gave rise to complex, although first-order, ^{19}F and ^1H NMR spectra. However, chemical shift differences were not observed in every case where chirality exists. The observed shifts (*) are noted in the Experimental Section.

Surprisingly, and in contrast with analogous SF_5-containing compounds, these CF_3SF_4-containing molecules are readily hydrolyzed by basic solutions or water. This precludes further chemistry in aqueous systems.

Experimental Section

Materials. *trans*-Chlorotetrafluoro(trifluoromethyl)sulfur,[9] thionyl fluoride,[10] sulfuryl fluoride,[10] and peroxydisulfuryl difluoride[11] were prepared according to literature methods. Trifluoroethylene, difluoroethylene, and 1,3-trifluoropropyne were obtained from PCR. Chlorine monofluoride was purchased from Ozark-Mahoning Co. All reagents were used without further purification.

General Procedures. Gases and volatile liquids were handled in a Pyrex vacuum apparatus equipped with a Heise–Bourdon tube gauge. Starting materials and purified products were measured quantitatively by using *PVT* techniques. Products were purified initially by trap-to-trap distillation and finally by use of a Hewlett-Packard 5712A gas chromatograph. Chromatographic columns were packed with 25% Kel-F No. 3 oil on Chromosorb P or 30% QF-1 on Chromosorb P. Infrared spectra were recorded with a Peerkin-Elmer 599B spectrometer using a 10-cm

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cell fitted with KBr windows for gaseous samples and a capillary film between AgCl windows for liquid samples. ^{19}F NMR and ^1H NMR spectra were obtained on a JEOL FX-90Q FT NMR spectrometer using CCl_3F and tetramethylsilane as external references, respectively. Mass spectra were recorded with a VG 7070 HS spectrometer. Elemental analyses were performed by Beller Mikroanlytisches Laboratorium, Göttingen, West Germany. Photolysis reactions were accomplished by using a Hanovia utility ultraviolet quartz lamp.

Preparation of $CF_3SF_4CF{=}CF_2$. Photolysis of trifluoroethylene and CF_3SF_4Cl gave $CF_3SF_4CHFCF_2Cl$[2] in 47% yield. The $CF_3SF_4CHFCF_2Cl$ (2 mmol) was condensed into a Pyrex reaction vessel fitted with a vacuum stopcock that contained dry powdered potassium hydroxide (6 mmol) at −196 °C. The vessel was warmed to and held at room temperature for 5 min. Volatile products were distilled through traps at −60, −78, and −98 °C. The olefin, $CF_3SF_4CF{=}CF_2$, was retained in a trap at −78 °C in 80% yield. Its vapor pressure is ∼100 torr at 25 °C. Further purification was accomplished by gas chromatography using a 12-ft column packed with Kel-F No. 3 oil on Chromosorb P and operating at room temperature. The infrared spectrum of $CF_3SF_4CF{=}CF_2$ is as follows: 1770 vs, 1340 s, 1240 vs, 1150 vs, 990 m, 845 vs, 795 vs, 720 vs, 640 vs, 575 w, 470 w cm^{-1}. The ^{19}F NMR spectrum for $CF_3SF_4CF^A{=}CF^BF^C$ consists of a multiplet at ϕ 38.0 (SF_4, $J_{CF_3-SF_4}$ = 23.4 Hz, $J_{SF_4-F^A}$ = 5.86 Hz, $J_{SF_4-F^B}$ = 11.64 Hz, $J_{SF_4-F^C}$ = 14.21 Hz), a pentet at ϕ −63.88 (CF_3), a multiplet at ϕ −98.81 (F^B, $J_{F^B-F^C}$ = 48.15 Hz), a multiplet at ϕ −97.04 (F^C), and a multiplet at ϕ −160.2 (F^A, $J_{F^A-F^B}$ = 73.34 Hz, $J_{F^A-F^C}$ = 133.5 Hz). The EI mass spectrum contains a molecular ion at m/e 258 ($CF_3SF_4CF{=}CF_2^+$, 100%) with other fragments at m/e 189 ($SF_4CF{=}CF_2^+$, 55%), 151 ($SF_2CF{=}CF_2^+$, 80%), 101 (CF_3S^+, 60%), and 69 (CF_3^+, 100%).

