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Some Group IVa Alkylmetal Difluorodithiophosphates

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Difluorodithiophosphoric acid, HPS_2F_2, has been found to react with metals[1] as well as metal[1] and organometal[2] halides of the transition elements to form difluorodithiophosphates. These reactions are characterized either by direct oxidation of the metal[1] or by displacement of a halide[1,2] or both a halide and carbonyl group.[2] It was therefore of interest to explore whether difluorodithiophosphates of main group metals can also be formed. Roesky and Dietl have discovered that the reaction between HPS_2F_2 and tin(IV) chloride results only in the reduction of the tin(IV) to the tin(II) chloride.[3] It has now been found that HPS_2F_2 will react with alkylmetallic compounds of some group IVa elements by replacing an alkyl group in the case of $(CH_3)_3SnCl$ or a hydrogen or a dialkylamino group when $(CH_3)_3SiH$ or $(CH_3)_3SiN(C_2H_5)_2$, respectively, are used as substrates. The new compounds dimethylstannyl chloride difluorodithiophosphate, $(CH_3)_2ClSnSP(S)F_2$, and trimethylsilyl difluorodithiophosphate, $(CH_3)_3SiSP(S)F_2$, have been prepared by these procedures.

Experimental Part

Reagents.—$(CH_3)_3SnCl$, $(CH_3)_3SiCl$, $(C_2H_5)_3GeCl$, $(CH_3)_3SiN(C_2H_5)_2$, and $(CH_3)_3SiH$ were obtained from Peninsular Chem-Research, Inc., and BF_3 was from the Matheson Co. These were employed without further purification. HPS_2F_2 was prepared and purified by the literature methods.[4,5]

Apparatus and Instrumentation.—A standard Pyrex high-vacuum system was used for the manipulation of volatile compounds. Otherwise transfer of chemicals was performed in a nitrogen drybox. The stopcocks and joints were lubricated with Kel-F no. 90 grease (3M Co.). The Pyrex reactors were either a 100-ml vessel fitted with a Fischer-Porter Teflon valve or a 300-ml vessel with a cold finger and equipped with a stopcock through a side arm. The top and bottom sections of the latter were connected *via* a 45/50 ₮ joint. These reactors contained Teflon-coated magnetic stirring bars.

Infrared spectra were recorded using liquid smears between potassium bromide disks with a Perkin-Elmer Model 621 spectrophotometer. A Varian Model V-4310 spectrometer operating at 40 and 12.8 Mc was used for obtaining ^{19}F and ^{31}P spectra, respectively, while proton spectra were obtained with a Varian HA-60 instrument. Samples were measured at ambient temperature in 5-mm o.d. Pyrex tubes using CCl_3F and $(CH_3)_4Si$ as internal standards for the fluorine and proton spectra, respectively, and orthophosphoric acid was used as an external standard for the ^{31}P spectra. The infrared and nmr spectroscopic data are included in the Results and Discussion. A Consolidated Engineering Corp. 61-620 mass spectrometer was employed for the analysis of gaseous mixtures. This instrument was calibrated by measuring the sensitivity and determining the cracking pattern of the pure gaseous substances.

Preparation of $(CH_3)_2SnClSP(S)F_2$.—Trimethyltin chloride (0.67 g, 3.4 mmol) was placed into the reactor containing a cold finger. Then HPS_2F_2 (8.1 mmol) was distilled into the reactor. The mixture was then heated to 65–70° for 48 hr. After this time the reactor was opened to the vacuum apparatus, the total quantity of the gaseous mixture was measured, and it was examined by infrared and mass spectral analysis. Methane (3.3 mmol) was present in this mixture along with a small quantity of HCl and trace amounts of PSF_3, H_2S, and SiF_4. All the volatile materials were passed through a cold trap at $-95°$. This trap retained the excess HPS_2F_2 (4.4 mmol). The remaining yellowish liquid was gently warmed to *ca.* 40° for 15 min while pumping. A small quantity of a white solid (unidentified) was removed. The reactor was disassembled under dry nitrogen, the cold finger was wiped clean, and a receptacle was placed into the reactor. The reactor was evacuated to 5×10^{-4} Torr and the cold finger was cooled with liquid nitrogen. Then the liquid was heated to 60° and distilled onto the cold finger. As warming occurred, the colorless liquid (0.51 g, 1.6 mmol, 47% recovery) was collected in the receptacle beneath the cold finger. *Anal.* Calcd for $C_2H_6ClF_2PSnS_2$: C, 7.57; H, 1.89; P, 9.75; mol wt 317.5. Found: C, 8.03; H, 1.79; P, 9.75; mol wt 294 (cryoscopic in benzene). Some yellow solid remained in the reactor. At 22° the vapor pressure of $(CH_3)_2SnClSP(S)F_2$ is *ca.* 0.1 mm, and it melts at $6.4 \pm 0.4°$.

