# Reactions of Chlorine Trifluoride with Pentafluoroiodobenzene and Related Compounds. Preparation of Pentafluorophenyliodine(v) Tetrafluoride †

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Pentafluoroiodobenzene is oxidised by chlorine trifluoride below room temperature to pentafluorophenyliodine(v) tetrafluoride and $C_6F_4(IF_4)_2$ is one of the products from the oxidation of 1,4-$I_2C_6F_4$ under similar conditions. Bromopentafluorobenzene is not oxidised by $ClF_3$ but addition of chlorine and fluorine to the ring occurs. Similar behaviour is observed with $C_6F_5IF_4$ and $ClF_3$.

SEVERAL perfluoroalkyliodine(v) tetrafluorides have been prepared by oxidation of the corresponding iodides with chlorine trifluoride.[1,2] The stability with respect to decomposition of the compounds $R_FIF_4$ depends on the identity of $R_F$; for example $CF_3IF_4$ is very much less stable than $(CF_3)_2CFIF_4$ and other compounds containing bulky $R_F$ groups.[2] Pentafluorophenyl derivatives of both metals and non-metals are often far more stable thermally than their perfluoroalkyl analogues,[3] therefore the $C_6F_5$ group should be a good ligand for iodine(v). We describe here the reactions of $ClF_3$ with $C_6F_5I$, 1,4-$I_2C_6F_4$, and $C_6BrF_5$, which were undertaken to prepare perfluoroaromatic derivatives of iodine(v) and bromine(v).

## EXPERIMENTAL

All manipulations and reactions were carried out *in vacuo* or in a dry inert atmosphere as described previously.[2a] $^{19}F$ N.m.r. spectra (at 56·4 MHz) and vibrational spectra were recorded on JEOL C60-HL, Perkin-Elmer 457, and Spex Ramalog instruments. Chemical shifts are given as $\delta$ values, in p.p.m. positive to low field of $CCl_3F$. $C_6F_6$ was used as a secondary internal reference. Mass spectra (at 70 eV) were obtained with a G.E.C./A.E.I. MS 12 spectrometer. Samples were inserted directly, probe temperatures were in the range 100—200 °C, and source pressures were $<1 \times 10^{-6}$ mmHg. Assignment of peaks due to $C_xF_y^+$ fragments was often aided by the observation of metastable peaks corresponding to the elimination of $CF_3$, $CF_2$, or CF. Similar transitions have been noted previously for $C_6F_6$ and its derivatives.[4] Although mass spectrometry did not lead to complete characterisation of the reaction products, it enabled oxidation and addition reactions to be distinguished. Full spectra are reported elsewhere [5] and are summarised in Tables 1—4.

$ClF_3$ (Matheson 98%) and the aromatic fluorocarbons (Fluorochem) were used as received. Microanalyses were carried out by A. Bernhardt.

TABLE 1

Mass spectrum of $C_6F_5IF_4$

| *m/e* % in parentheses | Assignment | |
|---|---|---|
| 370(3), 351(3), 332(1), 313(1), 294(100), 275 (1) | $C_6F_nI^+$ | $n = 9—4$ |
| 203(1), 184(1), 165(3), 146(1), 127(28) | $IF_n^+$ | $n = 4—0$ |
| 224(1), 205(2), 186(7), 167(58) | $C_6F_n^+$ | $n = 8—5$ |
| 117(56) | $C_5F_3^+$ [a] | |

| Metastable transitions | *m** | |
|---|---|---|
| | Found | Calc. |
| $C_6F_5I^+ \longrightarrow C_6F_5^+ + I$ | 94·9 | 95·0 |
| $C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2$ | 82·0 | 82·0 |

[a] Other $C_{\leqslant 6}F_n^+$ fragments which are also present in the spectrum of $C_6F_5I$ (J. Majer, *Adv. Fluorine Chem.*, 1961, **2**, 55) are not shown.

TABLE 2

Chlorine-containing fragments in the mass spectrum of the product from $C_6F_5I + ClF_3$ (in excess)

| *m/e* [a] | Relative intensity [b] (%) | Assignment | *m/e* [a] | Relative intensity [b] (%) | Assignment |
|---|---|---|---|---|---|
| 459 | 5 | $C_6Cl_2F_{10}I^+$ | 259 | 63 | $C_6ClF_8^+$ |
| 443 | 7 | $C_6ClF_{11}I^+$ | 209 | 20 | $C_5ClF_6^+$ |
| 424 | 3 | $C_6ClF_{10}I^+$ | 171 | 17 | $C_5ClF_4^+$ |
| 402 | 20 | $C_6Cl_2F_7I^+$ | 147 | 33 | $C_3ClF_4^+$ |
| 386 | 23 | $C_6ClF_8I^+$ | 85 | 58 | $CClF_2^+$ |
| 367 | 10 | $C_6ClF_7I^+$ | | | |

[a] Corresponds to $^{35}Cl$. The expected isotope patterns were observed in each case. [b] *m/e* 93 assigned to $C_3F_3^+$ is the base peak.

