Table I. Coordinates, Space Group $C2/c$ (x, y, z and $U_{eq}{}^a \times 10^4$)

atom	x	y	z	U_{eq}
Mn	0	1052 (0.8)	2500	269 (2)
Cl	733 (0.5)	1042 (1)	6265 (2)	341 (2)
O	−1802 (2)	1213 (3)	3056 (6)	487 (9)
N(1,3)	−1166 (2)	1938 (3)	2929 (5)	308 (8)
C(1,7)	−1314 (2)	3134 (4)	2714 (6)	302 (9)
C(2,6)	−645 (2)	3936 (4)	2565 (6)	263 (8)
N(2)	0	3282 (4)	2500	250 (10)
C(3,5)	−662 (3)	5271 (4)	2556 (6)	335 (10)
C(4)	0	5939 (6)	2500	371 (17)
C(8,9)	−2093 (3)	3712 (6)	2602 (12)	505 (14)

$^aU_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$.

the symmetry of $C2/c$. The problem lay in recognizing the symmetry.

Supplementary Material Available: Tables SI–SIII, listing anisotropic U_{ij}'s for the heavy atoms, coordinates and isotropic B's for the hydrogens, and bond distances for the $C2/c$ refinement (1 page); Table SIV, listing observed and calculated F's for the $C2/c$ refinement (4 pages). Ordering information is given on any current masthead page.

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Trifluoroamine Oxide: Reactions with Phosphorus Compounds and Selected Elements

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Earlier, we reported the utilization of carbonyl difluoride (COF_2) as a versatile and nondestructive fluorine-transfer reagent[1,2] and compared it with sulfinyl fluoride in a similar role.[3] The conversion of inorganic oxides to fluorides under mild conditions was also demonstrated by using carbonyl difluoride. Carbon dioxide is the only volatile product, and it is removed easily from the reaction vessel and absorbed in aqueous alkali.[4] Although this procedure has definite advantages over other methods, it also suffers from the fact that inorganic oxides that have high melting points could not be converted to fluorides and, in other cases, only oxyfluorides are formed. While fluorides have also been prepared by using vigorous fluorinating reagents, such as elemental fluorine or bromine trifluoride, or milder reagents, such as anhydrous hydrogen fluoride or sulfur tetrafluoride, none of these reagents is invariably the reagent of choice. Neither COF_2 nor SOF_2 reacts with the elements to form fluorides.

We now report the results obtained when trifluoroamine oxide, NF_3O, is reacted with main-group elements to give binary fluorides. Trifluoroamine oxide was found to fluorinate P(III) and P(V) compounds, also. The relative effectiveness of NF_3O, COF_2, and SOF_2 as fluorinating agents is examined.

Results and Discussion

Since its synthesis,[5-7] the physical, chemical, and spectral properties of trifluoroamine oxide have been studied extensively.[8,9] However, fluorination reactions of NF_3O have not been explored.[9]

Trifluoroamine oxide was found to react with phosphines at 110 °C to form difluorophosphoranes in good yields

$$R_3P + NF_3O \xrightarrow[4\ h]{110\ °C} R_3PF_2 + FNO + R_3PO$$

$$R\ (\%\ \text{yield}) = C_6H_5\ (80),\ CH_3\ (85)$$

Phosphites also reacted under similar conditions and formed the analogous oxidatively fluorinated products

$$(RO)_3P + NF_3O \xrightarrow[4\ h]{110\ °C} (RO)_3PF_2 + (RO)_2P(O)F + RF + (RO)_3PO$$

$$R\ (\%\ \text{yield}) = CH_3\ (80),\ C_2H_5\ (50),\ n\text{-}C_4H_9\ (70)$$

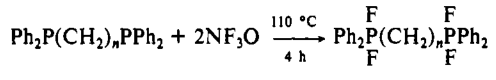
At higher temperatures, an Arbuzov–Michael reaction occurs, forming the respective fluoroalkane and monofluorophosphite. The extent of this latter reaction can be controlled but cannot be prevented, even when the reaction is carried out at low temperature; i.e., no reaction takes place at room temperature, but after 4 h at 50 °C, the difluorophosphorane is formed and the products due to the Arbuzov reaction are formed in small amounts. Products such as R_3PO and $(RO)_3PO$ resulted from reactions of NO_2 with the respective starting materials. The fluorinated products were isolated in high yield.

Oxidative fluorination of phosphites was achieved by using COF_2 and SOF_2 as fluorinating agents where the formation of additional products due to the Arbuzov reaction did not take place and the difluorophosphorane yields are high (Table I). The difference in the behavior of NF_3O compared to COF_2 and SOF_2 toward phosphites may be due to reaction temperature because the oxidative fluorination reaction with carbonyl difluoride and sulfinyl fluoride is achieved at room temperature in CH_2Cl_2, whereas NF_3O did not react under such conditions and, in fact, requires temperatures greater than 100 °C.