Anal. Calcd for $C_3F_{10}S$: S, 12.40. Found: S, 12.43.

Preparation of $CF_3SF_4CH{=}CF_2$. Photolysis of difluoroethylene and CF_3SF_4Cl gave $CF_3SF_4CH_2CF_2Cl$[2] in 57% yield. The $CF_3SF_4CH_2CF_2Cl$ was condensed into a Pyrex reaction vessel fitted with a vacuum stopcock that contained dried powdered potassium hydroxide (6 mmol) at −196 °C. The vessel was warmed to room temperature and held these for 5 min. Volatile products were distilled through traps held at −60, −78 and −98 °C. The trap at −78 °C retained $CF_3SF_4CH{=}CF_2$ in 80% yield. Its vapor pressure at 25 °C is ∼80 torr. Further purification was accomplished by gas chromatography using a 12-ft column packed with Kel-F No. 3 oil on Chromosorb P operating at room temperature. The infrared spectrum of $CF_3SF_4CH{=}CF_2$ is as follows: 1735 vs, 1235 vs, 1340 vs, 1240 vs, 1200 s, 1150 s, 1000 s, 890 w, 860 vs, 825 vs, 680 vs, 660 w, 630 m, 595 w, 480 w cm^{-1}. The ^{19}F NMR spectrum for $CF_3SF_4CH{=}CF^AF^B$ consists of a multiplet at ϕ 51.49 (SF_4, $J_{SF_4-CF_3}$ = 24.5 Hz, J_{SF_4-H} = 7.01 Hz, $J_{SF_4-F^A}$ = 15.57 Hz, $J_{SF_4-F^B}$ = 15.68 Hz), a pentet at ϕ −63.24 (CF_3), a multiplet at ϕ −62.88 (F^A, $J_{F^A-F^B}$ = 9.16 Hz, J_{F^A-H} = 18.80 Hz), and a multiplet at ϕ −83.80 (F^b, J_{F^B-H} = 2.5 Hz). The ^1H NMR spectrum consists of a multiplet at δ 5.90. The EI mass spectrum contains a molecular ion at m/e 240 ($CF_3SF_4CH{=}CF_2^+$, 20%) and other fragments at m/e 171 ($SF_3CHCF_2^+$, 40%), 152 ($SF_2CHCF_2^+$, 60%), 101 (CF_3S^+, 30%), 89 (SF_3^+, 95%), and 69 (CF_3^+, 80%).

Anal. Calcd for C_3F_9SH: S, 13.33. Found: S, 13.06.

Reaction of $CF_3SF_4CF{=}CF_2$ with Sulfuryl Fluoride. Sulfuryl fluoride (2 mmol) and $CF_3SF_4CF{=}CF_2$ (2 mmol) were condensed into a 75-mL Monel Hoke vessel that contained a catalytic amount of CsF (∼1 g) with diglyme as solvent at −196 °C. It was heated at 80 °C for 8 h. Volatile products were passed through traps at −60, −78, and −98 °C. The sulfone was stopped in a trap at −78 °C in 80% yield. The infrared spectrum of $(CF_3SF_4CFCF_2)_2SO_2$ is as follows: 1370 m, 1280 vs, 1248 vs, 1220 vs, 1150 vs, 990 m, 910 s, 840 vs, 830 vs, 770 vs, 670 vs, 630 s, 580 w, 530 w, 480 w, 460 w, 430 w cm^{-1}. The ^1F NMR spectrum consists of a multiplet at ϕ 30.81 (30.70*) (SF_4, $J_{SF_4-CF_3S}$ = 23.51 Hz, $J_{SF_4-CF_3C}$ = 10.11 Hz, J_{SF_4-CF} = 1.46 Hz), a pentet a ϕ −63.48 nCF_3S), a multiplet at ϕ −74.62 (−74.56*) (CF_3C, J_{CF_3C-CF} = 9.67 Hz), and a multiplet at ϕ −168.89 (−168.36*) (CF). The CI positive ion mass spectrum contains peaks at m/e 392 ($C_3S_3F_{12}O_2^+$, 0.58%), 304 ($C_2S_3F_8O_2^+$, 0.16%), 232 ($C_4F_8S^+$, 0.52%), 231 ($C_2S_3F_5O$, 10.18%), 212 ($C_2S_3F_4O$, 0.5%), 151 ($C_2F_5S^+$, 3.29%), 139 (CF_5S^+, 0.5%), 132 ($C_2F_4S^+$, 0.1%), 119 ($C_2F_5^+$, 18.12%), 101 (CF_3S^+, 3.26%), 100 ($C_2F_4^+$, 2.64%), and 69 (CF_3^+, 100%).