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† No reprints available.

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*Reactions of Chlorine Trifluoride.—With* $C_6F_5I$. (*a*) A mixture of $ClF_3$ (11·4 mmol) and $C_6F_5I$ (7·3 mmol) in n-$C_6F_{14}$ (3 ml), allowed to warm from −78 to −15 °C over 16 h, gave a white solid, m.p. 72—74 °C, and a green volatile liquid containing $Cl_2$, unchanged $ClF_3$, and n-$C_6F_{14}$. The solid was identified from its analysis (Found: C, 20·6; F, 45·2; I, 33·8. $C_6F_9I$ requires C, 19·45; F, 46·2; I, 34·3%) and mass (Table 1), $^{19}F$ n.m.r., and vibrational spectra as *pentafluorophenyliodine*(V) *tetrafluoride*; $\delta_F$ ($C_6F_6$) −6·4 (t, $^3J_{F-I-C-F}$ 26 Hz) and −128·0, −143·3, and −158·5 (complex multiplets, 2 : 1 : 2, *ortho*-, *para*-, and *meta*-F, assigned by analogy with $C_6F_5I$ and other $C_6F_5X$ compounds [6]). Its vibrational spectrum (solid) showed the presence of a $C_6F_5$ group [7] and in the region 600—400 cm$^{-1}$ was similar to that of $CF_3IF_4$: [2a] i.r. (2000—400 cm$^{-1}$) $\nu_{max.}$ 1638m, 1520sh, 1503s, 1495sh, 1350w, 1300w, 1268w, 1153w, 1127sh, 1099s, 1059w, 1004s, 987s, 807sh, 800m, 722m, 626m, 588s, 562s, 545sh, and 528s cm$^{-1}$; Raman $\nu_{max.}$ (relative peak height) 626(5), 587(18), 576(10), 558(13), 550(13), 538(12), 482(10), 443(7), 405(2), 385(5), 310(5), 285(5), 260(4), 223(1), 195(11), 170(2), 90(10), and 80(11) cm$^{-1}$.

TABLE 3

Mass spectrum of the product from $C_6F_4I_2$ + $ClF_3$ [a]

| *m/e* % in parentheses | Assignment | |
|---|---|---|
| 554(0·6), 535(1), 516(1), 497(4), 478(10), 459(4), 440(4), 421(3), 403(53) [b] | $C_6F_nI_2^+$ | $n$ = 12—4 |
| 389(3), 370(0·7), 351(5), 332(2), 313(1), 294(47), 275(22),[b] 256(2) [b] | $C_6F_nI^+$ | $n$ = 10—3 |
| 203(5), 184(3), 165(9), 146(11), 127(49) | $IF_n^+$ | $n$ = 4—0 |
| 224(5), 205(14), 186(45), 167(43), 148(100),[b] 129 (14) [b] | $C_6F_n^+$ | $n$ = 8—3 |

| | *m** | |
|---|---|---|
| Metastable transitions | Found | Calc. |
| $C_6F_4(IF_4)_2^+ \longrightarrow C_6F_5IF_4^+ + IF_3$ | 247·0 | 247·0 |
| $C_6F_5^+ \longrightarrow C_5F_4^+ + CF$ | 110·5 | 110·4 |
| $C_6F_5I^+ \longrightarrow C_6F_5^+ + I$ | 94·9 | 95·0 |
| $C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2$ | 82·0 | 81·9 |
| $C_6F_6^+ \longrightarrow C_5F_3^+ + CF_3$ | 73·8 | 73·6 |

[a] Peaks assigned to $C_{<6}F_x^+$ and $C_{<6}F_yI^+$ fragments are not shown. [b] Present in the spectrum of $C_6F_4I_2$.

