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REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH TRIS(PENTAFLUOROPHENYL)-PHOSPHINE, ARSINE AND STIBINE

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SUMMARY

Tris(pentafluorophenyl)phosphine is oxidised by bis(trifluoromethyl)-nitroxyl to form tris(pentafluorophenyl)phosphine oxide and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane). With the corresponding arsine and stibine, addition products are obtained, namely tris(pentafluorophenyl)-arsenicdi[bis(trifluoromethyl)nitroxide] and tris(pentafluorophenyl)-antimonydi[bis(trifluoromethyl)nitroxide] respectively. Some reactions of the new derivatives are described.

INTRODUCTION

Reports have already been made on the reactions of bis(trifluoromethyl)nitroxyl with compounds of group V elements such as $(CF_3)_3M$ (M = P, As, Sb), $(CF_3)_nPX_{3-n}$ (n = 1, 2; X = Cl, Br, I) and PX_3 (X = F, Cl, Br) [1-6]. This section presents the results of our continued investigations into the reactions between the nitroxyl radical with $(C_6F_5)_3M$ (M = P, As, and Sb).

DISCUSSION

The use of a solvent is necessary in this series of reactions because no reaction is found to occur when gaseous bis(trifluoromethyl)-nitroxyl is allowed to react with solid $(C_6F_5)_3M$ (M = P, As and Sb) even at elevated temperatures.

At room temperature, two moles of bis(trifluoromethyl)nitroxyl reacts smoothly with one mole of tris(pentafluorophenyl)phosphine in the presence of the solvent, 1,1,2-trichloro-1,2,2-trifluoroethane (b.p. 47.7°C), to form tris(pentafluorophenyl)phosphine oxide in 93% yield. Apart from elemental analysis, the phosphine oxide is confirmed by its melting point, 168-169°C (lit. 169-170°C) [7]. Its infrared spectrum gives vibrations due to C_6F_5 groups, and the absorption located at 1230 cm^{-1} is ascribed to P = O stretching vibration.

In addition to $(C_6F_5)_3PO$, another product is isolated which is identified as penfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (b.p. 48.5°C). Since both the solvent and the oxadiazapentane have comparable boiling points, they are trapped together at -86°C trap (passed -60°C trap) and cannot be separated by trap-to-trap fractionation.

Evidence for the formation of $(CF_3)_2NON(CF_3)_2$ is provided by comparing the infrared spectrum of the mixture with that of an authentic sample. Confirmation is obtained by gas chromatographic identification.

The overall reaction between the nitroxyl and $(C_6F_5)_3P$ can be represented by an equation:

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

The nature of this reaction is distinctively different to that with tristrifluoromethylphosphine which yields the phosphorane, $[(CF_3)_2NO]_2P(CF_3)_3$ [8], as well as its reaction with phosphorus tribromide [5], which affords the substituted phosphine oxide and $(CF_3)_2NON(CF_3)_2$, as shown by the equation:

$$PBr_3 + (\text{excess})\ (CF_3)_2NO \longrightarrow [(CF_3)_2NO]_3P{=}O + (CF_3)_2NON(CF_3)_2 + Br_2$$

The reaction of $(C_6F_5)_3P$ somewhat resembles that of phosphorus-trifluoride at ambient temperature, as illustrated by the equation,

$$PF_3 + 2(CF_3)_2NO \longrightarrow (CF_3)_2NON(CF_3)_2 + F_3PO$$

But at -45°C, the corresponding phosphorane $[(CF_3)_2NO]_2PF_3$ was formed [5].

When two moles of bis(trifluoromethyl)nitroxyl are allowed to react with one mole of tris(pentafluorophenyl)arsine at room temperature, an oxidative addition product, tris(pentafluorophenyl)arsenicdi[bis(trifluoromethyl)nitroxide], is formed in 85% yield. No other products are isolated.

This new pentavalent arsenic derivative, when freshly prepared, is a non-volatile colourless highly viscous liquid which is quite stable in air. Upon standing in air over a period of half an hour, it is slowly converted to a white paste which shows the same infrared absorptions as those given by the original compound. The compound is confirmed by elemental analysis as well as by its infrared spectrum.

