

Contribution from the Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322**Preparation of Allyldibromophosphine and Allyltrifluorophosphorane**

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The reaction of allyldifluorophosphine with HBr has been studied. The products characterized by mass, ir, and NMR spectroscopy and by analysis—allyltrifluorophosphorane, $\text{F}_3\text{PHCH}_2\text{CH}=\text{CH}_2$, and allyldibromophosphine, $\text{Br}_2\text{PCH}_2\text{CH}=\text{CH}_2$ —are consistent with initial addition of HBr to trivalent phosphorus followed by disproportionation through successive loss of HF and addition of more HBr.

The reaction $\text{PF}_2\text{CH}_2\text{CH}=\text{CH}_2$ with HBr was initially investigated in order to ascertain the feasibility of HBr free-radical addition across the C=C double bond. A reaction such as this would likely have produced $\text{PF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$. However, no evidence of free-radical addition was observed. A faster non-free-radical reaction to produce the new compounds $\text{PF}_3\text{HCH}_2\text{CH}=\text{CH}_2$ and $\text{PBr}_2\text{CH}_2\text{CH}=\text{CH}_2$ was found to occur.

Experimental Section

General Data. Standard high-vacuum techniques were used throughout. Hydrogen bromide (Matheson) was used without further purification. Allyldifluorophosphine was prepared as previously described.¹ NMR data were obtained on neat liquids using a Varian XL-100-12 spectrometer. Chemical shifts were determined by the tube-interchange technique. Ir data were recorded on a Beckman IR-20-A spectrometer. Solid-phase ir spectra were obtained at -196° using a low-temperature cell.² Mass spectral data were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer operating at 70 eV. Analysis was performed by Chemalytics, Inc., Tempe, Ariz.

Preparation of $\text{PBr}_2\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{PF}_3\text{HCH}_2\text{CH}=\text{CH}_2$. In a typical reaction 0.86 mmol of $\text{PF}_2\text{CH}_2\text{CH}=\text{CH}_2$ and 1.40 mmol of the HBr were condensed at -196° into a 100-ml quartz reaction tube. The reactants were allowed to warm slowly to room temperature. The almost immediate appearance of a yellow solid at low temperature was observed. This solid disappeared as the reaction mixture approached room temperature. At room temperature a pool of clear liquid was observed in the bottom of the reaction tube which indicated the occurrence of a reaction (vapor pressures and amounts of reactants used were such that, had no reaction occurred, all material would be vaporized). The reaction mixture was allowed to stand at room temperature for 2 min and then cooled to -196° . Yellow coloration of the mixture was observed upon condensation. The volatile products were distilled through traps held at -15 , -35.5 , -78 , -126 , and -196° . A yellow solid remained in the reaction tube. The trap held at -196° contained 0.81 mmol of HBr (ir). The trap held at -126° contained 0.19 mmol of $\text{PF}_2\text{CH}_2\text{CH}=\text{CH}_2$ (ir). The trap held at -35.5° contained 1 drop of unidentified material. The trap held at -15° contained 0.13 mmol of a clear liquid of low volatility ($\text{vp} = 1 \text{ mm}$ at 21°) which slowly discolored to a yellow solution upon standing at room temperature. This liquid was subsequently identified as $\text{PBr}_2\text{CH}_2\text{CH}=\text{CH}_2$. Anal. Calcd: C, 15.54; H, 2.17; Br, 68.93. Found: C, 15.34; H, 2.05; Br, 63.78. (Analyst reported Br was probably low as a result of experimental difficulty.) The trap held at -78° contained 0.47 mmol of a clear liquid which was subsequently identified as $\text{PF}_3\text{HCH}_2\text{CH}=\text{CH}_2$. Allyltrifluorophosphorane is unstable at room temperature decomposing rapidly to white solids. Decomposition in the liquid phase at temperatures as low as -30° was observed. However, vapor-phase samples appear to be reasonably stable at room temperature. The vapor pressure of $\text{PF}_3\text{HCH}_2\text{CH}=\text{CH}_2$ is 8.4 mm at -16.0° . The gas-phase molecular weight determined at 52 mm was found to be 127; calcd mol wt 130. It should be noted that the formation of trace amounts of what is thought to be $\text{PBrCH}_2\text{CH}=\text{CH}_2$ (mass spectrum) was observed in an investigation of preliminary distillation (-45 , -196°).

