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Comparative Study of Tris(trifluoromethyl)phosphine Oxide, Tris(nonafluorobutyl)phosphine Oxide, and Fluorobis(nonafluorobutyl)phosphine Oxide with Ammonia and Amines

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Under identical reaction conditions, the behavior of $(R_f)_3PO$ ($R_f = CF_3$, C_4F_9) or $(R_f)_2P(O)F$ ($R_f = C_4F_9$) with ammonia or amines is different, e.g., $(CF_3)_3PO$ with NH_3, CH_3NH_2, or $(CH_3)_2NH$ gives $(CF_3)_3P(NH_2)_2$, $(CF_3)_2P(O)(NHCH_3)$ or $(CF_3)P(O)(NHCH_3)_2$ (excess $(CH_3)_2NH$), or $(CF_3)_2P(O)N(CH_3)_2$, respectively. However, with the same reactants, $(C_4F_9)_3PO$ forms $(C_4F_9)_2P(O)NH^-NH_4^+$ or $C_4F_9P(O)(NH_2)_2$ (excess NH_3), $C_4F_9P(O)(NHCH_3)_2$ (excess CH_3NH_2), or $(C_4F_9)_3P(OH)[N(CH_3)_2]$, $(C_4F_9)_3P[N(CH_3)_2]_2$, and $(C_4F_9)_2P(O)N(CH_3)_2$. Similar products are found with $(C_4F_9)_2P(O)F$ except with $(CH_3)_2NH$ where $(C_4F_9)PF(O)[N(CH_3)_2]$ is the major product. In addition, new routes to $(C_4F_9)_3PO$, $(C_4F_9)_2PF_3$, and $(C_4F_9)_2P(O)F$ are described. These products and conditions are compared with those for analogous hydrolysis reactions.

Introduction

Although Burg earlier demonstrated that tris(trifluoromethyl)phosphine oxide gave (dimethylamino)bis(trifluoromethyl)phosphine oxide with dimethylamine,[1] little has been reported since that time on the interactions of bis- or tris(perfluoroalkyl)phosphine oxides with ammonia or amines. This may have been in part to the lack of easy availability of the appropriate precursors. We were particularly interested in the hydrolytic stability of these highly fluorinated materials that contain phosphorus–nitrogen–hydrogen bonds. Unfortunately no evidence for stability in aqueous solutions was found.

However, we did find quite striking differences in behavior between the title compounds and ammonia or organic bases in some cases. As a result of our study, we have synthesized a variety of tris-, bis-, and mono(perfluoroalkyl)phosphorus(V) derivatives.

Results and Discussion

Iodobis(trifluoromethyl)phosphine, $(CF_3)_2PI$, and tris(trifluoromethyl)phosphine were prepared by the Emelēus method[2] of causing white phosphorus to react with CF_3I

$$P_4 + 6CF_3I \xrightarrow[48\ h]{220\ °C} (CF_3)_3P + (CF_3)_2PI + CF_3PI_2 + PI_3$$

The relative amounts of the respective phosphines that form are a function of the stoichiometry used—a large excess of phosphorus enhances the yields of the iodophosphines, while larger amounts of CF_3I improve the yield of $(CF_3)_3P$. Starting with 61 mmol of CF_3I and 120.9 mmol of phosphorus, the yields of $(CF_3)_3P$, $(CF_3)_2$ PI, and CF_3PI_2 were 7, 10, and 8 mmol, respectively. The iodobis(trifluoromethyl)phosphine was converted to the chloro analogue[3] by using dry AgCl. Antimony (III) chloride has been used to chlorinate $C_2F_5PI_2$ to $C_2F_5PCl_2$ but we find a high yield of $(CF_3)_2PCl$ (~100%) when AgCl is the chlorinating reagent with $(CF_3)_2PI$. The oxidation of $(CF_3)_2PCl$ occurs easily with NO_2 at −20 °C to give $(CF_3)_2P(O)Cl$ (80%) as well as $[(CF_3)_2P(O)]_2O$ and NOCl.[1,2,5,6] Tris(trifluoromethyl)phosphine oxide[7,8] can be obtained similarly from $(CF_3)_3P$ with NO_2

$$(CF_3)_3P + NO_2 \xrightarrow[4\ h]{25\ °C} \underset{\sim 100\%}{(CF_3)_3PO} + NO$$

Burg[1] observed that the reaction between tris(trifluoromethyl)phosphine oxide and dimethylamine results in carbon–phosphorus bond breaking with concomitant formation of fluoroform. This is, of course, also the case when such compounds are hydrolyzed with aqueous base or even on heating of aqueous solutions.

$$(CF_3)_3PO + (CH_3)_2NH \xrightarrow{-78\ °C} (CF_3)_2P(O)N(CH_3)_2 + CF_3H$$

The product results from addition of $(CH_3)_2NH$ across the phosphorus–oxygen double bond followed by loss of CF_3H. The analogous reaction does not occur between $(CF_3)_3P$ and dimethylamine,[9] but interestingly $(CF_3)_3P$ can be caused to react slowly with ammonia.

$$(CF_3)_3P + NH_3 \xrightarrow{-70\ °C} (CF_3)_2PNH_2 + CF_3H$$

We commenced our work by examining the reactions of ammonia with several phosphine oxides, and the products varied widely; e.g., for equivalent amounts of reactants the yield of the diaminophosphorane is

$$(CF_3)_3PO + NH_3 \xrightarrow[+25\ °C]{-78\ to} (CF_3)_3P(NH_2)_2 + CF_3H + (CF_3)_2P(O)OH$$

80% based on the ammonia available. Unreacted $(CF_3)_3PO$ was recovered. The new phosphorane is a slightly volatile liquid that is stable at 25 °C. With the exception of (alkylamino)phosphoranes[10] and $PF_3(NH_2)_2$, which results from the gas-phase reaction of PF_5 with NH_3,[11]

$$PF_5 + NH_3 \rightarrow PF_3(NH_2)_2 + NH_4PF_6 + \text{solids}$$

no other pentasubstituted diaminophosphoranes have been reported.

