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REACTIONS OF TRIFLUORONITROSOMETHANE WITH BISTRIFLUOROMETHYLPHOSPHORUS COMPOUNDS, $(CF_3)_2PX$ (WHERE X = H, Cl, CF_3)

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SUMMARY

Trifluoronitrosomethane reacts with bis(trifluoromethyl)phosphine to give $(CF_3)_2P(O)N(OH)CF_3$ and a small amount of $(CF_3)_2NOH$. On the other hand, the reactions with tris(trifluoromethyl)phosphine and bis(trifluoromethyl)chlorophosphine afford $(CF_3)_2NOP(O)CF_3N(CF_3)_2$ and $(CF_3)_2NP(O)(CF_3)Cl$ respectively. Isomerisation of $>N-O-P<$ to $>N-P(O)<$ may be involved as found for the isomerisation of the phosphine, $(CF_3)_2NOP(CF_3)_2$, to the phosphoryl compound, $(CF_3)_2NP(O)(CF_3)_2$. Mechanisms for the above reactions are discussed.

INTRODUCTION

Hitherto, only a few reactions have been reported between trifluoronitrosomethane and inorganic compounds. These reactions are confined to compounds of silicon, nitrogen and phosphorus.

The gas phase photolysis of a mixture of trimethylsilane and trifluoronitrosomethane gives a 1:1 adduct, believed to be N-trifluoromethyl-O-trimethylsilylhydroxylamine, $CF_3(NH)OSiMe_3$, and N,N-bis(trifluoromethyl)-O-trimethylsilylhydroxylamine, $(CF_3)_2NOSiMe$ [1]. When both the gas and liquid phases are irradiated, the major product is $(CF_3)_2NOSiMe$. On the other hand, the platinum-catalysed reactions give the product, $CF_3(NH)OSiMe$, in high yield. The reactions of trifluoronitrosomethane with the halogenated silanes, $HSiX_3$ (where X = F or Cl), give only $CF_3(NH)OSiX_3$ [2].

Trifluoronitrosomethane gives distinct reactions with a number of compounds of nitrogen and phosphorus. Trifluoromethyl azide, CF_3N_3, is formed in 70% yield by reacting trifluoronitrosomethane with hydrazine [3]. Moreover, trifluoronitrosomethane affords N-trifluoromethyl-N'-methylcarbodiimide with methylisonitrile [4], a 1:1 adduct with ethyl azodicarboxylate [5], a 2:1 adduct with trifluorostyrene [5]

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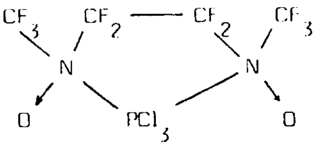
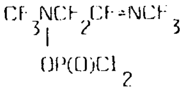
and both 1:1 and 2:1 adducts with styrene [4]. However, the reactions of trifluoronitrosomethane with phosphorus trichloride in the presence of fluoro-olefins, $CF_2{:}CFX$, have been reported by Ginsburg et al. to give compounds (I) and (II) [6,7].



(I) X = F



$$\underset{\displaystyle OP(O)Cl_2}{CF_3N}CF_2CF{=}NCF_3$$

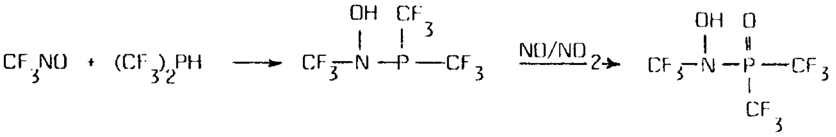
(II) X = Cl, Br

This paper reports the investigations of the reactions of trifluoronitrosomethane with a number of trifluoromethyl-substituted phosphines.

