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Phosphorus(III) and -(V) Bis(trifluoromethyl) Nitroxide Fluorides

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Careful temperature control of the reactions of $(CF_3)_2NO\cdot$ or $Hg(ON(CF_3)_2)_2$ with halophosphines or halophosphoryl compounds permits the synthesis of the phosphorus bis(trifluoromethyl) nitroxide fluorides $(CF_3)_2NOPF_2$, $((CF_3)_2NO)_2PF_3$, $((CF_3)_2NO)_3PF_2$, and $(CF_3)_2NOP(O)F_2$.

Several phosphorus compounds which contain the bis(trifluoromethyl) nitroxide moiety have been reported.[2-4] These include phosphorus bonded to a variety of groups, *e.g.*, CF_3, O, Cl, MeO, and $(CH_3)_2N$, in addition to $(CF_3)_2NO$, but only in the last case is phosphorus present as phosphorus(III)[4]

$$((CH_3)_2N)_2PCl + Hg(ON(CF_3)_2)_2 \rightarrow ((CH_3)_2N)_2PON(CF_3)_2$$

or

$$((CH_3)_2N)_3P + (CF_3)_2NO\cdot \xrightarrow{-50^\circ} ((CH_3)_2N)_2PON(CF_3)_2 + (CH_3)_2NON(CF_3)_2$$

Typically, phosphorus(III) compounds are oxidized by the radical $(CF_3)_2NO\cdot$

$$PBr_3 + (CF_3)_2NO\cdot \rightarrow OP(ON(CF_3)_2)_3{}^{5}$$

$$(MeO)_3P + (CF_3)_2NO\cdot \rightarrow (MeO)_3P(ON(CF_3)_2)_2{}^{4}$$

$$PF_3 + (CF_3)_2NO\cdot \rightarrow OPF_3 + \text{others}^{6}$$

There are no examples of bis(trifluoromethyl)nitroxy compounds which contain P-F bonds. However, *via* either the addition of $(CF_3)_2NO\cdot$ to fluorophosphines or the reaction of $Hg(ON(CF_3)_2)_2$ with halofluorophosphines, it is possible to form the new phosphorus(III) and -(V) nitroxide fluorides $(CF_3)_2NOPF_2$, $(CF_3)_2NOP(O)F_2$, $((CF_3)_2NO)_2PF_3$, and $((CF_3)_2NO)_3PF_2$.

Experimental Section

Starting Materials. Phosphorus trifluoride was obtained from Ozark-Mahoning Co. and was used without further purification. PF_2Cl,[7] $(CF_3)_2NO\cdot$,[8] and $Hg(ON(CF_3)_2)_2$[9] were prepared by the literature methods. Ammonia was obtained from Linde Air Products and CF_3NO from PCR, Inc.

Apparatus. The reactions were carried out in sealed small-volume Pyrex tubes. Infrared spectra were obtained on a Perkin-Elmer 457 or 621 infrared spectrometer with a 10-cm cell equipped with KBr windows. ^{19}F nmr spectra were recorded at 94.1 MHz on a Varian HA-100 with CCl_3F as internal reference. Molecular weights were determined by *PVT* measurements. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Gottingen, Germany.

Preparation and Properties of Phosphorus Bis(bis(trifluoromethyl) nitroxide) Trifluoride, $((CF_3)_2NO)_2PF_3$. Reaction temperature is of prime importance in this preparation (Table I) in order to prevent the occurrence of oxygenation only. The products of the reaction between PF_3 and $(CF_3)_2NO\cdot$ were separated by trap-to-trap distillation with $((CF_3)_2NO)_2PF_3$ held in a trap at $-63°$. Hydrolysis of this compound was followed by infrared analysis after a small amount of moist air was admitted to the cell in which it was contained. Bis(trifluoromethyl)hydroxylamine and phosphoryl fluoride result. $((CF_3)_2NO)_2PF_3$ is a colorless liquid whose vapor pressure is given by the equation $\log P_{\text{Torr}} = 7.570 - 1963/T$ (valid between 303.0 and 370.3°K). The extrapolated boiling point is 145.7° ($\Delta H_v = 9.0$ kcal/mol; $\Delta S_v = 21.5$ eu). No reaction occurs with anhydrous HCl at 25° or with elemental sulfur up to 160°. At $-40°$ and with $(CH_3)_3SiN(CH_3)_2$, $(CH_3)_3SiF$, $(CF_3)_2NOH$, $(CH_3)_3SiON(CF_3)_2$, and a yellow nonvolatile liquid are found. Infrared data for $((CF_3)_2NO)_2PF_3$ are given in Table II. The mass spectrum is listed in Table III. While a molecular ion was not observed, the highest peak (*m/e* 405) is assigned to M – F. Surprisingly, the base peak is at *m/e* 107 which is assigned to a recombination peak, PF_4^+. ^{19}F nmr and elemental analyses data are found in Table IV.