Strong absorptions at 1640, 1515, 1380, 1285, 1085 and 966 cm^{-1} which are characteristic of pentafluorophenyl groups are found in the infrared spectrum of $[(CF_3)_2NO]_2As(C_6F_5)_3$ [9]. Three peaks at 1310, 1255 and 1205 cm^{-1} are assigned as C-F stretching vibrations of the trifluoromethyl groups. N-O and C-N stretching vibrations are inferred because of peaks located at 1030 and 980 cm^{-1} respectively. These absorptions are typical of bis(trifluoromethyl)nitroxy derivatives.

Reaction of anhydrous hydrogen chloride with $[(CF_3)_2NO]_2As(C_6F_5)_3$ at 100°C does not yield bis(trifluoromethyl)hydroxylamine.

Bis(trifluoromethyl)nitroxyl reacts with tris(pentafluorophenyl)stibine at room temperature to afford tris(pentafluorophenyl)antimony-di[bis(trifluoromethyl)nitroxide] in 87% yield. This new **pentavalent** antimony derivative is a very stable, white crystalline solid which melts at 143-144°C and is not hydrolysed in moist air. The stibine has also undergoes an oxidative addition reaction as shown by the equation:

$$2(CF_3)_2NO + (C_6F_5)_3Sb \longrightarrow [(CF_3)_2NO]_2Sb(C_6F_5)_3$$

The product is confirmed by its elemental analysis and infrared spectrum. The presence of bis(trifluoromethyl)nitroxy groups are indicated by peaks located at 1040 and 965 cm^{-1} which are ascribed to the N-O and C-N stretching vibrations respectively, and the peaks in the region from 1250-1192 cm^{-1} are due to C-F stretching vibrations of trifluoromethyl **groups**.

Anhydrous hydrogen chloride does not react with the pentavalent antimony compound at room temperature. At 100°C for 6 days, however, bis(trifluoromethyl)hydroxylamine is isolated in high yields. The other product is tris(pentafluorophenyl)antimony dichloride, a white solid, which melts at 244-245°C. The reaction can be represented as follows:

$$[(CF_3)_2NO]_2Sb(C_6F_5)_3 + 2HCl \longrightarrow 2(CF_3)_2NOH + (C_6F_5)_3SbCl_2$$

The antimony derivative is stable up to 120°C. On heating at 160°C for 18 hours, tris(pentafluorophenyl)stibine, bis(trifluoromethyl)-nitroxyl and perfluoro-2-azapropene are formed.

CONCLUSION

The results obtained from the reactions between bis(trifluoromethyl)-nitroxyl and tris(pentafluorophenyl)phosphine, arsine and stibine are different and they also show marked contrast when compared with the reactions of tris(trifluoromethyl)phosphine, arsine and stibine.

Unlike tris(trifluoromethyl)phosphine which gives an addition product with bis(trifluoromethyl)nitroxyl, namely $(CF_3)_3P[ON(CF_3)_2]_2$, the reaction with tris(pentafluorophenyl)phosphine resembles that of phosphorus trifluoride. Mechanism of this reaction probably involves the formation of the phosphoranyl intermediate, $(CF_3)_2NOP(C_6F_5)_3$, followed by β-scission to give $(C_6F_5)_3PO$ and $(CF_3)_2N\cdot$ radical. The latter is readily coupled to the nitroxyl to give $(CF_3)_2NON(CF_3)_2$. The overall reactions are expressed as follows:

$$(CF_3)_2NO + (C_6F_5)_3P \longrightarrow (C_6F_5)_3\dot{P}ON(CF_3)_2$$

$$(C_6F_5)_3\dot{P}\text{-}O\text{-}N(CF_3)_2 \longrightarrow (C_6F_5)_3PO + (CF_3)_2N\cdot$$

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

In the reaction with many of the trivalent phosphorus compounds, the formation of $(CF_3)_2NON(CF_3)_2$ can be attributed to the preference of the substituted phosphine to undergo oxygenation reaction to give the corresponding phosphine oxide. As such, these reactions are distinctively different when compared to those of the corresponding arsines and stibines.