RESULTS AND DISCUSSION

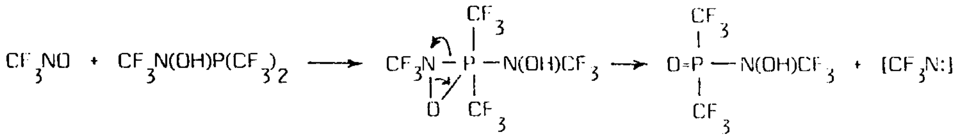
Reactions with bis(trifluoromethyl)phosphine

The reactions of an equimolar mixture of trifluoronitrosomethane and bis-(trifluoromethyl)phosphine at 100ºC for 22 hours gave the phosphoryl-substituted hydroxylamine, $CF_3N(OH)P(O)(CF_3)_2$, as shown by the following equations:



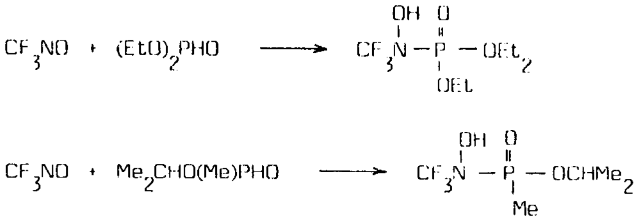
$$CF_3NO + (CF_3)_2PH \longrightarrow CF_3-\overset{OH}{N}-\overset{CF_3}{P}-CF_3 \xrightarrow{NO/NO_2} CF_3-\overset{OH}{N}-\underset{CF_3}{\overset{O}{\overset{\|}{P}}}-CF_3 \qquad (1)$$

Oxidation of trifluoromethyl-substituted phosphine by nitric oxide and nitrogen dioxide is similar to that reported by Burg [8], Griffith [9], Dobbie [10] and others [11-14]. The formation of the P=O bond via a pentacovalent phosphorus (V) intermediate cannot be discounted, as shown below:



$$CF_3NO + CF_3N(OH)P(CF_3)_2 \longrightarrow CF_3\underset{O}{N}-\underset{CF_3}{\overset{CF_3}{P}}-N(OH)CF_3 \longrightarrow O{=}\underset{CF_3}{\overset{CF_3}{P}}-N(OH)CF_3 + [CF_3N:]$$

Trifluoronitrosomethane has also been reported to give similar type of reactions with $(EtO)_2PHO$ and $Me_2CHO(Me)PHO$ to give the corresponding phosphoryl-substituted hydroxylamines, as shown below [15]:



$$CF_3NO + (EtO)_2PHO \longrightarrow CF_3\overset{OH}{N}-\overset{O}{\underset{OEt}{P}}-OEt_2$$

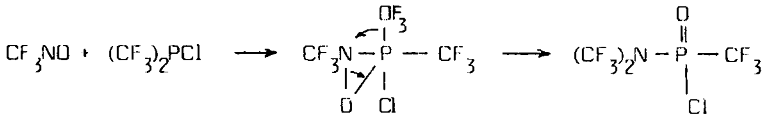
$$CF_3NO + Me_2CHO(Me)PHO \longrightarrow CF_3\overset{OH}{N}-\overset{O}{\underset{Me}{P}}-OCHMe_2$$

The above reactions with bis(trifluoromethyl)phosphine also generated a number of volatile compounds albeit in smaller amounts, namely bis(trifluoromethyl)-hydroxylamine, silicon tetrafluoride and an intractable phosphorus liquid.

Reactions with bis(trifluoromethyl)chlorophosphine

Trifluoronitrosomethane and bis(trifluoromethyl)chlorophosphine were reacted in a 1:1 ratio at 70ºC for 9 hours to give the following products, namely: a new compound bis(trifluoromethyl)amino-trifluoromethylchlorophosphine oxide (III) (n), $(CF_3)_2NP(O)(CF_3)_2Cl$, perfluoro-2-azapropene, carbonyl fluoride and silicon tetrafluoride.