Preparation and Properties of Phosphorus Tris(bis(trifluoromethyl) nitroxide) Difluoride, $((CF_3)_2NO)_3PF_2$. As shown in Table I, PF_2Cl and $(CF_3)_2NO\cdot$ react readily at $-78°$ to give good yields of this product. $((CF_3)_2NO)_3PF_2$ is a colorless liquid with a vapor pressure curve $\log P_{\text{Torr}} = 7.876 - 2054/T$. Based on these data, the extrapolated boiling point is 148.3°, $\Delta H_v = 9.4$ kcal/mol, and $\Delta S_v = 22.7$ eu. It hydrolyzes rapidly to produce $(CF_3)_2NOH$. Infrared and mass spectral data are in Tables II and III. The highest peak at *m/e* 405 is assigned to M – $(CF_3)_2NO$. The base peak is at 69 assigned to CF_3^+ and PF_2^+. ^{19}F nmr and elemental analyses data are in Table IV.

Preparation and Properties of Phosphorus Bis(trifluoromethyl) nitroxide Difluoride, $(CF_3)_2NOPF_2$. Reaction temperature is also important in this preparation as is illustrated in Table I. Warming from -98 to $-78°$ over a long period apparently prevents spot heating and thus the formation of the thermally induced decomposition products, OPF_3 and $CF_3N{=}CF_2$, whereas warming quickly from -183 to $-78°$ results in a rapid reaction to form decomposition products. $(CF_3)_2NOPF_2$ is a gas at 25°. The vapor pressure of the liquid between 191 and 273° is described by $\log P_{\text{Torr}} = 7.927 - 1456/T$. The extrapolated boiling point is 15.4°; the heat of vaporization, 6.7 kcal/mol, and the Trouton constant, 23.1 eu. The compound does not react with mercury and undergoes no decomposition during vapor pressure measurements. However, at 25° it slowly isomerizes to $(CF_3)_2NP(O)F_2$.

Infrared and mass spectral data are given in Tables II and III. A molecule ion at *m/e* 237 and a base peak at 69 assigned to CF_3^+ or PF_2^+ are observed. Elemental analysis and ^{19}F nmr data are in Table IV.

Pyrolysis of $(CF_3)_2NOPF_2$. Exposure of $(CF_3)_2NOPF_2$ (1 mmol) in a Pyrex tube to 70° for 1 hr results in total conversion to $(CF_3)_2NP(O)F_2$[10] with a trace of OPF_3 and $CF_3N{=}CF_2$,[11] as identified by infrared and ^{19}F nmr.[10]

Pyrolysis of $(CF_3)_2NP(O)F_2$. At 200°, $(CF_3)_2NP(O)F_2$ (0.3 mmol) remained unaffected. However, after 24 hr at 250° in Pyrex, the compound is completely decomposed.

Preparation and Properties of Phosphoryl Bis(trifluoromethyl) nitroxide Difluoride, $(CF_3)_2NOP(O)F_2$. This mercury salt reaction with OPF_2Cl goes smoothly at $-78°$ (Table I). Infrared and mass spectral data are in Tables II and III. The mass spectrum shows a molecule ion at *m/e* 253 and a base peak at *m/e* 69 for CF_3^+ and PF_2^+. The vapor pressure is given by the equation $\log P_{\text{Torr}} = 7.808 - 1697/T$. Based on these data, the boiling point is 71.3°, $\Delta H_v = 7.8$ kcal/mol, and $\Delta S_v = 22.6$ eu. Elemental analyses and ^{19}F nmr data are in Table IV.

