FLUORINATION WITH POSITIVE FLUORINE GENERATED FROM ISOELECTRONICALLY RELATED REAGENTS

M. CARTWRIGHT and A.A. WOOLF

School of Chemistry, University of Bath, Bath BA2 7AY (U.K.)

SUMMARY

Compounds such as $PhIF_2$, Ph_3PF_2 and XeF_2, which have been used previously as unrelated fluorinating agents, are shown to be periodically related as isoelectronic molecules E_3AF_2 of trigonal-bipyramidal shape, where E represents a bonded or non-bonded electron pair and A a main Group V-VIII element. These compounds are arranged in order of halogenating ability by estimating the magnitude of reduction couples, approximated by $\Delta H_f^O(E_3AF_2-E_3A)$, or by noting the direction of redox reactions involving the couples. The A sequence deduced Kr>Xe~Cl>Br>I>S>Se>Te~As~Sb>P agrees with the limited experimental data available. Evidence for an ionic mechanism involving 'onium' monohalide ions is given for halogenations with these reagents when carried out under "Friedel-Craft" conditions although no stable salts containing these ions have as yet been isolated because of intramolecular halogenation. These ions act as sources of positive fluorine. The use of ring deactivated reagents to achieve halogenation is discussed.
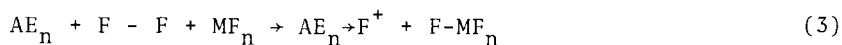
INTRODUCTION

There is a marked reluctance by fluorine chemists to accept the reality of positive fluorine [1]. Historically this stems from an improper use of the electronegativity concept and to the dogma that fluorine is the exceptional, rather than the extreme, halogen. Electronegativities are derived from atomic

or molecular properties of simple molecules like HF. They
cannot be applied predictively, especially when fluorine is
joined to delocalized electron systems, because the inductive
effect of fluorine is overcome by mesomeric or back-bonding
type effects.

Thus it is well known that aromatic carboxylic acids are
weakened, not strengthened, by o- and p-fluorine substitution;
the polarity $CF_3\overset{\delta-}{O}\overset{\delta+}{F}$ is required to explain fluorination
reactions even though fluorine is formally more electronegative
than the CF_3 group; the Lewis acidity of boron trihalides
increases from BF_3 to BI_3 and ionization increases along series
such as Ph_3AsF_2, Ph_3AsCl_2 and Ph_3AsBr_2 [29].

Recent work shows that difluorine resembles the other
dihalogens in electrophilically substituting aromatic compounds
if low temperatures and high dilutions are used [2]. The
difluorine polarization, necessary for aromatic substitution,
should be enhanced by withdrawal of fluorine ions with Lewis
acids, or conversely by ejection of fluoride ions with Lewis
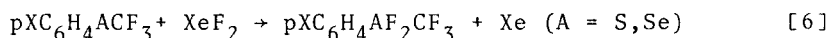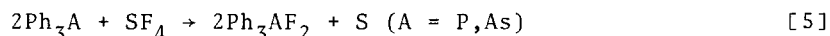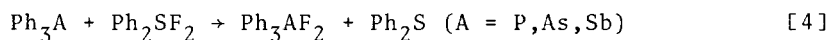bases, or by a combination of both processes.

$$\overset{\delta+}{F} - \overset{\delta-}{F} + MF_n \rightarrow F^+ + F\text{-}MF_n \tag{1}$$

$$AE_n + F - F \rightarrow AE_n{\rightarrow}F^+ + F^- \tag{2}$$

$$AE_n + F - F + MF_n \rightarrow AE_n{\rightarrow}F^+ + F\text{-}MF_n \tag{3}$$

where E_n represents bonded and non-bonded electron pairs to a
central atom A below its maximum valency state.

In this paper we show that products potentially equivalent
to those in (2) and (3) are already known, although not always
recognised as such, and they could provide a graded series of
fluorinating agents. Some of our evidence is extrapolated
from recent studies we have made on chlorinations with the
corresponding chloro-compounds as well as from fluorination
studies.

The recent preparation of aryl iodine difluorides by direct
fluorination [3] makes readily available a potentially useful
range of fluorinating agents. These compounds should not be
considered in isolation. They are penultimate members of an

isoelectronic series of compounds all derivable by oxidative
addition to Lewis bases with dihalogens. (Figure 1). The
halogenating power of these compounds should follow a regular
pattern provided they can be made to react with a common
mechanism. It can be seen that ionized forms of these
compounds correspond with products of equations (2) and (3)
albeit with the positive charge located on A. Positive
halogen will be released if the ion can be reduced to the
precursor bases AE_n without intramolecular decomposition. It
should be possible to predict the relative halogenating
ability in the series. Firstly, halogenating power increases
across a Period with increase in Group number of atom A. All
known reactions confirm this trend.

