Journal of Fluorine Chemistry, 21 (1982) 221–242

Received: March 9, 1982

REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH CF_3PX_2 (WHERE X = F, Cl, Br, I AND CN) and $P(CN)_3$

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SUMMARY

The reactions between bis(trifluoromethyl)nitroxyl and CF_3PX_2 (where X = F, Cl, Br and CN) in 2:1 molar ratio give addition products, $[(CF_3)_2NO]_2P(CF_3)X_2$. The bromo and cyano products are unstable. The former decomposes at room temperature to give bromine and perfluoro-2-azapropene, and the latter yields predominantly $(CF_3)_2NOCF_3$. With CF_3PI_2, iodine displacement occurs to afford $[(CF_3)_2NO]_2PCF_3$. On the other hand, $P(CN)_3$ affords $[(CF_3)_2NO]_3PO$, $(CF_3)_2NON(CF_3)_2$ and paracyanogen. Mechanisms for these reactions are proposed.

INTRODUCTION

The reactions of bis(trifluoromethyl)nitroxyl with compounds of group V elements have been a subject of active investigations in recent years. The bis(trifluoromethyl)nitroxyl radical reacts instantly with nitric oxide to give a quantitative yield of the corresponding O-nitroso-derivative [1, 2].

$$(CF_3)_2NO + NO \longrightarrow (CF_3)_2NONO$$

It also reacts with nitrogen dioxide to afford what is believed to be O-nitrobis(trifluoromethyl)hydroxylamine, $(CF_3)_2NONO_2$.

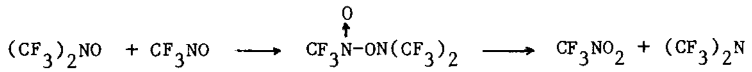
0022-1139/82/0000-0000/$02.75

The reactions with trifluoronitrosomethane follow a free radical pathway as shown by the following equations [3]:

$$(CF_3)_2NO + CF_3NO \longrightarrow (CF_3)_2NONO + CF_3$$

$$CF_3NO + CF_3 \longrightarrow (CF_3)_2NO$$

O-Nitrosobis(trifluoromethyl)hydroxylamine is reported as one of the products, the other being perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane). Formation of the latter can be similarly explained using the following free radical sequence:



$$(CF_3)_2NO + CF_3NO \longrightarrow CF_3\overset{\overset{O}{\uparrow}}{N}\text{-}ON(CF_3)_2 \longrightarrow CF_3NO_2 + (CF_3)_2N$$

$$(CF_3)_2NO + (CF_3)_2N \longrightarrow (CF_3)_2NON(CF_3)_2$$

The reactions of the bis(trifluoromethyl)nitroxyl with phosphorus compounds were undertaken by Makarov et al when the radical was first synthesized [4]. Its reactions with phosphorus trichloride are vigorous even at room temperature yielding two products, namely $(CF_3)_2NOPCl_4$ and $(CF_3)_2NOPCl_2$. On the other hand, phosphorus trifluoride at room temperature gives a mixture of products, namely $(CF_3)_2NON(CF_3)_2$, POF_3 and $CF_3N{=}CF_2$. But at -45°C, the corresponding phosphorane, $[(CF_3)_2NO]_2PF_3$, is formed [5]. The reactions with phosphorus tribromide however give a mixture of compounds, namely $[(CF_3)_2NO]_3PO$, $(CF_3)_2NON(CF_3)_2$ and bromine [6]. Furthermore, the reactions of substituted phosphines have been shown to give several types of reactions. For example, bis(trifluoromethyl)nitroxyl gives oxidation reactions with tris(pentafluorophenyl)phosphine as shown by the equation [7]:

$$2(CF_3)_2NO + (C_6F_5)_3P \longrightarrow (C_6F_5)_3PO + (CF_3)_2NON(CF_3)_2$$

Moreover, it undergoes addition reactions with $(CH_3O)_3P$ [8], substitution reactions with $[(CH_3)_2N]_3P$ [9], and hydrogen abstraction reactions with $(CF_3)_2PH$ [10].

In our present investigations, we have extended our study of bis-(trifluoromethyl)nitroxyl to several phosphorus compounds containing trifluoromethyl groups, halogens and pseudohalogens.

