*Journal of Fluorine Chemistry*
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

# OXIDATIVE ADDITION OF TRIFLUOROMETHYLHALOGENOPHOSPHINES WITH *N*-CHLOROBIS(TRIFLUOROMETHYL)AMINE

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(Received February 28, 1972)

## SUMMARY

*N*-Chlorobis(trifluoromethyl)amine gives addition compounds with a number of trifluoromethyl-substituted phosphorus halides, $(CF_3)_nPX_{3-n}$ ($n = 1$, X = F, Cl; $n = 2$, X = F, Cl, I). Other fluorinated phosphoranes produced in these reactions are explained. Infrared and $^{19}$F NMR spectra of the phosphoranes are discussed.

## INTRODUCTION

*N*-Chloro-and *N*-bromobis(trifluoromethyl)amine have been shown to display step-wise substitution reactions with tris(trifluoromethyl)phosphine to give a series of bis(trifluoromethyl)amino-phosphines, $[(CF_3)_2N]_n\ P(CF_3)_{3-n}$ ($n = 1, 2, 3$), and trifluoromethyl halides[1]. On the other hand, *N*-chlorobis(trifluoromethyl)amine undergoes addition reactions with $PF_2X$ (X = F, Cl) to yield the corresponding phosphoranes, $(CF_3)_2NPF_2ClX$ [2]. In these reactions, some perfluoro-2-azapropene was also produced, a feature common to many reactions involving compounds containing bis(trifluoromethyl)amino group(s). It was therefore of interest to investigate further reactions between *N*-chlorobis(trifluoromethyl)amine and phosphines containing trifluoromethyl group(s) and halogen in order to ascertain which way the reactions would proceed.

## EXPERIMENTAL

All reactions were carried out in sealed ampoules fitted with break seals. Infrared spectra were recorded on a Perkin–Elmer infracord spectrometer. $^{19}$F NMR spectra were measured on a Varian Associates V4300B spectrometer with trichlorofluoromethane as standard. The spectra were calibrated with audiofrequency side-bands generated by a Muirhead decade oscillator. Known compounds were identified by their infrared spectra unless other wise stated.

Trifluoromethylhalogenophosphines[4] and *N*-chlorobis(trifluoromethyl)-amine[5] were prepared by standard methods.

### *Reaction of* N-*chlorobis(trifluoromethyl)amine with bis(trifluoromethyl)chlorophosphine*

*N*-Chlorobis(trifluoromethyl)amine (0.724 g) and bis(trifluoromethyl)chlorophosphine (0.649 g) were allowed to react for 12 h at room temperature. Fractionation of the products gave (a) bis(trifluoromethyl)amino-bis(trifluoromethyl)-dichlorophosphorane (I) (0.479 g) (Found: Cl, 17.6; P, 7.2%. Calculated for $C_2F_{12}Cl_2P$: Cl, 18.1; P, 7.9%); (b) bis(trifluoromethyl)dichlorofluorophosphorane (II) (0.472 g) (Found: Cl, 27.1%; mol.wt., 262. Calculated for $C_2F_7Cl_2P$: Cl, 27.4%; mol.wt., 259); and (c) a mixture of perfluoro-2-azapropene and unreacted *N*-chlorobis(trifluoromethyl)amine (0.397 g).

### *Reaction with bis(trifluoromethyl)fluorophosphine*

*N*-Chlorobis(trifluoromethyl)amine (0.618 g) and bis(trifluoromethyl)fluorophosphine (0.611 g) were allowed to stand for 8.5 h at room temperature to give (a) bis(trifluoromethyl)amino-bis(trifluoromethyl)chlorofluorophosphorane (III) (0.208 g) (Found: Cl, 9.3%; mol.wt., 373. Calculated for $C_4F_{13}ClP$: Cl, 9.4%; mol.wt., 375); (b) bis(trifluoromethyl)chlorodifluorophosphorane (IV) (0.605 g) (Found: Cl, 14.5%; mol.wt., 241. Calculated for $C_2F_8ClP$: Cl, 14.6%; mol.wt., 242); and (c) a mixture of perfluoro-2-azapropene and *N*-chlorobis(trifluoromethyl)amine (0.358 g).