$$Ph_3A + Ph_2SF_2 \rightarrow Ph_3AF_2 + Ph_2S \ (A = P,As,Sb) \qquad [4]$$

$$2Ph_3A + SF_4 \rightarrow 2Ph_3AF_2 + S \ (A = P,As) \qquad [5]$$

$$pXC_6H_4ACF_3 + XeF_2 \rightarrow pXC_6H_4AF_2CF_3 + Xe \ (A = S,Se) \qquad [6]$$

$$Ph_3P + XeF_2 \rightarrow Ph_3PF_2 + Xe \qquad [7]$$

$$Ph_2S + XeF_2 \rightarrow Ph_2SF_2 + Xe \qquad [7]$$

$$ArI + XeF_2 \rightarrow ArIF_2 + Xe \qquad [8]$$

Similarly we have quantitatively converted Ph_3A (A = P,As,Sb)
and Ph_2S to their dichlorides with $PhICl_2$.

Secondly, predictions about variations in halogenating
power as Groups are descended can be made by considering the
free energy gap between oxidised and reduced forms of the
reagents. These reduction couples can be approximated with
standard enthalpy values when similar reactions along
isoelectronic series are to be compared. The simplest example
would be oxidation of xenon with argon difluoride for which

$$-\Delta H^O(XeF_2 - Xe) > -\Delta H^O(ArF_2 - Ar)$$

Unfortunately there is no thermochemical data on aryl
substituted difluorides and we are obliged to use couples
derived from simple binary fluorides as a first approximation.
(Table 1). Our recent measurements which show $\Delta H_f^O(PhICl_2 -$
$PhI) \sim \Delta H_f^O(ICl_3 - ICl)$ confirm that phenyl substitution does
not alter a couple appreciably.

ELEMENT A FROM

GROUP

$\underline{V}$ $\underline{VI}$ $\underline{VII}$ $\underline{VIII}$
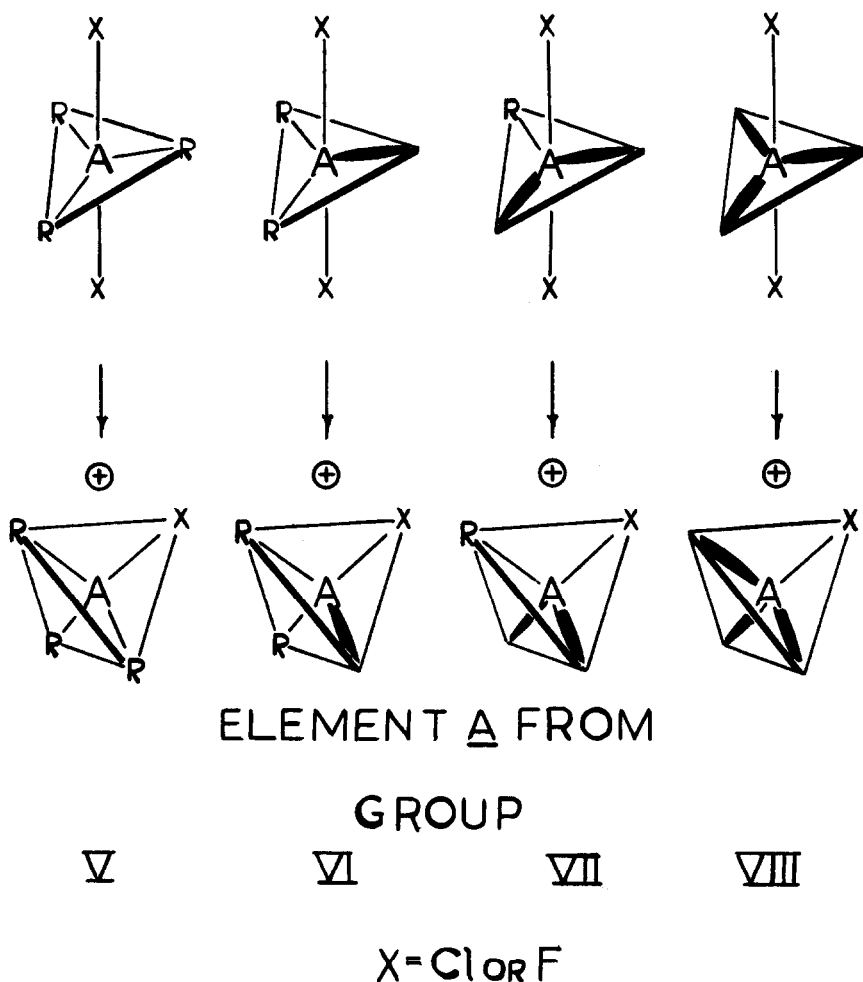
X = Cl OR F

Fig. 1. Isoelectronic halogenating reagents E_3AX_2 and
derived cations.