RESULTS AND DISCUSSION

Bis(trifluoromethyl)nitroxyl reacts with CF_3PX_2 (X = F, Cl, Br) at a low temperature of about -70°C to afford oxidative addition products, as shown by the equation:

$$CF_3PX_2 + 2(CF_3)_2NO \longrightarrow [(CF_3)_2NO]_2P(CF_3)X_2 \text{ (II)}$$

The reactions resemble those with $(CF_3)_3P$ [11], and $(CF_3)_2PX$ (X = F, Cl, Br and CN) [12]. However, the reactions with CF_3PBr_2 and $CF_3P(CN)_2$ also give side-products. The former affords bromine and perfluoro-2-azapropene, and the latter an appreciable amount of tris(trifluoromethyl)hydroxylamine.

The fluoro and chloro derivatives of (II) are stable. From vapour pressure measurements, the extrapolated physical constants are,

$[(CF_3)_2NO]_2P(CF_3)X_2$	b.p. °C	Kcal./mole
X = F	72	8.63
Cl	181	8.80

The bromo and cyano analogues are however unstable, and on prolonged standing at room temperature they undergo decomposition. The former on standing for a week gives perfluoro-2-azapropene and bromine, and the latter turns brown after a few days. On heating to 80°C for 36 hours, the cyano derivative undergoes 68% decomposition to give a mixture of carbonyl fluoride and perfluoro-2-azapropene together with an intractable brown liquid. The order of stability of the phosphorus derivatives $[(CF_3)_2NO]_2(CF_3)PX_2$ (X = F, Cl, Br and CN) follows the sequence $F \sim Cl > CN > Br$.

The reactions with trifluoromethyldiiodophosphine proceed by a displacement of iodine via either a four-coordinate intermediate as shown below:

$$\begin{tikzcd}
(CF_3)_2NO + CF_3PI_2 \arrow[r] & (CF_3)_2NOP(CF_3)I_2 \arrow[d] \\
& (CF_3)_2NOP(CF_3)I + \tfrac{1}{2}I_2
\end{tikzcd}$$

$$\begin{tikzcd}
(CF_3)_2NO + (CF_3)_2NOP(CF_3)I \arrow[r] & {[(CF_3)_2NO]_2P(CF_3)I} \arrow[d] \\
& {[(CF_3)_2NO]_2PCF_3 + \tfrac{1}{2}I_2}
\end{tikzcd}$$

or a five-coordinate intermediate:

$$\begin{tikzcd}
2(CF_3)_2NO + CF_3PI_2 \arrow[r] & {[(CF_3)_2NO]_2P(CF_3)I_2} \arrow[d] \\
& {[(CF_3)_2NO]_2PCF_3 + I_2}
\end{tikzcd}$$

The reactions of bis(trifluoromethyl)nitroxyl with phosphorus (III) cyanide follow a different course in that neither addition nor substitution products are obtained. Instead, tri[bis(trifluoromethyl)nitroxy]phosphine oxide, perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane, and a white residue probably polymeric paracyanogen were isolated. The overall equation is represented as follows:

$$5(CF_3)_2NO + P(CN)_3 \longrightarrow [(CF_3)_2NO]_3PO + (CF_3)_2NON(CF_3)_2 + \frac{3}{n}(CN)_n$$

which resembles the reactions with phosphorus tribromide. The radical mechanisms can be rationalised as shown below:

$$\begin{array}{lcl} (CF_3)_2NO + P(CN)_3 & \longrightarrow & (CF_3)_2NOP(CN)_3 \\ & & \downarrow \\ & & (CF_3)_2NOP(CN)_2 + \frac{1}{n}(CN)_n \end{array}$$

$$\begin{array}{lcl} (CF_3)_2NO + (CF_3)_2NOP(CN)_2 & \longrightarrow & [(CF_3)_2NO]_2P(CN)_2 \\ & & \downarrow \\ & & [(CF_3)_2NO]_2PCN + \frac{1}{n}(CN)_n \end{array}$$

$$\begin{array}{lcl} (CF_3)_2NO + [(CF_3)_2NO]_2PCN & \longrightarrow & [(CF_3)_2NO]_3PCN \\ & & \downarrow \\ & & [(CF_3)_2NO]_3P + \frac{1}{n}(CN)_n \end{array}$$

$$\begin{array}{lcl} (CF_3)_2NO + [(CF_3)_2NO]_3P & \longrightarrow & [(CF_3)_2NO]_3P\text{-}O\text{-}N(CF_3)_2 \\ & & \downarrow \\ & & [(CF_3)_2NO]_3PO + (CF_3)_2N \end{array}$$

$$(CF_3)_2NO + (CF_3)_2N \longrightarrow (CF_3)_2NON(CF_3)_2$$

All the new bis(trifluoromethyl)nitroxy derivatives of phosphorus undergo hydrolysis in air. Heating them with 20% sodium hydroxide cleaves the CF_3-P bonds to give trifluoromethane, the percentage yields are given in Table 1. On the other hand, the reactions of $[(CF_3)_2NO]_2P(CF_3)F_2$ with hydrogen chloride at 100°C for 2 days afford N,N-bis(trifluoromethyl)hydroxylamine in 17% yield. No reactions were observed with the chloro analogue.