Preparation of $(CH_3)_3SiSP(S)F_2$. A. From HSP_2F_2 and $(CH_3)_3SiN(C_2H_5)_2$.—*N,N*-Diethylaminotrimethylsilane (2.74 mmol) and HPS_2F_2 (5.50 mmol) were combined in the 100-ml reactor described above. Reaction took place below 0° on warming, and, after reaching ambient temperature, the mixture was stirred for an additional 15 min. The reactor was then placed in a cold bath set at $-45°$, and the volatile contents of the reactor at this temperature were pumped through a trap at $-80°$, which retained the unreacted HPS_2F_2 (1.6 mmol). The colorless liquid remaining in the reactor was vacuum distilled (5×10^{-4} Torr) and 0.261 g was obtained corresponding to 1.27 mmol of $(CH_3)_3SiSP(S)F_2$ (46.4% recovery). *Anal.* Calcd for $C_3H_9F_2PSiS_2$: C, 17.47; H, 4.40; F, 18.42; P, 15.02; mol wt 206. Found: C, 18.00; H, 4.93; F, 17.60; P, 14.51; mol wt 190 (cryoscopic in benzene). Vapor pressures were obtained by a null method using a diaphragm pointer gauge.[6] Several observed pressures are 21.8 mm (28.5°), 28.8 mm (33.4°), and 38.9 mm (39.8°). Noticeable decomposition occurs above the latter temperature. Some decomposition is also observed after several days when this compound is stored at ambient temperature. It melts at $-79.7 \pm 0.9°$.

B. From HPS_2F_2 and $(CN_3)_3SiH$.—The reactants HPS_2F_2 and $(CH_3)_3SiH$ (3.0 mmol each) were condensed in the reactor described in A. The mixture was allowed to warm to room temperature and then was heated to 45° for 3 hr. There was no evidence of reactant interaction under these conditions.

This reaction was repeated using HPS_2F_2 (6.70 mmol) and $(CH_3)_3SiH$ (6.77 mmol) as well as BF_3 (6.77 mmol). As the mixture warmed, reaction took place below 0°. After stirring at room temperature for 10 min, the mixture was cooled to $-196°$ and 6.42 mmol of H_2 was removed. The remaining products were then warmed to $-45°$ and the BF_3 and excess $(CH_3)_3SiH$ were pumped away. The remaining colorless liquid was distilled in the manner indicated above and 1.01 g (4.83 mmol, 74.3% recovery) of the $(CH_3)_3SiSP(S)F_2$ was obtained.

Other Reactions. A. $(CH_3)_3SiCl$ and HPS_2F_2.—Trimethylchlorosilane (2.66 mmol) and a slight excess of HPS_2F_2 (2.80 mmol) were placed in the reactor used in the experiment above. No reaction took place after heating at 50° for 2 hr. Boron trifluoride (2.66 mmol) was then added and still no reaction was observed after heating at 100° for 8 hr.

B. $(C_2H_5)_3GeCl$ and HPS_2F_2.—Triethylchlorogermane and HPS_2F_2 (2.77 mmol each) were placed together in the reactor

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with the cold finger. The reactants were heated to 100° for several hours when the mixture darkened. There was some evidence for a small amount of ethane. The addition of BF_3 had no effect on these results. All volatile components at $-45°$ were removed. The yellowish liquid did contain a small amount of a PS_2F_2-containing derivative indicated by the infrared spectrum [bands at 880 (s) and 887 cm^{-1} (m), P—F str; 725 (s) and 705 cm^{-1}, P=S str] and the ^{19}F nmr spectrum [resonance centered at ϕ 11.1 (J = 1195 cps)].

Results and Discussion

Not only is there a difference in the behavior of HPS_2F_2 toward transition organometal halides and the group IVa alkyl halides, but also there is a marked difference in action of this acid toward the different group IVa organometallic compounds in a related sequence. Stronger conditions are required for the group IVa metallic compounds than for the transition metallic compounds.