The smaller the enthalpy difference of the couple the greater
the fluorinating power. In Groups $\overline{VII}$ the well authenticated
reactivity series $ClF_5 > BrF_5 > IF_5$ and $ClF_3 > BrF_3$ parallels
the thermochemical trend. In Groups $\overline{VI}$ a similar decrease in
activity as the Group is descended is indicated by observations
on the stability of R_2ACl_2 (A = S,Se,Te) and salts in liquid
HCl [9]. However, in Groups $\overline{V}$ the order is reversed with
phosphorus compounds as the least reactive species.

TABLE 1

Enthalpy difference in fluorinating couples/Kjmol^{-1} of F_2.

H_f^o (oxidised form) $-$ H_f^o (reduced form)[a]				
Group $\underline{V}$	Group $\underline{V}$ [c]	Group $\underline{VI}$	Group $\underline{VII}$	Group $\underline{VIII}$
PF_5-PF_3	$Ph_3PF_{2(s)}-Ph_3P_{(s)}$	$SF_4-S_{(s)}$	ClF_3-ClF	–
-621	-601	-391	-101	
AsF_5-AsF_3	$Ph_3AsF_{2(s)}-Ph_3As_{(s)}$	$SeF_4-Se_{(s)}$	BrF_3-BrF	KrF_2-Kr
-409	-490	-401	-182	$+60$
SbF_5-SbF_3	$Ph_3SbF_{2(s)}-Ph_3Sb_{(s)}$	$TeF_7Te_{(s)}$	$IF_3^{b}\sim IF$	XeF_2-Xe
-494	-487	-486	-373	-107

[a] Gas phase values except where indicated as solids (s).

[b] Extrapolated value [12].

[c] Estimated as in text.

This conclusion can be supported if we estimate heats of formation of $Ph_3XF_{2(s)}$ (X = P,As,Sb) using the principle of isoelectronic heats [10], i.e. ΔH_f (Ph_3XF_2) $\equiv \Delta H_f$ (H_2O) + ΔH_f (Ph_3XO). The last have been measured from the following heats of reaction in benzene [11].

$$Ph_3X + t\text{-BuOOH} \to Ph_3XO + t\text{-BuOH} + \Delta H_r$$
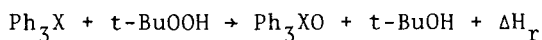
Hence values for fluorinating couples viz [ΔH_f(t-BuOH) + ΔH_r − ΔH_f(t-BuOOH) + ΔH_f(H_2O)] are independent of the large uncertainties in ΔH_f^o(Ph_3X). The smaller negative value for the AsF_5-AsF_3 couple compared with the $Ph_3AsF_2-Ph_3As$ couple reflects the comparative instability of AsF_5 (Figures 1 and 3 in reference [12]). The order in Group $\underline{V}$ is also supported by the ability of Ph_3AsF_2 to fluorinate Ph_3P.

A similar pattern emerges when other oxidations, such as iodine liberation from iodides or metal dissolution, are compared. Thus triphenyl arsenic dichloride and difluoride liberate iodine from potassium iodide unlike the corresponding

phosphorus and antimony dihalides. Phenyl iodine dichloride
in methyl cyanide solutions oxidises iron to ferric chloride,
whereas the latter chlorinates triphenyl stibine. Triphenyl
phosphine is chlorinated by cupric chloride, whereas copper
or cuprous chloride are oxidised by aryl iodine dichlorides.
The halogenating power of the species E_3AX_2 increases as the
basicity of E_3A decreases. Thus $(C_6F_5)_3SbCl_2$ and tris
(cyclohexyl) phosphorus dichloride oxidise potassium iodide
in contrast to the phenyl derivatives. Conversely they are
more difficult to halogenate.

Combination of periodic with group trends leads to the
following order of fluorinating power of difluorides
$Kr > Xe \sim Cl > Br > I > S > Se > Te \sim As \sim Sb > P$ where the ligands have been
omitted for brevity.