TABLE 1

Hydrolysis by 20% sodium hydroxide

Compound	(g, mole)	Temp.(°C)/hr	CF_3H: g, mole	Percent Yield
$R_2(CF_3)PF_2$	0.108, 0.23	90/24	0.0029, 0.04	17
$R_2(CF_3)PCl_2$	0.466, 0.92	120/48	0.0293, 0.42	46
$R_2(CF_3)PBr_2$	0.313, 0.53	130/24	0.0051, 0.07	14
R_2PCF_3	0.135, 0.31	110/24	0.145, 0.21	68

R = $(CF_3)_2NO$

Tentative assignments of infrared spectra of bis(trifluoromethyl)nitroxy derivatives of phosphorus are given in Table 2. The bands appearing in the region 1230-1325 cm^{-1} are due to the C-F stretching absorptions of bis(trifluoromethyl)nitroxy group(s) [1, 13, 14]; and the band located at 850-880 cm^{-1} is associated with the P-O-N stretching vibration. These frequencies together can be taken as diagnostic of compound formation. Further evidence can be obtained by the presence of a medium-to-strong peak at 1025-1035 cm^{-1} due to the N-O stretching vibration, while that at 920 cm^{-1} to the symmetric C-N-C skeletal stretching vibration. Moreover, peaks at 800-820 cm^{-1} region can be attributed to the symmetric C-N-C bending mode. The frequencies in the region 1120 to 1220 cm^{-1} are ascribed to the C-F stretching vibration of CF_3 group bonded to phosphorus [11], and those at about 715 cm^{-1} to CF_3 deformation mode.

EXPERIMENTAL

Infrared spectra were measured with a Perkin Elmer 337 Grating Infrared Spectrophotometer which carries the range 4000-400 cm^{-1}. Vapour pressures of new compounds were determined in vacuo using a spiral gauge. Difluorotrifluoromethylphosphine was prepared by reacting the diiodo analogue with antimony trifluoride; while the dichloro, dibromo and dicyano derivatives from the diiodo analogue and the corresponding mercuric salts. Phosphorus cyanide was prepared according to the method described by Staats and Morgan [16].

Reaction of trifluoromethyldifluorophosphine with bis(trifluoromethyl)nitroxyl

Trifluoromethyldifluorophosphine (0.4951 g, 3.59 mmoles) and bis(trifluoromethyl)nitroxyl (1.2276 g, 7.31 mmoles) were condensed in vacuo into a pyrex glass ampoule. The ampoule was allowed to warm up from -78°C to room temperature and then left to stand for one day. The purple colour of the radical was completely discharged, and a colourless liquid was formed.

On fractionation, a clear liquid collected at -65°C (passed the -35°C trap) was identified as di[bis(trifluoromethyl)nitroxy]trifluoromethyldifluorophosphorane. The yield was 0.8437 g (1.78 mmoles, 50% based on the amount of the phosphine used). Elemental analysis gave C, 12.99%, F, 65.5%, P, 6.53%; $C_5F_{17}N_2O_2P$ requires C,

TABLE 2

The vibrational spectra of bis(trifluoromethyl)nitroxy derivatives of phosphorus

$R_2(CF_3)PF_2$	$R_2(CF_3)PCl_2$	$R_2(CF_3)PBr_2$	$R_2(CF_3)P(CN)_2$	$R_2P(CF_3)_3$ [15]	Tentative assignment
			2200m		CN stretch
1315vs	1314vs	1325vs	1320vs	1324vs	C-F stretch of $(CF_3)_2N$
1275vs	1274vs	1270vs	1270vs	1265vs	
1270vs	1266vs				
1240vs	1238vs	1235vs	1240vs	1235vs	
	1230sh				
1220vs	1216s	1218vs	1222vs	1220vs	C-F stretch of CF_3P
1195w	1189v, sh		1186vs, sh	1209vs	
1175s	1175vs	1184vs	1178vs		
1160sh	1168m, sh	1150sh		1150m	
1140sh	1140w			1120sh	
1060w					
1035m	1034s	1025m	1032m	1026m	N-O stretch
975m	974s	970m	975m	972m	C-N stretch
900m					P-F stretch
		883w			
880m	849m	848m	878m	860m	P-ON stretch
				834w	
820vw	815w	825w	820w	820w	C-N-C stretch
			800w	800w	