However, instead of halogen substitution, which occurs with the transition metal compounds, the alkyl group is displaced when $(CH_3)_3SnCl$ is used as the substrate. The related germanium and silicon derivatives were unreactive even under the harsher conditions than those used for the tin congener, although there is some evidence for a germanium compound containing the PS_2F_2 group. On the other hand, when $(CH_3)_3SiH$ or $(CH_3)_3SiN(C_2H_5)_2$ is substituted for the chloride, reaction can be readily achieved below 0°. The hydride requires a catalyst (BF_3) while the dialkylamino compound requires no catalyst and $(CH_3)_3SiSP(S)F_2$ is formed in either case.

The infrared spectra of these compounds exhibit characteristic features. The spectrum of $(CH_3)_3SiSP(S)F_2$ has bands for which some tentative assignments have been made at 2960 (w) and 2900 (vw) [C—H str], 1416 (w), 1256 (m) [$Si(CH_3)_3$], 892 (s) [P—F str], 850 (s) [$Si(CH_3)_3$], 765 (wm) [$Si(CH_3)_3$], 716 (vs) [P=S str], 625 (wm), 525 (wm), 425 (wm), 385, 365, and *ca.* 340 cm^{-1}, and that of $(CH_3)_2SnClSP(S)F_2$ has bands at *ca.* 3000 (vw, br) and 2967 (w) [C—H str], 1397 (w) [C—H bend], 884 (s, br) [P—F str], 802 (ms), 707 (vs) [P=S str], 560 (w), 540 (s, sharp), 520 (w), 401 (ms), and 370 cm^{-1}. The ^{19}F nmr spectra show doublet resonance absorptions centered at ϕ 12.2 (J_{P-F_2} = 1200 cps) for $(CH_3)_3SiSP(S)F_2$ and at ϕ 14.3 (J_{P-F_2} = 1210 cps) for $(CH_3)_2SnClSP(S)F_2$ while the ^{31}P spectra exhibit triplet resonances centered at -1127 cps (J_{P-F_2} = 1196 cps) and at -1255 cps (J_{P-F_2} = 1210 cps), respectively. The proton spectrum of $(CH_3)_3SiSP(S)F_2$ has an absorption at τ 9.4, assigned to the methyl group while that of $(CH_3)_2SnClSP(S)F_2$ absorbs at τ 8.3, also assigned to the methyl group.

The reaction between trimethyltin chloride and oxy acids such as various sulfonic acids[7] and carboxylic acids[8] has been recently investigated. In the former case both the chlorine atom and one methyl group are removed and a bis(sulfonate) is produced. In this procedure the chlorine is reported to be displaced as HCl more facilely than the methyl group as methane. On the other hand, trimethyltin chloride reacts with carboxylic acids to displace only one methyl group as methane,[8] and monocarboxylates are formed. Both these types of oxy acids produce products that are white, crystalline, solid, polymeric substances involving five-[8] and six-coordinated[7] tin.

In this present work, the reaction between the monobasic dithio acid HPS_2F_2 and trimethyltin chloride causes the displacement of only the methyl group as methane with the formation of a monodifluorodithiophosphate, similar to the examples reported by Wang and Shreeve.[8] Molecular weight measurements of $(CH_3)_2SnClSP(S)F_2$ as well as of $(CH_3)_3SiSP(S)F_2$ indicate both are monomeric. Although intermolecular –S–P–S– bridged structures involving bidentate bonding of the S_2PF_2 group are ruled out, five-coordinated intramolecularly bonded structures cannot be discarded. However, the phosphorous–fluorine coupling constants, *ca.* 1200 cps, are more consistent with a unidentate structure.[1,2,9] In addition, expanded covalencies of the group IVa metals are reported for bonding with only the more electronegative elements such as oxygen. Therefore, structures of the type $\geqslant$M–SP(S)F_2 (where M = Si, Ge, Sn) appear to be the more reasonable.

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[9] The generalization of unidentate or bidentate bonding according to coupling constant data may not be well founded when comparing different sets of compounds.

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Difluoramidosulfuryl Chloride and Dichlorocyanodifluoraminomethane and Its Imine Derivatives[1]

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Although NF_2SO_2F is readily prepared by the photolysis of N_2F_4 and SO_2,[2] the sulfuryl chloride analog cannot be obtained using conventional methods for replacing fluorine bonded to sulfur in NF_2SO_2F by Cl, *e.g.*, with Al_2Cl_6, R_3SiCl, or HCl. However, NF_2SO_2Cl can be prepared in good yield by photolyzing a mixture of N_2F_4 and SO_2Cl_2 at 2537 Å. Although this new compound appears to have reasonable thermal

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[1] Presented at the Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970.

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