The halogenation mechanism with some of these reagents
has been conjectured from product distributions mainly when
conditions have been adjusted to favour radical mechanisms.
Such mechanisms have been suggested both for substitution and
addition reactions with phenyl iodine dichlorides [13,14]. A
dubious ionic mechanism was proposed in the presence of water
which involved a hypochlorite intermediate [15]. Such a
mechanism would not be feasible for the iodine difluorides
which readily hydrolyse to iodoso-compounds and hydrogen
fluoride. Previous studies on the thermal and photochemical
decomposition of $PhICl_2$, which produced similar product distri-
bution of o- and p-chloro-iodo and dichloro benzenes, were
interpreted as involving a major ionic pathway with $PhICl^+$
cations acting as chlorinating species [16]. It followed that
"Friedel-Craft" halides would enhance the electrophilic activity
as would acceptor solvents stablizing chloride ions and
encouraging cation dissociation. We have been unable to isolate
stable aryl iodonium monochloride salts in the solid state
because of rapid internal self-chlorination of the aryl group.
However, we can infer their presence in solution. Thus $PhICl_2$
can be conductometrically titrated with $SbCl_5$ in liquid sulphur
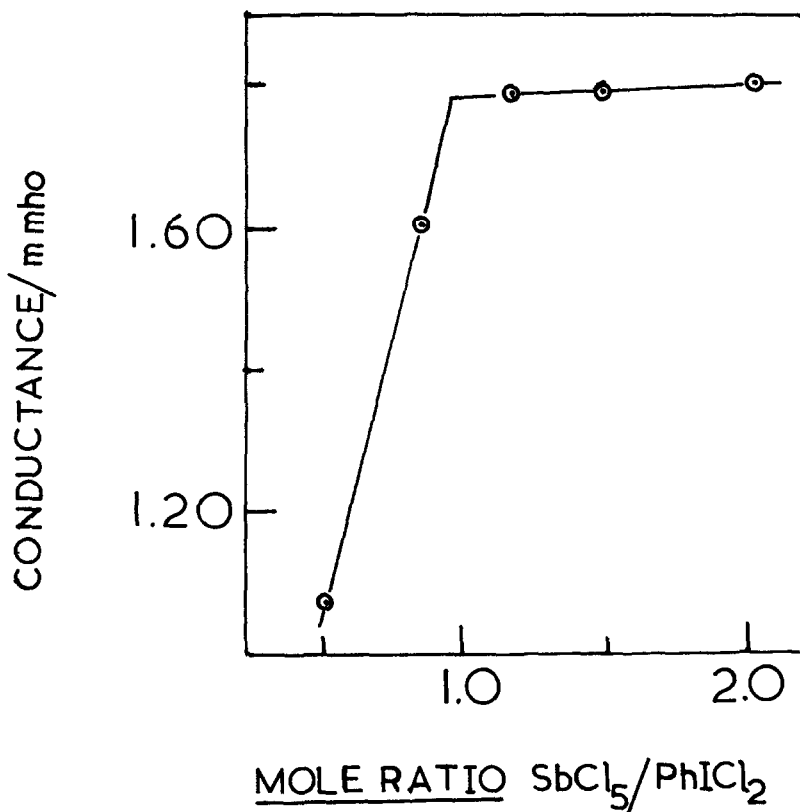dioxide to an equimolar end-point, suggesting an equilibrium

$$PhICl_2 + SbCl_5 \rightleftharpoons PhICl^+ + SbCl_6^-$$
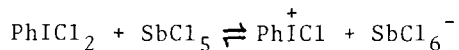
Fig. 2. Conductometric titration of PhICl$_2$ with SbCl$_5$ in
SO$_2$ at -20°C

The formation of such a cation is in agreement with the fact
that silver salts precipitate only <u>half</u> the available chlorine
from dilute solutions of aryl iodonium dichlorides in solvents
such as CH$_2$Cl$_2$, CHCl$_3$, Et$_2$O, or MeCN. Fortuitously the extent
of iodonium salt ionization can be deduced for the equilibrium

$$ArICl_2 + Ag PF_6 \xrightarrow{CH_3CN} Ag Cl_\downarrow + Ar\overset{+}{I}ClPF_6^-$$
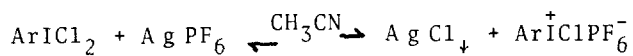
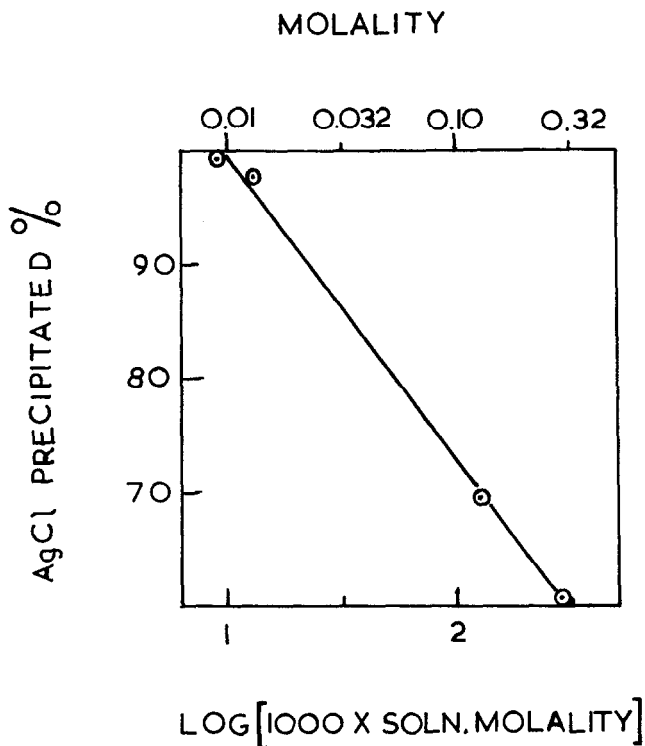because precipitation is incomplete in stronger solutions.