	778w		755vw		
713m	713m	713m	715m	715m	CF_3 deformation
622w	629m		655m		
615w	608w	610w	620w	615w	
	587m	565m	565w	580m	
	520w	518w			
		500w		505w	
		485w		490w	
		410w			

Note: (a) $R=(CF_3)_2NO$

(b) observed frequencies in cm^{-1}

(c) intensities: vs = very strong; s = strong; m = medium; w = weak; sh = shoulder

12.66%, F, 66.14%, P, 6.53%. The infrared spectrum of the compound showed absorptions at 1405w, 1315vs, 1275vs, 1270vs, 1240, 1220vs(doublet), 1195w, 1175s, 1160sh, 1140sh, 1060w, 1035m, 975m, 940m, 900m, 880m, 713m, and 632w, 615w(doublet) cm^{-1}.

TABLE 3

Vapour pressures of di[bis(trifluoromethyl)nitroxy]-trifluoromethyldifluorophosphorane

P(mm)	$\log_{10}P$(mm)	T(°C)	T(K)	$^1/T\times10^{-3}(K^{-1})$
27.0	1.431	0	273.0	3.663
35.5	1.550	5.0	278.0	3.597
51.0	1.708	10.0	283.0	3.534
58.0	1.764	13.5	286.5	3.490
74.5	1.872	18.5	291.5	3.431
87.5	1.942	21.5	294.5	3.396
98.5	1.993	23.5	296.5	3.373
117.0	2.068	27.0	300.0	3.333
135.5	2.132	30.0	303.0	3.300
163.0	2.212	34.0	307.0	3.257

Vapour pressure measurements of the compound from 0°C to 34°C gave a straight line as represented by the equation:

$$\log P(\mathrm{mm}) = 8.352 - \frac{1887}{T}$$

from which the following physical constants were obtained:

Latent heat of vaporisation, 7.63 Kcal/mole; and

Extrapolated boiling point, 72°C.

Hydrolysis of di[bis(trifluoromethyl)nitroxy]trifluoromethyldifluorophosphorane with 20% aqueous sodium hydroxide

0.1075 g (0.23 mmole) of di[bis(trifluoromethyl)nitroxy]trifluoromethyldifluorophosphorane was sealed with 5 ml 20% aqueous sodium hydroxide in a pyrex ampoule. A colourless solution remained in the ampoule after it was left at room temperature for one day. Upon heating the ampoule at 90°C for another day, a white precipitate was formed.

On fractionation, the only volatile product, identified by its infrared spectrum, was trifluoromethane (0.0029 g, 0.04 mmole; 17% yield).

Reaction of di[bis(trifluoromethyl)nitroxy]trifluoromethyldifluorophosphorane with anhydrous hydrogen chloride

Anhydrous hydrogen chloride (0.1455 g, 4.00 mmoles) was condensed in vacuo with di[bis(trifluoromethyl)nitroxy]trifluoromethyldifluorophosphorane (0.3809 g, 0.80 mmole) in a pyrex glass ampoule. After two days, only the original compounds were recovered. They were resealed into the glass ampoule and then heated to 100°C for another two days.

On fractionation, the mixture afforded:

(i) N,N-bis(trifluoromethyl)hydroxylamine (0.0474 g, 0.28 mmole, 18% yield), trapped at -83°C (passed the -60°C trap);

(ii) excess hydrogen chloride and a mixture of decomposition products which were trapped at -196°C (passed the -83°C trap). The infrared spectrum gave bands at 3460w, 1925m, 1800w, 1500m, 1415m, 1350s, 1320vs, 1270vs, 1240vs, 1195vs, 1145m, 1070m, 1025m, 990m, 945m, and 868w cm^{-1}. These peaks can be attributed to N,N-bis(trifluoromethyl)amine and perfluoro-2-azapropene; and

(iii) an intractable liquid remained in the ampoule.

Reaction of trifluoromethyldichlorophosphine with bis(trifluoromethyl)nitroxyl

Trifluoromethyldichlorophosphine (0.6206 g, 3.63 mmoles) was condensed together with bis(trifluoromethyl)nitroxyl (1.2255 g, 7.29 mmoles) in a pyrex ampoule. The ampoule was left in the dry ice/isopropanol mixture (-75°C) for 14 hours. By then, a light purple colour which persisted was due to excess bis(trifluoromethyl)nitroxyl.