As has been found with secondary amines where the abstraction of hydrogen from >NH by NF_3O at 0 °C occurs smoothly,[10] with diethyl phosphite and di-n-butyl phosphite the hydrogen–phosphorus bond is also broken and the stronger P–F bond is formed in the phosphorofluoridates.

$$(RO)_2P(O)H + NF_3O \rightarrow (RO)_2P(O)F$$

Compounds that contain more than one phosphorus atom also could be reacted with trifluoroamine oxide at 110 °C to form the oxidatively fluorinated products



$$Ph_2P(CH_2)_nPPh_2 + 2NF_3O \xrightarrow[4\ h]{110\ °C} Ph_2\overset{F}{\underset{F}{P}}(CH_2)_n\overset{F}{\underset{F}{P}}Ph_2$$

$$n\ (\%\ \text{yield}) = 1\ (75),\ 2\ (75)$$

Both SOF_2 and COF_2 behave similarly with phosphites and diphosphines to give products in comparable yields (Table I).

Although PF_3 and PCl_3 are oxidatively unsaturated, trifluoroamine oxide, under conditions employed in this study, did not fluorinate or react with them.[11] This lack of reactivity, also noted for COF_2 and SOF_2, arises from the reduced availability of the electron pair of phosphorus in PX_3 (X = Cl, F) compared to cases where X = RO and Ph.

Acyclic and cyclic nonaromatic secondary amines were reacted with NF_3O at ~0 °C to form N-fluoro and N-nitroso compounds.[10] With carbonyl fluoride and sulfinyl fluoride at 25 °C,

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Table I. Comparison of Fluorinated Products Obtained with NF_3O, COF_2, or SOF_2 with a Common Substrate

	products (% yield) for reaction with		
reactant (2 mmol)	NF_3O[a]	COF_2[b,c]	SOF_2[b,d]
$(C_6H_5)_3P$	$(C_6H_5)_3PF_2$ (80)	$(C_6H_5)_3PF_2$ (68)	$(C_6H_5)_3PF_2$ (44), $(C_6H_5)_3P{=}S$
$(CH_3)_3P$	$(CH_3)_3PF_2$ (60)	$(CH_3)_3PF_2$ (72)	$(CH_3)_3PF_2$ (25)
$(CH_3O)_3P$	$(CH_3O)_2P(O)F$ (~80) CH_3F (~60)		
$(C_2H_5O)_3P$	$(C_2H_5O)_2P(O)F$ (~50) C_2H_5F (~40)	$(C_2H_5O)_3PF_2$ (72)	$(C_2H_5O)_3PF_2$ (25)
$(n\text{-}C_4H_9O)_3P$	$(n\text{-}C_4H_9O)_2P(O)F$ (70) $n\text{-}C_4H_9F$ (~25)	$(n\text{-}C_4H_9O)_3PF_2$ (70)	$(n\text{-}C_4H_9O)_3PF_2$ (22)
$(C_2H_5O)_2P(O)H$	$(C_2H_5O)_2P(O)F$ (~100)	$(C_2H_5O)_2P(O)F$ (65)	$(C_2H_5O)_2P(O)F$ (~100)
$(n\text{-}C_4H_9O)_2P(O)H$	$(n\text{-}C_4H_9O)_2P(O)F$ (70)	$(n\text{-}C_4H_9O)_2P(O)F$ (60)	$(n\text{-}C_4H_9O)_2P(O)F$ (60)
$Ph_2PCH_2PPh_2$	$Ph_2PF_2CH_2PF_2Ph_2$ (75)		
$Ph_2PCH_2CH_2Ph_2$	$Ph_2PF_2CH_2CH_2PF_2Ph_2$ (75)	$Ph_2PF_2CH_2CH_2PF_2Ph_2$ (80)	
metal oxides	NR[e] at 200 °C, 24 h	metal fluorides and oxyfluorides	

[a] 100 °C, 2–4 h. [b] 25 °C, 10 h. [c] References 1 and 2. [d] Reference 3. [e] NR = no reaction.

Table II. Fluorination of Elements with NF_3O

element	product (% yield)	element	product (% yield)
Zn[a]	ZnF_2 (>99)	Pb[b]	PbF_2 (60)
Cd[a]	CdF_2 (>99)	As[d]	AsF_5 (90)
B[c]	BF_3 (80)	Sb[d]	SbF_5 (90)
Ga[a]	GaF_3 (>99)	Bi[e]	BiF_3 (>99)
Ge[a]	GeF_4 (75)	Fe[f]	NR[g]
Sn[c]	SnF_4 (>99)	Rh[f]	NR[g]
Se[a]	SeF_4/SeF_6 (80 combined)		

[a] 180 °C, 16 h. [b] 190 °C, 20 h. [c] 200 °C, 24 h. [d] 210 °C, 24 h. [e] 220 °C, 36 h. [f] 220 °C, 70 h. [g] No reaction.

