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AN IMPROVED PREPARATION OF SUBSTITUTED PHOSPHORYL DIFLUORIDES. SYNTHESIS OF TRIFLUOROMETHYLTHIODIFLUOROPHOSPHINE AND TRIFLUOROMETHYLTHIOPHOSPHORYL DIFLUORIDE

GEORGE H. SPRENGER AND JEAN'NE M. SHREEVE

Department of Chemistry, University of Idaho, Moscow, Idaho 83843 (U.S.A.)

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SUMMARY

Difluorobromophosphine reacts readily with bis(trifluoromethylthio)-mercury to yield the fluorophosphine CF_3SPF_2 in excellent yields. The resulting new phosphine is readily oxidized under very moderate conditions by ClF, Cl_2 and O_2 to give new chlorofluorophosphorane and fluorophosphoryl compounds which contain the CF_3S moiety. $CF_3SPF_2Cl_2$ and CF_3SPF_3Cl were not characterized because of their tendency to disproportionate. $CF_3SP(O)F_2$ has, however, been isolated and characterized. All the new compounds are relatively unstable and decompose with a fluoride shift from the methyl group to the phosphorus atom. A new synthetic route to the known difluorophosphoryl compounds OPF_2Cl, OPF_2Br, OPF_2NCS and $OPF_2(CH_3)_2$, by the direct oxidation of the respective difluorophosphine with oxygen, has been found.

INTRODUCTION

Utilization of a dialkylaminophosphorus difluoride compound in reaction with strong, non-oxidizing acids provides a powerful, high-yield route to substituted difluorophosphines[1]. However, application of this technique to the synthesis of difluorophosphoryl compounds by first forming $R_2NP(O)F_2$ from OPF_3 does not result in high yields of OPF_2X compounds[2]. In this work, we have found that essentially quantitative yields of OPF_2X compounds result when the corresponding difluorophosphine is reacted with elemental oxygen.

Many compounds which contain phosphorus and the trifluoromethylthio moiety are known[3-5] but none is known which contains both CF_3S and F bonded to phosphorus. We have now been able to prepare and characterize CF_3SPF_2 from the reaction of PF_2Br and $(CF_3S)_2Hg$, and $CF_3SP(O)F_2$ by the direct oxidation of CF_3SPF_2 with molecular oxygen. A single chlorine could be replaced by CF_3S from PF_2Cl_3 or PF_3Cl_2 in reaction with the mercurial but the products were not sufficiently stable to permit complete characterization.

DISCUSSION

Although there are 14 possible combinations of CF_3S and F with P^{III}, P^{V} and OP^{V}, prior to this work only $(CF_3S)_3P$ was known[3–5]. We now have succeeded in preparing the moderately stable compounds CF_3SPF_2 and $CF_3SP(O)F_2$.

The reaction of HCl with CF_3SPF_2 results in the severance of the phosphorus–sulfur bond to give CF_3SH and PF_2Cl. This fact precludes the utilization of a very attractive route to compounds of this type, namely the action of CF_3SCl on PF_2H, since the latter is not sufficiently basic to remove the product HCl as occurs in the case of PH_3[5]. Since earlier workers[4] successfully prepared $(CF_3S)_nPCl_{3-n}$ ($n = 1, 2, 3$) from $(CF_3S)_2Hg$ and PCl_3, we were prompted to use the mercurial as a ready source of the CF_3S group. Excellent yields of CF_3SPF_2 result from the reaction of $(CF_3S)_2Hg$ and PF_2Br, and, in addition, with PF_3Cl_2 and PF_2Cl_3 the somewhat unstable materials CF_3SPF_3Cl and $CF_3SPF_2Cl_2$ are obtained. Unsuccessful attempts were made to substitute the CF_3S moiety for bromine or chlorine in PF_2Cl, OPF_2Cl, OPF_2Br, SPF_2Cl, PBr_5 and PF_4Cl.

While pure CF_3SPF_2 in clean Pyrex glass at 25 °C and in diffuse light is stable for at least 6 h, it decomposes rapidly in the presence of unreacted starting materials or other impurities. Decomposition apparently proceeds *via* a fluoride-ion shift which breaks a carbon–fluorine bond in CF_3 to form a phosphorus–fluorine bond; *i.e.*, $2CF_3SPF_2 \rightarrow (CF_2S)_2 + 2PF_3$. It was of interest to compare this reaction with that of the nitrogen analogue, CF_3SNF_2, which decomposes at 25 °C in a 30% CCl_4 solution to give a variety of products including SF_5NF_2, CF_4, SOF_2, SO_2 and SiF_4[6]. Unfortunately, no data are available on the decomposition of the pure material.