On fractionation, a colourless liquid was obtained at -40°C (passed the -10°C trap). It was identified as di[bis(trifluoromethyl)nitroxy]trifluoromethyldichlorophosphorane (1.717 g, 3.39 mmoles), giving a yield of 93% based on the amount of trifluoromethyldichlorophosphine used. (Found: Cl, 13.91%; $C_5Cl_2F_{15}N_2O_2P$ requires Cl, 13.99%.) The compound was a clear heavy liquid, stable at room temperature in a sealed glass ampoule without showing any sign of decomposition. However, it was very sensitive to moist air which caused it to turn gradually to a light yellow liquid.

A small amount of the bis(trifluoromethyl)nitroxyl (0.1060 g, 0.63 mmoles) was recovered.

The infrared spectrum of the di[bis(trifluoromethyl)nitroxy]trifluoromethyldichlorophosphorane showed absorptions at 1314vs, 1292v, 1274vs, 1266vs, 1239vs, 1230sh, 1216s, 1189w(sh), 1175vs, 1168m(sh), 1140w, 1034s, 974s, 849m, 815w, 778w, 713m, 629m, 608w, 587m and 520w cm^{-1}.

TABLE 4

Vapour pressures of di[bis(trifluoromethyl)nitroxy] trifluoromethyldichlorophosphorane

P(mm)	$\log_{10}$P(mm)	T(°C)	T(K)	$^{1}/T\times10^{-3}(K^{-1})$
50.0	1.699	26.5	299.5	3.339
55.5	1.744	29.5	302.5	3.306
58.0	1.763	31.0	304.0	3.289
61.0	1.785	35.0	308.0	3.247
65.0	1.183	39.0	312.0	3.205
71.0	1.851	44.5	317.5	3.150
81.5	1.911	50.0	323.0	3.100
91.0	1.959	54.0	327.0	3.058
104.5	2.019	61.0	334.0	2.994
122.0	2.086	65.0	338.0	2.959

The vapour pressure measurements from 26.5°C to 65°C gave a straight line:

$$\log P(\text{mm}) = 5.189 - \frac{1048}{T}$$

from which the following physical constants were obtained:

Latent heat of vaporisation, 4.80 Kcal/mole; and

Extrapolated boiling point, 181°C.

Reaction of di[bis(trifluoromethyl)nitroxy]trifluoromethyldichlorophosphorane with anhydrous hydrogen chloride

Di[bis(trifluoromethyl)nitroxy]trifluoromethyldichlorophosphorane (0.2337 g, 0.46 mmole) was sealed with anhydrous hydrogen chloride (0.0990 g, 2.70 mmoles) in a pyrex ampoule. The ampoule was allowed to warm up from -50°C (dry ice/isopropanol mixture) to room temperature. There was no reaction. The mixture was then heated to

80°C for 16 hours. On fractionation, no N,N-bis(trifluoromethyl)-hydroxylamine was isolated. Instead, a small amount of trifluoromethane and bis(trifluoromethyl)amine were detected. Most of the phosphorane remained unreacted.

Hydrolysis of di[bis(trifluoromethyl)nitroxy]trifluoromethyldichlorophosphorane with 20% aqueous sodium hydroxide

Di[bis(trifluoromethyl)nitroxy]trifluoromethyldichlorophosphorane (0.4662 g, 0.92 mmole) was sealed with 5 ml 20% sodium hydroxide. The ampoule was heated to 120°C in the oven for two days. The solution remained clear after the heating. On fractionation, 0.0293 g (0.42 mmole) of trifluoromethane was obtained, giving a yield of 46%.

Reaction of trifluoromethyldibromophosphine with bis(trifluoromethyl)nitroxyl

Trifluoromethyldibromophosphine (0.3768 g, 1.45 mmoles) and bis(trifluoromethyl)nitroxyl (0.4960 g, 2.95 mmoles) were condensed in vacuo into a pyrex ampoule of 100 ml capacity at -196°C. The ampoule was sealed and left overnight in the dry ice/isopropanol mixture (-72°C). The next day, the temperature had warmed up to -30°C. The purple colour of the radical had completely disappeared, and a clear heavy liquid was formed. On standing for a few hours at room temperature, an orange red vapour appeared in the ampoule.

