Reactions of bis(trifluoromethyl)nitroxyl with hydrides of phosphorus and arsenic

H. G. Ang and C. H. Koh
Chemistry Department, National University of Singapore, Kent Ridge Road, Singapore 0511 (Republic of Singapore)

(Received May 17, 1991; accepted January 26, 1992)

Abstract

The reactions of bis(trifluoromethyl)nitroxyl with the Group 15 hydrides $(CF_3)_nMH_{3-n}$ (M = P, As; $n = 0$, 1) in a ratio of 2:1 proceed rapidly via free-radical mechanisms to afford *N,N*-bis(trifluoromethyl)hydroxylamine and products which can be rationalised in terms of unstable hydride intermediates $(CF_3)_2NOM(CF_3)_nH_{2-n}$. While the reactions with CF_3MH_2 (M = P, As) yielded mainly $CF_3M[ON(CF_3)_2]_2$ and $(CF_3)_2NOH$, those with AsH_3 gave $[(CF_3)_2NO]_3As$, arsenic metal and $(CF_3)_2NOH$. On the other hand, the reactions with PH_3 gave a mixture of $(CF_3)_2NOH$, $(CF_3)_2NH$, hydrogen gas and a polymeric yellow solid.

Introduction

Bis(trifluoromethyl)nitroxyl has been found to react with $(CH_3)_2NH$ to give $(CH_3)_2NON(CF_3)_2$ [1]. A number of bis(trifluoromethyl)nitroxy derivatives of trivalent phosphorus and arsenic have also been reported. These include $(CF_3)_2PON(CF_3)_2$ [1], $(CF_3)_2AsON(CF_3)_2$ [2], $(C_6F_5)_2PON(CF_3)_2$ [3] and the novel unsaturated derivatives $(CF_3)_2NON{=}PON(CF_3)_2$ [4] and $(CF_3)_2NON{=}AsON(CF_3)_2$ [5], which were derived from the corresponding hydrides $(CF_3)_2PH$, $(CF_3)_2AsH$, $(C_6F_5)_2PH$, $(CF_3)_2NON{=}PH$ and $(CF_3)_2NON{=}AsH$. In our present investigations, we have extended the study of the reactions of bis(trifluoromethyl)nitroxyl to a number of phosphorus and arsenic hydrides of the type $(CF_3)_nMH_{3-n}$ (M = P, As; $n = 0$, 1).

Experimental

All volatile compounds were manipulated in a high vacuum system with PTFE O-ring taps. The products were separated by trap-to-trap vacuum fractionation. Infrared spectra were recorded on a Perkin-Elmer 983G infrared spectrophotometer. Molecular weights were determined by Regnault's method.

Bis(trifluoromethyl)nitroxyl was prepared by the oxidation of bis(trifluoromethyl)hydroxylamine with silver(II) oxide [1]. Phosphine and arsine were purchased from AIRCO (USA) and purified before use. Tri-

0022-1139/92/$5.00

fluoromethylphosphine was prepared by the reaction of trifluoromethyldiiodophosphine with anhydrous hydrogen chloride in the presence of mercury [6], and trifluoromethylarsine from the reaction of trifluoromethyldiiodoarsine with arsine [7].

Reactions with phosphine

A mixture of phosphine (0.0526 g, 1.55 mmol) and bis(trifluoromethyl)nitroxyl (0.5199 g, 3.09 mmol) was allowed to warm up slowly in a Pyrex glass ampoule from −96 °C to room temperature. At the end of the reaction, the purple colour of bis(trifluoromethyl)nitroxyl was discharged completely and a colourless liquid and a yellow solid were formed. Fractionation of the product mixture yielded the following:

(i) *N*,*N*-Bis(trifluoromethyl)hydroxylamine (0.3693 g, 2.19 mmol), trapped at −96 °C (passed −50 °C). The yield was 70.1%, based on the amount of $(CF_3)_2NO$ used. The hydroxylamine was identified from its IR spectrum with bands located at 3614 m, 1394 m, 1312 s, 1270 vs, 1226 s, 1046 m, 972 m and 711 m cm^{-1}.

(ii) Bis(trifluoromethyl)amine (0.0730 g, 0.48 mmol; 15.5% yield based on the amount of $(CF_3)_2NO$ used), collected in the −126 °C bath (passed −96 °C). The identity of the amine was established from its molecular weight [found: 152 g mol^{-1}, $(CF_3)_2NH$ requires 153 g mol^{-1}] and its IR spectrum with peaks located at 3462 m, 1497 s, 1352 s, 1264 vs, 1205 vs, 1150 s, 951 ms, 885 w, 743 w and 682 m cm^{-1}. This observed spectrum was identical to that reported by Barr and Haszeldine [8].

