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EXCHANGE REACTIONS BETWEEN PERFLUORO-(2,4-DIMETHYL-3-OXA-2,4-DIAZAPENTANE) AND TRIS(TRIFLUOROMETHYL)PHOSPHINE, -ARSINE AND -STIBINE

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SUMMARY

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) reacts with tris(trifluoromethyl)phosphine and -arsine to afford $[(CF_3)_2N]_nM(CF_3)_{3-n}$ (M = P, n = 1, 2, and 3; and M = As, n = 1, and 2), tris(trifluoromethyl)hydroxylamine being eliminated in each case. The reactions with tris(trifluoromethyl)stibine, on the other hand, give antimony trifluoride, tris(trifluoromethyl)-hydroxylamine and perfluoro-2-azapropene.

INTRODUCTION

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane), a colourless volatile liquid, does not decompose by ultraviolet irradiation [1]. It reacts with a number of compounds such as nitric oxide, hydrogen iodide, and polyfluoroalkenes at ambient temperatures even in the dark. With perfluorobut-2-yne, however, the reactions proceed at elevated temperatures [2]. The facile reactions can be rationalised in terms of the relative ease of the cleavage of the

nitrogen-oxygen bond. Taking advantage of this distinct property, the authors report the exchange reactions between the diazapentane and trifluoromethyl-substituted compounds of Group V elements.

RESULTS AND DISCUSSION

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (I) reacts with tris(trifluoromethyl)phosphine in 1:1 molar ratio at room temperature to afford bis(trifluoromethyl)amino-bis(trifluoromethyl)phosphine and tris(trifluoromethyl)-hydroxylamine quantitatively. The same reaction in 2:1 molar ratio occurs at 60°C to give di[bis(trifluoromethyl)amino]-trifluoromethylphosphine (II) and tris(trifluoromethyl)-hydroxylamine, the yield being 47 per cent. Further substitution is achieved by heating a mixture of the phosphine (II) and diazapentane (I) in 1:1 molar ratio at about 100°C. Apart from the expected products obtained, namely tri[bis(trifluoromethyl)-amino]phosphine and tris(trifluoromethyl)hydroxylamine, some perfluoro-2-azapropene is also formed.

The reactions of the diazapentane (I) with tris(trifluoro-methyl)arsine follow a similar course at elevated temperatures. The reactions of 1:1 and 1:2 molar ratios give the mono-substituted and di-substituted derivatives, $[(CF_3)_2N]_nAs(CF_3)_{3-n}$ n = 1 and 2, respectively. In each case, the other products are tris(trifluoromethyl)hydroxylamine and a small trace of perfluoro-2-azapropene. The reaction between di[bis(trifluoromethyl amino]trifluoromethylarsine and the diazapropene (I) at 100°C, on the other hand, affords only tris(trifluoromethyl)hydroxyl-amine and perfluoro-2-azapropene. The latter is formed as a result of extensive fluorination by the bis(trifluoromethyl)amino

group(s). Tri[bis(trifluoromethyl)amino]arsine is not formed despite repeated attempts.

The above reactions can be summarised as follows:

$$n(CF_3)_2NON(CF_3)_2 + (CF_3)_3M \longrightarrow [(CF_3)_2N]_nM(CF_3)_{3-n} + n(CF_3)_2NOCF_3$$

M = P; n = 1, 2 and 3

M = As; n = 1 and 2

On extending the reactions of the diazapentane (I) with tris(trifluoromethyl)stibine, neither substituted trifluoromethyl- nor bis(trifluoromethyl)amino-stibine are formed. Instead, three products obtained in high yields are antimony trifluoride, tris(trifluoromethyl)hydroxylamine and perfluoro-2-azapropene. The overall reactions can be represented by the equation:

$$3(CF_3)_2NON(CF_3)_2 + (CF_3)_3Sb \longrightarrow 3(CF_3)_2NOCF_3 + 3CF_3N{=}CF_2 + SbF_3$$