Compound (III) was confirmed by its infrared spectrum and elemental analysis. Alkaline hydrolysis with 20% sodium hydroxide at 100ºC gives trifluoromethane in 74% yield. No reactions were observed with chlorine or hydrogen chloride even at elevated temperatures. The formation of compound (III) can be rationalised in terms of a pentavalent phosphorus intermediate, followed by a concommitmant oxidation and migration of a CF_3 group from phosphorus to nitrogen:



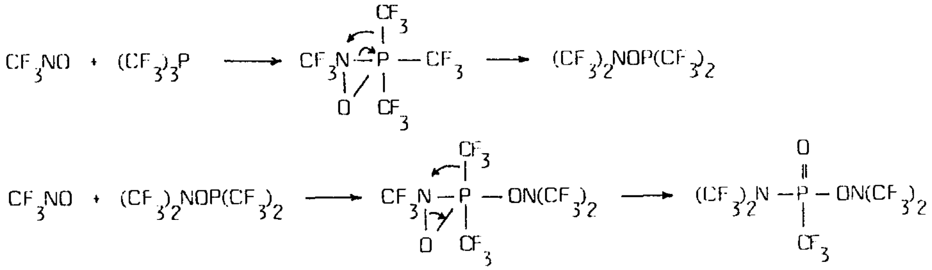
$$CF_3NO + (CF_3)_2PCl \longrightarrow CF_3\underset{O}{N}-\overset{OF_3}{\underset{Cl}{P}}-CF_3 \longrightarrow (CF_3)_2N-\overset{O}{\underset{Cl}{P}}-CF_3 \qquad (2)$$

The above reactions also yield a mixture of volatile compounds, namely: perfluoro-2-azapropene, carbonyl fluoride and silicon tetrafluoride.

Reactions with tris(trifluoromethyl)phosphine

The reactions of an equimolar mixture of trifluoronitrosomethane and tri(trifluoromethyl)phosphine were carried out at 100 to 150ºC. In each experiment about half the amount of tris(trifluoromethyl)phosphine was required although all the trifluoronitrosomethane had reacted.

Fractionation of the products gave bis(trifluoromethyl)aminobis(trifluoromethyl)nitroxytrifluoromethylphosphine oxide (IV), $(CF_3)_2NP(O)N(CF_3)_2$ Its structure was confirmed by its infrared spectrum and elemental analysis. Furthermore, no reactions were observed with chlorine or hydrogen chloride. Alkaline hydrolysis with 20% sodium hydroxide at 110ºC for 30 hours gave trifluoromethane in 100% yield. The formation of compound (IV) can be explained by the following reaction mechanisms:



<u>Isomerisation of bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine</u>

When bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine was heated at 100ºC for 42 hours, it underwent isomerisation to give 59% of the corresponding phosphine oxide according to the equation:

$$(CF_3)_2N-O-P(CF_3)_2 \longrightarrow (CF_3)_2NP(O)(CF_3)_2 \quad (V)$$

The infrared spectrum is identical to the phosphine oxide prepared according to the following equation:

$$2(CF_3)_2P(O)Cl + [(CF_3)_2NO]_2Hg \longrightarrow 2(CF_3)_2P(O)ON(CF_3)_2 + HgCl_2$$

Compound (V) did not give any addition reaction with chlorine, nor cleavage reaction with hydrogen chloride, unlike the reactions with bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine which proceed as follows:

$$(CF_3)_2NOP(CF_3)_2 + Cl_2 \longrightarrow (CF_3)_2NOP(CF_3)_2Cl_2$$

$$(CF_3)_2NOP(CF_3)_2 + HCl \longrightarrow (CF_3)_2NOH + (CF_3)_2PCl$$

Although the bis(trifluoromethyl)nitroxy phosphine, $(CF_3)_2NOP(CF_3)_2$, undergoes isomerisation at elevated temperatures, the corresponding difluoride $(CF_3)_2NOPF_2$, however, isomerises at room temperature and decomposes at elevated temperatures to give perfluoro-2-azapropene and trifluorophosphine oxide [16]:

$$(CF_3)_2NOPF_2 \longrightarrow (CF_3)_2NP(O)F_2 \xrightarrow{250^{\circ}C} CF_3N{=}CF_2 + OPF_3$$

