

Received: July 1, 1976

REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH $(CF_3)_2PX$
(X = F, Cl, Br, I and CN)

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SUMMARY

Bis(trifluoromethyl)nitroxyl gives oxidative addition products with $(CF_3)_2PX$ (X = F, Cl, Br and CN). With $(CF_3)_2PI$, iodine is eliminated to afford $(CF_3)_2NOP(CF_3)_2$. Mechanisms for the reactions are proposed and discussed, and spectral data of new compounds presented.

INTRODUCTION

Reactions of bis(trifluoromethyl)nitroxyl with compounds of phosphorus are varied. It has been reported to undergo addition reaction with $(CH_3O)_3P$ [1], substitution reaction with $[(CH_3)_2N]_3P$ [1], hydrogen abstraction reaction with $(CF_3)_2PH$ [2], and rather different kind of reactions with phosphorus trihalides. With phosphorus trifluoride at ambient temperatures, the reaction is as shown by the equation:



But at $-45^\circ C$, the corresponding phosphorane, $[(CF_3)_2NO]_2PF_3$, is formed [3]. The reaction with phosphorus trichloride at room temperature is different in that two products, namely, $(CF_3)_2NOPCl_4$ and $(CF_3)_2NOPCl_2$ are afforded [4]; and phosphorus tribromide, however, gives a mixture of $[(CF_3)_2NO]_3PO$, $(CF_3)_2NON(CF_3)_2$ and bromine [5]. This work discusses the reactions with a series of trifluoromethyl-substituted phosphines [6].

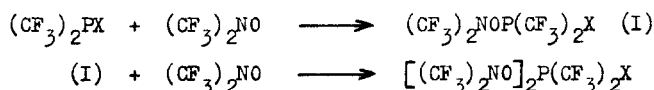
RESULTS AND DISCUSSION

Bis(trifluoromethyl)nitroxyl reacts with $(CF_3)_2PX$ ($X = F, Cl, Br$ and CN) readily to give oxidative addition products, as shown by the equation:



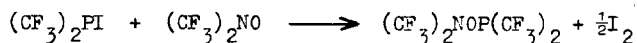
The reactions are similar to that with $(CF_3)_3P$ [7] but are distinctly different when compared with the reactions involving $[(CH_3)_2N]_3P$ or $(CF_3)_3M$ ($M = As$ and Sb) which give substitution products [1, 8].

Free radical mechanisms are most probably operative in the addition reactions, as illustrated by the equations:



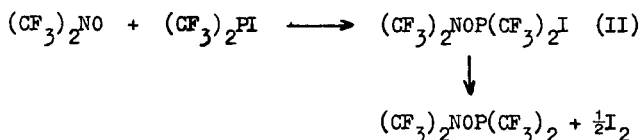
On prolonged standing (ca 3 months) only the fluoro- and cyano-phosphoranes, $[(CF_3)_2NO]_2P(CF_3)_2X$ ($X = F$ and CN), are stable, the least stable being the bromo-phosphorane since the liquid became coloured due to the presence of bromine as one of the decomposition products. Attempts at isolating the other decomposition products pure were unsuccessful. The order of stability of the phosphoranes $[(CF_3)_2NO]_2P(CF_3)_2X$ ($X = F, Cl, Br$ and CN) follows the sequence: $F \sim CN > Cl > Br$.

The reaction with bis(trifluoromethyl)iodophosphine proceeds by a displacement of iodine to afford the substituted phosphine,

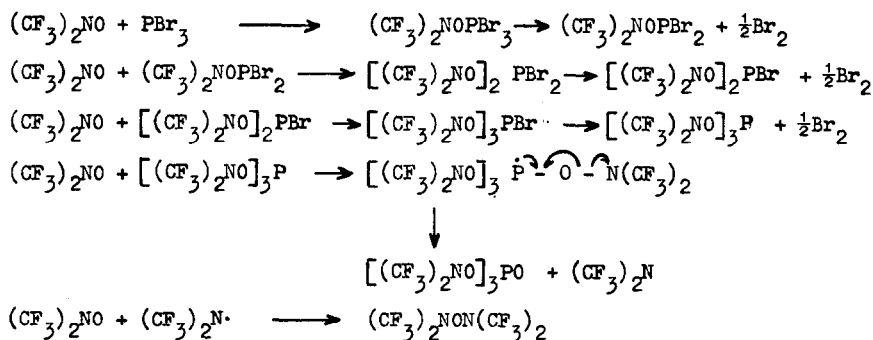


The above reactions demonstrate that for $(CF_3)_2PX$, the overriding factor that determines both the stability of the phosphoranes and the nature of the reactions is the halogen atoms attached to phosphorus. Thus, the stability sequence explains the difficulty that is associated with synthesizing the phosphoranes containing P-I bond.