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Table I. Preparation of Phosphorus(III) or -(V) Bis(trifluoromethyl) Nitroxide Fluorides

Reactants (mmol)	Conditions, °C, hr	Products (mmol)
PF_3 (2), $(CF_3)_2NO\cdot$ (4)	25, 5	OPF_3 (2), $(CF_3)_2NON(CF_3)_2$ (2)
PF_3 (2), $(CF_3)_2NO\cdot$ (4)	−20, 20	OPF_3 (2), $(CF_3)_2NON(CF_3)_2$ (2)
PF_3 (4.6), $(CF_3)_2NO\cdot$ (9.3)	−45, 20	$[(CF_3)_2NO]_2PF_3$ (4.1), OPF_3 (0.5), $(CF_3)_2NON(CF_3)_2$ (0.5)
PF_2Cl (2), $(CF_3)_2NO\cdot$ (4)	−78, 12	$[(CF_3)_2NO]_3PF_2$ (1.3), Cl_2, PF_2Cl
PF_2Cl (2), $(CF_3)_2NO\cdot$ (6)	−78, 4	$[(CF_3)_2NO]_3PF_2$ (1.9), Cl_2
PF_2Cl (1.4), $Hg(ON(CF_3)_2)_2$ (1.3)	−98 to −78, 12	$(CF_3)_2NOPF_2$ (1.2), PF_2Cl, PF_3, OPF_3, $CF_3N{=}CF_2$, Hg_2Cl_2
PF_2Cl (4.4), $Hg(ON(CF_3)_2)_2$ (4.2)	−78, 0.5	OPF_3 (4), $CF_3N{=}CF_2$, PF_2Cl (trace)
$(CF_3)_2NOPF_2$ (1), $(CF_3)_2NO\cdot$ (2)	−78, 10.5	$(CF_3)_2NOP(O)F_2$ (1), $(CF_3)_2NON(CF_3)_2$ (1)
$(CF_3)_2NOPF_2$ (0.3), O_2 (0.8)	−98 to −78, 12	$(CF_3)_2NP(O)_2F_2$ (0.3)
OPF_2Cl (2.6), $Hg(ON(CF_3)_2$ (1.9)	−78, 11	$(CF_3)_2NOP(O)F_2$ (2.5), OPF_2Cl, OPF_3

Table II. Infrared Spectra (cm^{-1})

$(CF_3)_2NOPF_2$:	1321 vs, 1273 vs, 1247 vs, 1223 s, sh, 1051 s, 1000 m, 970 s, 885 s, 854 s, 820 s, 706 m, 620 w, 543 w, 481 w
$((CF_3)_2NO)_2PF_3$:	1320 vs, 1274 vs, 1242 vs, 1223 vs, 1068 s, 981 s, 959 s, 916 s, 720 m, 645 m, 590 m, 572 w, sh, 538 m, 527 w, sh
$((CF_3)_2NO)_3PF_2$:	1318 vs, 1274 vs, 1238 vs, 1220 s, 1068 s, 979 s, 960 w, 932 m, 894 m, 848 w, 717 s, 674 w, 640 m, 580 w, 532 w, 518 m
$(CF_3)_2NOP(O)F_2$:	1410 vs, 1323 vs, 1270 vs, 1248 vs, 1224 vs, 1192 m, 1057 s, 980 s, 945 s, 862 m, 803 w, 719 m, 623 m, 545 w, 495 s
$(CF_3)_2NP(O)F_2$:	1410 vs, 1396 m, 1375 m, 1340 vs, 1255 vs, 1242 vs, 1175 vs, 991 s, 974 s, 901 s, 725 m, 593 s, 524 s, 424 w