OBSERVATIONS

From the foregoing reactions between trifluoronitrosomethane and $(CF_3)_2PX$ (X = H, Cl, CF_3), we observe that bis(trifluoromethyl)nitroxy group(s) are formed. This is probably due to the migration of CF_3 group from phosphorus to the nitrogen atom, as illustrated by equation (2). Similar reactions have also been observed in the reactions between tris(trifluoromethyl)antimony and O-nitroso-bis(trifluoromethyl)hydroxylamine [17]. The formation of the P=O bonds in the new phosphorus derivatives, namely $(CF_3)_2NP(O)(Cl)CF_3$ and $(CF_3)_2NP(O)(CF_3)ON(CF_3)_2$, is probably due to isomerisation of the corresponding phosphines $(CF_3)_2NOP(CF_3)X$ (where X = Cl and CF_3).

The infrared spectra of the new phosphorus compounds together with their tentative assignments are summarised in Table 1.

EXPERIMENTAL

All reactions are carried out in a vacuum system. Infrared spectra were recorded on Perkin Elmer Infrared 337 spectrometer. Known compounds were identified by their infrared spectra and molecular weights unless otherwise stated.

Reactions of bis(trifluoromethyl)phosphine with trifluoronitrosomethane

Bis(trifluoromethyl)phosphine (0.557 g, 3.27 mmoles) and trifluoronitrosomethane (0.334 g, 3.37 mmoles) were allowed to react in a sealed pyrex glass ampoule at 100ºC for 22 hours. Fractionation of the reaction mixture gave (a) a colourless liquid (0.0637 g, 0.230 mmole; 35% yield), trapped at -60ºC trap. Analyses gave F,59.8%; mol. wt. 287; $C_3F_9HNO_2P$ requires F,60.0%; mol. wt. 285. The major infrared absorptions were located at 3580m, 1870w, 1380m, 1270vs, 1250vs, 1204vs, 1166vs, 1131vs, 985m, 510w and 455m cm ; (b) N,N-bis(trifluoromethyl)hydroxylamine (0.0496 g, 0.290 mmole) was obtained in 9% yield at -78ºC trap; (c) 80% of bis(trifluoromethyl)phosphine (0.443 g, 2.61 mmole) at -126ºC trap; and (d) silicon tetrafluoride (0.0608 g, 0.580 mmole), at -196ºC trap. A heavy viscous liquid of a phosphorus compound (0.195 g) remained in the glass ampoule.

Table 1.

Infrared absorptions of some phosphorus derivatives

(I)	(II)	(III)	(IV)	Tentative Assignments
3580m				O-H stretching
1870w				N-O stretching of =N-O group
1380m	1350m	1350m	1340m	P=O stretching
1270vs	1325vs	1310vs	1330vs	C-F stretching of CF_3N group
	1252vs			
1250vs	1240vs	1280vs	1265vs	
	1219vs	1278vs	1242vs,sh	
1204vs	1200vs	1240vs	1230vs	
			1202vs	C-F stretching of CF_3P group
1166vs	1187vs	1150vs	1165vs,sh	
			1150vs	
1131vs	1130s		1140s,sh	
			1120s	
		1028m		N-O stretching of $(CF_3)_2NO$ group
985m		985m		C-N stretching
	970m	969m	972m	
		858m		P-O stretching
		735m	745w	-
		722m		-
	710m	710m	712m	CF_3 deformation
	610m			P-Cl stretching
		587m	579m	-
510w	500m	500m	500w	P=O bending
455w			460w	-

(I): $CF_3N(OH)P(O)(CF_3)_2$; (II): $(CF_3)_2NP(O)(CF_3)Cl$; (III): $(CF_3)_2NP(O)(CF_3)ON(CF_3)_2$; (IV): $(CF_3)NP(O)(CF_3)_2$.