Fractionation of the products gave 3 main fractions:

(i) a reddish solid, trapped at -50°C (passed the -20°C trap) was obtained. The reddish colour was due to the presence of bromine, which was subsequently removed by shaking the fraction with mercury for a few minutes. On refractionation, a clear liquid obtained was identified as di[bis(trifluoromethyl)nitroxy]trifluoromethyldibromophosphorane (0.5893 g, 0.99 mmole; found: C, 9.05%, F, 47.3%, Br, 26.76%; $C_5F_{15}N_2O_2PBr_2$ requires C, 10.07%, F, 47.8%, Br, 26.84%.), giving a yield of 68% based on the amount of the phosphine used. The infrared spectrum of di[bis(trifluoromethyl)nitroxy]trifluoromethyldibromophosphorane showed absorptions at 1375m, 1335m, 1325vs, 1270vs, 1235vs, 1218vs, 1184vs, 1150sh, 1025m, 970m, 883w, 848m, 713m, 610w, 565m, 518w, 500w, 485w and 410w cm^{-1};

(ii) a small quantity of red solid was trapped at -83°C (passed -60°C) (0.1010 g, 0.63 mmoles). The vapour showed no infrared absorptions but gave a pale yellow precipitate of silver bromide with acidified silver nitrate; and

(iii) perfluoro-2-azapropene (0.0532 g, 0.40 mmole) was trapped at -196°C. The yield was 14% based on the amount of bis(trifluoromethyl)nitroxyl used. The infrared spectrum showed absorptions at 1800vs, 1330s, 1292s, 1270s, 1250m, 1205s, 1150s, 1010s, 1000s(doublet) and 730m cm^{-1}.

Reaction of di[bis(trifluoromethyl)nitroxy]trifluoromethyldibromophosphorane with 20% aqueous sodium hydroxide

Di[bis(trifluoromethyl)nitroxy]trifluoromethyldibromophosphorane (0.3129 g, 0.53 mmole) was sealed with 10 ml 20% aqueous sodium hydroxide into a glass ampoule. The ampoule was heated to 130°C for one day. On fractionation, it gave trifluoromethane (0.0051 g, 0.07 mmole; 14% yield). The aqueous solution, after acidification, reacted with silver nitrate solution to give silver bromide (0.1974 g).

Stability of di[bis(trifluoromethyl)nitroxy]trifluoromethyldiboromophosphorane

A sample of di[bis(trifluoromethyl)nitroxy]trifluoromethyldibromophosphorane (0.3830 g) was sealed in a glass ampoule and kept for one week at room temperature. Orange-red vapour was found in the ampoule and the liquid became viscous. Fractionation of the mixture through a series of traps cooled at -20°C, -50°C, -83°C and -196°C yielded the following fractions:

(i) a small amount of clear liquid (0.0118 g) was trapped at -20°C. The infrared spectrum of the fraction showed a strong absorption band at 1350 cm^{-1} which is attributed to the P=O stretching vibration. A medium-to-strong broad band was also observed at 870 cm^{-1}. The other major bands were located at 1350s, 1320vs, 1275vs, 1240vs, 1220vs, 1180m, 1030m(broad), 975m, 870m(broad), 720m, 650w, 620w and 570v cm^{-1};

(ii) the original compound di[bis(trifluoromethyl)nitroxy]trifluoromethyldibromophosphorane (0.3625 g) was trapped at -50°C, giving a 95% recovery;

(iii) a trace amount of bromine was trapped at -83°C;

(iv) a trace amount of perfluoro-2-azapropene was trapped at -196°C as a white solid, identified from its infrared spectrum; and

(v) a droplet of colourless liquid was found in the ampoule. It changed to a white solid when exposed to air.

Reaction of trifluoromethyldiiodophosphine with bis(trifluoromethyl)nitroxyl

Trifluoromethyldiiodophosphine (0.8850 g, 2.5 mmoles) was condensed in vacuo with bis(trifluoromethyl)nitroxyl (0.6440 g, 3.8

mmoles) into a pyrex ampoule. The sealed ampoule was placed in a dry ice/isopropanol mixture (-78°C). Solid iodine appeared after the ampoule was placed in the coolant for about 15 minutes.

On fractionation, a mixture of colourless liquid and iodine solid was trapped at -45°C. The fraction was refractionated many times to remove the iodine. After refractionation, a light brown liquid (0.3735 g) was found trapped at -55°C (most of the iodine was trapped at -45°C). The last trace of iodine in the brown liquid was removed by shaking the mixture with dry mercury. A colourless liquid (0.3010 g, 0.69 mmole) obtained was identified as di[bis(trifluoromethyl)nitroxy]trifluoromethylphosphine. Analysis gave F, 65.2%, P, 7.0%; $C_5F_{15}N_2O_2P$ requires F, 65.3%, P, 7.1%. The yield was 36%, based on the amount of bis(trifluoromethyl)nitroxyl used. The major infrared absorption bands were located at 1319vs, 1267vs, 1234vs, 1215vs, 1182vs, 1160m, 1122m, 1024m, 970m, 832m and 710m cm^{-1}.