The reactions with $(C_6F_5)_3M$ (where M = As and Sb) give addition products, presumably by stepwise free radical addition:

$$(C_6F_5)_3M + (CF_3)_2NO \longrightarrow (C_6F_5)_3MON(CF_3)_2$$

$$(C_6F_5)_3MON(CF_3)_2 + (CF_3)_2NO \longrightarrow (C_6F_5)_3M[ON(CF_3)_2]_2$$

Unlike $(C_6F_5)_3As[ON(CF_3)_2]_2$, the corresponding stibine derivative, $(C_6F_5)_3Sb[ON(CF_3)_2]_2$, reacts with anhydrous hydrogen chloride to give bis(trifluoromethyl)hydroxylamine and $(C_6F_5)_3SbCl_2$. The relative ease of cleavage of Sb-O bonds can be attributed to the more electro-positive nature of antimony when compared to arsenic.

In contrast to tris(trifluoromethyl)-arsine and -stibine, no group exchange reaction is observed with the pentafluorophenyl analogues even at elevated temperatures. This could be attributed to the stronger bond formed between the group VB elements and the sp^2 hybridized carbon of the pentafluorophenyl groups.

EXPERIMENTAL

Many of the compounds that are handled are either gases or susceptible to hydrolysis. Manipulations were carried out in a vacuum line. Infrared spectra were recorded on Perkin Elmer 337 spectrophotometer.

Reaction of tris(pentafluorophenyl)phosphine

In the absence of a solvent, bis(trifluoromethyl)nitroxyl did not react with tris(pentafluorophenyl)phosphine either at room temperature or at 97°C for 30 hours. In another experiment, bis(trifluoromethyl)-nitroxyl (0.503 g, 2.98 m mole) and tris(pentafluorophenyl)phosphine (0.791 g, 1.49 m mole) were sealed in an evacuated ampoule (85 ml capacity) containing 5 ml of pure 1,1,2-trichloro-1,2,2-trifluoroethane as a solvent. The reaction ampoule was left at a -70°C for a day. The liquid turned purple and a lump of white solid deposited. The mixture was shaken at room temperature for 20 minutes and left standing for another day. As a result, the purple colour was discharged to give a colourless liquid and fine white solid in the ampoule. Fractionation of the reaction mixture under vacuum gave a volatile mixture and a white solid remaining in the ample.

The white solid is non-volatile and has a melting point 164-165°C. It was identified as tris(pentafluorophenyl)phosphine oxide (0.758 g, 1.38 m mole; 93.0% based on the nitroxyl consumed). It was recrystallised from petroleum ether (40-60°C) to give white crystalline needles with melting point 168-169°C (lit., 169-170°C [7]). Analytical results are, Found: C, 38.21%; F, 50.73%; P, 5.88%; $C_{18}F_{15}OP$ requires C, 39.42%; F, 52.00%; P, 5.66%. The infrared spectrum gave a peak of medium intensity at 1230 cm^{-1} which is attributed to the P-O stretching vibration.

On vacuum fractionation of the volatile mixture, colourless liquid was trapped at -86°C and liquid air trap. Both passed -60°C trap. The infrared spectra gave peaks due to the solvent as well as peaks located at 1305, 1280, 1235, 970 and 718 cm^{-1}. These peaks are those expected for bis(trifluoromethyl)arsino **groups**. Separation of the mixture by further refractionation was unsuccessful.

The mixture was identified using gas chromatograph under the following conditions: column, 10 ft. x 0.25 in., packed with methyl silicone gum (10%) on celite (60-80 mesh); temperature maintained at 60°C; flow rate was ca. 45 ml/min and carrier gas was nitrogen.

The retention time of 1,1,2-trichloro-1,2,2-trifluoroethane with respect to trichloroethane was 0.500 and that of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) was 0.208. The data agree with those obtained from an authentic sample.

Reaction with tris(pentafluorophenyl)arsine

Bis(trifluoromethyl)nitroxyl (0.427 g, 2.54 m mole) and tris(pentafluorophenyl)arsine (0.72 g, 1.25 m mole) were sealed in a 50 ml capacity ampoule containing 5 ml 1,1,2-trichloro-1,2,2-trifluoroethane as solvent. The colour of the solution was changed from purple to pink after it has been left standing at room temperature for 7 days. Separation of the mixture under vacuum gave four fractions.