Spectral Data for $\text{PBr}_2\text{CH}_2\text{CH}=\text{CH}_2$. Ir data (solid phase, -196°) (relative intensities and tentative assignments in parentheses) (cm^{-1}): 3055 (w, $\nu(\text{CH}$ vinyl)), 2980 (vw, $\nu(\text{CH})$), 2950 (vw, $\nu(\text{CH})$), 2923 (vw, $\nu(\text{CH})$), 2870 (vw, $\nu(\text{CH})$), 1840 (vw), 1629 (m, $\nu(\text{C}=\text{C})$), 1410 (m, $\delta(\text{CH}_2)$), 1380 (m, $\delta(\text{HCH})$), 1290 (vw), 1200 (vw, $\rho(\text{CH}_2)$), 1180 (w), 1050 (w), 1035 (w), 983 (ms, $\delta(\text{HCC}$ in $\text{CH}_2=\text{CH}$)), 918 (s,

$\delta(\text{HCC}$ in $\text{CH}=\text{CH}$)), 820 (m), 801 (m), 731 (w), 702 (vw), 570 (m), 400 (s, $\nu(\text{PBr})$), 378 (s, $\nu(\text{PBr})$).

The mass spectrum displays the following m/e values (relative intensities and assignments in parentheses) (peaks not essential to characterization omitted): 234 (1.0, $\text{P}^{81}\text{Br}_2\text{C}_3\text{H}_5^+$), 232 (2.0, $\text{P}^{81}\text{Br}^{79}\text{BrC}_3\text{H}_5^+$), 230 (1.0, $\text{P}^{79}\text{Br}_2\text{C}_3\text{H}_5^+$), 193 (0.5, $\text{P}^{81}\text{Br}_2^+$), 191 (1.0, $\text{P}^{81}\text{Br}^{79}\text{Br}^+$), 189 (0.5, $\text{P}^{79}\text{Br}_2^+$), 153 (3.5, $\text{P}^{81}\text{BrC}_3\text{H}_5^+$), 151 (3.5, $\text{P}^{79}\text{BrC}_3\text{H}_5^+$), 112 (1.0, P^{81}Br^+), 110 (1.0, P^{79}Br^+), 41 (100, C_3H_5^+), 39 (62, C_3H_3^+).

NMR data: ^1H (100.1 MHz, $+14^\circ$): broad unresolved peak, δ 3.7 ppm (TMS), area 2; multiplets, δ 5.8 and 6.7, combined area 3. ^{31}P (40.5 MHz, $+14^\circ$): broad apparent singlet at δ -177.8 ppm (85% H_3PO_4).

Spectral Data for $\text{PF}_3\text{HCH}_2\text{CH}=\text{CH}_2$. Ir data (gas phase) (relative intensities and tentative assignments in parentheses) (cm^{-1}): 3080 (w, $\nu(\text{CH}$ vinyl)), 3012 (vw, $\nu(\text{CH})$), 2980 (vw, $\nu(\text{CH})$), 2882 (vw, $\nu(\text{CH})$), 2429 (m, $\nu(\text{PH})$), 1840 (w), 1630 (w, $\nu(\text{C}=\text{C})$), 1410 (w, $\delta(\text{CH}_2)$), 1370 (m, $\delta(\text{CH}_2)$), 1230 (w), 1185 (w), 1065 (w), 1016 (ms, $\delta(\text{HCC}$ in $\text{CH}_2=\text{CH}$)), 950 (s, $\delta(\text{HCC}$ in $\text{CH}=\text{CH}$)), 920 (s, sh), 805 (s, $\nu(\text{PF})$), 760 (s, $\nu(\text{PF})$), 575 (m), 469 (w).

The mass spectrum displays the following m/e values (relative intensities and assignments in parentheses) (peaks not essential to characterization omitted): 111 (1.5, $\text{PF}_2\text{C}_3\text{H}_6^+$), 110 (13.1, $\text{PF}_2\text{C}_3\text{H}_5^+$), 91 (1.5, PFC_3H_5^+), 89 (16.7, PFC_3H_3^+ or PF_3H^+), 69 (19.4, PF_2^+), 41 (100, C_3H_5^+), 39 (66.7, C_3H_3^+).