Reaction of $CF_3SF_4CF{=}CF_2$ with SF_4. Sulfur tetrafluoride (2.1 mmol) and $CF_3SF_4CF{=}CF_2$ (2 mmol) were condensed into a 25-mL Monel Hoke vessel containing dried powdered cesium fluoride (∼1 g) at −196 °C, and the vessel was heated at 70° C for 6 h. Volatile products were passed through traps at 0 and −50 °C. The trap at −50 °C retained $CF_3SF_4CF[S(O)F]CF_3$ in 50% yield. It was further purified by gas chromatography using a 2-ft column packed with Kel-F No. 3 oil on Chromosorb P operating at 40 °C. The infrared spectrum of $CF_3SF_4CF[S(O)F]CF_3$ is as follows: 1240 vs, 1150 vs, 1080 w, 1030 vs, 840 vs, 790 s, 740 vs, 680 vs, 630 vw, 570 vw, 465 vw cm^{-1}. The ^{19}F NMR spectrum consists of a multiplet at ϕ 35.88 (36.84*) (SF_4, $J_{SF_4-CF_3S}$ = 23.31 Hz, $J_{SF_4-CF_3C}$ = 9.76 Hz, J_{SF_4-SF} = 5.37 Hz), a pentet at ϕ −62.03 (−62.08*) (CF_3S), a multiplet at ϕ −67.35 (−66.72*) (CF_3C, J_{CF_3-CF} = 7.25 Hz), a multiplet at ϕ −5.22 (−5.44*) [S(O)F (Figure 1), J_{SF-CF} = 2.68 Hz, J_{SF-CF_3} = 20.0 Hz], and a multiplet at ϕ −132.51 (−131.11*) (CF). The EI mass spectrum contains peaks at m/e 258 ($CF_3SF_4C_2F_3^+$, 1.06%), 170 ($SF_3C_2F_3^+$, 41.18%), 151 ($SF_2CFCF_2^+$, 12.80%), 89 (SF_3^+, 21.36%), 69 (CF_3^+, 100%), and 67 (SOF^+, 26.83%).

Anal. Calcd for $C_3F_{12}S_2O$: S, 18.60. Found: S, 18.83.

Reaction of $CF_3SF_4CF{=}CF_2$ with CF_3SF_4Cl. The reactants, $CF_3SF_4CF{=}CF_2$ (2 mmol) and CF_3SF_4Cl (2.1 mmol), were condensed into a 75-mL Hoke metal vessel containing dry powdered cesium fluoride (∼1 g) at 196 °C. The vessel was then heated for 6 h at 60 °C, and the volatile products were passed through traps at −60, −78, and −98 °C. In the trap at −78 °C, $CF_3SF_4CFClCF_3$ was collected in 70% yield. It was further purified by gas chromatography using a 2-ft column packed with Kel F No. 3 oil on Chromosorb P operating at room temperature. The infrared spectrum of $CF_3SF_4CFClCF_3$ is as follows: 1240 vs, 1210 vs, 1135 vs, 955 vs, 900 m, 890 m, 845 vs, 790 vs, 735 vs, 680 vs, 670–660 w, 485 s cm^{-1}. The ^{19}F NMR spectrum contains a multiplet at ϕ 26.80 (SF_4, $J_{SF_4-CF_3S}$ = 22.95 Hz, J_{SF_4-CF} = 10.19 Hz, $J_{SF_4-CF_3C}$ = 10.25 Hz), a pentet at ϕ −63.42 (CF_3S), a multiplet at ϕ −76.10 (CF_3C, J_{CF_3C-CF} = 6.8 Hz), and a multiplet at ϕ −94.42 (CF). The EI mass spectrum contains peaks at m/e 139 ($CF_3SF_2^+$, 6.71%), 137 ($CF_3CF^{37}Cl^+$, 26.67%), 135 ($CF_3CF^{35}Cl^+$, 85.76%), 119 ($CF_3CF_2^+$, 10.66%), 101 (CF_3S^+, 1.54%), 89 (SF_3^+, 25.40%), 87 ($CF_2{}^{37}Cl^+$, 14.60%), 85 ($CF_2{}^{35}Cl^+$, 48.30%), and 69 (CF_3^+, 100%).