These findings suggest that the reactions first involve addition to give an unstable intermediate, namely $(CF_3)_3Sb[ON(CF_3)_2][N(CF_3)_2]$, followed by an elimination reaction to afford tris(trifluoromethyl)hydroxylamine and bis(trifluoromethyl)amino-bis(trifluoromethyl)stibine. Intramolecular fluorination of the latter yields perfluoro-2-azapropene and bis(trifluoromethyl)fluorostibine which, by successive disproportionation, produces antimony trifluoride, as shown by the following equations:

$$(CF_3)_3Sb + (CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2NSb(CF_3)_2 + (CF_3)_2NOCF_3$$

$$(CF_3)_2NSb(CF_3)_2 \longrightarrow CF_3N{=}CF_2 + (CF_3)_2SbF$$

$$2(CF_3)_2SbF \longrightarrow (CF_3)_3Sb + CF_3SbF_2$$

$$2CF_3SbF_2 \longrightarrow (CF_3)_2SbF + SbF_3$$

An alternative pathway leading to antimony trifluoride could involve further substitution of trifluoromethyl-substituted fluorostibine as shown by the equations:

$$(CF_3)_2SbF + (CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2SbF.N(CF_3)_2.ON(CF_3)_2$$

$$\downarrow$$

$$(CF_3)_2NSbCF_3F + (CF_3)_2NOCF_3$$

$$\downarrow$$

$$CF_3SbF_2 + CF_3N{=}CF_2$$

$$CF_3SbF_2 + (CF_3)_2NON(CF_3)_2 \longrightarrow CF_3SbF_2.N(CF_3)_2.ON(CF_3)_2$$

$$\downarrow$$

$$(CF_3)_2NSbF_2 + (CF_3)_2NOCF_3$$

$$\downarrow$$

$$SbF_3 + CF_3N{=}CF_2$$

MECHANISMS OF EXCHANGE REACTIONS

In the foregoing exchange reactions, free radical mechanisms can be eliminated for the following reasons: (a) the diazapentane (I) has been found to undergo dissociation only on prolonged irradiation to afford traces of the corresponding bis(trifluoromethyl)nitroxyl and tetrakis-(trifluoromethyl)hydrazine. Moreover, among the compounds $(CF_3)_3M$ (M = P, As and Sb), only the arsenic derivative gives the $(CF_3)_2As$ and CF_3 radicals at 350 - 400^{o}C; and (b) if the reaction between the diazapentane (I) and tris(trifluoromethyl)phosphine had proceeded along the free radical pathway, the same could have been expected of the

arsenic analogue. Such is not the case since reactions with the arsenic derivative had to be conducted at elevated temperatures. At no instance was hexafluoroethane nor tetrakis(trifluoromethyl)hydrazine detected, as would have been the case if a free radical mechanism was operative.

The most probable mechanism is the formation of the pentacovalent intermediate, $(CF_3)_3P[N(CF_3)_2][ON(CF_3)_2]$, followed by an elimination of tris(trifluoromethyl)hydroxylamine, according to the equation:

$$(CF_3)_3P + (CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2\overset{\overset{CF_3}{|}}{\underset{\underset{N(CF_3)_2}{|}}{P}}\!\!-\!\!ON(CF_3)_2 \longrightarrow (CF_3)_2PN(CF_3)_2 + (CF_3)_2NOCF_3$$

That the yield is quantitative implies that the reaction is irreversible.

CONCLUSIONS

From the above investigations concerning the reactions between perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) with tris(trifluoromethyl)phosphine, -arsine and -stibine, several interesting features emerge:

(a) The reactions clearly demonstrate the relative ease of cleavage of the N - O bond in the diazapentane (I). This is also shown in the way it reacts with various organic compounds.

(b) With respect to the above exchange reactions, there appears to be close resemblance in the way the diazapentane (I) and $(CF_3)_2NX$ (where X = Cl and Br) react.