Reactions of bis(trifluoromethyl)chlorophosphine with trifluoronitrosomethane

Bis(trifluoromethyl)chlorophosphine (0.613 g, 3.00 mmole) and trifluoronitrosomethane (0.296 g, 2.99 mmole) were allowed to react at 70ºC for 9 hours. Fractionation of the reaction mixture gave (a) an unidentified liquid (0.108 g) at -55ºC trap, whose infrared absorption bands are located at 1350vs (P=O stretching) 1320vs, 1270vs, 1250vs, 1190vs (C-F stretching), 1032m, 970w, 950m, 910m, 855m, 720m and 610w cm^{-1}; (b) a colourless liquid (0.504 g, 1.66 mmole; 55% yield), at -78ºC, was identified as bis(trifluoromethyl)aminotrifluoromethylchlorophosphine oxide (III) (n) (Found: F,56.2%; Cl,11.4%; C_3ClF_9NOP requires F,56.3%; Cl,11.7%). The infrared spectrum gave bands located at 1350m, 1325vs, 1252vs, 1240s, 1219vs, 1200vs, 1187vs, 1130s, 970m, 710m, 610m and 525m cm ; and (c) a mixture (0.118 g) of carbonyl fluoride perfluoro-aza-propene and silicon tetrafluoride.

Hydrolysis of compound (III) by sodium hydroxide

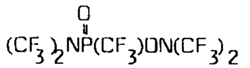
0.125 g (0.410 mmole) of compound (III) and 5 ml of 20% aqueous sodium hydroxide were heated at 120ºC for 3 days to give trifluoromethane (0.0214 g, 0.306 mmole; 74% yield).

Reactions of tris(trifluoromethyl)phosphine with trifluoronitrosomethane

Equimolar quantities of tris(trifluoromethyl)phosphine and trifluoronitrosomethane were found to react at temperatures above 100ºC. Table 2 summarises the results of 3 experiments.

Table 2.

Reactions between tris(trifluoromethyl)phosphine and trifluoronitrosomethane

Experiment	(1)	(2)	(3)
$(CF_3)_2P$ (g, mmole)	0.273,1.16	0.598,2.51	0.728,3.06
CF_3NO (g, mole)	0.129,1.30	0.250,2.54	0.325,3.28
Temperature (ºC)	150	130	110
Products:			
(a)  $(CF_3)_2N\overset{O}{\overset{\parallel}{P}}(CF_3)ON(CF_3)_2$ (g, mole)	0.0490,0.112	0.244,0.560	0.243,0.558
(b) $(CF_3)_3P$ (g, mmole)	0.141,0.592	0.447,1.88	0.121,0.509
(c) SiF_4 + COF_2 (g)	0.0605	0.0757	0.0716 (only COF_2)

Fractionation of the reactions gave as the principal component bis(trifluoromethyl)aminobis(trifluoromethyl)nitroxytrifluoromethylphosphine oxide (IV) (n) at -65ºC trap. Elemental analysis gave F,66.4%; $C_5F_{15}N_2O_2P$ requires F, 66.4%. Its infrared spectrum showed bands located at 1350s, 1310s, 1300sh, 1280s, 1278s, 1240s, 1200vs, 1185vs, 1150sh, 1120w, 1090w, 1028m, 985m, 969m, 930w, 880vw, 858m, 735m, 722m, 710m, 587m and 500m cm $^{-1}$. Hydrolysis of compound (IV) (0.243 g, 0.560 mmole) with 10ml 20% sodium hydroxide at 120ºC for 24 hours yielded trifluoromethane (0.0011 g, 0.020 mmole). No reactions were obtained with chlorine even at 100ºC.

Preparation of bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine

A mixture of bistrifluoromethyliodophosphine (0.854 g, 2.88 mmoles) and bis(trifluoromethyl)nitroxyl (0.509 g, 3.03 mmole) was allowed to warm up from -78ºC to room temperature over a period of 12 hours. Bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine was obtained at -78ºC trap (0.649 g, 1.93 mmole; 67% yield). Its infrared spectrum gave the following peaks: 1330m, 1319vs, 1265vs, 1240vs, 1219,1208 (doublet)vs, 1180,1168 (doublet)vs, 1135vs, 1120m,sh, 1026m, 972m, 820m, 745w, 710m, 620w, 560w and 438m cm^{-1} ; and molecular weight gave 336; C $C_4F_{12}NOP$ requires mol. wt. 337.