The radical mechanisms that can be proposed for the displacement reaction is as follows:



which suggests the unstable nature of the phosphoranyl intermediate (II). The reactions with phosphorus tribromide probably follow a similar course:



All the new bis(trifluoromethyl)nitroso-phosphorus compounds formed in the present study are susceptible to hydrolysis when exposed to air. Heating them with 20% sodium hydroxide at elevated temperatures eliminates the trifluoromethyl groups bonded to phosphorus as trifluoromethane. The results are given below.

TABLE 1

Hydrolysis by 20% sodium hydroxide

Compound (g., mmole)	Temp. (°C)/hr	CF ₃ H: g.mmole	Per cent Yield
R ₂ (CF ₃) ₂ PF (0.092, 0.176)	120/48	0.0241, 0.345	96.4
R ₂ (CF ₃) ₂ PCL (0.197, 0.365)	129/53	0.0504, 0.715	98.2
R ₂ (CF ₃) ₂ PBr (0.166, 0.284)	130/96	0.0240, 0.0343	60.5
R ₂ (CF ₃) ₂ PCN (0.206, 0.388)	130/48	0.0270, 0.386	99.5
RP(CF ₃) ₂ (0.412, 1.22)	130/30	0.170, 9.44	99.8

R = (CF₃)₂NO

Attempts at conformational studies by undertaking F^{19} n.m.r. measurements at low temperatures (ca -60°C) met with no success. In $[(\text{CF}_3)_2\text{NO}]_2-(\text{CF}_3)_2\text{PX}$ ($X = \text{F}$ and Cl), only two peaks were obtained: $X = \text{F}$: $\delta(\text{CF}_3\text{N})$, 68.1 p.p.m.; $\delta(\text{CF}_3\text{P})$, 55.4 p.p.m.; $J(\text{CF}_3-\text{P})$, 114 Hz; and $X = \text{Cl}$: $\delta(\text{CF}_3\text{N})$, 68.2 p.p.m.; and $\delta(\text{CF}_3\text{P})$, 59.0 p.p.m. In both the spectra, the peaks associated with CF_3P are broad.

Tentative assignments of infrared data of bis(trifluoromethyl)nitroxyl derivatives of phosphorus are given in Table 2. The new peak located at 850 cm^{-1} is associated with the P-O-N stretching vibration, and can be taken as diagnostic of compound formation.

EXPERIMENTAL

Since all the compounds used in this study are volatile, inflammable and/or susceptible to hydrolysis, a vacuum system is used. The infrared spectra were recorded on an Infracord Spectrometer 337. All the phosphorus compounds were prepared by known methods.

Reaction of bis(trifluoromethyl)nitroxyl with bis(trifluoromethyl)fluorophosphine

A mixture of bis(trifluoromethyl)fluorophosphine (0.345 g., 1.84 mmole) and bis(trifluoromethyl)nitroxyl (0.717 g., 4.27 mmole) was condensed in an evacuated ampoule which was allowed to warm gradually to room temperature. After standing for a day, a liquid tinged by the purple nitroxyl was obtained. Fractionation under vacuum gave a colourless liquid at -45°C trap, identified to be di[bis(trifluoromethyl)nitroxyl]bis(trifluoromethyl)-phosphorane, $[(\text{CF}_3)_2\text{NO}]_2(\text{CF}_3)_2\text{PF}$, (0.792 g., 1.51 mmole; 91% yield). Analysis: F, 70.3%; $\text{C}_6\text{F}_{19}\text{N}_2\text{O}_2\text{P}$ requires F, 70.3%. Vapour pressures ($24^{\circ} - 55^{\circ}\text{C}$) were represented by $\log_{10} P(\text{mm}) = 6.270 - 1.390/T$, giving an extrapolated b.p. of 138°C and latent heat of vapourisation of $6.380\text{ kcal. mole}^{-1}$.

Reaction with bis(trifluoromethyl)chlorophosphine

Bis(trifluoromethyl)chlorophosphine (0.723 g., 3.53 mmole) and bis(trifluoromethyl)nitroxyl (1.29 g., 6.09 mmole) were allowed to react in an