### *Reaction with trifluoromethyldichlorophosphine*

A mixture of trifluoromethyldichlorophosphine (0.335 g) and *N*-chlorobis(trifluoromethyl)amine (0.365 g) was allowed to react in a sealed tube at −60° for 1 h and at room temperature for another hour. The products were (a) bis(trifluoromethyl)amino-(trifluoromethyl)trichlorophosphorane (V) (0.329 g) (Found: Cl, 29.3%; mol.wt., 355. Calculated for $C_3F_9Cl_3NP$: Cl, 29.7%; mol.wt., 358); (b) (trifluoromethyl)trichlorofluorophosphorane (VI) (0.195 g) (Found: Cl, 47.5%; mol.wt., 224. Calculated for $CF_4Cl_3P$: Cl, 47.2%; mol.wt., 225); and (c) perfluoro-2-azapropene and unreacted *N*-chlorobis(trifluoromethyl)amine (0.152 g).

### *Reaction with trifluoromethyldifluorophosphine*

*N*-Chlorobis(trifluoromethyl)amine (0.994 g) and trifluoromethyldifluorophosphine (0.706 g) were allowed to react for 12 h at room temperature. Fractionation of the products gave (a) bis(trifluoromethyl)amino-(trifluoromethyl)chlorodifluorophosphorane (VII) (0.378 g) (Found: Cl, 10.1%; mol.wt., 323. Calculated for $C_3F_{11}ClP$: Cl, 10.9%; mol.wt., 325); (b) (trifluoromethyl)chlorotrifluorophosphorane (VIII) (0.389 g) (Found: Cl, 18.1; P, 10.1%; mol.wt., 192. Calculated for $CF_6ClP$: Cl, 18.4; P, 10.1%; mol.wt., 192); and (c) a mixture of perfluoro-2-azapropene and (trifluoromethyl)chlorotrifluorophosphorane and *N*-chlorobis(trifluoromethyl)amine (0.945 g). Complete separation of the mixture was difficult. However, it was possible to isolate sufficient quantity of each compound for identification by means of its infrared spectrum.

### *Reaction of bis(trifluoromethyl)iodophosphine*

A mixture of bis(trifluoromethyl)iodophosphine (1.08 g) and *N*-chlorobis(trifluoromethyl)amine (0.703 g) was transfered into a sealed ampoule which was slowly warmed from −196° to −50°. Vigorous reaction proceeded at −126°, giving a liquid fraction together with some greyish-black solid. Fractionation of the products gave (a) perfluoro-2-azapropene and *N*-chlorobis(trifluoromethyl)amine (0.480 g); (b) bis(trifluoromethyl)fluorophosphine (0.307 g); and (c) bis(trifluoromethyl)chlorodifluorophosphorane (0.279 g) (Found: Cl, 14.9%. Calculated for $C_2F_8ClP$: Cl, 14.6%). Its infrared spectrum was identical to the product formed by the thermal decomposition of $(CF_3)_2NP(CF_3)_2ClF$.

## RESULTS AND DISCUSSION

The reaction of bis(trifluoromethyl)chlorophosphine with *N*-chlorobis(trifluoromethyl)amine at temperatures not greater than 20° gave perfluoro-2-azapropene and two phosphoranes, namely bis(trifluoromethyl)amino-bis(trifluoromethyl)dichlorophosphorane (I) and bis(trifluoromethyl)dichlorofluorophosphorane (II). The phosphorane (I) is a colourless, heavy liquid which underwent decomposition at room temperature to afford compound (II) and perfluoro-2-azapropene,

$$(CF_3)_2NP(CF_3)_2Cl_2 \rightarrow (CF_3)_2PCl_2F + CF_3N = CF_2$$

Prepared in this way, it differed from the isomeric crystalline solid obtained by the addition of chlorine to bis(trifluoromethyl)amino-bis(trifluoromethyl)phosphine[3].