NMR data: ^1H (100.1 MHz, $+30^\circ$): broad unresolved multiplets at δ 2.4 ppm, area 2, δ 4.8 and 5.3 ppm, combined area 3; doublet of quartets at δ 6.77 ppm, area 1, $J_{\text{PH}} = 886 \text{ Hz}$, $J_{\text{HPF}} = 92 \text{ Hz}$. ^1H (100.1 MHz, -40°): broad unresolved multiplets at δ 3.3 ppm, area 2, δ 5.8 and 6.3 ppm of combined area 3; doublet of triplets of doublets at δ 6.22 ppm, area 1, $J_{\text{PH}} = 843 \text{ Hz}$, $J_{\text{HPF}_a} = 126 \text{ Hz}$, $J_{\text{HPF}_e} = 30 \text{ Hz}$. (a = axial and e = equatorial in assumed trigonal-bipyramidal structure.) ^{19}F (94.1 MHz, -80°): doublet of doublets at δ $+25.1$ ppm (CFCl_3), area 2, $J_{\text{PF}_a} = 800 \text{ Hz}$, $J_{\text{F}_a\text{F}_e} = 28 \text{ Hz}$, $J_{\text{HPF}_a} = 120 \text{ Hz}$; doublet of triplets of doublets at δ $+99.7$ ppm, area 1, $J_{\text{PF}_e} = 966 \text{ Hz}$, $J_{\text{F}_a\text{F}_e} = 28 \text{ Hz}$, $J_{\text{HPF}_e} = 28 \text{ Hz}$. ^{31}P (40.5 MHz, -80°): doublet of doublets of triplets at δ $+11$ ppm (85% H_3PO_4), $J_{\text{PF}_e} = 1045 \text{ Hz}$, $J_{\text{PH}} = 920 \text{ Hz}$, $J_{\text{PF}_a} = 875 \text{ Hz}$.

Results and Discussion

Characterization of $\text{Br}_2\text{PCH}_2\text{CH}=\text{CH}_2$. Allyldibromophosphine is a clear liquid of low volatility which decomposes to a yellow solution upon standing at room temperature for periods of minutes. Its characterization has been completed by means of ir, NMR, and mass spectral data as well as elemental analyses.

The ir spectrum (see Experimental Section) is consistent with the proposed structure and formula. Absorption bands at 3055, 1629, 983, and 918 cm^{-1} indicate the presence of a vinyl group in the molecule.³ The absorption bands at 400 and 378 cm^{-1} suggest the presence of a PBr_2 moiety in the molecule.⁴

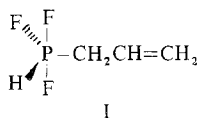
The fragmentation pattern observed in the mass spectrum further supports the structure. The isotope peaks of the molecular ion (m/e 234, 232, and 230) have the appropriate masses and isotope ratio (1:2:1) for the molecule with two bromine atoms. The isotopic ratios of fragment ions containing bromine are also appropriate and aid in their assignment. The strong peaks at m/e 41 and 39 support the assignment of an allyl group to the molecule.

The relative areas and chemical shifts of the signals observed in the proton NMR spectrum are consistent with those expected of the $-\text{CH}_2\text{CH}=\text{CH}_2$ moiety in the molecule.^{1,3} The chemical shift of the broad singlet in the ^{31}P NMR spectrum compares favorably with those observed for alkyl-dibromophosphines.⁵ No fine structure could be resolved in the ^{31}P spectrum.

Characterization of $\text{F}_3\text{PHCH}_2\text{CH}=\text{CH}_2$. Allyldifluorophosphorane is a clear liquid which rapidly decomposes to white solids at room temperature. The new compound has been characterized by ir, mass, and NMR spectra and by its vapor density molecular weight. The molecular ion peak is not seen in the mass spectrum; however, strong peaks corresponding to the fragments PF_3H^+ and C_3H_5^+ support the assigned structure. The vapor density molecular weight of 127 agrees well with the calculated value of 130.

The ir spectrum proves quite useful in assigning the structure. An absorption band at 2429 cm^{-1} lies within the range associated with P-H stretch in a pentavalent phosphorus compound.⁴ Bands at 3080 and 1630 cm^{-1} indicate the vinyl group is intact in the molecule.³ P-F bonding is reflected in bands at 805 and 760 cm^{-1} .

The ^1H NMR spectrum (-40°) displays the typical complex pattern, with appropriate chemical shifts, of molecules containing a $-\text{CH}_2\text{CH}=\text{CH}_2$ function.³ In addition to these signals, a doublet of triplets of doublets is observed which is consistent with a proton bound to phosphorus in a trigonal-bipyramidal structure. The signal is first split to a doublet by the bound phosphorus nucleus and then further to triplets by the two axial fluorine nuclei. Each member of the triplets is further split by the one equatorial fluorine nucleus (structure I).