TABLE 2

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

$R_2(CF_3)_2PF$	$R_2(CF_3)_2PCL$	$R_2(CF_3)_2PBr$	$R_2(CF_3)_2PCN$	$R_2(CF_3)_3$	Tentative assignment
1314 vs	1310 vs	1319 vs	2200 w		CN stretch
1205 vs	1268 vs	1275 vs	1320 vs	1324 vs	
1235 vs	1234 vs	1235 s	1270 vs	1265 vs	C-F stretch (of CF_3N)
1215 vs	1215 vs	1220 s	1240 vs	1235 vs	
1182 s	1173 s	1175 s	1220 vs	1220 vs	
1150 sh	1154 s	1151 sh	1190 s	1209 vs	C-F stretch (of CF_3P)
		1134	1160 m	1150 m	
1030 s	1032 s	1025 m		1120 sh	
974 s	972 s	972 m	1035 s	1026 m	N-O stretch
893 s		972 m	975 s	972 m	C-N stretch
850 s	858 s	853 m			P-F stretch
832 sh	823 m	825 w	865 s	860 m	P-CN stretch
	815 sh		820 w	834 w	C-N-C stretch
	786 w		790 w	820 w	
			760 w	800 w	
730 w			735 w		

716 s	717 s	718 m	716 s	715 m
625 m	638 s	652 w	665 s	-
590 m	614 m	610 w	600 m	615 w
	590 m			
497 w	512 m	575 w	555 w	580 m
473 m	408 m	500 w	510 w	505 w
			470 w	490 w

CF₃ deformation

* observed frequencies in cm⁻¹

R = (CF₃)₂NO

ampoule for a day. Fractionation yields di[bis(trifluoromethyl)nitroxy]-bis(trifluoromethyl)chlorophosphorane, $[(CF_3)_2NO]_2(CF_3)_2PCl$ (1.78 g., 3.29 mmole; 93.5% yield). Analysis:- Found: Cl, 6.55%; $C_6F_{18}PN_2O_2Cl$ requires Cl, 6.57%. The vapour pressure measurements over a temperature range of 24° to 77°C can be represented by the equation $\log_{10} p(\text{mm}) = 8.120 - 2125/T$, giving an extrapolated b.p. of 132°C and latent heat of vapourisation of 9.750 kcal. mole⁻¹.

Reaction with bis(trifluoromethyl)bromophosphine

Bis(trifluoromethyl)bromophosphine (0.744 g., 2.98 mmole) and bis(trifluoromethyl)nitroxyl (1.170 g., 6.97 mmole) were allowed to react at room temperature for three days. Fractionation gave di[bis(trifluoromethyl)nitroxy] bis(trifluoromethyl)bromophosphorane, $[(CF_3)_2NO]_2(CF_3)_2PBr$, (1.34 g., 2.30 mmole, 76.8% yield). Analysis:- Found: Br, 13.2%; $C_6F_{18}BrN_2O_2P$ requires Br, 13.7%. Vapour pressure measurements over a temperature range of 26° to 53°C can be represented by $\log_{10} p(\text{mm}) = 6.340 - 1600/T$, giving an extrapolated b.p. of 190°C and latent heat of vapourisation of 7.350 kcal. mole⁻¹.

Reaction with bis(trifluoromethyl)iodophosphine

When bis(trifluoromethyl)iodophosphine (0.737 g., 2.49 mmole) and bis(trifluoromethyl)nitroxyl (0.436 g., 2.59 mmole) were allowed to stand at -74°C, iodine was immediately discharged. After standing for three days, the mixture was fractionated to give (a) bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine (0.624 g., 1.85 mmole, 74.4% yield) at -74°C trap. Traces of iodine was removed by shaking with mercury. Analysis:- Found: mol. wt. 328; F, 67.3%; $C_4F_{12}NOP$ requires mol. wt., 337; F, 67.7%; and (b) iodine found at -25°C and -45°C traps. Vapour pressure measurements over a temperature range of -7° to 40°C can be represented by $\log_{10} p(\text{mm}) = 7.940 - 1800/T$, giving an extrapolated b.p. of 83°C and latent heat of vapourisation of 8.250 kcal. mole⁻¹.

Reaction with bis(trifluoromethyl)cyanophosphine

Reaction of bis(trifluoromethyl)cyanophosphine (0.439 g., 2.25 mmole) and bis(trifluoromethyl)nitroxyl (0.892 g., 5.31 mmole) at -74°C for 16

hours gave di[bis(trifluoromethyl)nitroxyl] bis(trifluoromethyl)cyanophosphorane (0.970 g., 1.83 mmole; 88.4% yield). Analysis:- Found: F, 64.4%; $C_7F_{18}N_3O_2P$ requires F, 64.4%. Vapour pressure measurements over a temperature range of 26° to 68°C can be represented by $\log_{10} p(\text{mm}) = 7.600 - 1950/T$, giving an extrapolated b.p. of 140°C, latent heat of vapourisation of 8.940 kcal. mole, and Trouton constant of 21.6.

ACKNOWLEDGEMENTS

We thank Professor R. Schmutzler, Braunschweig, for measurements of the F^{19} n.m.r. spectra.

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