With $(C_4F_9)_3PO$, two quite different products were obtained with ammonia depending on the relative amounts of reactants utilized. In both cases the products were not analogous to those obtained with $(CF_3)_3PO$. For equimolar amounts of reactants, $(C_4F_9)_3PO$ and NH_3, $(C_4F_9)_2P(O)NH^-NH_4^+$ was the major product with equal amounts of of C_4F_9H and unreacted $(C_4F_9)_3PO$ being isolated. When the ratio of reactants was $(C_4F_9)_3PO{:}NH_3$ = 1:2, all of the reactants were consumed at 25 °C and 1 part of C_4F_9H was recovered. The white solid, $C_4F_9P(O)(NH_2)_2$, remaining was formed in 80% yield based on the ammonia available. The same product is obtained with $(C_4H_9)_2P(O)F$ and ammonia, although in lower yield. The products obtained are

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analogous to those obtained from the reactions of $(C_4F_9)_3PO$ and $(C_4F_9)_2P(O)F$ with water with the exception that because water is less basic than ammonia, slightly higher temperatures are required.[2]

$$(C_4F_9)_3PO + H_2O \xrightarrow{44\ ^\circ C} (C_4F_9)_2P(O)OH + C_4F_9H$$

$$(C_4F_9)_2P(O)OH + H_2O \xrightarrow{150\ ^\circ C} C_4F_9P(O)(OH)_2 + C_4F_9H$$

Raising the temperature to 195 °C causes complete hydrolysis of the phosphonic acid to form H_3PO_4 and C_4F_9H. In order to synthesize $(C_4F_9)_3PO$ and $(C_4F_9)_2P(O)F$, advantage was taken of the fluorinating action of sulfur tetrafluoride on bis(nonafluorobutyl)phosphinic acid to form the new bis(nonafluorobutyl)trifluorophosphorane.[12,13] Depending upon the ratio of reactants used, sulfur tetrafluoride also was useful as a reagent to dehydrate the acid starting material.

$$(C_4F_9)_2P(O)OH{\cdot}H_2O + SF_4 \rightarrow (C_4F_9)_2P(O)OH + SOF_2 + 2HF$$

$$2[(C_4F_9)_2P(O)OH{\cdot}H_2O] + \text{excess } SF_4 \rightarrow \underset{85\%}{2(C_4F_9)_2PF_3} + 6SOF_2 + 6HF$$

The hydrogen fluoride was readily removed by allowing the volatile product mixture to contact anhydrous CsF briefly. Conversion of $(C_4F_9)_2PF_3$ to $(C_4F_9)_2P(O)F$ occurred in the reaction with $(Me_3Si)_2O$.

$$(C_4F_9)_2PF_3 + (Me_3Si)_2O \xrightarrow{-Me_3SiF} (C_4F_9)_2P(O)F + (C_4F_9)_2PF_2(OSiMe_3) \xrightarrow{75\ ^\circ C} (C_4F_9)_2P(O)F + Me_3SiF$$

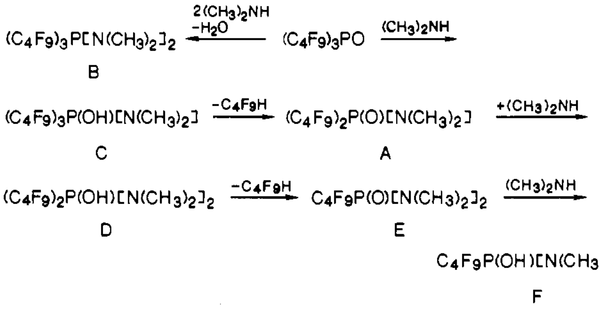
overall yield ~90%

Since $(C_4F_9)_2P(O)F$ is more volatile than $(C_4F_9)_2PF_2(OSiMe_3)$, it can be removed easily from the reaction mixture. Reaction with $(Me_3Si)_2O$ also allows the conversion of $(C_4F_9)_3PF_2$ to $(C_4F_9)_3PO$ in 88% yield. It is not possible to hydrolyze $(C_4F_9)_3PF_2$ to give $(C_4F_9)_3PO$ since invariably carbon–phosphorus bond breaking occurs to form the corresponding acid.[2]

$$(C_4F_9)_3PF_2 + 2H_2O \rightarrow (C_4F_9)_2P(O)OH + C_4F_9H + 2HF$$

Hydrolysis reactions of $(R_f)_nPF_{5-n}$ (n = 1, 2) also only result in acid formation and not phosphine oxide. It is interesting to note that the behavior of $(Me_3Si)_2O$ varies. While Schmutzler[14,15] reported ready synthesis of $(C_6H_5)_2P(O)F$, $C_6H_5P(O)F_2$, and $C_2H_5P(O)F_2$ using $(Me_3Si)_2O$ and the appropriate fluorophosphoranes, Cavell[16] has demonstrated that $(Me_3Si)_2O$ with $(CF_3)_3PO$ gives $(CF_3)_3P(OSiMe_3)_2$. The latter when heated rearranged to form $(CF_3)_2P(O)(OSiMe_3)$, identical with the product obtained when $(CF_3)_2P(O)Cl$ is reacted with $(Me_3Si)_2O$. Our yield of $(C_4F_9)_3PO$ was high, and we observed no Arbuzov rearranged product that could have come from subsequent reaction between $(C_4F_9)_3PO$ and $(Me_3Si)_2O$.