The P–F stretching frequency of bis(trifluoromethyl)dichlorofluorophosphorane (II) is located at 840 $cm^{-1}$ which is comparable to 855 $cm^{-1}$ observed in the infrared spectrum of $(CF_3)_3PF_2$ where the fluorine atoms are known to reside in the apical positions. Muetterties and co-workers have in fact shown that for a large number of fluorophosphoranes the apical P–F stretching frequencies are significantly lower than the equatorial frequencies[6]. Thus, structures (A) and (B) can be eliminated.

$^{19}F$ NMR spectrum of compound (II) gave resonances at 77.1 ppm for the fluorine in $PCF_3$ and 94.5 ppm for PF fluorine. Hyperfine structure due to spin–spin coupling of PF fluorine and fluorine atoms in $PCF_3$ was evident ($J$ = 14 Hz). Therefore, spectroscopic equivalence is not due to some intermolecular exchange

TABLE 1

REACTIONS OF *N*-CHLOROBIS(TRIFLUOROMETHYL)AMINE WITH SUBSTITUTED PHOSPHINES

| *N*-chloroamine mmoles (g) | Phosphine mmoles (g) | Phosphoranes mmoles (g) | | Perfluoro-2-azapropene and *N*-chloroamine (g) |
|---|---|---|---|---|
| 3.86(0.724) | $(CF_3)_2PCl$<br>3.18(0.649) | $(CF_3)_2NP(CF_3)_2Cl_2$<br>1.22(0.479) | $(CF_3)_2PCl_2F$<br>1.82(0.472) | (0.397) |
| 3.29(0.618) | $(CF_3)_2PF$<br>3.25(0.611) | $(CF_3)_2NP(CF_3)_2ClF$<br>0.555(0.208) | $(CF_3)_2PClF_2$<br>2.49(0.605) | (0.358) |
| 1.95(0.365) | $CF_3PCl_2$<br>1.96(0.335) | $(CF_3)_2NPCF_3Cl_3$<br>0.918(0.329) | $CF_3PCl_3F$<br>0.865(0.195) | (0.152) |
| 5.30(0.994) | $CF_3PF_2$<br>5.93(0.706) | $(CF_3)_2NPCF_3ClF_2$<br>1.24(0.378) | $CF_3PClF_3$<br>1.27(0.389) | and $CF_3PClF_3$<br>(0.945) |
| 3.75(0.703) | $(CF_3)_2PI$<br>3.63(1.08) | $(CF_3)_2PClF_2$<br>0.115(0.279) | $(CF_3)_2PF$*<br>1.63(0.307) | (0.480) |

* Phosphine.

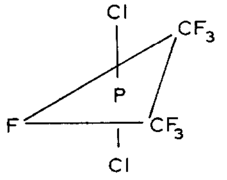
TABLE 2

INFRARED DATA OF SOME PHOSPHORANES

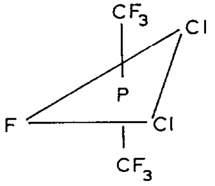
| (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) | (VIII) | |
|---|---|---|---|---|---|---|---|---|
| 1315 (w) | | 1320 (vs) | 1390 (w) | 1310 (w) | 1320 (w) | 1340 (vs) | 1300 (m) | ν(C–F) |
| 1305 (s) | | | 1290 (w) | | | | | |
| 1238 (s) | 1240 (w) | 1245 (vs) | 1230 (m) | 1235 (s) | 1240 (w) | 1264 (vs) | 1245 (m) | |
| | 1235 (w) | 1210 (m) | 1210 (vs) | 1200 (m) | | 1245 (vs) | 1200 (sh) | |
| | | | | | | 1213 (s) | | |
| 1175 (vs) | 1180 (vs) | 1180 (vs) | 1185 (vs) | 1170 (s) | 1175 (vs) | 1190 (s) | 1170 (vs) | |
| 1143 (m) | 1120 (w) | 1160 (vs) | 1120 (w) | 1145 (s) | 1150 (s) | 1170 (s) | | |
| | | 1125 (m) | | 1110 (w) | | 1120 (w) | | ν(C–N) |
| 1130 (sh) | | | | | | | | |
| | | 1035 (w) | | 1100 (w) | | 1045 (w) | | |
| 960 (w) | | 960 (m) | | 960 (w) | | | | C–N–C bending |
| | 840 (s) | 840 (s) | 850 (m) | | 810 (s) | 875 (s) | 960 (m) | ν(P–F) |
| | | | | | | | 880 (s) | |
| | | | | | | | 830 (s) | |
| 740 (m) | 760 (w) | 760 (m) | 770 (w) | 760 (w) | 730 (m) | 770 (w) | 760 (m) | δ($CF_3$) |
| | | | | | | 733 (w) | | |
| | | | 660 (w) | | 610 (s) | | | |