(c) The exchange reactions between the diazapentane (I) and trifluoromethyl-substituted compounds of Group V elements can therefore be summarised as follows:

$$(CF_3)_2NON(CF_3)_2 + (CF_3)_3M \xrightarrow{1:1} (CF_3)_2NM(CF_3)_2 + (CF_3)_2NOCF_3 \quad - (1)$$

$$\xrightarrow{2:1} [(CF_3)_2N]_2MCF_3 + 2(CF_3)_2NOCF_3 \quad - (2)$$

$$\downarrow (CF_3)_2NON(CF_3)_2$$

$$[(CF_3)_2N]_3M + (CF_3)_2NOCF_3 \quad - (3)$$

where M = P : equations (1), (2) and (3); and
M = As: equations (1) and (2).

and

$$(CF_3)_3Sb + 3(CF_3)_2NON(CF_3)_2 \longrightarrow 3(CF_3)_2NOCF_3 + 3CF_3NCF_2 + SbF_3$$

(d) For a given atom M, the ease of intramolecular fluorination increases in the order,

$$(CF_3)_2NM(CF_3)_2 < [(CF_3)_2N]_2MCF_3 < [(CF_3)_2N]_3M$$

where M = P and As.

(e) For a given series of compounds containing one or more bis(trifluoromerhyl)amino group(s), such as the compounds $(CF_3)_2NM(CF_3)_2$ (where M = P, As and Sb), the ease of intramolecular fluorination increases in the order P < As < Sb. This can be attributed to the increase in electropositivity in the order P < As < Sb.

EXPERIMENTAL

All reactions were carried out in sealed evacuated ampoules of capacity ranging from 30-100 ml., each carrying a break seal at the side arm to facilitate transferring of compounds into a vacuum line. The vacuum system consisted of a series of traps, and a spiral gauge to facilitate molecular weight determination, quantitative transfer of compounds for reactions and infrared measurements. Each infrared spectrum was measured on the Perkin Elmer 337 spectrophotometer using a gas cell fitted with potassium bromide optics.

The following compounds were prepared and purified by published methods: tris(trifluoromethyl)phosphine [3], tris-(trifluoromethyl)arsine [4, 5], tris(trifluoromethyl)stibine [6], bis(trifluoromethyl)nitroxyl [7, 8], and perfluoro-(2,4-dimethyl-3-oxa-diazapentane) [9].

Reactions of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) with trifluoromethyl-substituted compounds of phosphorus, arsenic and antimony

(a) Reactions with tris(trifluoromethyl)phosphine in 1:1 molar ratio

A mixture of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.522 g., 1.63 mmoles) was allowed to react in a sealed ampoule (40 ml capacity) at -78^{o}C for about 15 hours. Black solids were formed and the solution was coloured pink. The colour, however, was discharged after further reaction was allowe to continue for 3-4 hours at room temperature.

Vacuum trap-to-trap fractionation gave the following fractions:

(i) a colourless liquid trapped at -88°C (passed -62°C trap) (0.438 g., 1.36 mmoles; 99.2% yield based on the phosphine consumed). This fraction was identified as bis(trifluoromethyl)-amino-bis(trifluoromethyl)phosphine by comparison of its infrared spectrum with that of an authentic sample [10]. Hydrolysis of the phosphine (0.137 g., 0.43 mmole) by 5 ml. of 20% sodium hydroxide solution was carried out at 100°C for 15 hours to give fluoroform (0.0526 g., 0.75 mmole; 88.2% yield).

(ii) a colourless liquid trapped at -126°C (0.314 g., 1.35 mmoles; 96.0% yield based on the phosphine consumed; found: M, 239; calc. for C_3F_9NO: M, 237. Its infrared spectrum was identical with that of pure tris(trifluoromethyl)hydroxylamine;

(iii) a trace of colourless volatile liquid (0.094 g.), trapped at -196°C, was not identified.