Further dissimilarity of the products obtained is demonstrated by the reactions of $(CF_3)_3PO$ and $(C_4F_9)_3PO$ or $(C_4F_9)_2P(O)F$ with $(CH_3)_2NH$. As Burg has shown[1] and we have duplicated, $(CF_3)_2P(O)N(CH_3)_2$ is formed quantitatively when $(CF_3)_3PO$ is reacted with $(CH_3)_2NH$. However, in the nonafluorobutyl case, we were able to isolate and characterize the intermediate acid that slowly loses C_4F_9H to form $(C_4F_9)_2P(O)[N(CH_3)_2]$, the analogue of which was the only product isolated with $(CF_3)_3PO$. It is interesting to note that after a reaction time of 14 h the products as identified by $^{31}P\{^1H\}$ NMR were (relative amounts based on peak areas) $(C_4F_9)_2P(O)[N(CH_3)_2]$ (A, 63%) $(C_4F_9)_3P[N(CH_3)_2]_2$ (B, 15%), $(C_4F_9)_3P(OH)[N(CH_3)_2]$ (C, 12%), and $(C_4F_9)_2P(OH)[N(CH_3)_2]_2$ (D, 10%). After a reaction time of 42 h, the relative amounts of A, B, C, and D were reduced to 38, 9.6, 8.1, and 11.1% with the additional compounds $C_4F_9P(O)[N(CH_3)_2]_2$ (E, 16.5%) and $C_4F_9P(OH)[N(CH_3)_2]_3$ (F, 16.2%). An appropriate additional amount of C_4F_9H was observed. The formation of these products may occur as follows:



$$\underset{B}{(C_4F_9)_3P[N(CH_3)_2]_2} \xleftarrow[-H_2O]{2(CH_3)_2NH} (C_4F_9)_3PO \xrightarrow{(CH_3)_2NH}$$

$$\underset{C}{(C_4F_9)_3P(OH)[N(CH_3)_2]} \xrightarrow{-C_4F_9H} \underset{A}{(C_4F_9)_2P(O)[N(CH_3)_2]} \xrightarrow{+(CH_3)_2NH}$$

$$\underset{D}{(C_4F_9)_2P(OH)[N(CH_3)_2]_2} \xrightarrow{-C_4F_9H} \underset{E}{C_4F_9P(O)[N(CH_3)_2]_2} \xrightarrow{(CH_3)_2NH}$$

$$\underset{F}{C_4F_9P(OH)[N(CH_3)_2]_3}$$

It is surprising that the P–F bond in $(C_4F_9)_2P(O)F$ is stable toward attack by $(CH_3)_2NH$ but succumbs to NH_3, CH_3NH_2, and H_2O.

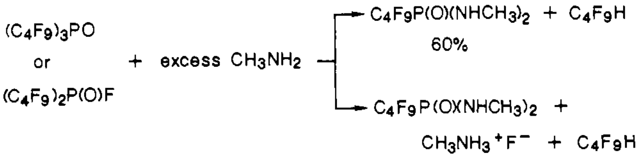
$$(C_4F_9)_2P(O)F + (CH_3)_2NH \rightarrow (C_4F_9)P(O)F[N(CH_3)_2] + C_4F_9H$$

However, with CH_3NH_2 the products obtained are analogous to those from $(CF_3)_3PO$. No intermediates were isolated.

$$(CF_3)_3PO + CH_3NH_2 \rightarrow (CF_3)_2P(O)(NHCH_3) + CF_3H$$

$$(CF_3)_3PO + 2CH_3NH_2 \rightarrow CF_3P(O)(NHCH_3)_2 + 2CF_3H$$

and



$$\left.\begin{array}{c}(C_4F_9)_3PO\\ \text{or}\\ (C_4F_9)_2P(O)F\end{array}\right\} + \text{excess } CH_3NH_2 \rightarrow \left\{\begin{array}{l}\underset{60\%}{C_4F_9P(O)(NHCH_3)_2} + C_4F_9H\\ C_4F_9P(O)(NHCH_3)_2 + CH_3NH_3{}^+F^- + C_4F_9H\end{array}\right.$$

Experimental Section

Materials. Commercially available reagents were used as received: NH_3, CH_3NH_2, and $(CH_3)_2NH$ (Matheson); $(Me_3Si)_2O$ (Aldrich); SF_4 and CF_3I (PCR). Phosphorus (Alfa) was dried under vacuum, and CsF (Baker) was dried and powdered at 150 °C.

General Procedure. A conventional Pyrex glass vacuum line equipped with Heise Bourdon tube and Televac thermocouple gauges was used for manipulation of volatile materials. Trap-to-trap distillation was employed to separate components in volatile mixtures. Reactions between −80 and +25 °C were carried out in 100-mL round-bottomed Pyrex flasks that were equipped with Chem Glass Teflon stopcocks. Fluorination reactions requiring temperatures ≥75 °C were run in 150-mL Hoke stainless-steel reactors that were equipped with Hoke valves. Hydrogen fluoride was removed by condensing product mixtures into a 150-mL Hoke stainless reactor that contained dry CsF and was equipped with a Hoke valve. Infrared spectra were obtained on a Perkin-Elmer 599B or a Perkin-Elmer 1710 FT spectrometer by using a 10-cm cell equipped with KBr windows. ^{19}F, ^{31}P, and ^1H NMR spectra were recorded on a JEOL FX 90Q FT NMR spectrometer with CCl_3F or H_3PO_4 as external reference and $CDCl_3$ or $CFCl_3$ as internal reference and solvent. Negative values were assigned to signals upfield from the reference. Mass spectra were recorded with a VG HS7070 mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, FRG.

Reaction of Phosphorus with CF_3I. Trifluoromethyl iodide (11.95, 61 mmol) was treated with white phosphorus (15 g, 120.9 mmol) in a 75-mL Hoke stainless-steel reactor for 48 h at 220 °C.[4] Upon trap-to-trap (t-t-t) distillation, CF_3PI_2 (8 mmol) was retained at −40 °C, $(CF_3)_2PI$ (10 mmol) at −78 °C, and $(CF_3)_3P$ (7 mmol) at −110 °C. ^{19}F NMR: CF_3PI_2, ϕ −59.30 d (J_{P-CF_3} = 50.3 Hz); $(CF_3)_2PI$, ϕ −54.15 d (J_{P-CF_3} = 68.36 Hz); $(CF_3)_3P$, ϕ −49.67 d (J_{P-CF_3} = 83.01 Hz). ^{31}P NMR: δ 57.99 q, 0.97 sept, −3.06 dectet, respectively.