Anal. Calcd for $C_3F_{11}SCl$: S, 10.25. Found: S, 10.62.

Reaction of $CF_3SF_4CF{=}CF_2$ with ClF. Chlorine monofluoride (2.2 mmol) and $CF_3SF_4CF{=}CF_2$ (2 mmol) were condensed into a 75-mL Hoke metal vessel at −196 °C. The vessel was allowed to stand for 24 h at room temperature. The $CF_3SF_4CFClCF_3$ that was formed was purified as outlined above. The yield was essentially quantitative.

Reaction of $CF_3SF_4CF{=}CF_2$ with $S_2O_6F_2$. To a 1-L Pyrex reaction vessel fitted with a vacuum stopcock and charged with $CF_3SF_4CF{=}CF_2$ (2 mmol) diluted with nitrogen (2 mmol) was slowly introduced $S_2O_6F_2$ (2.1 mmol) at room temperature until it was present in slight excess. The reaction mixture was held at room temperature for 0.25 h, and then it was passed through a trap at 0 °C. $CF_3SF_4CF(SO_3F)CF_2(SO_3F)$ was collected in a trap at −20 °C in 50% yield. Its infrared spectrum is as follows: 1480 vs, 1250–1070 br, vs, 975 vs, 940 w, 880–820 br, vs, 795 s, 735 vs, 725 s, 710 s, 685 vs, 665 s, 625 s, 565 s, 475 m, 465 m cm^{-1}. The ^{19}F NMR spectrum of $CF_2{}^FSF_4{}^ECF^D(SO_3F^B)CF_2{}^C(SO_3F^A)$ shows a multiplet at ϕ 55.02 (1, SO_3F^B, $J_{F^B-F^D}$ = 9.76 Hz, $J_{F^B-F^E}$ = 3.29 Hz), a triplet at ϕ 53.92 (1, SO_3F^A, $J_{F^A-F^C}$ = 8.42), a multiplet at ϕ 28.03 (4, $SF_4{}^E$, $J_{F^E-F^F}$ = 22.70 Hz, $J_{F^E-F^C}$ = 10.26 Hz, $J_{F^E-F^D}$ = 12.49 Hz), a pentet at ϕ −61.28 (3, $CF_3{}^F$), a multiplet at ϕ −78.59 (2, $CF_2{}^C$), and a multiplet at ϕ −105.35 (1, CF^D). The CI^+ mass spectrum contains peaks at m/e 279 ($C_2S_2F_5O_6^+$, 0.62%), 201 ($C_3F_7S^+$, 0.08%), 199 ($C_2F_5SO_3^+$, 2.13%), 177 (CF_3S^+, 0.23%), 149 ($CF_3SO_3^+$, 4.24%), 139 (CF_5S^+, 5.70%), 120 (CF_4S^+, 0.5%), 119 ($C_2F_5^+$, 4.63%), 89 (SF_3^+, 11.60%), 83 (SO_2F^+, 100%), 70 (SF_2^+, 8.30%), 69 (CF_3^+, 92.50%), 67 (SOF^+, 17.23%), and 64 (SO_2^+, 6.98%).

Reaction of CF_3SF_4Cl with $FO_2SCF(CF_3)CF_2OCF_2CF{=}CF_2$. CF_3SF_4Cl (2 mmol) and $FO_2SCF(CF_3)CF_2OCF_2CF{=}CF_2$ (2 mmol) were condensed into a quartz vessel, and the mixture was photolyzed for 24 h. Products were passed through traps at 0 and −10 °C. $FO_2SCF(CF_3)CF_2OCF_2CFClCF_3$ was retained in the trap at −10 °C (30% yield). It was further purified by gas chromatography using a 50-cm column of QF-1 on Chromosorb P operating at 90 °C.