A small amount of perfluoro-2-azapropene (0.0815 g, 0.61 mmoles) was trapped at -196°C (passed -96°C trap). It was identified by its infrared spectrum which gave peaks at 1800vs, 1330vs, 1292vs, 1270vs, 1250m, 1150s, 1010s, 1000s(doublet) and 730m cm^{-1}.

Hydrolysis of di[bis(trifluoromethyl)nitroxy]trifluoromethylphosphine with 20% aqueous sodium hydroxide

Di[bis(trifluoromethyl)nitroxy]trifluoromethylphosphine (0.1348 g, 0.31 mmole) was condensed in a glass ampoule containing 3.5 ml of 20% aqueous sodium hydroxide. The sealed ampoule was heated to 110°C for 24 hours. On fractionation, the only volatile compound was found to be trifluoromethane (0.0145 g, 0.21 mmole; 68% yield based on the amount of the phosphine used).

Reaction of trifluoromethyldicyanophosphine with bis(trifluoromethyl)nitroxyl

Trifluoromethyldicyanophosphine (0.3316 g, 2.18 mmoles) was condensed together with the bis(trifluoromethyl)nitroxyl (0.7325 g, 4.37 mmoles) into a pyrex ampoule of 100 ml capacity. The sealed ampoule was left in the dry ice/isopropanol mixture (-78°C). After one day, the temperature increased to -20°C. A colourless liquid was left in the ampoule.

Fractionation of the reaction mixture gave 3 fractions:

(i) a colourless liquid, trapped at -30°C (passed the -10°C trap) was identified as di[bis(trifluoromethyl)nitroxy]trifluoromethyldicyanophosphorane (0.6975 g, 1.43 mmoles; found: F, 58.3%; $C_7F_{15}N_4O_2P$ requires F, 58.4%.). The yield was 66% based on the amount of the phosphine used. The compound was not stable at room temperature. Appreciable decomposition took place on standing for a few days, as shown by the appearance of a heavy brown liquid. The infrared spectrum of di[bis(trifluoromethyl)nitroxy]trifluoromethyldicyanophosphorane showed absorptions located at 2200m, 1370w, 1320vs, 1270vs, 1240vs, 1222vs, 1186vs, 1178vs(doublet), 1032m, 975m, 878m, 820w, 800w, 755vw, 715m, 655m 620w and 565v cm^{-1};

(ii) tris(trifluoromethyl)hydroxylamine (0.1162 g, 0.49 mmoles) was obtained in the -196°C trap (passed the -96°C trap). It was identified by its infrared spectrum and molecular weight; and

(iii) a droplet of intractable liquid was left in the ampoule.

Hydrolysis of di[bis(trifluoromethyl)nitroxy]trifluoromethyldicyanophosphorane with 20% aqueous sodium hydroxide

0.2600 g (0.53 mmole) of di[bis(trifluoromethyl)nitroxy]trifluoromethyldicyanophosphorane was sealed with 5 ml 20% aqueous sodium hydroxide in a large ampoule and heated to 120°C for three days. Some white crystalline solid appeared after heating. On fractionation, the only volatile fraction trapped at -196°C (passed the -126°C trap), was found to be impure trifluoromethane (0.0116 g). The infrared spectrum showed absorption bands at 2220m(doublet), 1370m, 1210m, 1150vs, 965s, 920m, 700w and 590w cm^{-1}. This fraction (0.0116 g) was treated with acidified silver nitrate solution to give a white precipitate.

Pyrolysis of di[bis(trifluoromethyl)nitroxy]trifluoromethyldicyanophosphorane

The phosphorane (0.3003 g, 0.62 mmole) was sealed in vacuo in a glass ampoule and heated to 80°C for 36 hours. A heavy brown liquid remained in the ampoule. Fractionation of the mixture yielded 4 fractions:

(i) a colourless liquid (0.0980 g) was trapped at -55°C (passed -10°C). It was identified by the infrared spectrum to be the original phosphorane (32% recovery);

(ii) a colourless liquid (0.0104 g) was trapped at -126°C (passed the -96°C trap). The infrared spectrum showed absorption bands at 2260w, 1880m, 1380vs, 1350w, 1320m, 1270s, 1240vs, 1185m, 1030w, 990m, 730m and 710m cm^{-1};