Oxidation of $(CF_3)_3P$ with NO_2.[10,11] Tris(trifluoromethyl)phosphine (5 mmol, 1.19 g) and NO_2 (4.9 mmol, 0.22 g) were condensed into a 250-mL Pyrex round-bottomed flask at −196 °C. After the mixture was allowed to warm to and remain at 25 °C for 10 h, the $(CF_3)_3PO$ (~5 mmol) was isolated in a trap at −100 °C (t-t-t). ^{19}F and ^{31}P NMR resonances: ϕ −64.35 d (J_{P-CF_3} = 117.2 Hz); δ 4.2 dectet, respectively.

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Reaction of $(CF_3)_3PO$ with NH_3 To Form $(CF_3)_3P(NH_2)_2$. Tris(trifluoromethyl)phosphine oxide (5 mmol, 1.27 g) and anhydrous ammonia (5 mmol, 0.085 g) were condensed into a 50-mL Pyrex flask equipped with a Kontes Teflon stopcock at −196 °C. After the mixture was warmed slowly from −78 to +25 °C over 10 h, CF_3H (1 mmol) was found at −120 °C and $(CF_3)_3P(NH_2)_2$ (2.0 mmol) at −78 °C (t-t-t). Fluoroform was identified by using NMR: ^{19}F, ϕ −78.45 d (J_{CF_3-H} = 78.13 Hz); ^1H, δ 6.44 q. NMR spectra for $(CF_3)_3P(NH_2)_2$: ^{19}F, ϕ −68.07 d, pentet (J_{P-CF_3} = 63.47 Hz; J_{CF_3-H} = 11.96 Hz); ^{31}P, δ −94.4 pentet, dectet (J_{P-NH_2} = 12 Hz); $^{31}P\{^1H\}$ dectet. MS (CI) (*m*/*e* (species), %): 254 ($M^+ - NH_2$), 1.4; 201 ($M^+ - CF_3$), 6.9; 151 ($C_2HF_5P^+$), 4.5; 131 ($CH_3F_3N_2P^+$), 1.1; 100 (CF_3P^+), 7.2; 69 (CF_3^+), 100; 63 ($H_4N_2P^+$), 2.0. IR: 3530 s, 3430 s ($\nu_{NH_{sym}}$), 1595 m ($\delta_{NH_{asym}}$), 1215 s, 1175 s, 1160 w, 1140 w, 1110 s, 1040 s, 998 m, 900 w, 800 w, 749 w, 708 w, 611 w, 589 w, 511 m, 498 m, 388 m cm^{-1}. Anal. Calcd for $C_3H_4F_9N_2P$: C, 13.35; H, 1.48; P, 11.48. Found, C, 13.84; H, 1.50; P, 11.05.

Preparation of $(C_4F_9)_2PF_3$. Sulfur tetrafluoride (40 mmol, 4.32 g) and $(C_4F_9)_2P(O)OH\cdot H_2O$ (10 mmol, 5.20 g) were transferred into a 150-mL stainless-steel Hoke vessel equipped with a Hoke valve.[2] The mixture was warmed to 25 °C, where an exothermic reaction occurred, after which the reaction mixture was agitated for 2 h. All of the volatile materials were then transferred into a second Hoke vessel that contained dry CsF. After the reaction mixture was shaken for 0.5 h at 25 °C and after t-t-t distillation, $(C_4F_9)_2PF_3$ was found in a trap at −35 °C (85% yield). ^{19}F NMR: ϕ −53.02 d (PF, J_{P-F} = 1177 Hz), −83.86 s (CF_3), −114.6 (CF_2, J_{P-CF_2} = 131.8 Hz), −121.8 (CF_2), −128.3 (CF_2). ^{31}P NMR: δ −37.32 pentet of quartets. IR: 1352 s, 1251 s, 1222 s, 1149 s, 1037 s, 1015 m, 993 s, 891 s, 796 m, 747 m, 697 m, 660 w, 616 s, 589 m, 530 s cm^{-1}. MS (EI) (*m*/*e* (species), %): 507 ($M^+ - F$), 0.4; 307 ($C_4F_{12}P^+$), 5.8; 219 ($C_3F_8P^+$, $C_4F_9^+$), 17.3; 169 ($C_2F_6P^+$), 7.2; 131 ($C_2F_4P^+$), 33.2; 119 ($C_2F_5^+$), 13.1; 100 ($C_2F_4^+$, CF_3P^+), 9.4; 81 (CF_2P^+, $C_2F_3^+$), 1.9; 69 (CF_3^+), 100. Anal. Calcd for $C_8F_{21}P$: C, 18.25; F, 75.85; P, 5.89. Found: C, 18.20; F, 75.4; P, 5.92.