Reaction of $FO_2SCF(CF_3)CF_2OCF_2CF{=}CF_2$ with ClF. Chlorine monofluoride (2.2 mmol) and $FO_2SCF(CF_3)CF_2OCF_2CF{=}CF_2$ (2 mmol) were condensed into a 75-mL Monel Hoke vessel at −196 °C and allowed to stand at room temperature for 24 h. Purification was carried out as mentioned above. The infrared spectrum is as follows: 1450 vs, 1290–1090 br, vs, 900–865 br, vs, 810 vs, 760 s, 740 s, 700 vs, 610 vs, 540 vs, 480 vs, 465 s, 450 w cm^{-1}. The ^{19}F NMR spectrum of $FO_2S^GCF^E(CF_3{}^F)CF_2{}^DOCF_2{}^CCF^BClCF_3{}^A$ contains a mulltiplet at ϕ 56.20 (1, SO_2F^G), a pentet at ϕ −70.48 (3, $CF_3{}^A$), a multiplet at ϕ −73.96 (2, $CF_2{}^C$), a quartet at ϕ −77.08 (3, $CF_3{}^F$), a multiplet at ϕ −79.52 (2, $CF_2{}^D$), overlapping pentets at ϕ −139.3 (1, CF^B), and doublets of overlapping pentets at ϕ −164.8 (1, CF^E). The EI mass spectrum contains peaks at m/e 235 ($CF_2CF_2CFClCF_3^+$, 0.98%), 233 ($FSO_2CF(CF_3)CF_2^+$, 19.07%), 187 ($CF_2CF^{37}ClCF_3^+$, 9.68%), 185 ($CF_2CF^{35}ClCF_3^+$, 30.8%), 137 ($CF_3CF^{37}Cl^+$, 3.13%), 135 ($CF_3CF^{35}Cl^+$, 9.63%), 131 ($CF_3CCF_2^+$, 3.5%), 83 (SO_2F^+, 2.23%), 69 (CF_3^+, 73%), and 67 (SOF^+, 100%).

Anal. Calcd for $C_6F_{13}O_3SCl$: S, 7.37. Found: S, 7.25.

Reaction of CF_3SF_4Cl with $CF_3C{\equiv}CH$. Trifluoropropyne (5 mmol) and CF_3SF_4Cl (5.2 mmol) were condensed into a Pyrex reaction vessel fitted with a vacuum stopcock at −196 °C and then photolyzed for 3 days

at room temperature. The product mixture was passed through traps held at -10 and -50 °C. The product was retained in the trap at -50 °C in 30% yield. It was further purified by gas chromatography using a 4-ft column packed with 25% Kel-F No. 3 oil on Chromosorb-P. Two isomers II and III were isolated in equal amounts. The infrared spectrum of II consists of bands at 1290 m, 1250 vs, 1200 w, 1150 vs, 1090 m, 1025 w, 980 s, 890 w, 830 vs, 730 vs, 660 vs, 620 vs, 570 w, 550 m, and 485 m, cm^{-1}. The ^{19}F NMR spectrum consists of a multiplet at ϕ 46.10 (SF_4), a pentet at ϕ -64.11 (CF_3S), and a pentet at ϕ -63.07 (CF_3C). The ^1H NMR spectrum consists of a multiplet at δ 6.94. The infrared spectrum of III consists of bands at 1280 m, 1250 vs, 1210 m, 1285 vs, 1150 vs, 1090 m, 1025 s, 980 vs, 890 m, 840 vs, 730 vs, 690 m, 650 vs, 620 vs, 550 m, and 485 w cm^{-1}. The ^{19}F NMR spectrum consists of a multiplet at ϕ 42.97 (SF_4), a pentet at ϕ -64.39 (CF_3S), and a singlet at ϕ -69.20 (CF_3C). The ^1H NMR spectrum consists of a multiplet at δ 7.35. The EI mass spectrum contains a molecular ion at m/e 306 [$CF_3C(CF_3SF_4)CHCl^+$, 0.8%] with other fragments at m/e 239 ($CF_3SF_4C_2H^{37}Cl^+$, 1.37%), 235 ($CF_3SF_4C_2H^{35}Cl^+$, 3.82%), 199 ($CF_3SF_2CHCCl^+$, 13.35%), 139 ($CF_3SF_2^+$, 2.70%), 131 ($SF_2CC^{37}Cl^+$, 4.30%), 129 ($SF_2C_2^{35}Cl^+$, 13%), 89 (SF_3^+, 21.3%), and 69 (CF_3^+, 100%).

