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REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH CYANOPENTAFLUOROPHENYLPHOSPHINES

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SUMMARY

Bis(trifluoromethyl)nitroxyl undergoes substitution reactions with $(C_6F_5)_{3-n}P(CN)_n$ (where n = 1, 2, 3) to afford $(CF_3)_2NO(C_6F_5)_{3-n}P(CN)_{n-1}$ respectively, together with the hitherto unreported $(CF_3)_2NOCN$. The latter oxidises hydrogen chloride to give N, N-bis(trifluoromethyl)hydroxylamine, chlorine and paracyanogen.

INTRODUCTION

The reactions of bis(trifluoromethyl)nitroxyl with compounds of phosphorus have been a subject of active investigations in recent years. Its reactions with phosphorus trichloride are vigorous even at room temperature yielding two products, namely $(CF_3)_2NOPCl_4$ and $(CF_3)_2NOPCl_2$ [1]. 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 [2]. The reactions with phosphorus tribromide however give a mixture of compounds, namely $[(CF_3)_2NO]_3PO$, $(CF_3)_2NON(CF_3)_2$ and bromine [3]. Furthermore, the reactions of substituted

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phosphines have been shown to give several types of reactions. For example, bis(trifluoromethyl)nitroxyl undergoes addition reactions with $(CH_3O)_3P$ [4] and $(CF_3)_2PX$ (where X = Cl, CN and CF_3) [5,6], iodine displacement reactions with $(CF_3)_2PI$ [6], substitution reactions with $[(CH_3)_2N]_3P$ [7], and hydrogen abstraction reactions with $(CF_3)_2PH$ [8]. We now report the interactions between the nitroxyl radical and $(C_6F_5)_nP(CN)_{3-n}$ (n = 0, 1, 2).

RESULTS AND DISCUSSION

At room temperature, a mixture of bis(trifluoromethyl)nitroxyl radical and $(C_6F_5)_2PCN$ in 2:1 molar ratio reacted to afford $(C_6F_5)_2PON(CF_3)_2$ (A) and $(CF_3)_2NOCN$ (C), according to the following equation:

$$2(CF_3)_2NO + (C_6F_5)_2PCN \longrightarrow \underset{(A)}{(C_6F_5)_2PON(CF_3)_2} + \underset{(C)}{(CF_3)_2NOCN}$$

Compound (A) is a white hygroscopic solid, m.p. 157°C.

The reaction of bis(trifluoromethyl)nitroxyl with $C_6F_5P(CN)_2$ follows a similar course to give the substitution product, $(CF_3)_2NOP(CN)C_6F_5$ (B):

$$2(CF_3)_2NO + C_6F_5P(CN)_2 \longrightarrow \underset{(B)}{C_6F_5(CN)PON(CF_3)_2} + \underset{(C)}{(CF_3)_2NOCN}$$

Compound (B) is a yellow hygroscopic solid, m.p. 140°C. Traces of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) were also isolated as a minor product.

Products (A) and (B) were purified by recrystallisation from acetonitrile, and their structures confirmed by elemental analysis and ^{19}F NMR spectroscopy.

The volatile O-cyanobis(trifluoromethyl)hydroxylamine (C) was isolated from both the above substitution reactions by trapping it at -96°C during vacuum fractionation. It is a new compound hitherto unreported. The EI MS (70 ev) spectrum of O-cyanobis(trifluoromethyl)hydroxylamine did not show the parent ion but exhibited characteristic fragmentation peaks at m/z