Preparation of $(C_4F_9)_2P(O)F$. In a dry atmosphere, $(C_4F_9)_2PF_3$ (10 mmol, 5.26 g) was transferred into a thick-walled Pyrex tube equipped with a ChemGlass Teflon stopcock. After the vessel was cooled to −196 °C and evacuated, $(Me_3Si)_2O$ (10 mmol, 1.6 g) was condensed into it. The mixture was held at 25 °C for 24 h and separated by t-t-t distillation. The Me_3SiF was found at −78 °C, and $(C_4F_9)_2P(O)F$ (3 mmol) was found at −30 °C. Remaining in the glass vessel was an involatile compound $(C_4F_9)_2PF_2(OSiMe_3)$ that upon heating at 75 °C for 24 h gave 6 mmol each of $(C_4F_9)_2P(O)F$ and Me_3SiF. Spectral data for Me_3SiF: ^1H NMR, δ 2.01 d (J_{CH_3-F} = 7.32 Hz); ^{19}F NMR, ϕ −160.5 dectet. ^{19}F NMR for $(C_4F_9)_2P(O)F$: ϕ −80.53d (PF, J_{P-F} = 1211 Hz), −83.5 (CF_3), −119.6 d (CF_2, J_{P-CF_2} = 107.6 Hz), −122.0 (CF_2), −127.8 (CF_2). ^{31}P NMR: δ 16.69 doublet of pentets. IR: 1350 s ($\nu_{P=O}$), 1251 s, 1224 s, 1150 s, 1016 m, 991 m, 909 w, 873 m, 823 w, 796 m, 746 m, 556 w cm^{-1}. MS (CI^+) (*m*/*e* (species), %): 505 ($M^+ + 1$), 19.9; 485 ($M^+ - F$), 4.5; 285 ($C_4F_{10}OP^+$), 1.0; 219 ($C_4F_9^+$), 8.1; 169 ($C_3F_7^+$), 14.0; 147 ($C_2F_4OP^+$), 1.8; 119 ($C_2F_5^+$), 20.4; 100 ($C_2F_4^+$), 3.3; 69 (CF_3^+), 100. Anal. Calcd for $C_8F_{19}OP$: C, 19.05; F, 71.62; P, 6.15. Found: C, 18.93; F, 71.3; P, 6.11. ^{19}F NMR for $(C_4F_9)_2PF_2(OSiMe_3)$: ϕ −34.95 d (PF, J_{P-F} = 1206 Hz), −83.39 s (CF_3), −117.2 d (CF_2, J_{P-CF_2} = 122.1 Hz), −121.9 (CF_2), −128.2 (CF_2). ^{31}P NMR: δ 53.4 triplet of pentets. MS (EI) (*m*/*e* (species), %): 563 ($C_{10}H_7F_{19}OPSi^+$), 2.2; 547 ($C_9H_3F_{19}OPSi^+$), 0.7; 219 ($C_4F_9^+$), 1.5; 169 ($C_2F_6P^+$), 8.0; 150 ($C_2F_5P^+$), 3.4; 143 ($C_2H_6F_2OPSi^+$), 1.3; 131 ($C_2F_4P^+$), 71.7; 119 ($C_2F_5^+$), 17.2; 113 (F_2OPSi^+), 3.2; 100 ($C_2F_4^+$), 31.7; 85 (F_2OP^+), 4.9; 69 (CF_3^+), 100. Total yield of $(C_4F_9)_2P(O)F$ was 90%.

Preparation of $(C_4F_9)_3PO$. Into a thick-walled Pyrex glass vessel equipped with a Kontes stopcock was placed $(C_4F_9)_3PF_2$ (10 mmol, 7.26 g), and then $(Me_3Si)_2O$ (10 mmol, 1.62 g) was added at −196 °C under vacuum. After 48 h at 25 °C, Me_3SiF was distilled away leaving involatile $(C_4F_9)_3PO$ (8.8 mmol). ^{19}F NMR for $(C_4F_9)_3PO$: ϕ −83.57 s (CF_3), −113.9 d (CF_2, J_{P-CF_2} = 83 Hz), −120.2 (CF_2), −128.0 (CF_2). ^{31}P NMR: δ 22.67 septet. IR: 1349 s ($\nu_{P=O}$), 1311 m, 1235 br, s, 1211 br, s, 1143 br, s, 1009 s, 987 s, 967 m, 947 w, 916 w, 856 br, m, 807 s, 751 m, 739 s, 696 s, 639 w, 609 w, 575 w, 555 w, 489 br, s cm^{-1}. MS (EI) (*m*/*e* (species), %): 685 ($M^+ - F$), 1.0; 485 ($C_8F_{18}OP^+$), 1.0; 219 ($C_4F_9^+$), 16.0; 200 ($C_4F_8^+$), 1.0; 119 ($C_2F_5^+$), 16.0; 97 (CF_2OP^+), 3.0; 69 (CF_3^+), 100; 47 (OP^+), 7.0.

Reaction of $(CF_3)_2P(O)Cl$ with NH_3. Anhydrous ammonia (5 mmol, 0.085 g), triethylamine (5 mmol, 0.50 g), and $(CF_3)_2P(O)Cl$[6] (5 mmol, 1.1 g) were condensed into a 50-mL Pyrex flask at −196 °C. A white solid formed on warming to 25 °C. It was sublimed at 55 °C (1 Torr) to give 1 mmol of $[(CF_3)_2P(O)]_3NH^+Cl^-\cdot NEt_3$. ^1H NMR: δ 11.9 s (NH), 2.6 q (CH_2, $J_{CH_2-CH_3}$ = 7.34 Hz), 1.0 tr (CH_3). ^{19}F NMR: ϕ −74.03 d (J_{CF_3-P} = 112.3 Hz). $^{31}P\{^1H\}$ NMR: δ −13.82 septet. ^{31}P NMR: δ −13.82 septet of doublets (J_{P-NH} = 9.8 Hz). MS (CI) (*m*/*e* (species), %): 707 ($M^+ + 1$), 0.96; 689 ($M^+ + 2 - F$), 9.6; 638 ($M^+ + 1 - CF_3$), 1.12; 506 ($M^+ + 1 - (CF_3)_2PO_2$), 4.90; 338 ($C_4F_9P_2ON_2CH^+$), 2.86; 272 ($C_3F_7P_2N_2CH^+$), 8.96; 222 ($C_2F_5P_2N_2CH^+$), 4.81; 100 (CF_3P^+), 19.9; 86 ($HPOF_2^+$), 100; 72 ($C_4H_{10}N^+$), 7.28; 69 (CF_3^+), 13.25.