(iii) a mixture (0.0852 g) of perfluoro-2-azapropene and carbonyl fluoride was trapped at -196°C (passed the -120°C trap). The infrared spectrum of this fraction showed absorptions at 2250w, 1940m(triplet), 1800s, 1360m, 1320m, 1292s, 1270s(doublet), 1250s, 1000m(triplet), 960m, 770w(sharp), and 730w(triplet) cm^{-1}; and

(iv) a heavy brown liquid (0.1177 g) remained in the ampoule. Its infrared spectrum in Nujol gave only one broad absorption at about 3500 cm^{-1}.

Reaction of Phosphorus(III) cyanide with bis(trifluoromethyl)nitroxyl

Bis(trifluoromethyl)nitroxyl (1.398 g, 7.80 mmoles) was condensed in vacuo into a pyrex glass ampoule containing 0.1028 g (0.94 mmole) of phosphorus(III) cyanide. The ampoule was left in the dry ice/isopropanol mixture (-78°C) for 16 hours. By then the temperature had risen to room temperature. Excess radical and some white solid were observed in the ampoule.

On fractionation of the reaction mixture, three volatile fractions were collected. They were:

(i) a white solid, which sublimed into the vacuum line and condensed at 0°C trap. It was found to be phosphoryl bis(trifluoromethyl)nitroxide (0.4963 g, 0.90 mmole; found: C, 12.93%; $C_6F_{18}N_3O_4P$ requires C, 13.1%). The yield was 96% based on the amount of phosphorus(III) cyanide used. The major infrared bands were located at 1380s, 1320vs, 1275vs, 1235s, 1215s, 1184m, 1029s, 971s, 897s, 800w, 714s, 621m and 493m cm^{-1};

(ii) a colourless liquid, trapped at -83°C (passed the -70°C trap) and found to be perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.1536 g, 0.48 mmole; 51% yield based on $P(CN)_3$; found: mol. wt. 322, $C_4F_{12}N_2O$ requires mo. wt.

320). The major infrared bands were located at 1315vs, 1280vs, 1270vs, 1240vs, 1220s, 1200s, 1190s, 1040w, 990m, 970s, 795w, 720s and 625w cm^{-1}; and

(iii) excess bis(trifluoromethyl)nitroxyl (0.5289 g, 3.15 mmoles), was recovered. A white solid which remained in the ampoule could not be identified as it was hygroscopic and did not give a satisfactory infrared spectrum with Nujol.

REFERENCES

1 W.D. Blackley and R.R. Reinhard, J. Amer. Chem. Soc. 87, 802, 1965.

2 R.E. Banks, W.M. Cheng, R.N. Haszeldine and G.J. Shaw, J. Chem. Soc. (C), 55, 1970.

3 R.E. Banks, R.N. Haszeldine and M.J. Stevenson, J. Chem. Soc. (C), 901, 1966.

4 S.P. Makarov, M.A. Englin, A.F. Videiko, V.A. Tobolin and S.S. Dabov, Dokl. Akad. Nauk SSSR, 168(2), 344, 1966; Proc. Acad. Sci. USSR, Chem. Sec. 168, 483, 1966.

5 J.M. Shreeve and C.S.C. Wang, Inorg. Chem. 12, 81, 1973.

6 H.J. Emeleus, P.M. Spaziante and S.M. Williamson, J. Inorg. Nucl. Chem. 32, 3219, 1970.

7 H.G. Ang and W.S. Lien, J. Fluorine Chem. 9, 73, 1977.

8 Y.O. El Nigumi and H.J. Emeleus, J. Inorg. Nucl. Chem. 32, 3213, 1970.

9 Y.O. El Nigumi and H.J. Emeleus, J. Inorg. Nucl. Chem. 32, 3211, 1970.

10 H.G. Ang, Chem. Commun. 1320, 1968.

11 H.G. Ang and Y.C. Syn, J. Fluorine Chem. 8, 481, 1976.

12 H.G. Ang and K F Ho, J. Fluorine Chem. 7, 497, 1976.

13 D.P. Babb and J.M. Shreeve, Inorg. Chem. 6, 351, 1967.

14 G.G. Flaskerad and J.M. Shreeve, Inorg. Chem. 8, 2065, 1969.

15 H.G. Ang and K.F.Ho, J. Flourine Chem. 27, 349, 1971.

16 P.A. Staats and H.W. Morgan, Inorganic Synthesis 6, 84, 1960