MOLALITY

Fig. 3. Completeness of Ag Cl precipitation from solutions
of Ag PF$_6$ + FC$_6$H$_4$ICl$_2$ in MeCN

The ionization ArICl$_2$ $\rightleftharpoons$ ArICl$^+$ + Cl$^-$ provides insufficient
chloride ion to exceed the solubility product for silver
chloride in methyl cyanide [17] which indicates a chloride ion,
and corresponding iodonium cation, concentration of about
$10^{-6.5}$ molar at 25°C. However precipitation is complete even
at high concentrations in solvents such as Et$_2$O, iso-Pr$_2$O
which are attacked by the cation. Sufficient chloride ion is
provided by ionization of the liberated hydrogen chloride. The
instability of iodonium (I) salts such as I$^+$(ClO$_4$)$^-$ and
I$^+$(F$_3$CCOO)$^-$ in ethers is similar [18]. Previous work by Alcock
and Waddington [19] requires re-interpretation because they
neglected the reactivity of PhICl$^+$ and similar cations as well
as concentration effects on precipitations.

Finally, the same products which are formed slowly in thermal or photo-decomposition are quickly formed when traces of stannous chloride are added to $PhICl_2$ in MeCN.

$$PhICl_2 + SnCl_2 \longrightarrow PhI + SnCl_4$$

$$PhICl_2 + SnCl_4 \xrightarrow{MeCN} Ph\overset{+}{I}Cl\ SnCl_5(MeCN)^-$$
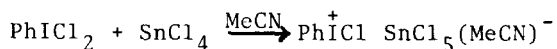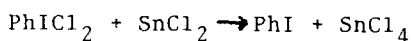
Similar ionizations are encountered with other members of the series including difluorides. Salts of Me_3PF^+ have been isolated [20] and Ph_3PCl_2 is almost a strong electrolyte in MeCN [21]. Fluorine exchange occurs in compounds R_2SeF_2. The rate of exchange, monitored by F^{19} n.m.r., increases in the order R = Me<Et<Pr and is independent of concentration but is greatly accelerated by traces of BF_3 or water (i.e. HF generated). These results support a rate-determining ionization $R_2SeF_2 \rightarrow R_2\overset{+}{Se}F + F^-$ [22]. Aromatic chlorination under Friedel-Craft conditions has been observed

$$Ph_2SeCl_2 + C_6H_6 \xrightarrow{AlCl_3} Ph_2Se + PhCl + HCl$$
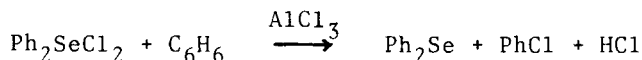
Ph_3SeCl has also been reported as a product [23]. Side chain bromination occurs as expected in the following decomposition

$$\begin{array}{c} Ph \\ \diagdown \\ \quad\quad SeBr_2 \rightarrow PhSeBr + PhCH_2Br \quad\quad\quad [23] \\ \diagup \\ PhCH_2 \end{array}$$
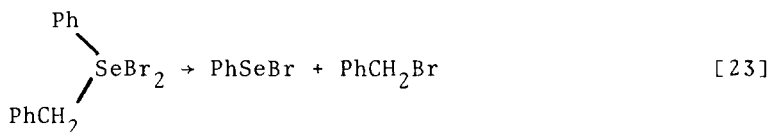
The introduction of tellurium into aromatics using $TeCl_4$ and $AlCl_3$ most likely involves phenyl tellurium chloronium ions although not formulated as such [24]. Catalytic fluorination with aryl iodonium difluorides and hydrogen fluorides [25], xenon difluoride and boron trifluoride etherate [26], and xenon difluoride-hydrogen fluoride [26,27] at or below room temperatures should also involve ionic intermediates. For example, norbornene and norbornadiene form 1, 3 and 1, 4 difluorinated products which can only result from Wagner-Meerwein rearrangements of carbonium-ion intermediates formed by addition of $ArIF^+$ or XeF^+ to an unsaturated 1, 2 bond. The corresponding alkylating iodonium ions e.g. $ArIMe^+$ are well authenticated by n.m.r. spectra in solution [28], KrF^+ in salts is one of the most powerful fluorinaters known.