Anal. Calcd for $C_4HF_{10}SCl$: S, 10.45. Found: S, 9.43.

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Preparation of New Bis(dialkylamino)phosphine Species via Reduction of Bis(dialkylamino)halophosphines[1a]

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Four new bis(dialkylamino)phosphine species, $(Me_2N)_2PH$, $CH_3\overline{NCH_2CH_2N(CH_3)}PH$, $(CO)_3Ni[(Me_2N)_2PH]$, and $(CO)_3Ni[CH_3\overline{NCH_2CH_2N(CH_3)}PH]$, have easily been prepared in good yields through reduction of corresponding bis(dialkylamino)halophosphines by lithium tri-*sec*-butylborohydride. The preparation and characterization of these compounds are discussed. An improved synthesis for obtaining quantitative yields of $(CO)_3NiL$ [L = Me_2NPF_2, $(Me_2N)_2PF$, $CH_3\overline{NCH_2CH_2N(CH_3)}PF$] is also described.

Introduction

Secondary phosphines can now be prepared quite easily by a number of methods, the most common being the reduction of halophosphine derivatives or the alkylation of phosphine species.[2] In contrast, previous attempts to prepare the secondary aminophosphine $(Me_2N)_2PH$ have been unsuccessful. Recently the syntheses of $(i\text{-}Pr_2N)_2PH$, and $(Et_2N)_2PH$ were reported by King, Sadanani, and Sundaram.[3,4] The compounds were prepared by the reaction of the corresponding $(R_2N)_2PCl$ precursor with $LiAlH_4$ in diethyl ether. An analogous reaction of $(Me_2N)_2PCl$, however, did not produce any evidence of $(Me_2N)_2PH$ formation.[3,4] Nöth and Vetter monitored the reaction of $LiBH_4$ with $(Me_2N)_2PCl$ and were able to obtain the borane adduct of bis(dimethylamino)phosphine, $(Me_2N)_2PH{\cdot}BH_3$, but not the free phosphine itself.[5] The use of $LiAlH[OC(CH_3)_3]_3$ as a reducing agent on $(Me_2N)_2PCl$ was also unsuccessful as a method for preparing $(Me_2N)_2PH$.[6]

The only other examples of trivalent phosphorus derivatives of the type $(R_2N)_2PH$ are silylphosphines, $(Me_3Si)_2NP(R)H$,[7] and heterocycles of the type $R\overline{NCH_2CH_2CHR'N(R)}PH$ or $R\overline{NCH_2CH_2N(R)}PH$, where R groups are usually large alkyl structures and R' is H or an alkyl group.[4]

These results suggest interesting possibilities relative to the mechanism of the process. A number of dicoordinated phosphorus cations of the type $(R_2N)_2P^+$ are known.[9] These cations are strong Lewis acids,[10] and the ring structures are particularly stable. If they were to form, even briefly, in solution due to the precipitation of lithium halide, one would expect rapid reaction with any hydride to produce bis(dialkylamino)phosphines. The reported results show that this description is too simplistic. The data now available show that the reactions are very sensitive to the reducing agent chosen and to the type of organic group attached to the nitrogen.

In this study the reactivity of a number of bis(dialkylamino)halophosphines with hindered borohydride reducing agents such as the commercial "Selectrides" (lithium, sodium, or potassium tri-*sec*-butylborohydride) has been examined. The general equation for the reduction process is

$$(R_2N)_2PX + M[HBR_3] \rightarrow (R_2N)_2PH + MX + BR_3 \quad (1)$$

By use of this method it has been possible to synthesize easily and in high yield the elusive $(Me_2N)_2PH$, along with the new cyclic bis(methylamino)phosphine $CH_3\overline{NCH_2CH_2N(CH_3)}PH$.

We were also interested in the coordination chemistry of these new phosphine species. The coordination chemistry of aminohalophosphines is quite rich and has been extensively studied,[11] and the coordination chemistry of the phosphenium cation species is an area of current interest.[12] By use of the L-Selectride

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