(iii) Excess phosphine (0.0433 g, 1.31 mmol), identified from its IR spectrum, which was recovered at the −196 °C trap.

(iv) Some non-condensable gas, which was presumably hydrogen.

(v) A hygroscopic yellow solid which burned with white fumes, most probably due to the presence of white phosphorus. It was insoluble in all common solvents. The infrared spectrum in KBr pellet exhibited broad bands located at 1200–1300 cm^{-1}, which most probably are due to the C−F vibrations. Two strong peaks were also observed at 1398 and 833 cm^{-1}, which were assigned to P=O and P−O stretching vibrations, respectively. Chemical analyses also confirmed the presence of phosphorus and fluorine. The solid was thus a mixture of elemental phosphorus and a polymeric compound containing the CF_3 group.

Reactions with arsine

Bis(trifluoromethyl)nitroxyl (0.4851 g, 2.89 mmol) was sealed in an evacuated glass ampoule together with arsine (0.1102 g, 1.41 mmol). The reaction mixture was then allowed to warm up gradually from −126 °C. On attaining room temperature, the reaction vessel was found to be coated with a layer of grey metallic solid. The following fractions were obtained upon fractionation of the volatile components:

(i) A colourless crystalline solid trapped at −20 °C (passed 0 °C). It was identified as tri[bis(trifluoromethyl)nitroxy]arsine (0.2051 g, 0.354 mmol;

36.7% yield) from its IR spectrum. The spectrum with the following peaks was identical to that of an authentic sample [2]: 1308 vs, 1270 vs, 1236 s, 1225 s, sh, 1027 ms, 971 ms, 800 w, 748 w, 712 m and 584 w cm^{-1}.

(ii) *N,N*-bis(trifluoromethyl)hydroxylamine (0.2897 g, 1.71 mmol), trapped at −96 °C (passed −40 °C), in 59.1% yield.

(iii) A trace of colourless liquid trapped at −126 °C, which was found to be mainly bis(trifluoromethyl)amine (0.0024 g, 0.016 mmol) from its IR spectrum.

(iv) Excess arsine (0.0674 g, 0.86 mmol), which was collected in the −196 °C trap.

(v) A small amount of non-condensable gas.

The metallic solid did not show any absorption in its IR spectrum and was confirmed by chemical analysis to be arsenic metal.

Reactions with trifluoromethylphosphine

Trifluoromethylphosphine (0.1065 g, 1.04 mmol) and bis(trifluoromethyl)nitroxyl (0.3537 g, 2.10 mmol) were sealed *in vacuo* in a Pyrex glass ampoule. The ampoule was slowly allowed to warm up from −96 °C to room temperature. The purple colour of bis(trifluoromethyl)nitroxyl was discharged at −20 °C, yielding a colourless liquid. Fractionation of the product mixture gave the following:

(i) A colourless liquid which was collected at −60 °C, passed −40 °C (0.1362 g, 0.312 mmol; 29.7% yield). Its IR spectrum with the following peaks was identical to an authentic sample of di[bis(trifluoromethyl)nitroxy]trifluoromethylphosphine [9]: 1312 vs, 1271 vs, 1238 vs, 1215 s, 1160 vs, 1020 ms, 972 ms, 813 ms and 713 ms cm^{-1}. Molecular weight determination gave 436 g mol^{-1} ($C_3F_9N_2O_2P$ requires 436 g mol^{-1}).

(ii) *N,N*-Bis(trifluoromethyl)hydroxylamine (0.1628 g, 0.963 mmol; 45.9% yield), trapped at −86 °C.

(iii) A colourless liquid trapped at the −126 °C bath which was identified as bis(trifluoromethyl)amine (0.0461 g, 0.301 mmol; 14.3% yield) from its IR spectrum.

(iv) Trifluoromethylphosphine (0.0374 g, 0.367 mmol), identified from its IR spectrum, which was recovered in the liquid nitrogen trap.

(v) A trace of an intractable liquid was left in the ampoule. The liquid was hygroscopic and its IR spectrum showed the following bands: 1308, 1270, 1208, 1138, 1040, 968, 833 and 711 cm^{-1}. It was insoluble in all common solvents and chemical analysis confirmed the presence of phosphorus.

Reactions with trifluoromethylarsine

A mixture of trifluoromethylarsine (0.1578 g, 1.08 mmol) and bis(trifluoromethyl)nitroxyl (0.3838 g, 2.28 mmol) in an evacuated glass ampoule was allowed to warm up slowly from −126 °C to room temperature.