Reaction of $(C_4F_9)_3PO$ with NH_3. Ammonia (5 mmol, 0.085 g) and $(C_4F_9)_3P(O)$ (5 mmol, 3.52 g) were condensed into a 100-mL Pyrex flask equipped with a ChemGlass Teflon stopcock at −196 °C. The temperature was raised from −78 to +25 °C over 4 h. Upon t-t-t distillation, C_4F_9H (2.5 mmol) was found at −98 °C, unreacted $(C_4F_9)_3PO$ (2.5 mmol) was found at 0 °C and $(C_4F_9)_2P(O)NH^-NH_4^+$ (40% yield) remained in the reaction vessel. Spectral data for C_4F_9H: ^{19}F NMR, ϕ −82.0 (CF_3), −128.5 (CF_2), −130.1 (CF_2) −138.1 d (J_{CF_2-H} = 4.88 Hz) ^1H NMR, δ 6.02 tr of tr (CH). Spectral data for $(C_4F_9)_2P(O)NH^-NH_4^+$: ^1H NMR, δ 7.66, 7.09, 6.5 (NH_4^+), 7.2 d (NH, J_{P-NH} = 9.16 Hz); ^{19}F NMR, ϕ −81.6 (CF_3), −121.7 d (CF_2P, J_{P-CF_2} = 79.18 Hz), −121.5 (CF_2), −126.5 (CF_2); $^{31}P\{^1H\}$ NMR, δ 13.7 p. MS (CI) (*m*/*e* (species), %): 519 ($M^+ + 1$), 0.7; 517 ($C_8F_{18}P(O)N_2H_3^+$), 1.3; 516 ($C_8F_{18}P(O)N_2H_3^+$), 12.7; 503 ($C_8F_{18}P(O)NH_4^+$), 4.6; 502 ($C_8F_{18}P(O)NH_3^+$), 49.2; 485 ($C_8F_{18}OP^+$), 0.5; 482 ($C_8F_{17}P(O)NH_2^+$), 7.1; 433 ($C_7F_{15}P(O)NH_3^+$), 0.5; 283 ($C_4F_9P(O)NH_3^+$), 0.5; 282 ($C_4F_9P(O)NH_2^+$), 9.2; 266 ($C_4F_9P(O)^+$), 3.6; 219 ($C_4F_9^+$), 11.6; 213 ($C_3F_6P(O)NH_2^+$), 1.4; 181 ($C_2F_4PON_2H_6^+$), 8.8; 163 ($C_2F_4PONH_2^+$), 1.3; 131 ($CF_2PON_2H_6^+$), 42.9; 119 ($C_2F_5^+$), 14.6; 100 ($C_2F_4^+$), 13.6; 85 (F_2PO^+), 20.6; 69 (CF_3^+), 100; 63 ($PONH_2^+$), 3.3.

Reaction of $(C_4F_9)_2P(O)F$ with NH_3. This reaction was carried out as with $(C_4F_9)_3PO$. Ammonium fluoride is sublimed out of the reaction vessel, leaving behind $(C_4F_9)_2P(O)NH^-NH_4^+$ (70%). It was characterized as above.

Reaction of $(C_4F_9)_3PO$ or $(C_4F_9)_2P(O)F$ with Excess NH_3. These reactions were carried out as above except the molar ratio of $(C_4F_9)_3PO$ or $(C_4F_9)_2P(O)F$ to NH_3 was 1:3.5. The solid product that remained after removing C_4F_9N, NH_3, and NH_4F was solid $C_4F_9P(O)(NH_2)_2$ (80%). ^{19}F NMR for $C_4F_9P(O)(NH_2)_2$: ϕ −81.78 (CF_3), −121.0 (CF_2), −123.1 d (CF_2, J_{CF_2-P} = 75.11 Hz), −125.5 (CF_2). $^{31}P\{^1H\}$ NMR: δ 10.67 tr. ^1H NMR, δ 4.9 br. MS (CI) (*m*/*e* (species), %): 299 ($M^+ + 1$), 5.14; 282 ($C_4F_9PONH_2^+$), 0.57; 279 ($C_4F_8PON_2H_5^+$), 0.67; 266 ($C_4F_9PO^+$), 0.58; 248 ($C_4F_8POH^+$), 2.46; 219 ($C_4F_9^+$), 25.37; 200 ($C_4F_8^+$), 1.09; 179 ($C_2F_4PON_2H_4^+$), 0.57; 119 ($C_2F_5^+$), 10.75; 100 ($C_2F_4^+$), 11.25; 85 (PF_2O^+), 22.08; 79 ($PON_2H_4^+$), 20.33; 69 (CF_3^+), 100; 63 ($PONH_2^+$), 2.0.

Reaction of $(C_4F_9)_3PO$ or $(C_4F_9)_2P(O)F$ with Excess CH_3NH_2. These reactions were accomplished as above. After C_4F_9H and $CH_3NH_3^+F^-$ were removed, a solid that was characterized to be $C_4F_9P(O)(NHCH_3)_2$ (60%) remained. ^{19}F NMR for $C_4F_9P(O)[NHCH_3]_2$: ϕ −81.54 (CF_3), −121.5 d (CF_2, J_{CF_2-P} = 74.78 Hz), −121.7 (CF_2), −126.4 (CF_2). ^{31}P NMR: δ 10.06 tr. ^1H NMR: δ 6.8 (NH), 2.72 (CH_3). IR: 3439 (ν_{N-H}), 3011 (ν_{C-H}), 1471 w, 1350 s ($\nu_{P=O}$), 1235 br, s, 1134 s, 1030 m, 1011 m, 868 w, 797 w, 748 m, 731 m, 641 m, 614 w, 589 w, 530 m cm^{-1}. MS (CI) (*m*/*e* (species), %): 327 ($M^+ + 1$), 33.9; 307 ($C_6F_8PON_2H_8^+$), 3.3; 219 ($C_4F_9^+$), 7.5; 127 ($CF_2PON_2H_2^+$, $C_2F_2PONH_4^+$), 1.1; 119 ($C_2F_5^+$), 17.2; 107 ($C_2PON_2H_8^+$), 95.7; 92 ($CPON_2H_5^+$), 3.9; 77 ($CPONH_4^+$), 1.7; 69 (CF_3^+), 100.

Reaction of $(C_4F_9)_2P(O)F$ with $(CH_3)_2NH$. This reaction was carried out as above ($(C_4F_9)P(O)F:(CH_3)_2NH$ = 1:1). After C_4F_9H was removed, slightly volatile $C_4F_9P(O)F[N(CH_3)_2]$ was removed under dynamic vacuum (70% yield). ^{19}F NMR for $C_4F_9P(O)F(N(CH_3)_2)$: ϕ −79.19 d (PF, J_{F-P} = 1069 Hz), −82.1 (CF_3), −122.8 (CF_2), 122.9 d (CF_2, J_{CF_2-P} = 87.89 Hz), −127.0 (CF_2). ^{31}P NMR: δ 14.7 tr of d. IR: 2940 w, 2820 w (ν_{C-H}), 1472 m, 1400 w, 1350 m ($\nu_{P=O}$), 1290 s, 1228 s, 1208 s, 1190 s, 1131 s, 1110 m, 1080 m, 1028 m, 1005 w, 750 m, 740 m (ν_{P-F}), 695 w, 511 s, 490 m, 462 m cm^{-1}. MS (EI) (*m*/*e* (species), %): 329 (M^+), 6.6; 310 ($M^+ - F$), 1.8; 244 ($M^+ - C_2H_4F_3$), 2.0; 169 ($C_3F_7^+$), 0.9; 128 (?), 9.0; 119 ($C_2F_5^+$), 5.4; 110 ($M^+ - C_4F_9$), 100; 100 ($C_2F_4^+$), 8.7; 69 (CF_3^+), 33.6.