To complete a spectrum of reagents we have now examined some properties of triphenyl arsenic difluoride (TAD) which we anticipated would be a very mild fluorinating agent. This, and the corresponding antimony compound, can be quantitatively prepared from aqueous solutions. It is barely ionized in methyl cyanide [29], or in sulphur dioxide, but is appreciably ionized in arsenic trifluoride, in which it is freely soluble, and also in the molten state. It can be conductometrically titrated with SbF_5 in arsenic trifluoride producing a similar titration curve to the $SbCl_5$ - $PhICl_2$ titration in SO_2 described above (Figure 2) and the interhalogen - Ph_3AsCl_2 titrations in MeCN [30]. Because SbF_5 is known to form a 1:1 adduct with AsF_3 which conducts in AsF_3 [31] and whose structure permits facile ionization into $AsF_2^+SbF_6^-$ [32] we interpret the titration as follows. Initially the conductivity increases as the more conducting salt $Ph_3AsF^+SbF_6^-$ is formed. After equivalence the conductivity levels off because dissociation of $AsF_2^+SbF_6^-$ is repressed by the common SbF_6^- ion. The titration is essentially a neutralization reaction in AsF_3.

$$Ph_3AsF^+AsF_4^- + AsF_2^+SbF_6^- \rightleftharpoons Ph_3AsF^+SbF_6^- + 2AsF_3$$
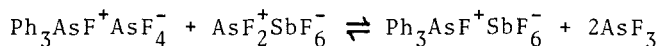
Solid T.A.D. reacted with excess PF_5 or BF_3 at room temperatures and 1:1 adducts were isolated after removing excess gas in vacuo. The infra-red, Ramman and ^{19}F n.m.r. spectra conclusively showed the presence of PF_6^- and BF_4^- anions. However, the PF_6^- salt had new broad i.r. bands at 2,270, 2,260 and 2,900 cm^{-1} in place of the sharp 3,095 and 3060 peaks of T.A.D. The 'H n.m.r. spectrum also contained a small subsidiary peak at 7.04 p.p.m. displaced from the main peak at 7.79 p.p.m. These results suggest an As-H bond in an arsonium cation which could arise from partial self-fluorination, i.e. $Ph_3AsF^+ \rightarrow (C_{18}H_{14}F)AsH^+$. Evidentally even the mildest reagents in the series are liable to undergo intramolecular fluorination and further evidence for this was obtained from a study of alkene fluorinations. These were followed in situ using n.m.r. T.A.D. solutions in CD_2Cl_2 did not react with cyclohexene, norbornene, norbornadiene or cyclo-octadiene (C.O.D.). However, addition of PF_5 brought about a reaction with C.O.D.
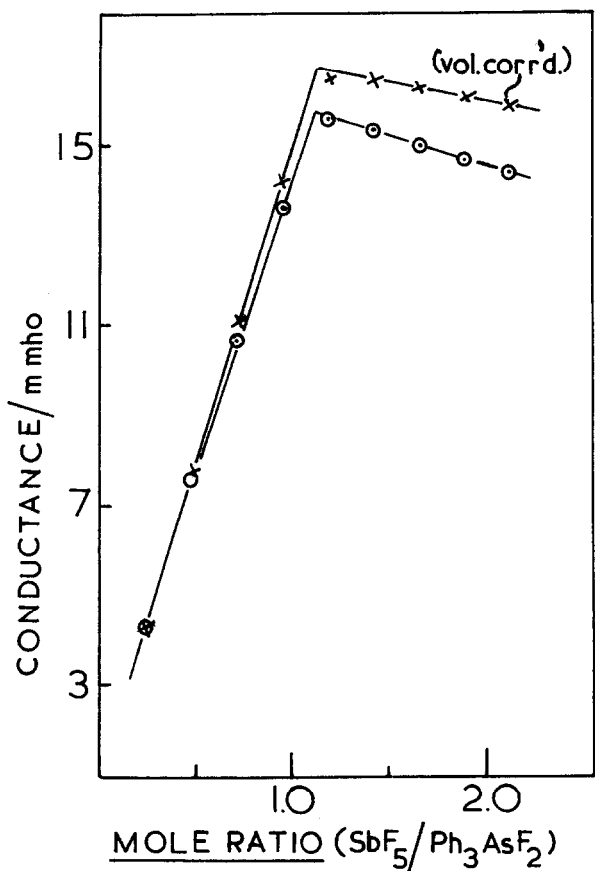
FIG. 4. Conductometric titration of Ph_3AsF_2 with SbF_5
     in AsF_3 at $25^\circ C$.