TABLE 4

Mass spectrum of the product from $C_6BrF_5$ and $ClF_3$ [a]

| *m/e* [b] % in parentheses [c] | Assignment |
|---|---|
| 338(1) | $C_6BrClF_8^+$ [d] |
| 322(1), 303(1), 284(18), 265(5) | $C_6BrF_n^+$ $n$ = 9—6 |
| 259(2) | $C_6ClF_8^+$ |
| 243(2), 224(3), 205(66), 186(42) | $C_6F_n^+$ $n$ = 9—6 |
| 209(1), 171(1), 147(1) | $C_5ClF_6^+$, $C_5ClF_4^+$, $C_3ClF_4^+$ |
| 85(7) | $CCl_2F^+$ |

| | *m** | |
|---|---|---|
| Metastable transitions | Found | Calc. |
| $C_6F_7^+ \longrightarrow C_5F_6^+ + CF$ | 147·5 | 147·6 |
| $C_6F_7^+ \longrightarrow C_5F_5^+ + CF_2$ | 117·3 | 117·1 |
| $C_6F_4^+ \longrightarrow C_5F_3^+ + F$ | 100·8 | 100·7 |
| $C_6F_6^+ \longrightarrow C_5F_3^+ + CF_2$ | 73·8 | 73·8 |

[a] Fragments observed in the spectrum of $C_6BrF_5$ (J. Majer, *Adv. Fluorine Chem.*, 1961, **2**, 55) and corresponding to $C_{<5}F_n^+$ are not shown. [b] Corresponds to $^{79}Br$ and $^{35}Cl$. The expected isotope patterns are observed in each case. [c] *m/e* 69 assigned to $CF_3^+$ as the base peak. [d] Metastable peaks tentatively assigned to loss of $CBrF_2$ from this fragment.

(*b*) $ClF_3$ (7·6 mmol) and $C_6F_5I$ (3·85 mmol) in n-$C_6F_{14}$, allowed to warm from −78 to 20 °C over 16 h, gave a colourless, viscous liquid on removal of the volatile material. Its mass spectrum consisted of peaks assigned to chlorine-containing fragments (Table 2) and peaks identical with those found in the spectrum of $C_6F_5IF_4$; i.r. (2000—625 cm$^{-1}$) $\nu_{max.}$ 1780vw, 1660s, 1300s, 1290w, 1200—1230vs,br, 1140—1160vs,br, 1110vs, 1060m, 1045m, 1030m, 990m, 970s, 950s, 915w, 865w, 855w, 760w, 725m, 700w, 680m, and 650 cm$^{-1}$.

*With* $C_6F_5IF_4$. $ClF_3$ (5·3 mmol) and $C_6F_5IF_4$ (1·3 mmol) in n-$C_6F_{14}$, allowed to warm from −78 to 20 °C over 16 h, gave a colourless, viscous liquid on removal of the volatile material; $\delta_F$ 11·4 (d, $J$ 90 Hz, $IF_5$), −5·5br ($W_{\frac{1}{2}}$ 140 Hz), and seven complex multiplets of low intensity between −80 and −156. Its i.r. and mass spectra were very similar to those described above [reaction (*b*)] but additionally several metastable peaks corresponding to loss of $CF_2$, $CF_3$, or F from $C_6F_n^+$ ($n$ = 9—4) fragments were identified in its mass spectrum.

*With* 1,4-$I_2C_6F_4I_2$. $ClF_3$ (7·85 mmol), $C_6F_4I_2$ (2·3 mmol), and n-$C_6F_{14}$ (3 ml) were allowed to warm from −60 to −20 °C over 16 h. At all times a solid was observed in the mixture but the liquid slowly became green. The solid isolated was insoluble in $IF_5$, $C_6F_6$, and MeCN (Found: C, 14·1; F, 36·6; I, 49·35. $C_6F_{10}I_2$ requires C, 14·0; F, 36·8; I, 49·2%). Above 580 cm$^{-1}$ its i.r. spectrum was very similar to that of $C_6F_4I_2$. Below this the spectrum ($\nu_{max.}$ 571s, 562sh, 525sh, 506s, 476s, 429m, and 418w cm$^{-1}$) suggested that $IF_n$ groups were present, consistent with the mass spectrum (Table 3). No n.m.r. spectrum was obtained owing to the solid's insolubility.

*With* $C_6BrF_5$. A mixture of $ClF_3$ (8·2 mmol) and $C_6BrF_5$ (6·0 mmol) in n-$C_6F_{14}$ (3 ml), allowed to warm from −78 to −36 °C over 16 h, gave a colourless liquid after removal of $ClF_3$ and n-$C_6F_{14}$. Its $^{19}F$ n.m.r. spectrum showed that $C_6BrF_5$ was the major component but 12 weak multiplets between δ −98 and −159 were also observed. Several ions containing chlorine were identified in its mass spectrum (Table 4).