The completion of the reaction was marked by the disappearance of the radical colour. The following products were obtained:

(i) A colourless crystalline solid which was isolated at −50 °C, passed −30 °C. It was identified as di[bis(trifluoromethyl)nitroxy]trifluoromethylarsine (0.2305 g, 0.481 mmol; 42.2% yield). Its IR spectrum gave absorptions located at 1307 vs, 1259 vs, 1235 vs, 1215 sh, 1190 m, 1143 s, 1027 ms, 971 ms, 801 m, 748 w and 712 m cm^{-1}. Its ^{19}F NMR spectrum revealed two signals at 11.612 ppm and 7.008 ppm, with an intensity ratio of 1:4.

(ii) *N,N*-Bis(trifluoromethyl)hydroxylamine (0.2212 g, 1.31 mmol) trapped at −96 °C in 57.5% yield.

(iii) A very volatile fraction trapped at −196 °C (0.0696 g), containing mainly trifluoromethylarsine with a small trace of bis(trifluoromethyl)amine.

(iv) A trace amount of intractable orange solid which remained in the reaction ampoule.

(v) A small amount of a non-condensable gas.

Results and discussion

Reactions with phosphine

The reaction of bis(trifluoromethyl)nitroxyl with phosphine in a 2:1 molar ratio proceeded at low temperatures to afford bis(trifluoromethyl)-hydroxylamine, bis(trifluoromethyl)amine, a hygroscopic yellow solid which contains phosphorus and fluorine and a non-condensable gas which was presumably hydrogen. From the infrared spectrum, the yellow solid probably consists of a mixture of yellow phosphorus and the polymeric compound $[(CF_3)_2NOP{=}O]_n$.

The formation of bis(trifluoromethyl)hydroxylamine can be explained by hydrogen abstraction from phosphine by the nitroxyl radical, whereupon the substituted phosphine, $(CF_3)_2NOPH_2$, is formed as shown below:

$$(CF_3)_2NO + PH_3 \longrightarrow (CF_3)_2NOH + PH_2\cdot$$

$$PH_2\cdot + (CF_3)_2NO \longrightarrow (CF_3)_2NOPH_2$$

$(CF_3)_2NOPH_2$, being unstable, probably undergoes elimination reactions involving the cleavage of the P–O bond to afford $(CF_3)_2NOH$, phosphorus and hydrogen gas, as shown below:

$$(CF_3)_2NOPH_2 \longrightarrow (CF_3)_2NOH + PH$$

$$4PH \longrightarrow P_4 + 2H_2$$

while a second process could involve the cleavage of the N–O bond with hydrogen transfer to give $(CF_3)_2NH$ and a polymeric product as illustrated below:

$(CF_3)_2NOPH_2 \longrightarrow (CF_3)_2NH + HP{=}O$

$HP{=}O + 2(CF_3)_2NO \longrightarrow (CF_3)_2NOP{=}O + (CF_3)_2NOH$

$n(CF_3)_2NOP{=}O \longrightarrow [(CF_3)_2NOP{=}O]_n$

Hydrogen abstraction of both PH_3 and HPO by the nitroxyl radical, together with break down of $(CF_3)_2NOPH_2$, could account for the high yield of $(CF_3)_2NOH$ (70%).

Reactions with arsine

The reaction of bis(trifluoromethyl)nitroxyl with arsine in a 2:1 molar ratio was rapid at low temperatures, yielding tri[bis(trifluoromethyl)-nitroxy]arsine, bis(trifluoromethyl)hydroxylamine, a trace amount of bis(trifluoromethyl)amine and a coating of arsenic metal on the wall of the reaction vessel.

The nitroxyl radical, being a good hydrogen abstractor and a powerful radical scavenger, can be considered to attack arsine to form bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOAsH_2$. The latter then undergoes disproportionation to give tri[bis(trifluoromethyl)nitroxy]arsine and arsine.

$$3(CF_3)_2NOAsH_2 \longrightarrow [(CF_3)_2NO]_3AsH + 2AsH_3 \quad (1)$$

The formation of arsenic metal would be similar to the reaction of $(CF_3)_2NOPH_2$:

$$(CF_3)_2NOAsH_2 \longrightarrow (CF_3)_2NOH + AsH \quad (2)$$

$$nAsH \longrightarrow As_n + \frac{n}{2} H_2$$

The higher than expected yields of $(CF_3)_2NOH$ (about 59%) are probably due to the relative rates of reactions (1) and (2) above.

Reactions with trifluoromethylphosphine

The reaction of bis(trifluoromethyl)nitroxyl with trifluoromethylphosphine in 2:1 molar ratio also afforded a number of products, namely, di[bis(trifluoromethyl)nitroxy]trifluoromethylphosphine, bis(trifluoromethyl)-hydroxylamine, bis(trifluoromethyl)amine and an intractable colourless liquid.