not due to PF_5 alone which does not react with C.O.D. in
CD_2Cl_2. Addition of traces of PF_5 to Ph_3AsF_2 in CD_2Cl_2
reduced the original ^{19}F signal of Ph_3AsF_2 at 8.14 p.p.m. and
a new signal due to PF_6^- appeared at -6.5 (d) p.p.m., together
with peaks at 5 and 16 p.p.m. with P-F coupling. The former
may be due to Ph_3AsF^+ since its intensity was a sixth of the
PF_6^- intensity. On adding C.O.D. to the PF_5-$PhAsF_2$ mixture
the -6.5 and 5 p.p.m. peaks decreased without affecting the
16 p.p.m. peak and a new broad peak appeared between the PF_6^-
doublet. Further new peaks at -86 and 74 p.p.m. grew as
reaction progressed. The former corresponds with an HF signal,
the latter to fluorinated C.O.D. The half time of reaction

was about 90 minutes. After the reaction the ^{1}H n.m.r. spectrum was examined. The 8.04 and 7.66 p.p.m. signals of Ph_3AsF_2 and the 5.53 and 2.32 p.p.m. signals from C.O.D. were replaced by 7.32 and 7.52 p.p.m. signals of Ph_3As and broad 3.4 and 1.6 p.p.m. signals of fluorine substituted C.O.D. (A small ^{19}F peak at 69 p.p.m. of CD_2F_2 due to solvent attack also appeared after a few hours.)

The preformed adduct $Ph_3AsF_2PF_5$ behaved differently as expected for a substance which had undergone some self substitution. In the original solution the ^{19}F doublet peak of PF_6^- was observed as with an $AgPF_6$ solution. Addition of C.O.D. caused the -86 and 74 p.p.m. peaks to appear but at a much slower rate than above. Similarly the $Ph_3AsF_2 \cdot BF_3$ adduct gave a BF_4^- signal and after reaction with C.O.D. a weak -86 p.p.m. signal.

The only reported organic fluorinations with Group $\underline{V}$ reagents are essentially thermal fluorinations of oxy-organic compounds with Ph_3PF_2. They are oxygen abstractions and not phosphorus$(\underline{V})$ reductions (e.g. $Ph_3PF_2 + ROH \rightarrow Ph_3PO + RF + HF$). A similar periodic treatment of difluoride reagents in this type of reaction will be made elsewhere, but it should be pointed out that conductivity measurements on Group $\underline{V}$ triphenyl dihalides in oxygentated solvents should be treated with caution. Part of the conductivity could be due to hydrogen halide liberated in oxygen abstractions rather than from simple dissociation of dihalides (see for example figures quoted in ref. [33]).

The tendency of the intermediate onium cations to undergo self-halogenation will increase with the more reactive reagents especially when reacting with more resistant substrates. This will reduce yields, quite apart from complicating product separation. Hence it is advisable to deactivate the reagents by ring substitution with electron withdrawing groups. Perfluorination is too drastic because perfluoro-alkyl and aryl iodides resist oxidative addition of chlorine [34,35] and $P(C_6F_5)_3$ is only slowly chlorinated [36]. (An attempt to catalyse the chlorination of C_6F_5I with $SbCl_5$ and Cl_2 led to fluorine displacement and conversion to hexachloro-benzene.) However, fluorine or halogen fluorides

are powerful enough oxidants to form $C_6F_5IF_2$ [34,35],
$C_6F_5BrF_2$ [38] and $C_6F_5ClF_2$ [39] albeit under vigorous con-
ditions. We have found that p-fluoro substitution is
sufficiently deactivating to prevent ring self-chlorination
without greatly delaying addition of chlorine. (The rate of
chlorination decreases in the order $CH_3 > H > F > NO_2$ for
p-substituted phenyl iodides. The last is only chlorinated
at an appreciable speed in the more polar solvents.) A
balance has to be struck between resistance to ring halogena-
tion and ease of preparation by oxidative halogenation.

Some experiments on the rate of loss of oxidising power
under conditions when the reagent is activated by cation
formers or deactivated by fluorine substitution are summarized
(Table 2). We interpret the losses as follows. The self
chlorination of $PhICl^+$ in reaction 1) (Table 2) is much slower
than its attack on the substrate PhI, reaction 2), presumably
because of the lower electron density in the cation ring.
Reaction 3) shows the effect of enhancement in ionization over
reactions 1) or 2) which were only catalysed by a weak catalyst
($SnCl_4$). Reactions 4) and 5), when compared with 2) and 3)
respectively, show the deactivation arising from p-fluoro
substitution. (It is assumed that the loss in oxidising power
varies linearly with time, although in practice the rate will
accelerate as more ArI is generated on reduction of $ArICl_2$.)