The first fraction is a non-volatile highly viscous colourless liquid, which was identified as tris(pentafluorophenyl)arsenicdi[bis-(trifluoromethyl)nitroxide]. After treating it with acetone, it gave 0.94 g (1.03 m mole; 82.5% yield base on the arsine consumed) of the product. Elemental analysis gave C, 27.44%; F, 54.76%; and $AsC_{22}F_{27}N_2O_2$ requires C, 26.75%; F, 56.24%. The arsenic derivative appeared as a white crystalline solid in acetone, but become gummy on removing the solvent. Its infrared spectrum gave peaks at 1640 (s), 1515 (vs), 1480 (vs), 1380 (s), 1310 (vs), 1285 (s), 1255 (vs), 1205 (vs), 1095 (vs), 1085 (vs), 1030 (s), 980 (vs), 966 (vs), 930 (m, doublet), 809 (m), 712 (m), 628 (vw), 555 (vw), and 490 (vw)cm^{-1}.

The second fraction which was trapped at -60°C consists of a white crystalline solid (0.012 g). Its infrared spectrum gave absorptions at 1315 - 1210 cm^{-1} (C-F stretching), 970 cm^{-1} (C-N stretching) and 710 cm^{-1} (C-F deformation).

The third fraction trapped at -87°C is the solvent, 1,1,2-trichloro-1, 2,2-trichloroethane, identified by its infrared spectrum. The last fraction at the liquid air trap consists mainly of the solvent and a trace of the nitroxyl radical.

Reaction with tris(pentafluorophenyl)stibine

Bis(trifluoromethyl)nitroxyl (0.311 g, 1.85 m mole) and tris(pentafluorophenyl)stibine (0.570 g, 0.91 m mole) were sealed in an 85 ml capacity ampoule containing 5 ml of pure 1,1,2-trichloro-1,2,2-trifluoroethane as a solvent. The reaction was completed within a few minutes, giving a light yellow solution. Removal of the solvent gave a white solid, m.p. 143 - 144°C. This was identified as tris(pentafluorophenyl)-antimonydi [bis(trifluoromethyl)nitroxide] (0.760 g, 0.79 m mole); 86.8% yield based on stibine consumed. Its elemental analyses gave C, 26.03%; F, 51.48%; and N, 2.91%. $C_{22}F_{27}N_2O_2Sb$ requires C, 26.51%; F, 51.51% and N, 2.81%. The infrared spectrum of the compounds gave peaks located at 1643 (s), 1515 (s), 1495 (vs), 1395 (s), 1290 (vs, doublet), 1250 (vs), 1220 (s), 1205 (vs), 1192 (s), 1150 (vw), 1095 (vs), 1040 (vs), 980 (vs), 965 (vs), 801 (m), 735 (vw), 722 (vw), 710 (s), 680 (vw), 619 (vw) and 540 (w) cm^{-1}.

Reaction of tris(pentafluorophenyl)antimonydi [bis(trifluoromethyl)-nitroxide] with anhydrous hydrogen chloride

There was very little interaction between the antimony (v)-derivatives and hydrogen chloride at room temperature. Only a very small trace of bis(trifluoromethyl)hydroxylamine was isolated after being left for four hours at room temperature.

In another reaction, tris(pentafluorophenyl)antimonydi [bis(trifluoromethyl)nitroxide] (0.230 g, 0.24 m mole) and hydrogen chloride (0.138 g, 3.80 m mole) were heated in an evacuated 50 ml ampoule at 100°C for 6 days. The products obtained were tris(pentafluorophenyl)antimony dichloride (0.179 g, 0.25 m mole). Elemental analysis gave C, 30.44%; Cl, 9.03%; F, 39.86%. $C_{18}Cl_2F_{15}Sb$ requires C, 31.13%; Cl, 10.23%; and F, 41.06%.

The dichloride, m.p. 244 - 245°C, is insoluble in water. Its infrared spectrum showed absorptions at 1640 (s), 1500 (s), 1490 (s), 1390 (m), 1320 (vw), 1290 (vw), 1152 (vw), 1100 (vs), 1086 (s), 1025 (w), 1005 (m), 980 (vs, sh), 812 (s), 750 (vw, doublet), 720 (vw), 618 (w), 582 (vw) and 492 (vw) and 492 (vw) cm^{-1}.

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