The coupling constants and the chemical shift are consistent with those observed in similar compounds.⁶⁻⁸ At ambient temperature, the proton spectrum consists of the $-\text{CH}_2-\text{CH}=\text{CH}_2$ pattern and a pattern corresponding to a single PH proton, which appears as a doublet of quartets in contrast to the spectrum at -40° . This change reflects the expected fluxional character of the molecule as each member of the doublet due to PH coupling is further split by three fluorine nuclei now equivalent in the NMR time scale. The low-temperature spectrum reflects, then, the ground-state structure of the molecule.

The ^{19}F NMR spectrum supports structure I. The signals assignable by area to the equatorial fluorine occur at higher chemical shift and with larger coupling constants than those due to the axial fluorines. This is consistent with general observations of fluorophosphoranes and is considered to be characteristic of them.⁶⁻⁸ The magnitudes of the coupling constants are similarly consistent with other trifluorophosphoranes.^{7,8}

In the ^{31}P NMR spectrum, the positive chemical shift value corresponds well with those reported for trifluorophosphoranes.⁷ The splitting pattern also supports structure I.⁶⁻⁸ The coupling constants obtained in the ^{31}P spectrum are in each case ~ 75 Hz larger than those from ^1H or ^{19}F spectra. This was likely due to instrument drift resulting from absence of internal lock in obtaining the spectrum; the J values thus obtained are therefore suspect.

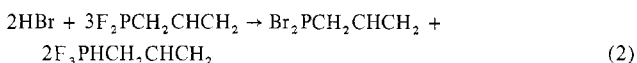
General Comments. The formation of alkyl- and aryltrifluorophosphoranes has been reported to result from the reaction of hydrogen fluoride with the corresponding dichlorophosphines.⁷ Further treatment with tertiary amines

caused dehydrofluorination and formation of the alkyl- or aryl-difluorophosphines.⁹ Hydrogen fluoride also will add to alkyl- or aryl-difluorophosphines to give the corresponding trifluorophosphorane.⁷ The reaction of hydrogen chloride with methyl-difluorophosphine is reported to result in the absorption of 3 mol of HCl /mol of F_2PCH_3 but no products were characterized.⁷ The present case is similar in that hydrogen bromide has been shown to react with allyldifluorophosphine but now the principal products have been characterized.

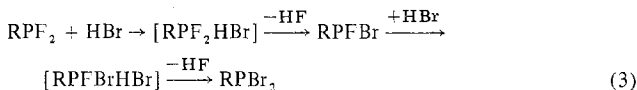
A mechanism for the reaction of RPHCl_2 with HF has been proposed^{7,9} which suggests the formation of (mixed-halo)-alkylphosphorane intermediates (eq 1). (More complex



intermediates are also possible.) The formation of RPHF_3 from RPF_2 and HF likely proceeds similarly by direct adduct formation. The reaction products of HBr with $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{PF}_2$ may be accounted for in a similar way. The formation of yellow solid products in addition to those characterized precludes determination of exact stoichiometry but the amounts of unrecovered HBr and $\text{PCH}_2\text{CH}=\text{CH}_2$ suggest a 2:1 ratio of $\text{HBr}:\text{PBr}_2\text{CH}_2\text{CH}=\text{CH}_2$ in the solid material. With that assumption, the formation of volatile products may be written as



This stoichiometry is satisfied by a reaction sequence such as (1) in which the displaced HF reacts further with starting material



The isolation of RPFBr from the mixture would lend strong support to this sequence but, as in earlier cases, there was no unequivocal evidence for its formation. A mass spectrum of the crude volatile products did, however, have a substantial pair of peaks which corresponded to this product, though we were unable to isolate the material in pure form. It has been shown¹⁰ that CH_3PFBr disproportionates to CH_3PF_2 and CH_3PBr_2 in the absence of excess HBr so that the formation of RPBr_2 in this case may be due to such a process occurring after the initial formation of RPFBr . However, it was noted¹⁰ that a slight excess of HBr accelerated the disproportionation of CH_3PFBr and that some $\text{CH}_3\text{PF}_2\text{H}$ was then recovered. These observations are consistent with the results obtained in this work and with the reaction scheme suggested above.