Table III. Mass Spectra

$(CF_3)_2NOPF_2$:	237 $C_2F_6NOPF_2^+$ (0.8), 218 $C_2F_6NOPF^+$ (2.5), 153 $C_2F_6NH^+$ (1.3), 152 $C_2F_6N^+$ (24.5), 150 $C_2F_5NOH^+$ (1.0), 149 CF_3NOPF^+ (1.2), 134 $C_2F_5NH^+$ (5.0), 133 $C_2F_5N^+$ (2.1), 114 $C_2F_4N^+$ (10.7), 104 PF_3O^+ (2.9), 99 CF_3NO^+ (23.6), 88 PF_3 (1.4), 85 OPF_2^+ (9.7), 81, $C_2F_3^+$ (1.4), 70 $^{13}CF_3^+$ (1.0), 69 CF_3^+ (100.0), 64 CF_2N^+ (1.4), 63 PO_2^+ (1.4), 50 CF_2^+ (6.0), 47 PO^+ (1.5)
$((CF_3)_2NO)_2PF_3$:	405 $(C_2F_6NO)_2PF_2^+$ (1.2), 256 $C_2F_6NOPF_3^+$ (89.3), 168 $(CF_3)_2NO^+$, $CF_2NOPF_3^+$ (1.5), 150 $C_2F_5NOH^+$ (1.4), 121 ? (1.2), 119 CF_3PF^+ (3.3), 117 $PO_3F_2^+$ (3.4), 107 PF_4^+ (100.0), 104 F_3PO^+ (3.1), 99 CF_3NO^+ (1.2), 85 POF_2^+ (2.5), 81 $C_2F_3^+$ (1.6), 69 CF_3^+ (53.7), 64 CF_2N^+ (1.1), 50 CF_2, PF^+ (1.3), 47 PO^+ (1.1)
$((CF_3)_2NO)_3PF_2$:	405 $(C_2F_6NO)_2PF_2^+$ (4.2), 256 $C_2F_6NOPF_3^+$ (5.0), 169 $C_2F_6NOH^+$ (1.0), 168 $C_2F_6NO^+$ (2.0), 150 $C_2F_5NOH^+$ (6.4), 114 $C_2F_4N^+$ (2.0), 107 PF_4^+ (3.6), 104 F_3PO^+ (3.0), 99 CF_3NO^+ (2.4), 85 F_2PO^+ (8.4), 81 $C_2F_3^+$ (5.5), 70 $^{13}CF_3^+$ (1.0), 69 CF_3^+ (100.0), 64 CF_2N^+ (1.1), 50 CF_2^+, PF^+ (4.0), 47 PO^+ (1.0)
$(CF_3)_2NOP(O)F_2$:	253 $C_2F_6NOP(O)F_2$ (2.1), 234 $C_2F_5NOP(O)F_2$ (1.3), 169 $C_2F_6NOH^+$ (1.3), 168 $C_2F_6NO^+$ (1.5), 150 $C_2F_5NOH^+$ (1.7), 135 $CF_3P(O)F$ (1.2), 104 F_3PO^+ (6.5), 99 CF_3NO^+ (10.8), 85 F_2PO^+ (7.2), 81 $C_2F_3^+$ (2.3), 70 $^{13}CF_3^+$ (1.0), 69 CF_3^+ (100.0), 50 CF_2^+, PF^+ (1.8)

Results and Discussion

These fluorophosphorus bis(trifluoromethyl) nitroxides are colorless liquids at 25° which are extremely sensitive to hydrolysis and which boil well above room temperature. With the exception of $(CF_3)_2NOPF_2$, which even at 25° undergoes slow isomerization to $(CF_3)_2NP(O)F_2$, the new phosphorus(V) compounds are stable to at least 100°.