Substituted organic phosphines are oxidized readily to phosphoryl or thiophosphoryl compounds with elemental oxygen or sulfur[7]. CF_3SPF_2 is also converted readily and in high yield to $CF_3SP(O)F_2$ with oxygen under mild conditions. The analogous oxidation of $(CF_3S)_3P$ has been attempted under conditions that varied from 14 days at 25 °C with no resultant reaction to 3 h at 90 °C when OPF_3, SO_2, $(CF_2S)_2$ and other unidentified phosphorus(III) fluorides were recovered. Attempts to oxidize CF_3SPF_2 with sulfur at a variety of temperatures, with or without solvents, only gave rise to decomposition products.

After 24 h at 25 °C, CF_3SPF_2 and CF_3SCl react completely to give mainly CF_3SSCF_3 and PF_2Cl accompanied by traces of $(CF_2S)_2$ and PF_3. With excess ammonia, CF_3SPF_2 gives an involatile liquid, probably $CF_3SP(NH_2)_2$, whose mass spectrum contains a molecule ion at 164 and other fragments which support the diamine structure.

Both CF_3SPF_2 and $CF_3SP(O)F_2$ are hydrolyzed rapidly by water. Large quantities of PF_3 and CF_3SH, accompanied by traces of CF_3SSCF_3, SiF_4 and traces of fluorophosphoric acids, are obtained when CF_3SPF_2 is hydrolyzed, while $CF_3SP(O)F_2$ upon hydrolysis gives mainly CF_3SSCF_3 and involatile fluorophosphoric acids. Small amounts of OPF_3 and CF_3SH were also observed in the latter reaction. Hydrogen chloride attacks $CF_3SP(O)F_2$ to form CF_3SH and $OPClF_2$.

The low-temperature oxidation of difluorophosphines resulted in high yields of substituted phosphoryl difluorides. This method appears to be superior to that in the literature[2].

EXPERIMENTAL

General methods

A standard Pyrex high-vacuum system equipped with a Heise–Bourdon tube gauge was used in all reactions. Purification of starting materials and products was accomplished by fractional condensation. Infrared spectra were obtained on a Perkin–Elmer Model 457 spectrometer using a 10 cm Pyrex gas cell fitted with sodium chloride or potassium bromide discs depending on the corrosiveness of the sample. ^{19}F NMR spectra were obtained using a Varian HA-100 spectrometer at 94.1 MHz with trichlorofluoromethane as an internal reference. ^{31}P NMR spectra were obtained using a Varian HA-100 spectrometer at 40.5 MHz with 85% phosphoric acid as an external reference. A Hitachi–Perkin–Elmer RMU-6E spectrometer operated at an ionization potential of either 70 or 17 eV was used to obtain mass spectra. Molecular weight determinations were obtained by the method of Regnault. Compounds were fused with excess sodium metal and their fluorine content determined with a fluoride-ion electrode. Sulfur was determined by oxidizing the sulfide ion to sulfate ion with hydrogen peroxide and precipitating as $BaSO_4$.

Materials

Commercially available reagents were purchased from the following sources: PF_3, OPF_3 and ClF from Ozark-Mahoning Co.; CF_3SSCF_3 and CF_3SCl from PCR, Inc.; HBr, HCl and $(CH_3)_2NH$ from the Matheson Co. PF_2Cl, PF_2Br, SPF_2Cl and SPF_2Br were synthesized *via* literature methods[2]. PF_3Cl_2, PF_3Br_2, PF_2Cl_3 and PF_4Cl[8] resulted from the direct oxidation of PF_3 or PF_2Cl with the halogen or ClF. ClF was freed from any ClF_3 by holding the mixture at −130 °C and removing the more volatile ClF under dynamic vacuum. $(CF_3S)_2Hg$ was obtained from the photolysis of CF_3SSCF_3 in the presence of mercury[9]. Photolysis of a mixture of CF_3SSCF_3 and H_2S gave essentially quantitative yields of CF_3SH[10].

Preparation of CF_3SPF_2

Freshly-prepared $(CF_3S)_2Hg$ (8 g, 20 mmol) was sublimed into a 500 cm^3 Pyrex glass vessel and 9 mmol of PF_2Br added. The mixture was allowed to remain at 25 °C except for the periodic condensation of the PF_2Br on to the surface of the mercurial followed by warming to 25 °C. Total reaction time was 6–8 h. The yield of CF_3SPF_2 was 8.7 mmol.