processes. The possibility that spectroscopic equivalence of like substituents could arise in structure (C) from some intramolecular process is considered unlikely because of the large size of $CF_3$ groups. The coupling constant of 14 Hz is comparable to that found in tris(trifluoromethyl)difluorophosphine, $J(F_P–F_C) = 16$ Hz. The highfield multiplet is a basic doublet, $J(P–F) = 1298$ Hz, in which each component is further split into a multiplet due to $F_P$ and $F_C$ coupling. The lowfield quartet is made up of a doublet, $J(P–F_C) = 183$ Hz, and each peak is further split into a 1 : 1 doublet by the fluorine atom directly bonded to phosphorus.

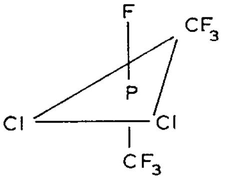
On the basis of the above evidence, structure (D) could be assigned for compound (II).



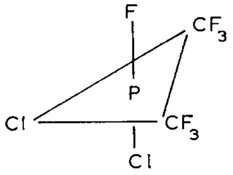
(A)



(B)



(C)



(D)

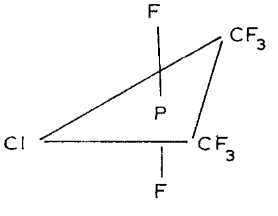
A stoichiometric mixture of *N*-chlorobis(trifluoromethyl)amine and bis(trifluoromethyl)fluorophosphine displayed a similar reaction as above, yielding bis(trifluoromethyl)amino-bis(trifluoromethyl)chlorofluorophosphorane (III) and bis(trifluoromethyl)chlorodifluorophosphorane (IV).

Unlike $(CF_3)_2NP(CF_3)_2Cl_2$, $(CF_3)_2NP(CF_3)_2ClF$ was found to be stable at room temperature. Perfluoro-2-azapropene was also liberated in this reaction. Both phosphoranes (III) and (IV) gave infrared absorptions at about 850 $cm^{-1}$ and appeared to be in the region which is associated with apical fluorine. The $^{19}F$ NMR spectrum of $(CF_3)_2PClF_2$ gave chemical shifts at 78.2 and 72.2 ppm due to $CF_3$ and PF fluorine respectively. The highfield spectrum consists essentially of a doublet, $J(F_{CP}–P) = 180$ Hz, which is further split into a 1 : 2 : 1 triplet by the two PF fluorine atoms, $J(F_{CP}–F_P) = 15$ Hz. The lowfield spectrum consists of a 1 : 1 doublet resulting from the spin coupling between the fluorine atoms and phosphorus, $J(F_P–P) = 1304$ Hz and each is again split into a multiplet by the fluorine in $CF_3$ groups, $J(F_{CP}–F_P) = 15$ Hz. The spectroscopic data suggest structure (E) for compound (IV) and structure (F) can therefore be inferred for compound (III).