Attempts to prepare $(CF_3)_2NOPF_2$ from mixing PF_3 or PF_2Cl with the $(CF_3)_2NOH{\cdot}CsF$ adduct[12] have resulted only in no reaction or in the formation of PF_3 and $(CF_3)_2NOH$. With PF_3, $(CF_3)_2NO\cdot$ neither abstracts a fluorine nor adds *via* oxidative addition, but rather the oxygenation product OPF_3 and $((CF_3)_2N)_2O$ are formed. Careful control of the reaction temperature is critical in ensuring the successful preparation of $(CF_3)_2NOPF_2$ from $Hg(ON(CF_3)_2)_2$ with PF_2Cl. If the temperature is not lower than −78°, only OPF_3 and $CF_3N{=}CF_2$ are obtained; however, slow warming from −98 to −78° gives the phosphorus(III) compound in high yield. From pyrolysis studies, it is found that decomposition occurs

$$(CF_3)_2NOPF_2 \xrightarrow[\text{or days at } 25^{\circ}]{70^{\circ}} (CF_3)_2NP(O)F_2 \xrightarrow{250^{\circ}} CF_3N{=}CF_2 + OPF_3$$

The appearance of the last two compounds when the reaction occurs at −78° or above suggests that the mercurial reaction is highly exothermic which contributes to the subsequent decomposition of the product sought.

The reaction of $(CF_3)_2NO\cdot$ with PF_3 reportedly resulted in the formation of a peroxide, bis(hexafluorodimethylamino)peroxide, OPF_3, and $CF_3N{=}CF_2$.[6] But in our examination of this reaction at 25°, the only products obtained after 5 hr are OPF_3 and $(CF_3)_2NON(CF_3)_2$. Similarly these are obtained quantitatively at −20°. No trace of the peroxide or $CF_3N{=}CF_2$ is found. Since the peroxide is reported to be stable at 25°, if it is formed in this study, it should be isolable. When the reaction is carried out at lower than −40°, only addition occurs to form $((CF_3)_2NO)_2PF_3$.

It is of interest to note that the reaction products of PF_2Cl and $(CF_3)_2PCl$ with $(CF_3)_2NO\cdot$ differ, for in the former case the chlorine is displaced and a total of 3 mol of radical/mol of PF_2Cl is added. With $(CF_3)_2PCl$, no chlorine is released with 2 mol of radical/mol of $(CF_3)_2PCl$ being added.[13]

Oxidation of phosphorus(III) to form $\equiv P{=}O$ is very common with radicals containing oxygen.[14] Nitrogen oxide reacts with triethyl phosphite,[15] trimethylphosphine,[16] and triphenylphosphine[17] to give dinitrogen oxide and phosphoryl compounds. The reaction $2NO + P(OC_2H_5)_3 \rightarrow N_2O + OP(OC_2H_5)_3$ is bimolecular and rates are insensitive to solvent. These results are consistent with a phosphoranyl radical scheme. The low-temperature reaction of PF_3 with $(CF_3)_2NO\cdot$ likely proceeds through an analogous intermediate

$$(CF_3)_2NO\cdot + PF_3 \rightarrow [(CF_3)_2NO\dot{P}F_3]$$

which combines with the nitroxide radical at low temperature to form the stable product which can be heated subse-

$$\begin{tikzcd}((CF_3)_2NO\dot{P}F_3) + (CF_3)_2NO\cdot \arrow[r, "0^{\circ}"] \arrow[dr, "-40^{\circ}"] & (CF_3)_2NON(CF_3)_2 + OPF_3 \\ & ((CF_3)_2NO)_2PF_3\end{tikzcd}$$

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Table IV. Elemental Analyses and ^{19}F Nmr Data

Compd	% C	% F	% N	% P	Mol wt	ϕ,[b] ppm CF_{3ax}	ϕ,[b] ppm CF_{3eq}	ϕ,[b] ppm $F_{P_{eq}}$	J_{P-F}, Hz
$(CF_3)_2NOPF_2$	10.21	63.5	5.91	12.93	236	67.4 s		47.0 d	1343
	(10.30)[a]	(64.1)	(5.91)	(13.08)	(237)	(3)		(1)	
$((CF_3)_2NO)_2PF_3$	11.65	66.5	6.61	7.00	424	69.2 s		57.6 d	932
	(11.33)	(67.2)	(6.60)	(7.30)	(424)	(4)		(1)	
$((CF_3)_2NO)_3PF_2$	12.30	66.5	7.08	5.44	574	68.68 s	68.79 s	8.0 d	993
	(12.57)	(66.3)	(7.33)	(5.41)	(573)	(6)	(3)	(1)	
$(CF_3)_2NOP(O)PF_2$	10.52	61.5	5.53		252	68.7 d, tr		86.0 d, hept	1077
	(9.49)	(60.1)	(5.53)		(253)	(3)		(1)	

[a] Calculated values in parentheses. [b] Key: s, singlet; d, doublet; tr, triplet; hept, heptet. Intensities in parentheses.

quently to at least 130° without decomposition. However, hydrolysis occurs readily.