If the mercurial was not freshly sublimed or had been transferred in the air, the yield of CF_3SPF_2 was reduced and was accompanied by large amounts of PF_3, OPF_3 and $(CSF_2)_2$ and minor amounts of CF_3SH and CF_3SSCF_3. Elemental analysis gave F, 56.34% and S, 17.30% (calc. 55.88 and 18.82 respectively). The experimental molecular weight was 168 (calc. 170). A molecular ion, $CF_3SPF_2^+$, at 170 was observed in the mass spectrum. Bands in the infrared spectrum were 1228 (w), 1182 (s), 1170 (s), 1117 (s), 850 (s), 760 (m), 571 (m) and 502 (m), cm^{-1}. Nuclear magnetic resonance data included ^{19}F chemical shifts for CF_3 at φ 29.3 and PF at φ 69.2, and a ^{31}P chemical shift at -215 MHz. Spin–spin coupling constants are $J(CF_3\text{–}PF) = 5.1$ Hz, $J(CF_3\text{–}P) = 26.7$ Hz and $J(PF\text{–}P) = 1302$ Hz. CF_3SPF_2 boils at 3.9 °C, with $\Delta H_v = 5.8$ kcal mol^{-1} and $\Delta S_v = 21$ cal K^{-1} mol^{-1} and obeys the equation $\log p(\text{Torr}) = 7.086 - 1164.2/T$.

Preparation of $CF_3SP(O)F_2$

Pure CF_3SPF_2 (3.0 mmol) was condensed into a 500 cm^3 Pyrex glass vessel that was completely immersed in a bath at -78 °C. Pure dry oxygen was introduced into the vessel to a pressure of 1 atm. After 12 h at -78 °C, the volatile materials which consisted of O_2, PF_3 and OPF_3 were removed under dynamic vacuum. $CF_3SP(O)F_2$ (2.8 mmol, 93%), slightly contaminated with CF_3SSCF_3, remained in the vessel. Trap-to-trap separation through a trap at -63 °C retained the pure $CF_3SP(O)F_2$. Elemental analysis gave F, 50.67% and S, 16.78% (calc. 51.08 and 17.20 respectively). The experimental molecular weight was 183 (calc. 186). A molecular ion, $CF_3SP(O)F_2^+$, at 186 was observed in the mass spectrum. Bands in the infrared spectrum were 1375 (s), 1350 (w, sh), 1310 (w), 1200 (s), 1115 (s), 945 (s), 887 (s), 763 (m), 602 (s) and 550 (m), cm^{-1}. Nuclear magnetic resonance data included ^{19}F chemical shifts for CF_3 at φ 31.9 and PF at φ 41.2, and a ^{31}P chemical shift at -0.8 MHz. Spin–spin coupling constants are $J(CF_3\text{–}PF) = 7.9$ Hz, $J(CF_3\text{–}P) = 11.5$ Hz and $J(PF\text{–}P) = 1296$ Hz. $CF_3SP(O)F_2$ boils at 27.3 °C with $\Delta H_v = 5.5$ kcal mol^{-1} and $\Delta S_v = 18.3$ cal K^{-1} mol^{-1} and obeys the equation $\log p(\text{Torr}) = 6.902 - 1207.4/T$.

Preparation of OPF_2X

This method is equally applicable for the preparation of phosphoryl compounds where X = Cl, Br, NCS and $N(CH_3)_2$. Typically, 3.4 mmol of PF_2Br were reacted with an excess of pure dry oxygen at -78 °C for 12 h. Good yields (3.2 mmol) of OPF_2Br were isolated. The conditions for the conversion of other

PF_2X compounds include: PF_2Cl at −50 °C for 12 h yielded 100% OPF_2Cl; PF_2NCS at 25 °C for 1 h yielded 80% OPF_2NCS; $PF_2N(CH_3)_2$ at 60 °C for 12 h yielded 100% $OPF_2N(CH_3)_2$; and PF_2NCO at 150 °C for 6 h resulted in no reaction. The products were identified by their infrared spectra.

Reaction of PF_3Cl_2 or PF_2Cl_3 with $(CF_3S)_2Hg$

When 2 mmol of either PF_3Cl_2 or PF_2Cl_3 was allowed to react with an excess of $(CF_3S)_2Hg$, a single chlorine was replaced to form the unstable new compound which is probably CF_3SPF_3Cl or $CF_3SPF_2Cl_2$. Based on a comparison of infrared data, the same compounds were formed by the oxidation of CF_3SPF_2 with ClF at −98 °C or with Cl_2 (free from HCl) at −78 °C. Both CF_3SPF_3Cl and $CF_3SPF_2Cl_2$ are relatively unstable with respect to $(CSF_2)_2$ and PF_4Cl or PF_3Cl_2. Better yields of both compounds were obtained from reactions involving mercurials.

Reactions of $(CF_3S)_2Hg$ with other phosphorus compounds

Attempted mercurial reactions with PF_2Cl, POF_2Cl, OPF_2Br, SPF_2Cl, PBr_5 and PF_4Cl gave only starting materials or disproportionation products of the respective phosphorus halides at 25 °C.

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