(b) Reactions with tris(trifluoromethyl)phosphine in 2:1 molar ratio

Several reactions of the diazapentane (I) and the phosphine were carried out at elevated temperatures in the usual way, followed by fractionation using traps at -40°, -60°, -86°, -126° and -196°C. The products of the reactions were (a) di[bis(trifluoromethyl)amino]-trifluoromethylphosphine, trapped at -60°C, and (b) tris(trifluoromethyl)phosphine, trapped at -126°C. Unreacted starting materials were trapped at -86°C trap. The results of three experiments are summarised in Table 1.

TABLE 1

Reaction between perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) and tris(trifluoromethyl)phosphine in 2:1 ratio

Experiment	1	2	3
Reactants:			
$(CF_3)_3P$ (g, mmole)	0.1774, 0.745	Products from	Products from
$(CF_3)_2NON(CF_3)_2$ (g, mmole)	0.5135, 1.605	experiment 1	experiment 2
Condition:			
Volume of ampoule (ml)	30	15	15
Oven temperature (^oC)	60	70	70
Length of heating (hrs)	11.5	16	46
Products:			
(i) $[(CF_3)_2N]_2PCF_3$ (g, mmole, % yield) based on phosphine used)	0.1424, 0.353, 47.4	0.1726, 0.427, 57.3	0.1845, 0.457, 61.4
(ii) Unreacted $(CF_3)_3P$ + $(CF_3)_2NON(CF_3)_2$ (g, mmole)	0.1987	0.1036	Pure $(CF_3)_2NON(CF_3)_2$, 0.0705, 0.22
(iii) $(CF_3)_2NOCF_3$ (g , mmole, % yield based on phosphine used)	0.2418, 1.02, 68.5	0.2812 1.185 79.6	0.2868, 1.21, 81.2
(iv) traces of unidentifiable gas(es)	0.0620	0.0662	0.0719

(c) Reactions with di[bis(trifluoromethyl)amino]-trifluoromethylphosphine

Di[bis(trifluoromethyl)amino]trifluoromethylphosphine (II) (0.185 g., 0.457 mmole) and the diazapentane (0.172 g., 0.530 mmole) were reacted in a 15 ml ampoule at 70°C for 44 hours. Fractionation of the reaction mixture gave (i) the unreacted phosphine (II) (0.175 g., 0.430 mmole) trapped at -60°C), (ii) the unreacted diazapentane (0.170 g., mmole) trapped at -86°C, and (iii) a trace of tris(trifluoromethyl)-hydroxylame and perfluoro-2-azapropene trapped at -196°C trap, (0.0069 g.).

The unreacted reactants were further reacted at 100°C for another 70 hours to afford (i) a colourless liquid at -45°C trap, and identified as tris[bis(trifluoromethyl)amino]phosphine (III) (0.047 g., 0.09 mmole; 22.6% yield based on the phosphine (consumed) by comparing its i.r. spectrum with that of an authentic sample [10], (ii) unreacted perfluoro-(2,3-dimethyl-3-oxa-2,4-diazapentane) (0.1355 g, 0.423 mmole) which was trapped at -86°C (passed -53°C) trap), (iii) a very light pink liquid (0.107 g, 0.42 mmole; 97.6% yield based on the phosphine (II) used) which was trapped at -126°C (passed -86°C trap). Its infrared spectrum was similar to that of tristrifluoromethyl-hydroxylamine; and (iv) a volatile liquid, trapped at -196°C (passed -126°C trap). Its infrared spectrum indicated that this fraction contained mainly perfluoro-2-azapropene (0.154 g, 1.16 mmole).

(d) Reactions with tris(trifluoromethyl)arsine in 1:1 molar

A mixture of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane (0.631 g., 2.09 mmoles) and tris(trifluoromethyl)arsine

(0.590 g., 2.90 mmoles) was allowed to warm up in a 50 ml. ampoule from -78°C to room temperature, the duration of reaction being 24 hours. Practically all the starting materials were recovered. Further reactions carried out at 98°C for 60 hours gave the following products:

(i) a colourless liquid trapped at -89°C (passed -70°C trap), (0.594 g., 1.63 mmoles; 82.5% yield based on $(CF_3)_2NON(CF_3)_2$ consumed), which was identified as bis(trifluoromethyl)amino-bis(trifluoromethyl)arsine by comparison ith the infrared spectrum of the authentic sample.