The infrared spectra of these compounds are given in Table II. As is typical of $(CF_3)_2NO$ derivatives[2] the >NO-X stretch occurs in the range 1051-1068 cm^{-1} and ν_{aP^V-F} and ν_{sP^V-F} occur at 959-932 and 645-623 cm^{-1}. $\nu_{P^{III}-F}$ is assigned to 820 cm^{-1}. In comparing the spectra for $(CF_3)_2NP(O)F_2$ and $(CF_3)_2NOP(O)F_2$, the P=O stretching frequencies at 1410 cm^{-1} are identical but the latter exhibits a band at 1057 cm^{-1} assigned to >NO-X while the former does not absorb in this region. The energy of the $\nu_{P=O}$ absorption reflects the electronegativity of groups bonded to phosphorus(V) and others have proposed the following series:[18] $F > (CF_3)_2NO, (CF_3)_2N > CF_3 > C_3F_7 > Cl > Br > C_2H_5 > CH_3$. In line with this order, $\nu_{P=O}$ for $(CF_3)_2NOP(O)F_2$ at 1410 cm^{-1} is higher than for $((CF_3)_2NO)_3$-P=O[5] at 1382 cm^{-1} and lower than for $F_3P{=}O$[19] at 1415 cm^{-1}.

The ^{19}F nuclear magnetic resonance spectra (Table IV) are helpful in determining the structure of some of these compounds. In $(CF_3)_2NOPF_2$, there is no fluorine-fluorine coupling and P-F coupling of 1343 Hz is typical of phosphorus(III) compounds. The simplicity of the spectrum of $((CF_3)_2NO)_2PF_3$ with a singlet at ϕ 69.2 ($(CF_3)_2NO$) and a doublet at ϕ 57.6 (P-F) in the ratio of 4:1 leads to the conclusion that the molecule has a trigonal-bipyramidal structure and that the three equivalent fluorine atoms attached to phosphorus are equatorial while the two bis(trifluoromethyl) nitroxide groups are in the apical positions. This is entirely analogous to $(CF_3)_2PF_3$. For $((CF_3)_2NO)_3PF_2$, low resolution shows a doublet and a singlet in a 1:9 ratio. However, at high resolution the singlet becomes two peaks in the ratio 1:2 at ϕ 68.79 and 68.68 which indicates chemically different $(CF_3)_2NO$ groups in the molecule. Therefore, $((CF_3)_2NO)_3PF_2$ is a trigonal bipyramid with two equivalent fluorines and one $(CF_3)_2NO$ group occupying equatorial positions and the two additional equivalent $(CF_3)_2NO$ groups in the axial position.

In the case of the phosphoryl compound $(CF_3)_2NOP(O)F_2$ (four-coordinated phosphorus) all nuclei with nuclear spins are coupled. The two equivalent PF fluorines couple with phosphorus to give a doublet (J = 1077 Hz) which is split into two heptets by the $(CF_3)_2NO$ group (J_{CF_3-F} = 4 Hz). The $(CF_3)_2NO$ resonance occurs as a doublet of triplets from interaction with both fluorine (PF) and phosphorus (J_{P-CF_3} = 1 Hz). This compound must have a distorted OPF_3 structure.

Registry No. $(CF_3)_2NOPF_2$, 36544-19-1; $((CF_3)_2NO)_2PF_3$, 36544-20-4; $((CF_3)_2NO)_3PF_2$, 36544-21-5; $(CF_3)_2NOP(O)F_2$, 36544-22-6; $(CF_3)_2NP(O)F_2$, 13105-59-4; $Hg(ON(CF_3)_2)_2$, 21799-99-5; bis(trifluoromethyl) nitroxide, 2154-71-4.

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