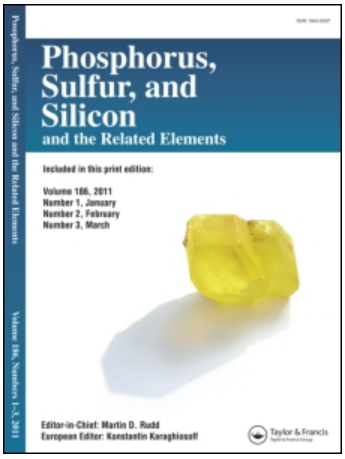

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F-(TRI-*tert*-BUTOXY)PHOSPHINE AND F-(PENTA-*tert*-BUTOXY)PHOSPHORANE

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Oxidative displacement and addition reactions occur when F-(*tert*-butyl)hypochlorite is reacted with PCl_3 and PCl_5 to give $[(CF_3)_3CO]_3P$ (III) and $[(CF_3)_3CO]_5P$ (VIII), respectively. (VIII) is hydrolyzed to $OP[(CF_3)_3CO]_3$. With PF_3, oxidative addition occurs with $(CF_3)_3COCl$ to form $[(CF_3)_3CO]_2PF_3$ (II). Analogous reactions between F-methylhypochlorite and PCl_3, PCl_5 and $SPCl_3$ were examined for comparison. Fluorination is the principal reaction mode.

INTRODUCTION

In recent studies, we have demonstrated that with simple fluoro or chloro sulfur compounds, F(*tert*-butyl)hypochlorite exhibits oxidative addition as well as oxidative displacement reactions[1,2] at the central sulfur atom. With phosphorus compounds,[3] however, only oxidative displacement reactions have been described. Both a mono- and a di-substituted F-alkoxyfluorophosphorane resulted from oxidative displacement of chlorine atoms

$$(CF_3)_3COCl + PClF_4 \xrightarrow{25^\circ C} (CF_3)_3COPF_4 + Cl_2 \quad (I)$$

$$2(CF_3)_3COCl + PCl_2F_3 \xrightarrow{25\ C} [(CF_3)_3CO]_2PF_3 + 2Cl_2 \quad (II)$$

on phosphorus from $PClF_4$ and PCl_2F_3 by F(*tert*-butyl)hypochlorite. When F(*tert*-butyl)hypochlorite reacted with PCl_3 and PCl_5, it was possible to displace all the chlorine atoms on phosphorus to obtain F-(tri-*tert*-butoxy)phosphine and a F-(penta-*tert*-butoxy)phosphorane.

RESULTS AND DISCUSSION

The phosphine, $P[OC(CF_3)_3]_3$ is easily prepared by condensing $(CF_3)_3COCl$ onto PCl_3. The reaction takes place readily at 0°C to give the product in quantitative yield. Compound III is a white solid which melts at 127°C. A molecular ion is observed in the mass spectrum. The ^{19}F nmr spectrum has a single resonance band at $\phi - 74.8$. An analogous compound resulted when PCl_3 was treated with $Li[OCH(CF_3)_2]$.[4] It is particularly interesting to use that IV undergoes further oxidative addition reactions with Cl_2 or Br_2 to give penta-coordinated dichloro or dibromo phosphoranes, while chlorine is formed concomitantly with III. No further addition could be made at this point.

$$3Li[OCH(CF_3)_2] + PCl_3 \longrightarrow$$

$$P[OCH(CF_3)_2]_3 \xrightarrow{Cl_2} Cl_2P[OCH(CF_3)_2]_3 \quad (V)$$

$$P[OCH(CF_3)_2]_3 \xrightarrow{Br_2} Br_2P[OCH(CF_3)_2]_3 \quad (VI)$$

(IV)

$$3(CF_3)_3COCl + PCl_3 \xrightarrow{0\ C} P[OC(CF_3)_3]_3 + 3Cl_2 \quad (III)$$

Despite several attempts at synthesis, only a few penta-alkoxy and phenoxy phosphoranes were known, in most cases low yields were obtained[5–7] and, of these, only the penta-phenoxy derivative and compound (VII) have been isolated as pure compounds. The reaction between V and $Li[OCH(CF_3)_2]$ resulted in a 73% yield of VII.[4]

$$Cl_2P[OCH(CF_3)_2]_3 + 2Li[OCH(CF_3)_2] \longrightarrow P[OCH(CF_3)_2]_5 + 2LiCl \quad (VII)$$