If proven to be general, the reaction described here provides a convenient preparation of RPF_3H compounds in small quantities. Previously reported syntheses^{8,11} provide, perhaps, more suitable approaches to large-scale preparation.

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Registry No. $\text{PBr}_2\text{CH}_2\text{CH}=\text{CH}_2$, 54566-76-6; $\text{PF}_3\text{HCH}_2\text{C}-\text{H}=\text{CH}_2$, 54566-75-5; $\text{PF}_2\text{CH}_2\text{CH}=\text{CH}_2$, 52124-33-1; HBr , 10035-10-6.

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Silicon-Substituted Derivatives of Trifluoro(trifluoromethyl)silane. Some Chemistry of the Silicon-Iodine Bond in a Polyhalo System

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The fluoriodosilane $\text{CF}_3\text{SiF}_2\text{I}$ has been utilized to generate a series of compounds of formula $\text{CF}_3\text{SiF}_2\text{X}$, where $\text{X} = \text{Br}$, Cl , F , and OSiF_2CF_3 ; all but $\text{X} = \text{F}$ are new compounds. Conversion of Si-I bonds to Si-X is effected by antimony(III) halides or, for oxygen, mercury(II) oxide. Each of the halodifluoro(trifluoromethyl)silanes undergoes pyrolytic decomposition at 100° to generate SiF_3X and CF_2 , although the thermal decomposition of $\text{CF}_3\text{SiF}_2\text{I}$ is quite complex. Each of the $\text{CF}_3\text{SiF}_2\text{X}$ species (other than CF_3SiF_3) reacts with water vapor to generate CF_3SiF_3 and, for $\text{X} = \text{Br}$ or I , CF_2HX . The halodifluoromethanes evidently result from the reaction of CF_2 with HX —the CF_2 in turn resulting from the interaction of water vapor and CF_3SiF_3 at room temperature. Correlations of fluorine chemical shifts and directly bonded silicon-fluorine coupling constants between $\text{CF}_3\text{SiF}_2\text{X}$ species and the corresponding SiF_3X species are presented.

Introduction

The known chemistry of the silicon-iodine bond in polyhalo systems is quite limited. Trichloriodosilane has been described, but its known reaction chemistry consists of a single reaction.¹ Trifluoriodosilane remains a rather elusive molecule; several synthetic routes to SiF_3I have been described,²⁻⁴ but no definitive evidence for isolation of the pure compound exists, and its chemical properties remain unknown, except for a purported susceptibility toward redistribution at 700° .² The absence of a well-characterized reaction chemistry for SiF_3I is particularly unfortunate in view of the extensive use of CF_3I both in generating trifluoromethyl derivatives of main group elements and as a convenient homolytic source of the trifluoromethyl radical.⁵

An attractive feature of the silicon-iodine bond apparent in the chemistry of iododisilane and iodotrimethylsilane is its ability to serve as the basis for a "conversion series" whereby iodine can be selectively exchanged for a variety of halo or pseudohalo functions via silver⁶ or mercury(II)⁷ halides or pseudohalides. The extension of such a series to Si-I bonds in polyhalo systems has not yet been established, nor has a wide range of halogenating agents been explored.

The synthesis of difluoriodo(trifluoromethyl)silane, $\text{CF}_3\text{SiF}_2\text{I}$,⁸ has provided a polyhalosilane (or perhalo if the CF_3 group is accorded a pseudohalogen status) containing a Si-I bond whose accessibility and stability permit the systematic development of its reaction chemistry. This compound has recently been utilized in the first synthesis of CF_3SiF_3 ,^{9,10} the simplest perfluoro(alkylsilane). The chemical and physical properties of several new derivatives of CF_3SiF_3 —of general formula $\text{CF}_3\text{SiF}_2\text{X}$ —will be discussed in the following sections.

Experimental Section

All volatile materials were manipulated in a grease-free vacuum system constructed of borosilicate glass, fluorocarbon polymer stopcocks, and glass "O" ring connectors. Solids were handled in an inert-atmosphere glove box. Reagents were obtained from commercial sources and, subsequent to purity verification, were used as received. Molecular weights were calculated from vapor density measurements (Dumas method). Infrared spectra were taken on a commercial double-grating instrument (Beckman IR-20A) in the range 4000–350 cm^{-1} . ^{19}F NMR spectra were run on a Varian T-60 (56.4 MHz).