Reactions of bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine

Bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine (0.184 g, 0.550 mmole) and anhydrous hydrogen chloride (0.0643 g, 1.76 mmole) were reacted at 60ºC for a day to give on fractionation (a) N,N-bis(trifluoromethyl)hydroxylamine (0.0837 g, 0.500 mmole; 90% yield); and (b) bis(trifluoromethyl)chlorophosphine (0.105 g, 0.520 mmole; 95% yield; mol. wt. 204; C_2ClF_6P requires mol. wt. 204). Its infrared spectrum showed three strong C-F absorptions located at 1215, 1270 and 1135 cm^{-1} .

A mixture of bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine (0.224 g, 0.660 mmole) and chlorine (0.130 g, 1.83 mmole) was slowly warmed up from -78ºC to -20ºC to give, on fractionation, a white crystalline solid of bis(trifluoromethyl)nitroxybis(trifluoromethyl)dichlorophosphorane (0.161 g, 0.400 mmole; 61% yield) at the -40ºC trap. Elemental analysis gave: Cl, 17.4%; $C_4Cl_1F_{12}NOP$ requires Cl, 17.4%). Its infrared spectrum gave the following bands: 1318vs, 1268vs, 1245m,sh, 1233s, 1218s, 1180s, 1158,1148 (doublet)s, 1031m, 970m, 829m, 800w, 712m, 615m, 599m, 579m, 535m and 478m cm^{-1} .

Bis(trifluoromethyl)nitroxybis(trifluoromethyl)dichlorophosphorane (0.161 g, 0.0400 mmole) was reacted with 5 ml of 20% sodium hydroxide at 130ºC for 3 days to give trifluoromethane (0.0289 g, 0.410 mmole; 99% yield; found: Cl, 17.4%; $C_4Cl_2F_{12}NOP$ requires Cl, 17.4%).

Isomerisation of bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine

Bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine (0.598 g, 1.76 mmole) was heated at 100ºC for 42 hours to give, on fractionation, bis(trifluoromethyl)aminobis(trifluoromethyl)phosphine oxide (V) (n) (0.350 g, 1.04 mmole; 59% yield; found: F, 68.1%; $C_4F_{12}NOP$ requires F, 67.6%). Its infrared spectrum gave bands located at 1360m, 1330vs, 1265vs, 1240vs,sh, 1230vs, 1200vs, 1165sh, 1150vs, 1145sh, 1120vs, 1020w, 970m, 745w, 710m, 650w and 578m cm^{-1}. No cleavage reactions were obtained with chlorine and hydrogen chloride.

Reactions of mercury(II) bis(trifluoromethyl)nitroxide with bis(trifluoromethyl)-phosphinic chloride in 1:2 molar ratio

Bis(trifluoromethyl)phosphinic chloride (0.511 g, 2.32 mmole) and the mercurial, prepared by the reaction of bis(trifluoromethyl)nitroxyl (0.387 g, 2.31 mmole) with mercury (0.323 g, 1.63 mmole $[(CF_3)_2NO:Hg = 1.4:1]$ were allowed to react at room temperature to give bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide (n) (0.783 g, 2.22 mmole; 96% yield; found: F,62.3%; P,8.6%; $C_4F_{12}NO_2P$ requires F, 64.6%; P,8.8%).

Hydrolysis of the phosphine oxide (V)

Hydrolysis of the phosphine oxide (V) (0.407 g, 1.15 mmole) with 10 ml of 20% sodium hydroxide was undertaken at 120ºC for 24 hours to give trifluoromethane (0.0807 g, 1.15 mmole; 100% yield; found: mol. wt. 70; calc. for CF_3H: 70).

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