(ii) a colourless liquid trapped at -196°C (passed -89°C trap) (0.470 g., 1.98 mmoles; 100.5% based on $(CF_3)_2NON(CF_3)_2$ consumed), which was confirmed to be tris(trifluoromethyl)-hydroxylamine on the basis of its infrared spectrum.

(e) Reactions with tris(trifluoromethyl)arsine in 2:1 molar ratio

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.513 g., 1.60 mmoles) and tris(trifluoromethyl)arsine (0.226 g., 0.80 mmoles) were reacted in a 15 ml. evacuated ampoule at 70°C for 42 hours. Fractionations yield the following fractions:

(i) a light colourless liquid trapped at -60°C (passed -40°C trap) (0.322 g., o.718 mmoles; 89.5% based on $(CF_3)_2NON(CF_3)_2$ consumed). It was identified as di[bis-(trifluoromethylamino]trifluoromethylarsine by comparing its infrared spectrum with that of an authentic sample.

(ii) a trace of an unidentified liquid (0.034 g.) trapped at -89°C. Its infrared spectrum indicates the presence of bis(trifluoromethyl)amino group;

(ii) tris(trifluoromethyl)hydroxylamine trapped at -126°C trap, (o.331 g., 1.40 mmoles; 87.2% yield based on $(CF_3)_2NON(CF_3)_2$ consumed);

(iv) a trace of colourless gases (0.022 g.) trapped at -196°C, whose infrared spectrum indicated a mixture of both tris(trifluoromethyl)hydroxylamine and perfluoro-2-azapropene.

(f) Reactions with di[bis(trifluoromethyl)amino]-trifluoromethylarsine

A mixture of di[bis(trifluoromethyl)amino]trifluoro-methylarsine (0.321 g., 0.69 mmole) and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.242 g., 0.72 mmole) was heated to 100°C for 72 hours. The liquid in the ampoule turned light pink. Vacuum separation yielded the following fractions:

(i) white discrete particle at -65°C trap (passed -45°C trap) (0.105 g.) became a liquid at room temperature. The liquid undergoes decomposition on standing, and despite repeated fractionations, no pure compiund could be obtained;

(ii) a light pink liquid, trapped at -126°C (passed -86°C trap), was found to be mainly tris(trifluoromethyl)-hydroxylamine (0.145 g., 0.06 mmole);

(iii) a light pink liquid (0.197 g.) trapped at -196°C, consists mainly perfluoro-2-azapropene.

(g) Reactions with tris(trifluoromethyl)stibine

Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.385 g., 1.20 mmoles) and tris(trifluoromethyl)stibine (0.388 g., 1.18

mmoles) were allowed to react in a 30 ml. ampoule from -60°C to room temperature for 10 hours. A white solid was gradually formed during the course of the reactions.

Fractionations of the products afforded:

(i) a colourless liquid (0.058 g., 0.18 mmoles; 7.5% of the total weight of the reactants) trapped at -74°C (passed -52°C trap), which was mainly tris(trifluoromethyl)stibine on the basis of its infrared spectrum;

(ii) a colourless liquid (0.292 g., 1.23 mmoles; found: M, 234; calc. for C_3F_9NO: M, 237), trapped at -126°C (passed -74°C trap), containing mainly tris(trifluoromethyl)hydroxylamine with a samll trace of perfluoro-2-azapropene;

(iii) a colourless solid at -196°C (0.146 g., 1.10 mmoles; 92.5% yield based on the stibine consumed; found: M, 133; calc.: M, 133). Its infrared spectrum is identical to that of pure perfluoro-2-azapropene; and

(iv) a non-volatile solid with a pungent smell, (0.277 g., ca 36% of the total weight of reactants), which generated a trace of fluoroform on addition of 20% sodium hydroxide solution. It gave a positive fluoride test, and has a m.p. of 291°C, confirming it to be antimony trifluoride.

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