Reaction of $(C_4F_9)_3PO$ with $(CH_3)_2NH$. This reaction was carried out as above $(C_4F_9)_3PO:(CH_3)_2NH$ = 1:1). After 14 h, ~1.21 mmol of C_4F_9H was recovered when 2.6 mmol of each reactant was used. The nonvolatile liquid that remained when all of the volatile material (C_4F_9H) had been removed was a mixture of $(C_4F_9)_2P(O)N(CH_3)_2$ (A, 63%), $(C_4F_9)_3P[N(CH_3)_2]_2$ (B, 15%), $(C_4F_9)_3P(OH)[N(CH_3)_2]$ (C, 12%) and $(C_4F_9)_2P(OH)[N(CH_3)_2]_2$ (D, 10%). The $^{31}P\{^1H\}$ NMR spectral data for these compounds is as follows: A, δ 13.2 pentet (J_{P-F} = 79.2 Hz); B, δ −40.4 septet (J_{P-F} = 70.4 Hz); C, δ −69.9 septet (J_{P-F} = 70.4 Hz); D, δ 1.21 pentet (J_{P-F} = 70.4 Hz). The fluorine α-CF_2 chemical shifts, as well as the other fluorine resonances, are relatively invariant, and the former fall in the ϕ −115 to −119 region. Resonances for CF_3 are at approximately ϕ −81, and those for the other difluoromethylene groups lie between ϕ −118 and −127. A single OH proton shift was observed at δ 8.2. When the solution is allowed to stand, new resonances attributed to $C_4F_9P(O)[N(CH_3)_2]_2$ and $C_4F_9P(OH)[N(CH_3)_2]_3$ with $^{31}P\{^1H\}$ at δ

20.5 tr (J_{P-F} = 88.0 Hz) and −9.2 tr (J_{P-F} = 92.4 Hz) appeared.

Reaction of $(CF_3)_3PO$ with CH_3NH_2. One millimole of CH_3NH_2 was condensed into a 50-mL Pyrex flask that contained 3 mmol of $(CF_3)_3PO$. The mixture was allowed to warm overnight from −78 °C to room temperature. After volatile CF_3H (~1 mmol) and CH_3NH_2 were removed, a light yellow solid, $(CF_3)_2P(O)NHCH_3$, remained. ^1H NMR: δ 7.67 s; br (NH), 2.43 s (CH_3). ^{19}F NMR: ϕ −73.35 d (CF_3, J_{P-F} = 102.5 Hz). $^{31}P\{^1H\}$ NMR: δ −2.67 septet. IR: 3050 s, br, 2900 w, 2800 w, 2610 w, 2510 w, 1658 w, 1645 w, 1550 w, br, 1475 w, 1395 w, 1295 s, 1252 m, 1212 s, 1140 s, 1105 s, 1070 m, 980 m, 755 m, 585 vs, 510 s cm^{-1}. MS (EI) (*m/e* (species), %): 218 ($(CF_3)_2PONH_3CH_3^+$), 7.36; 198 ($(CF_3)_2PNCH_3^+$), 1.72; 157 ($C_2F_3PONCH_3^+$), 5.24; 146 ($CF_3PONCH_4^+$), 1.1; 133 (CF_3PONH^+), 4.25; 119 (CF_4P^+), 11.0; 100 (CF_3P^+), 6.59; 81 (CF_2P^+), 3.53; 78 ($P(O)NCH_5^+$), 3.7; 69 (CF_3^+), 100.

Reaction of $(CF_3)_3PO$ with Excess CH_3NH_2. Six millimoles of CH_3NH_2 as condensed into a 50-mL Pyrex flask that contained 2 mmol of $(CF_3)_3PO$. The mixture was allowed to warm overnight from −78 °C to room temperature. After volatile CF_3H (3.45 mmol) and CH_3NH_2 were removed, 0.34 g of a light yellow viscous liquid, $CF_3P(O)[NHCH_3]_2$, remained. ^1H NMR: δ 5.52 s, br (NH), 2.69 dd (CH_3, J_{CH_3-P} = 11.7 Hz, J_{CH_3-NH} = 4.4 Hz). ^{19}F NMR: ϕ −72.41 d (CF_3, J_{P-F} = 107.4 Hz); $^{31}P\{^1H\}$ NMR: 10.56 q. IR: 3250 m, br, 2940 w, 1390 s, br ($\nu_{P=O}$), 1293 m, 1235 s, 1210 s, 1110 s, br, 975 w, 890 m, 825 w, 810 m, 585 m, 565 m, 510 m cm^{-1}. MS (EI) (*m/e* (species), %): 175 ($M^+ - 1$), 1.43; 125 ($FPON_2HC_2H_6^+$), 1.42; 107 ($PON_2H_2C_2H_6^+$), 100; 96 (CF_2PNH^+), 8.48; 93 ($PON_2H_3CH_3^+$), 3.29; 78 ($PONH_2CH_3^+$), 35.71; 69 (CF_3^+), 7.06.