168[$(CF_3)_2NO$], 69[CF_3] and 26[CN]. Its identity was further confirmed by molecular weight determination using Regnault's method and fluorine analysis. Its infrared spectrum was consistent with the structure assigned. Compound (C) was not affected by ultra-violet light or elevated temperatures (up to 160° C), but treatment with anhydrous hydrogen chloride under ambient conditions led to cleavage of the NO-CN bond, giving N, N-bis(trifluoromethyl)hydroxylamine, chlorine and most probably paracyanogen:

$$2(CF_3)_2NOCN + 2HCl \longrightarrow 2(CF_3)_2NOH + Cl_2 + \frac{2}{n}(CN)_n$$

The above substitution reactions between bis(trifluoromethyl)nitroxyl and $(C_6F_5)_nP(CN)_{3-n}$ (n = 1 and 2) are different from those with $(C_6F_5)_3P$ [9] and with $(CF_3)_nP(CN)_{3-n}$ (n = 1 and 2) [6, 10], as seen from the equations below:

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

$$2(CF_3)_2NO + (CF_3)_nP(CN)_{3-n} \longrightarrow [(CF_3)_2NO]_2P(CF_3)_n(CN)_{3-n}$$

On extending our investigation to phosphorus cyanide, bis(trifluoromethyl)nitroxyl and $P(CN)_3$ in a 2:1 molar ratio at room temperature gave the substitution product $(CF_3)_2NOP(CN)_2$ (D):

$$2(CF_3)_2NO + P(CN)_3 \longrightarrow \underset{(D)}{(CF_3)_2NOP(CN)_2} + \underset{(C)}{(CF_3)_2NOCN}$$

Compound (D), was recrystallised from acetonitrile as a white solid m.p. 71° C and the structure was confirmed by elemental analysis and infrared spectroscopy.

By contrast, reaction between the nitroxyl radical and $P(CN)_3$ in 5:1 ratio affords tri[bis(trifluoromethyl)nitroxy]phosphine oxide, perfluoro-(2, 4-dimethyl-3-oxa-2, 4-diazapentane) and paracyanogen [10], according to the equation:

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

EXPERIMENTAL

Infrared spectra were measured with a Perkin Elmer 983G Grating Infrared Spectrophotometer (range 4000 to 200 cm^{-1}). ^{19}F NMR spectra were recorded on on a Jeol NMR Spectrophotometer operating at 90 MHz (w.r.t. CF_3COOH). Mass spectra (70 ev) were measured on a Micromass Mass Spectrometer. Molecular weights were determined by Regnault's method.

Phosphorus cyanide were prepared according to the method described by Staats and Morgan [11]. $(C_6F_5)_2PCN$ and $C_6F_5P(CN)_2$ were prepared by treating the chloro analogues with silver cyanide [12].

Compounds (A)-(D) are new.

Reaction of bis(trifluoromethyl)nitroxyl with phosphorus cyanide

Phosphorus cyanide (0.3428 g, 3.14 mmole) was evacuated in a pyrex glass ampoule (100 ml) and bis(trifluoromethyl)nitroxyl (1.0380 g, 6.20 mmole) was condensed on it. The reaction proceeded over a period of twenty-four hours at 28° C with eventual discharge of the radical's purple colour. Vacuum fractionation gave $(CF_3)_2NOCN$ (C) (0.3785g, 1.95 mmole; 62% yield) trapped at -96°C (passed -60°C). Infrared absorptions were detected at 2105 cm^{-1} (m) (ν C=N); 1310 cm^{-1} (s), 1280 cm^{-1} (s), 1240 cm^{-1} (s), 1210 cm^{-1} (s)(ν C-F); 1080 cm^{-1} (m) (ν N-O); 960 cm^{-1} (m) (ν C-N) and 780 cm^{-1} (m)(δ C-F). (Elemental analysis gave: F, 58.46%; mol. wt. 194; $C_3F_6N_2O$ requires F, 58.76%; mol. wt. 194).