## RESULTS AND DISCUSSION

The oxidation of $C_6F_5I$ by $ClF_3$ proceeds smoothly and, providing that the temperature of the mixture is kept below *ca.* −10 °C and the molar ratio of $ClF_3$ to $C_6F_5I$ does not greatly exceed 4 : 3, substantially pure $C_6F_5IF_4$ is obtained. The compound is a white, moisture-sensitive solid whose thermal stability is similar to that of $(CF_3)_2CFIF_4$. It is more stable than either $C_6F_5IF_2$, which has been reported to decompose above −5 °C,[8] or $C_6H_5IF_4$, which apparently loses HF readily.[9] The spectroscopic properties of $C_6F_5IF_4$ are related to those of $R_FIF_4$ compounds, in particular its $^{19}F$ n.m.r. spectrum in $C_6F_6$ or $IF_5$ indicates either that the $C_6F_5$ group occupies the apical position in a square pyramidal molecule, or that a fast intramolecular exchange process occurs.

Unlike the mass spectra of the perfluoroalkyl derivatives, that of $C_6F_5IF_4$ (Table 1) contains a peak attribut-

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able to the molecular ion, and peaks at *m/e* 351, 332, and 313 may reasonably be assigned to $C_6F_5IF_n^+$ ($n$ = 3—1). It is suggested that the peaks assigned to $C_6F_8^+$, $C_6F_7^+$, and $C_6F_6^+$ result from fluorine migrations involving the elimination of IF, $IF_2$, or $IF_3$ fragments. Such processes are the reverse of those found in $C_6F_5PF_2$, and many $C_6F_5$ derivatives of Group V, Group IV, and transition elements, where migration of fluorine to the central atom is observed,[10] but are consistent with the expected order of bond energies C–F > I–F.

The isolation of $C_6F_5IF_4$ is dependent on the reaction temperature and stoicheiometry, as further reaction, indicated by the appearance of a viscous liquid, can occur. Thus both the reaction of $C_6F_5I$ with a large excess of $ClF_3$ and the reaction of $C_6F_5IF_4$ with $ClF_3$ yield viscous liquids which appear to be mixtures. Fragments containing one or two chlorine atoms are identified in their mass spectra (Table 2), their i.r. spectra suggest the presence of a cyclic olefinic group,[11] and additional bands are observed in the region 1000—900 cm$^{-1}$. Some C–I bond scission also occurs. The formation of $I^V$–Cl bonds under these conditions is unlikely,[12] and although the mass spectra do not establish the identities of the compounds formed, they suggest that $C_6Cl_2F_7IF_4$ and $C_6ClF_8IF_4$ may be present.

$ClF_3$ oxidises 1,4-$I_2C_6F_4$ under similar conditions but the oxidation is not complete, probably owing to the insolubility of the iodide and product in the reaction medium. A similar situation exists in the oxidation of $SF_5(CF_2)_2I$ where a mixture of $SF_5(CF_2)_2IF_2$ and $SF_5(CF_2)_2IF_4$ is obtained.[2b] There is no evidence for chlorine-containing products and the solid's composition is $C_6F_{10}I_2$. Its mass spectrum (Table 3) indicates the presence of $C_6F_4(IF_4)_2$ and we suggest that the solid is a mixture of this and $C_6F_4(IF_2)_2$ or $C_6F_4I_2$.

Although both $Br_2$ and $I_2$ react with $ClF_3$ giving $BrF_3$ and $IF_5$ respectively,[13] neither $C_6BrF_5$ nor n-$C_3F_7Br$ is oxidised by $ClF_3$ under the conditions used. The different behaviour from the compounds $R_FI$ is probably a reflection of the greater thermodynamic stability of iodine fluorides.[14] Reaction does occur between $C_6BrF_5$ and $ClF_3$, however, to give a mixture of products resulting from the addition of fluorine and chlorine to the aromatic ring. The origin of many of the fragments observed in the mixture's mass spectrum (Table 4) cannot be stated with certainty, but the spectrum is consistent with the presence of the cyclohexenes $C_6BrClF_8$ and $C_6BrF_9$.

$XeF_2$ is known to add two fluorines to $C_6F_6$ and other perfluoroaromatic compounds,[15] and related behaviour by a $Br_2$–$BrF_3$ mixture, or in some cases by $BrF_3$ alone, has been briefly reported.[16] For example a $Br_2$–$BrF_3$ mixture reacts with $C_6F_5Br$ to give 1-bromoheptafluorocyclohexa-1,4-diene and $C_6Br_2F_8$ isomers, $C_6Br_3F_9$ isomers being formed with an excess of reagent. The addition reactions observed in the present work are similar to these and may be initiated either by $ClF_3$ alone or by $ClF_3$ and $Cl_2$, the latter being present either as a reaction product or in small quantities as an impurity in $ClF_3$.

We thank the S.R.C. and the S.E.D. for maintenance awards to G. O. and J. A. B., respectively.

[3/1901 *Received*, 14*th September*, 1973]

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