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Registry No. CF_3I, 2314-97-8; CF_3PI_2, 421-59-0; $(CF_3)_2PI$, 359-64-8; $(CF_3)_3P$, 432-04-2; $(CF_3)_3PO$, 423-01-8; CF_3H, 75-46-7; $(CF_3)_3P(NH_2)_2$, 115421-79-9; SF_4, 7783-60-0; $(C_4F_9)_2P(O)OH$, 52299-25-9; $(C_4F_9)_2PF_3$, 115421-80-2; $(Me_3Si)_2O$, 107-46-0; $(C_4F_9)_2PF_2(OSiMe_3)$, 115421-81-3; $(C_4F_9)_2P(O)F$, 115421-82-4; Me_3SiF, 420-56-4; $(C_4F_9)_3PF_2$, 91543-34-9; $(C_4F_9)_3PO$, 58431-34-8; $(CF_3)_2P(O)Cl$, 115421-83-5; $[(CF_3)_2P(O)]_3NH^+Cl^-{\cdot}N(Et)_3$, 115436-91-4; C_4F_9H, 375-17-7; $(C_4F_9)_2P(O)NH^-NH_4^+$, 115421-84-6; NH_4F, 12125-01-8; $C_4F_9P(O)(NHCH_3)_2$, 115421-85-7; $C_4F_9P(O)(N(CH_3)_2)$, 115421-86-8; $(C_4F_9)_2P(O)N(CH_3)_2$, 115421-87-9; $(C_4F_9)_3P[N(CH_3)_2]_2$, 115421-88-0; $(C_4F_9)_3P(OH)[N(CH_3)_2]$, 115421-89-1; $(C_4F_9)_2P(OH)[N(CH_3)_2]_2$, 115436-92-5; $C_4F_9P(O)[N(CH_3)_2]_2$, 115421-90-4; $C_4F_9P(OH)[N(CH_3)_2]_3$, 115436-93-6; $(CF_3)_2P(O)NHCH_3$, 31411-29-7; $CF_3P(O)[NHCH_3]_2$, 115421-91-5; $C_4F_9P(O)(NH_2)_2$, 115421-92-6.

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A New Pentafluorothio (SF_5) Sultone: Rearrangement and Pathway to $SF_5CH_2SO_3H$. New Pentafluorothio Fluoro Esters

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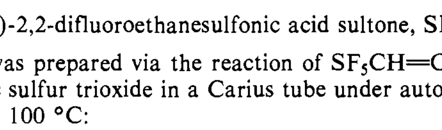
The new fluorosultone $SF_5\overline{CHCF_2OSO}_2$ has been prepared along with its rearranged isomer ($SF_5CH(SO_2F)COF$) and hydrolysis product ($SF_5CH_2SO_2F$); further reaction of $SF_5CH_2SO_2F$ with base and acid affords the corresponding sulfonic acid and salt: $SF_5CH_2SO_3H{\cdot}H_2O$ and $Ca(SF_5CH_2SO_3)_2$. New pentafluorothio (SF_5) esters, $SF_5CX(SO_2F)C(O)OR_f$ ($R_f = CF_3CH_2$, $(CF_3)_2CH$; X = H, F), have been synthesized by using the fluorosultones $SF_5\overline{CFCF_2OSO}_2$ and $SF_5\overline{CHCF_2OSO}_2$ with appropriate polyfluoro alcohols in the presence of sodium fluoride. In a like manner, the diester $[SF_5CF(SO_2F)C(O)OCH_2CF_2]_2CF_2$ was prepared from $HOCH_2(CF_2)_3CH_2OH$ and $SF_5\overline{CFCF_2OSO}_2$. These new esters, unlike fluorinated esters with fluorine at the alkoxy α-carbon atoms, are stable in the presence of fluoride ion at 25 °C or higher temperature. The new compounds are characterized by their IR, NMR (^1H, ^{19}F, ^{13}C), and mass spectra.

Introduction

Fluorinated sultones are occupying an ever-increasing importance in the synthesis of new sulfonyl fluorides (RSO_2F, R = hydrocarbon or fluorocarbon moieties). The incorporation of the sulfonyl fluoride group into molecular systems can lead to compounds useful as ion-exchange resins, surface-active agents, and thermally stable and strong sulfonic acids.[1-5] Since fluorinated sultones lead to new RSO_2F systems, it is of considerable interest that new sultones with unique structural features be prepared. While there are a number of fluorocarbon sultones, only one sultone with the unique pentafluorothio group (SF_5) exists.[3] We wish to present our success in preparing the second SF_5-containing sultone and its rearrangement, hydrolysis, and reaction chemistry leading to $SF_5CH_2SO_3H$; in addition, results obtained by using both SF_5-containing sultones in preparing new SF_5-containing fluorosulfonyl fluoro esters will be reported.

Results and Discussion

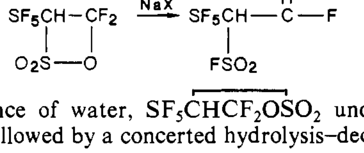
The new pentafluorothio β-sultone 2-hydroxy-1-(pentafluoro-λ^6-sulfanyl)-2,2-difluoroethanesulfonic acid sultone, $SF_5\overline{CHCF_2OSO}_2$, was prepared via the reaction of $SF_5CH{=}CF_2$ with monomeric sulfur trioxide in a Carius tube under autogeneous pressure at 100 °C:



$$SF_5CH{=}CF_2 + SO_3 \longrightarrow \begin{array}{l} SF_5CH{-}CF_2 \\ \quad\;\, | \qquad | \\ \quad O_2S{-}O \end{array} \qquad (1)$$

The $SF_5\overline{CHCF_2OSO}_2$ product is a stable crystalline solid with a vapor pressure of 9 Torr at 22 °C; it melts at 47–48 °C.

The SF_5 sultone undergoes rearrangement in the presence of NaX (X = I, F), giving the isomeric bifunctional fluoride 2-(fluorosulfonyl)-2-(pentafluoro-λ^6-sulfanyl)acetyl fluoride:



$$\begin{array}{l} SF_5CH{-}CF_2 \\ \quad\;\, | \qquad | \\ \quad O_2S{-}O \end{array} \xrightarrow{NaX} \begin{array}{l} \qquad\qquad\;\; O \\ \qquad\qquad\;\; \| \\ SF_5CH{-}C{-}F \\ \qquad | \\ \quad\; FSO_2 \end{array} \qquad (2)$$

In the presence of water, $SF_5\overline{CHCF_2OSO}_2$ undergoes rearrangement, followed by a concerted hydrolysis–decarboxylation reaction:

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