Recrystallisation of the solid product from acetonitrile gave $(CF_3)_2NOP(CN)_2$ (D) amount as a white crystalline solid (m.p. 71°C). Infrared absorptions were located at 2130 cm^{-1} (m) (ν C=N), 1240 cm^{-1} (s), 1205 cm^{-1} (s),1180 cm^{-1} (s)(ν C-F); 1050 cm^{-1} (m)(ν N-O), 980 cm^{-1} (m)(ν P-O), 960 cm^{-1} (m)(ν C-N), 720 cm^{-1} (m)(δ C-F). (Elemental analysis gave: C, 19.90%; N, 16.65%; $C_4F_6N_3OP$ requires : C, 19.12%; N, 16.73%).

Reaction of $(CF_3)_2NOCN$ (C) with anhydrous hydrogen chloride

$(CF_3)_2NOCN$ (0.3695 g, 1.90 mmole) and anhydrous hydrogen chloride (0.0694 g, 1.91 mmole) were condensed in an evacuated Pyrex glass ampoule (100 ml). Fractionation of the product after the tube had stood at room temperature for ten hours gave N,N-bis(trifluoromethyl)hydroxylamine (0.0695 g, 1.37 mmole) (-86°C trap; passed -60°C trap). This was identified by its infrared spectrum and molecular weight. Chlorine gas was trapped -196°C (mol wt. 71 g mol^{-1}; Cl_2 requires 71 g mol^{-1}). A white solid identified as paracyanogen was formed on the walls of the reaction tube.

Reactions of bis(trifluoromethyl)nitroxyl with pentafluorophenylphosphorus dicyanide

Pentafluorophenylphosphorus cyanide (0.4375 g, 1.75 mmole) was evacuated into a Pyrex glass reaction tube and bis(trifluoromethyl)nitroxyl (0.5800 g, 3.49 mmole) was condensed on it. On attaining room temperature from -96°C, the colour of the radical was discharged and a brown solid was formed. Fractionation of the volatile products yield $(CF_3)_2NOCN$ (C) (0.2037 g, 1.05 mmole) (-96°C trap; passed -40°C trap). Traces of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) were obtained at -40°C trap and identified by its infrared spectrum. Recrystallisation of the solid residue gave $C_6F_5P(CN)ON(CF_3)_2$ (B) as a yellow hygroscopic solid, m.p. 140°C. Its ^{19}F NMR spectrum in $CDCl_3$ gave peaks at -59.07 ppm (singlet)(δ CF_3), -60.18 ppm (multiplet)(δ o-F of C_6F_5 group), -76.10 ppm (multiplet)(δ p-F) and -87.97 ppm (multiplet)(δ m-F) w.r.t. CF_3COOH as external reference. (Elemental analysis gave: C, 27.59%; N, 7.61%; $C_9F_{11}N_2OP$ requires : C, 27.55%; N, 7.14%).

Reactions of bis(trifluoromethyl)nitroxyl with bis(pentafluorophenyl)phosphorus cyanide

Bis(pentafluorophenyl)phosphorus cyanide (0.6289g, 1.75 mmole) was placed in an evacuated Pyrex glass Schlenk tube (100 ml) and bis(trifluoromethyl)nitroxyl (0.5810 g, 3.52 mmole) was condensed on it. After eight hours at room temperature, the colour of the radical was discharged. Trap-to-trap fractionation under vacuum gave $(CF_3)_2NOCN$ (C) (0.3201 g, 1.02 mmole) (-96°C trap; passed -40°C trap). Recrystallisation of the solid residue from acetonitrile gave $(C_6F_5)_2PON(CF_3)_2$ (A) as a white hygroscopic solid, m.p. 157°C. Its ^{19}F NMR spectrum in $CDCl_3$ gave peaks at -57.11 ppm (singlet)(δ CF_3); -62.44 ppm (multiplet)(δ o-F of C_6F_5 group), -75.00 ppm (multiplet)(δ p-F) and -85.43 ppm (multiplet)(δ m-F), w.r.t. CF_3COOH as external reference. (Elemental analysis gave: C, 27.92%; N, 2.08%. $C_{12}F_{16}NPO$ requires: C, 28.29%; N, 2.75%).

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