Synthesis of $\text{CF}_3\text{SiF}_2\text{I}$. Difluoriodo(trifluoromethyl)silane was synthesized from the low-temperature reaction of silicon difluoride

with trifluoriodomethane, as previously described.⁸ Although the reaction of SiF_2 with CF_3I has been shown to be quite complex, use of a moderate excess of CF_3I in the reaction mixture allows recovery of the desired product in up to 40% overall yield, based on estimated SiF_2 production.

Reactions of $\text{CF}_3\text{SiF}_2\text{I}$ with SbX_3 . "Conversion" reactions were conducted by distilling the $\text{CF}_3\text{SiF}_2\text{I}$ into a bulb containing an excess of the antimony halide and, for $\text{X} = \text{Cl}$, SbCl_5 , isolating the bulb from the vacuum system and shaking the contents of the bulb as they warmed from liquid nitrogen temperature. Color changes indicative of reaction occurred in the solid well below room temperature in the fluoride and chloride systems. For the synthesis of $\text{CF}_3\text{SiF}_2\text{Cl}$, the following data correspond to a representative reaction. A 0.93-mmole sample of $\text{CF}_3\text{SiF}_2\text{I}$ was distilled into a bulb containing 29.6 g (130 mmol) of SbCl_3 and 0.97 g (3.2 mmol) of SbCl_5 . The reaction produced 0.47 mmol of $\text{CF}_3\text{SiF}_2\text{Cl}$ (51% theoretical yield), with the remainder of the products consisting of approximately equal quantities of CF_3SiF_3 and $(\text{CF}_3\text{SiF}_2)_2\text{O}$, along with a much smaller amount of unreacted $\text{CF}_3\text{SiF}_2\text{I}$. The source of the oxygen is either water in the "anhydrous" SbCl_3 or Sb-O bonds in the solid, or both. Yields for the system where $\text{X} = \text{Br}$ were somewhat lower than for $\text{X} = \text{Cl}$; yields for the production of CF_3SiF_3 were considerably higher, often surpassing 90%.

Purification of the compounds described in this work was effected by either simple trap-to-trap or low-temperature column distillation. Molecular weights for $\text{CF}_3\text{SiF}_2\text{X}$, where $\text{X} = \text{F}$, Cl , Br , I : calcd, 154.1, 170.5, 215.0, 262.0; found, 154.6, 170.5, 216.5, 260.8.

Reaction of $\text{CF}_3\text{SiF}_2\text{I}$ with HgO , Sb_2O_3 , and Ag_2CO_3 . Several oxygen-containing compounds were employed in attempts to convert the Si-I function in $\text{CF}_3\text{SiF}_2\text{I}$ into a siloxane (i.e., $\text{CF}_3\text{SiF}_2\text{OSiF}_2\text{CF}_3$). $\text{CF}_3\text{SiF}_2\text{I}$ reacts rapidly with antimony(III) oxide at or below room temperature, but $(\text{CF}_3\text{SiF}_2)_2\text{O}$ could not be isolated among the products. Instead, SiF_4 , C_2F_4 , and CF_3SiF_3 are generated in substantial quantities, along with smaller amounts of $\text{SiF}_3\text{OSiF}_3$. Silver carbonate has been utilized in conversion of a P-I bond into a diphenoxane containing a P-O-P linkage;¹¹ however, interaction of $\text{CF}_3\text{SiF}_2\text{I}$ with Ag_2CO_3 led to formation of CF_3SiF_3 in the presence or absence of added SbCl_5 .

Mercury(II) oxide did prove to be effective in the generation of the desired siloxane if small amounts of SbCl_5 were present. In a typical run, 2.81 mmol of $\text{CF}_3\text{SiF}_2\text{I}$ was distilled into a bulb containing 26 g (120 mmol) of HgO and 1.0 g (3.3 mmol) of SbCl_5 . The bulb was allowed to warm to room temperature and the bulb contents were shaken for 5 min. The reaction generated 0.53 mmol of $\text{CF}_3\text{SiF}_2\text{OSiF}_2\text{CF}_3$ (38% theoretical yield), with the balance of the products being largely CF_3SiF_3 . Smaller amounts of $\text{CF}_3\text{SiF}_2\text{Cl}$ (from the apparent activity of SbCl_5 as a chlorinating agent) and unreacted starting material were also present. Longer contact times of $\text{CF}_3\text{SiF}_2\text{I}$