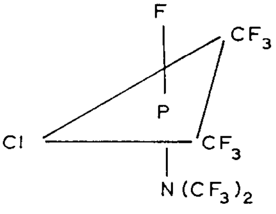
TABLE 3

$^{19}$F NMR DATA OF SOME PHOSPHORANES

| Compound | Chemical shift (ppm) | *J* (Hz) | |
|---|---|---|---|
| $(CF_3)_2NP(CF_3)_2Cl_2$ | $F_{CP}$ + 77.4 | $F_{CP}$–P | 187 |
| | $F_{CN}$ + 48.2 | | |
| $(CF_3)_2NPCF_3Cl_3$ | $F_{CP}$ + 75.5 | $F_{CP}$–P | 157 |
| | $F_{CN}$ + 45.8 | $F_{CN}$–$F_{CP}$ | 4 |
| $(CF_3)_2NPCF_3ClF_2$ | $F_{CP}$ + 68.1 | $F_{CP}$–P | 190 |
| | $F_{CN}$ + 51.5 | $F_{CN}$–$F_{CP}$ | 2 |
| | $F_P$ — 16.7 | $F_P$–$F_{CP}$ | 18 |
| | | $F_P$–P | 999 |
| $(CF_3)_2PCl_2F$ | $F_{CP}$ + 77.1 | $F_{CP}$–P | 183 |
| | $F_P$ + 94.5 | $F_{CP}$–$F_P$ | 14 |
| | | $F_P$–P | 1298 |
| $(CF_3)_2PClF_2$ | $F_{CP}$ + 78.2 | $F_{CP}$–P | 180 |
| | | $F_{CP}$–$F_P$ | 15 |
| | $F_P$ + 72.2 | $F_P$–P | 1304 |
| $CF_3PClF_3$ | $F_{CP}$ + 72.3 | $F_{CP}$–P | 173 |
| | | $F_{CP}$–$F_P$ | 13 |
| | $F_P$ + 64.9 | $F_P$–P | 1123 |



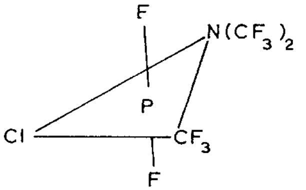
(E)



(F)

The reaction of *N*-chlorobis(trifluoromethyl)amine with trifluoromethyldichlorophosphine gave bis(trifluoromethyl)amino(trifluoromethyl)trichlorophosphorane (V), (trifluoromethyl)trichlorofluorophosphorane (VI) and some perfluoro-2-azapropene. Compound (V) is unstable at room temperature, as indicated by the formation of perfluoro-2-azapropene and compound (VI) if it is left to stand for a day at room temperature. Its $^{19}$F NMR spectrum shows basically two peaks of intensity 1 : 2 which are due to the fluorine in trifluoromethyl and bis(trifluoromethyl)amino groups, whose chemical shifts have been found to be 75.5 ppm and 45.8 ppm, respectively. The former gives a spin–spin coupling with the phosphorus atom, $J(F_C\text{–}P) = 157$ Hz and a long-range coupling with the distant fluorine is also present, $J(F_{CP}\text{–}F_{CN}) = 4$ Hz. The unusual feature is that there is no coupling of the central phosphorus with fluorine in bis(trifluoromethyl)amino group.

Trifluoromethyldifluorophosphine reacted with the chloroamine to afford bis(trifluoromethyl)amino-(trifluoromethyl)difluorochlorophosphorane (VII) as one of the products. Its $^{19}F$ NMR spectrum contains essentially three bands whose chemical shifts are $\delta(F_{CN}) = 51.5$ ppm, $\delta(F_{CP}) = 68.1$ ppm and $\delta(F_P) = -16.7$ ppm. Hyperfine splittings due to spin–spin coupling are also noted: $J(F_P\text{–}P) = 999$ Hz, $J(F_{CP}\text{–}P) = 190$ Hz, $J(F_{CP}\text{–}F_P) = 18$ Hz and $J(F_{CP}\text{–}F_{CN}) = 2$ Hz. Splitting arising from $F_{CN}$–P coupling was absent. The equivalence of the fluorine atoms (bonded to phosphorus) does not reveal the positions of the fluorine atoms, since the spectrum was measured at about 25°. However, the presence of an absorption at 875 $cm^{-1}$ in the infrared spectrum does suggest that the fluorine atoms are in the apical positions. Thus, the following structure is implied:



Similar structure has been assigned by Onak and Emeléus for $(CF_3)_2NPF_2Cl_2$[2].