The preparation of $Cl_2P[OCH(CF_3)_2]_3$ and the subsequent separation from LiCl, however, require considerable effort. In addition, the reaction

does not occur without heating. When F(*tert*-butyl)hypochlorite reacted with PCl_5 at 0°C, the yield of pure F-(penta-*tert*-butoxy)phosphorane, $P[OC(CF_3)_3]_5$, was nearly quantitative. It is a white solid which melts at 110°C. The structure of

$$5(CF_3)_3COCl + PCl_5 \xrightarrow{0°C} P[OC(CF_3)_3]_5 + 5Cl_2$$
(VIII)

this phosphorane is supported by its spectral data. The $(M-F)^+$ fragment was observed as the highest mass peak in the mass spectrum. The ^{19}F nmr spectrum has a resonance band at $\phi - 68.0$, and the ^{31}P nmr spectrum has a singlet at -68.97. At first sight, it may be surprising that when PCl_5, which is ionic $(PCl_4)^+ (PCl_6)^-$, reacted with $(CF_3)_3COCl$ a covalent penta-alkoxy phosphorane was obtained. Although we are aware that there is evidence for the existence of molecular PCl_5 in solutions of benzene or methylene chloride,[5] it is our feeling that in the case of the very polar $(CF_3)_3COCl$, the phosphorus compound would likely be present in its ionic form and that reaction occurs *via* nucleophilic attack of $(CF_3)_3CO^-$ on phosphorus in $[PCl_4]^+$.

The compounds, VII[4] and VIII, have interesting parallel reactions and properties. First, both are extremely hygroscopic solids, which hydrolyze to give one molecule of the phosphoryl compound and two molecules of alcohol. Compound IX is also

$$P[OC(CF_3)_3]_5 + H_2O \longrightarrow OP[OC(CF_3)_3]_3 + 2(CF_3)_3COH$$
(IX)

$$P[OCH(CF_3)_2]_5 + H_2O \longrightarrow OP[OCH(CF_3)_2]_3 + 2(CF_3)_2CHOH$$

a colorless solid which melts at 68°C. When phosphoryl trichloride, $OPCl_3$, reacted with $(CF_3)_3COCl$, IX was not obtained. This may be due to the strong electronegative oxygen on phosphorus which makes the P—Cl bond less susceptible to $(CF_3)_3COCl$ attack.

Secondly, both compounds have single ^{19}F and ^{31}P nmr resonance bands. This excludes the possible contributions from either 4-coordinate or 6-coordinate phosphorus (i.e. no self redistribution species such as $P(OR)_4^+$ or $P(OR)_6^-$ were found as noted in the literature). Since the resonance band in the ^{31}P nmr spectrum of VIII has a band width at half height of 17 Hz, it is likely that VIII possesses a trigonal bipyramidal structure in which rapid exchange of axial and equatorial ligands occurs.

As was mentioned above, no oxidative addition reaction mode has been reported for phosphorus compounds with F(*tert*-butyl)hypochlorite. When PF_3 reacted with the latter, II resulted, but in a

$$2(CF_3)_3COCl + PF_3 \longrightarrow [(CF_3)_3CO]_2PF_3^3 + Cl_2$$
(II)

lower yield, and a longer reaction time was required than in the displacement reaction with PCl_2F_3. However, this indeed is an example of oxidative addition to phosphorus with F(*tert*-butyl)hypochlorite. The lower yield and longer reaction time may be owing to the lower availability of the electron pair of PF_3 thus increasing the barrier to oxidation.

Since we had observed very different modes of behavior for $(CF_3)_3COCl$ and CF_3OCl with sulfur compounds,[2] e.g., with CF_3OCl in reactions with compounds containing S—Cl bonds, where fluorination was the favored reaction, it was of interest to compare products obtained with phosphorus-chlorine compounds. When PCl_3 reacted with CF_3OCl, a white solid, which was identified as $[PCl_4]^+F^-$, was formed on warming from -196 to 0°C. The only volatile compound formed was carbonyl fluoride. No chlorine was observed. Since $[PCl_4]^+F^-$ has been reported to result from the low temperature chlorination of phosphorus (III) chlorofluorides, such as PCl_2F,[8] the exact nature of the reaction pathway is not clear.

Furthermore, when thiophosphoryl chloride, $SPCl_3$, reacted with CF_3OCl at 0°C, a white solid, in addition to volatile compounds, SCl_2, S_2Cl_2 and COF_2, was found. Mass spectral and elemental analysis data indicate that the white solid likely was $(PCl_4)^+F^-$. Upon warming a mixture of CF_3OCl and PCl_5 to 0°C, chlorine was formed and the solid PCl_5 disappeared. The reaction mixture after separation by trap-to-trap techniques, and mass spectral analyses, was found to contain $OP(OCF_3)_3$, (M^+); $OP(OCF_3)_2Cl$, $(M+, M+2)$; $OP(OCF_3)Cl_2$ $(M^+, M+2, M+4)$. However, although sets of doublets in the ^{19}F nmr spectra between $\phi - 52$ and -53, supported such structures, it was not possible to assign any $\nu_{P=O}$ bands in the infrared spectra. In addition, on standing at 25° for 10 hr the volatile compounds decomposed to give white solids and new volatile materials such as COF_2 and OPF_3. The study was not continued.