The formation of the above products can be rationalised in terms of the intermediate $(CF_3)_2NOP(H)CF_3$ produced in accordance with the equation:

$$2(CF_3)_2NO + CF_3PH_2 \longrightarrow (CF_3)_2NOP(H)CF_3 + (CF_3)_2NOH$$

The intermediate being unstable, could either disproportionate to give di[bis(trifluoromethyl)nitroxy]trifluoromethylphosphine and trifluoromethyl-phosphine:

$2(CF_3)_2NOP(H)CF_3 \longrightarrow [(CF_3)_2NO]_2PCF_3 + CF_3PH_2$

or undergo cleavage of the N—O bond to afford bis(trifluoromethyl)amine and a polymeric product, as shown below:

$(CF_3)_2NOP(H)CF_3 \longrightarrow (CF_3)_2NH + CF_3P{=}O$

$nCF_3P{=}O \longrightarrow (CF_3P{=}O)_n$

The colourless liquid has been found to contain P=O and CF_3 groups.

Reactions with trifluoromethylarsine

In contrast to the above reactions, only two major products were obtained in the reaction between bis(trifluoromethyl)nitroxyl and trifluoromethylarsine in 2:1 molar ratio, viz. di[bis(trifluoromethyl)nitroxy]trifluoromethylarsine and bis(trifluoromethyl)hydroxylamine. Bis(trifluoromethyl)amine was isolated in trace amounts.

The formation of di[bis(trifluoromethyl)nitroxy]trifluoromethylarsine is probably due to the disproportionation of the intermediate $(CF_3)_2NOAs(H)CF_3$, as shown below:

$2(CF_3)_2NO + CF_3AsH_2 \longrightarrow (CF_3)_2NOAs(H)CF_3 + (CF_3)_2NOH$

$2(CF_3)_2NOAs(H)CF_3 \longrightarrow [(CF_3)_2NO]_2AsCF_3 + CF_3AsH_2$

Conclusions

The above reactions between bis(trifluoromethyl)nitroxyl and the hydrides of phosphorus and arsenic demonstrate that the bis(trifluoromethyl)nitroxy-substituted phosphines and arsines $(CF_3)_2NOM(CF_3)_nH_{2-n}$ (M = P, As; $n = 0$, 1) are unstable. They undergo disproportionation and elimination reactions to afford more stable products. While $(CF_3)_2NOPH_2$ was found to undergo elimination reactions to give $(CF_3)_2NOH$, $(CF_3)_2NH$, elemental phosphorus, hydrogen and a polymeric solid, $(CF_3)_2NOAsH_2$ undergoes both elimination and disproportionation to afford $[(CF_3)_2NO]_3As$, $(CF_3)_2NOH$, arsenic metal and hydrogen. Similarly, $(CF_3)_2NOP(H)CF_3$ also undergoes elimination reaction via the cleavage of the N—O bond to give $(CF_3)_2NH$ and $(CF_3P{=}O)_n$, as well as disproportionation reactions to afford $[(CF_3)_2NO]_2PCF_3$. On the other hand, $(CF_3)_2NOAs(H)CF_3$ undergoes mainly disproportionation to yield $[(CF_3)_2NO]_2AsCF_3$.

Although all four reactions investigated gave bis(trifluoromethyl)hydroxylamine and bis(trifluoromethyl)amine as common products, some differences are observed in the reactions with the phosphines and the arsines. In the reactions of $(CF_3)_2NO$ with AsH_3 and CF_3AsH_2, only a trace amount of $(CF_3)_2NH$ was isolated. On the other hand, reactions with PH_3 and CF_3PH_2 yielded substantial amounts of $(CF_3)_2NH$. It is thus concluded that the modes of decomposition for the bis(trifluoromethyl)nitroxy-substituted

phosphines and arsines are different. In the case of $(CF_3)_2NOP(CF_3)_nH_{2-n}$ ($n=0$, 1), the preferred mode of decomposition is via cleavage of the N–O bond, whereas in the case of $(CF_3)_2NOAs(CF_3)_nH_{2-n}$ ($n=0$, 1) cleavage of the As–O bond is preferred. This is probably due to formation of the more stable P=O group compared to the N–O–P moiety.

Acknowledgements

We thank the National University of Singapore for a Research Grant (RP820035) and one of us (K.C.H.) is grateful to the University for a Research Scholarship.

References

1 H. G. Ang, *Chem. Commun.*, (1968) 1320.
2 H. G. Ang and K. F. Ho, *J. Organomet. Chem.*, *27* (1971) 349.
3 H. G. Ang and F. K. Lee, unpublished results.
4 H. G. Ang and F. K. Lee, *Polyhedron*, *8* (1989) 379.
5 H. G. Ang and F. K. Lee, *Polyhedron*, *8* (1989) 1461.
6 A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, *79* (1957) 4242.
7 H. G. Ang and C. H. Koh, unpublished results.
8 D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, (1955) 4169.
9 H. G. Ang and K. K. So, *J. Fluorine Chem.*, *21* (1982) 221.