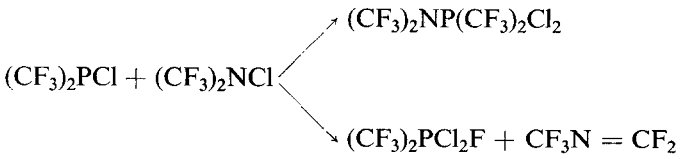
Compound (VII) is a colourless liquid which is fairly stable at room temperature, but is rapidly hydrolysed in air to release a strong odour of bis(trifluoromethyl)amine. Its vapour pressures can be expressed by $\log P_{mm} = 7.457 - 1571/T$, which gives an extrapolated boiling point of 70°, a latent heat of vapourisation of 7.19 kcal $mole^{-1}$ and a Trouton constant of 20.9.

The other products from the reaction with trifluoromethyldifluorophosphine are (trifluoromethyl)chlorotrifluorophosphorane (VIII) and perfluoro-2-azapropene. $^{19}F$ NMR and infrared data suggest that both the trifluoromethyl group and the chlorine atom are in the equatorial positions.

The reaction of bis(trifluoromethyl)iodophosphine with an equimolar quantity of the chloroamine proceeded vigorously even at −126°, liberating iodine almost immediately. The other products formed were bis(trifluoromethyl)fluorophosphine, bis(trifluoromethyl)chlorodifluorophosphorane and perfluoro-2-azapropene. The absence of bis(trifluoromethyl)amino derivatives of phosphorus in this reaction shows that the addition product if formed was certainly very unstable.

A study of a series of reactions involving *N*-chlorobis(trifluoromethyl)amine and phosphines permits a number of conclusions to be drawn:

(a) *N*-Chlorobis(trifluoromethyl)amine, in general, undergoes addition reactions with $(CF_3)_nPX_{3-n}$ and $PF_2X$ ($X = F$, Cl; $n = 1, 2$). In all cases, the reactions also afforded the corresponding fluorophosphoranes, derived from intramolecular fluorination by bis(trifluoromethyl)amino group, and perfluoro-2-azapropene. For example,



$$(CF_3)_2PCl + (CF_3)_2NCl \begin{array}{l} \nearrow (CF_3)_2NP(CF_3)_2Cl_2 \\ \searrow (CF_3)_2PCl_2F + CF_3N = CF_2 \end{array}$$

The unstable nature of bis(trifluoromethyl)aminophosphoranes containing more than one chlorine atom is of interest in that it indicates the difficulty that might be associated with the preparation of phosphoranes containing either a bromine or an iodine atom or an electropositive group. This explains the peculiar reaction between bis(trifluoromethyl)iodophosphine and the chloroamine.

(b) The new bis(trifluoromethyl)aminophosphoranes display different degrees of stability, the stability sequence, on the basis of the ease of decomposition at room temperature, appears to be in the order $(CF_3)_2NP(CF_3)_2Cl_2 \sim (CF_3)_2NP(CF_3)Cl_3 < (CF_3)_2NP(CF_3)_2ClF < (CF_3)_2NPCF_3F_2Cl$.

(c) The successful isolation of a number of bis(trifluoromethyl)aminophosphoranes strengthens the postulated mechanisms that the interactions between $(CF_3)_3M$ (M = P, As) and *N*-halogenobis(trifluoromethyl)amine involves radical exchange in which the formation of a pentacovalent addition intermediate is suggested[1].

## ACKNOWLEDGEMENT

The author thanks Professor H. J. Emeléus, F.R.S. for useful discussions. He is grateful for the award of Research Fellowships of Peterhouse, Cambridge and the Royal Commission for the Exhibition of 1851, London, while this investigation was being undertaken.

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