The observed differences in the behavior of CF_3OCl and $(CF_3)_3COCl$ may arise from the lower stability of the CF_3O group because of the ease with which fluorine may be lost to form the stable molecule, COF_2, particularly if there is the possibility of forming a strong bond, such as P—F. Remembering that $B(OCF_3)_3$ decomposed at $-20°C$ to form BF_3 and COF_2,[9] and that attempts to make $S(OCF_3)_4$ were unsuccessful,[2] while the analogous $(CF_3)_3CO$ analogs are well characterized and very stable at 25°, it is not unexpected that CF_3OCl once again acts as a fluorinating reagent in these cases.

EXPERIMENTAL

General

The appropriate precautions were taken in handling moisture-sensitive compounds. Standard high vacuum procedures were used throughout. ^{19}F nmr spectra were obtained by using a Varian HA-100 spectrometer with CCl_3F as an internal std. ^{31}P nmr spectra were taken on a Bruker WH90 instrument with 85% H_3PO_4 as external reference. Mass spectra were recorded with a Hitachi Perkin–Elmer RMU-6E spectrometer at 17 or 70 eV. All nuclear magnetic resonance shifts are assigned negative values for positions upfield from the reference.

Preparation of $P[OC(CF_3)_3]_3$ (III).

Phosphorus trichloride (1 mmole) and $(CF_3)_3COCl$ (3.2 mmole) were condensed into a 25 ml Pyrex vessel and reacted at 0°C for 10 hr. The chlorine was removed by opening briefly the vessel to a static vacuum at 25°C. It was identified from its color and mass spectrum. The white solid left behind can be further purified by sublimation under dynamic vacuum at 25°C. The ^{19}F nmr spectrum contains a singlet at ϕ −74.8. Anhydrous ether was used as solvent. The mass spectrum has speaks at M^+ 736; $(M—F)^+$, 717; $(M—OC(CF_3)_3^+$, 501. Anal. Calc. 19.56; F, 69.9; P 4.2. Found, C, 18.99; F, 67.5; P, 3.71.

Preparation of $P[OC(CF_3)_3]_5$ (VIII).

Phosphorus pentachloride (0.178 g, 0.9 mmole) was reacted with 4.8 mmole $(CF_3)_3COCl$ at 0°C for 10 hr. After removal of chlorine, the white solid was purified via sublimation at 40°C and the pure $P[OC(CF_3)_3]_5$ remained unsublimed. The yield is nearly 100%. The ^{19}F nmr has a singlet at ϕ −68.0 and the ^{31}P nmr has a band at −68.97. A molecular ion was not observed in the mass spectrum. The fragment $(M—F)^+$, m/e 1187, was the highest mass peak. Other fragments appeared appropriately, m/e (1068) $CF_3COP[OC(CF_3)_3]_4^+$, and m/e 736 $P[OC(CF_3)_3]_3^+$. Anal. Calc. C, 19.90; F, 70.89; P, 2.57. Found, C, 18.9; F, 67.6; P, 3.2.

Preparation of $OP[OC(CF_3)_3]_3$ (IX).

Compound VIII (0.5 mmole) was reacted with excess H_2O at 25°C for 1 hr. After removal of $(CF_3)_3COH$ via trap-to-trap distillation, the $OP[O(CF_3)_3]_3$ was sublimed onto a cold finger at 0°C. The ^{19}F nmr has a band at ϕ −71.0. A molecular ion was observed in the mass spectrum. Anal. Calc. C, 19.1. Found, C, 18.08.

Preparation of $PF_3[OC(CF_3)_3]_2$ (II).

Phosphorus trifluoride (2 mmole) and $(CF_3)_3COCl$ (4.2 mmole) were condensed into a 25 ml Pyrex vessel and reacted at 0°C for 7 days. Trap-to-trap distillation was used to separate the products and $PF_3[OC(CF_3)_3]_2$ was retained in a bath at −31°C. The product was confirmed based on spectral data cited in the literature[3] (yield = 15%, based on PF_3 recovered).

Reaction of CF_3OCl *with* PCl_3, $SPCl_3$ *and* PCl_5.

In each case, one mmol of phosphorus compound reacted with three or five mmol of CF_3OCl (depending on number of P—Cl bonds) while increasing the temperature slowly from −196 to 0°C. Infrared, mass, ^{19}F nmr spectral and elemental analysis data were used to identify the products.

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