>NC(O)F- and >NS(O)F-containing compounds were prepared, respectively.

$$>NH + NF_3O \xrightarrow{0\ °C} >NF + >NNO + \text{salt}$$

$$>NH + COF_2 \xrightarrow[CH_2Cl_2]{Et_3N} >NC(O)F + Et_3N{\cdot}HF$$

$$>NH + SOF_2 \xrightarrow[CH_2Cl_2]{Et_3N} >NS(O)F + Et_3N{\cdot}HF$$

Only $(CH_3)_2NH$ was found to form $(CH_3)_2NF$ when reacted with COF_2.[3] In the case of the nitrogen–hydrogen bond, the behavior of NF_3O is in sharp contrast to that of COF_2 and SOF_2 with similar systems.

Compounds with active C–H bonds, such as $(C_6H_5)_3CH$, CF_3CF_2H, and $CF_3C{\equiv}CH$ did not react with NF_3O under various conditions. That is, no reaction occurred between $(C_6H_5)_3CH$ and NF_3O at 0 or 25 °C for 12 h, between CF_3CF_2H and NF_3O at 0 or 25 °C in the presence of aqueous KOH, or between $CF_3C{\equiv}CH$ and NF_3O at 0, 25, or 80 °C. With these or similar systems, abstraction of hydrogen from tertiary carbon was observed in the case of COF_2 and SOF_2.

Trifluoroamine oxide was reacted with a variety of free elements at ~200 °C for 24 h

$$M + nNF_3O \xrightarrow{100\text{–}220\ °C} MF_y$$

$$M = As, Sb, Bi, Ge, Sn, Pb, B, Ga, Zn, Cd, Se$$

with 95–100% conversion in nearly every case (Table II). Only the binary fluorides were characterized.

The oxides of these elements were also exposed to NF_3O at 200–220 °C for ~24 h, but in all cases, only the unreacted starting materials were recovered. Interestingly, in contrast with the behavior of NF_3O toward free elements, COF_2 and SOF_2 did not react at all, but they could be reacted with metal oxides to form the corresponding fluorides.

Experimental Section

Caution! Trifluoroamine oxide is a strong oxidizer. Mixtures with both inorganic and organic materials are potentially explosive. Attempts to scaleup the synthetic methods presented in this paper should be avoided. Proper safety precautions should be taken when reacting trifluoroamine oxide with any substrate.

General Procedures. A conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube gauge was used to handle gases and volatile liquids. Most of the starting materials and products were measured quantitatively by using *PVT* techniques. Volatile products were purified by fractional condensation (trap-to-trap distillation) and, when necessary, bulb-to-bulb distillation (Kugelrohr). ^{19}F NMR spectra were obtained on either a JEOL FX-90FT or a Varian EM360 NMR spectrometer with CCl_3F as an internal reference. Chemical shifts upfield of the reference are assigned negative values. Mass spectra were recorded with a VG 7070HS mass spectrometer operating at 10 eV.

Materials. Trifluoroamine oxide (Allied) was passed through two traps cooled at −78 °C to remove NO_2. Starting materials were obtained and treated as follows: $(C_2H_5O)_3P$, $(CH_3O)_3P$, and $(n\text{-}C_4H_9O)_3P$ (Aldrich) were distilled over $PbCO_3$ before use; $(CH_3)_3P$ (Strem), $(C_6H_5)_3P$ (Aldrich), $Ph_2PCH_2PPh_2$ (Strem), and $Ph_2PCH_2CH_2PPh_2$ (Strem) were used as received. The powdered elements As, Sb, Bi, Ge, Sn, Pb, B, Ga, Zn, Cd, and Se were used as received.

Reaction of Elements with NF_3O. A stainless-steel or Monel Hoke cylinder fitted with a stainless-steel or Monel Whitey valve was loaded with a known amount (~2 mmol) of the dry powdered element. A slight excess over the stoichiometric amount of NF_3O required was condensed into the cylinder at −196 °C by using standard vacuum-line techniques. The mixture was heated at 180–200 °C for 24 h. The progress of the reaction was checked by recording the IR spectrum of any volatile materials, including NF_3O. The formation of the fluoride products was confirmed by comparison of infrared and ^{19}F NMR spectral data with literature values.

Reaction of Phosphines and Phosphites with NF_3O. A 75-mL Monel Hoke cylinder fitted with a stainless-steel or Monel Whitey valve was charged with a known amount of compound (2–3 mmol) and cooled to −196 °C and evacuated. A slight excess over the stoichiometric amount of NF_3O required was condensed into the cylinder by standard vacuum-line techniques. A check was done for the completion of the reaction by following the IR spectrum of NF_3O. Trap-to-trap distillation or bulb-to-bulb distillation (Kugelrohr) was employed as necessary. The products were confirmed by comparison of infrared spectra, ^{19}F NMR spectra, and ^{31}P NMR spectral data with literature values.

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A Newly Proposed Cycle for the Water Gas Shift Reaction Homogeneously Catalyzed by Platinum and Tin Chloride

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A mechanism for catalysis of the water gas shift (WGS) reaction ($H_2O + CO = H_2 + CO_2$) by K_2PtCl_4 and $SnCl_4$ in a mixture of acetic and hydrochloric acids[1] has been described in

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