TABLE 2

Loss in oxidising power (Δ) of aryl iodonium
dichlorides in methyl cyanide solutions[a]

Reaction	Δ/%	x/hrs.	$\Delta \div x$
1) $PhICl_2$ + $SnCl_4$	5	3	1.7
2) $PhICl_2$ + $SnCl_4$ + PhI	20	1	20
3) $PhICl_2$ + $AgPF_6$ + PhI	100	0.25	400
4) $pFC_6H_4ICl_2$ + $SnCl_4$ + pFC_6H_4I	3	3	1
5) $pFC_6H_4ICl_2$ + $AgPF_6$ + pFC_6H_4I	10	1	10

a) $ArICl_2$ and $ArICl^+$ have the same oxidising power. The loss
is measured by the decrease in iodine liberated from aqueous
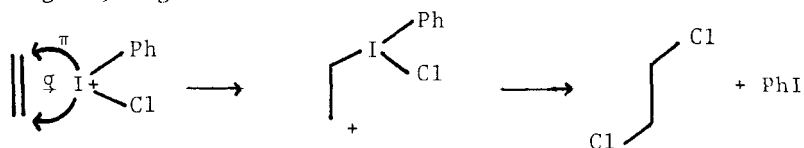potassium iodide.

We have carried out numerous chlorinations with the $FC_6H_4ICl_2$ - $SnCl_4$ combination. For example the chlorination of cyclohexene in $CDCl_3$ can be followed quantitatively by p.m.r. At a 2/1 mole ratio $FC_6H_4ICl_2/C_6H_{10}$ the exclusive conversion to trans 1, 2 dichlorocyclohexane was complete in seven hours. If $SnCl_4$ (0.2 mole) was added the reaction was complete in less than 0.1 hour.

Self-fluorination in aryl iodonium difluorides has not been described but probably occurs judging from the reported differences in 'melting points' and the low decomposition temperatures.
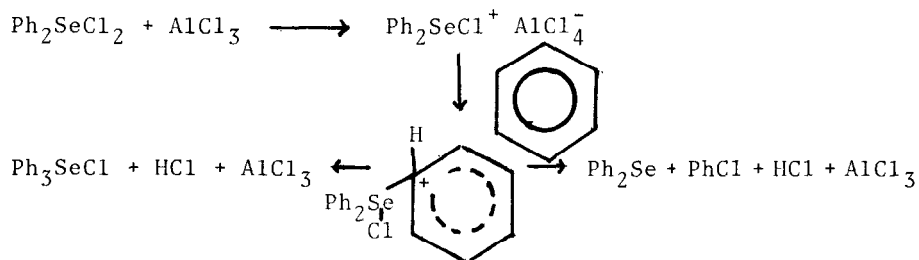
viz.

$$ \text{Ph–}IF_2 \longrightarrow \text{F–Ph–}I + HF $$
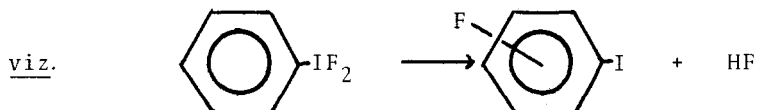
The process would accelerate because of salt formation $ArIF^+FHF^-$ especially if traces of water were present. The wide range of melting points reported for Ph_3PF_2 is also significant since it is also easily hydrolysed.

A common mechanism can be envisaged for all these reagents when catalysed by "Friedel-Craft" halides. An initial formation of low concentrations of monohalo-cations which will attach themselves to high electron density regions by a synergic combination of sigma-donor and pi-acceptor orbitals. The counter-anion will neutralize the combined cation, usually in a trans-position, followed by extrusion of the reduced form of the reagent, e.g. for addition:

and for substitution:

$$ Ph_2SeCl_2 + AlCl_3 \longrightarrow Ph_2SeCl^+ \ AlCl_4^- $$

$$ Ph_3SeCl + HCl + AlCl_3 \longleftarrow \quad \longrightarrow Ph_2Se + PhCl + HCl + AlCl_3 $$

Some general conclusions concerning the use of these isoelectronic reagents for fluorination can be drawn.

1) Aryl iodonium difluorides can be used for in-situ preparation of less reactive (potentially more selective) reagents according to the sequence given.

2) Reagents less reactive than XeF_2 or $ArIF_2$ should be used with more reactive substrates and reaction rates enhanced when required with the weaker Friedel-Craft halides.

3) The use of solvents which stabilize anions is an alternative method for enhancing reaction rates. SO_2 or HCl would be suitable for dichlorides, SO_2ClF, HF, CF_3COOH for difluorides. The range of solvents, which is restricted to those which resist halogenation, is greater with the less reactive reagents. Thus XeF_2 fluorinates CH_2Cl_2 and has to be used at low temperature [27].

4) Aromatic ring substituted reagents or possibly saturated ring systems are required to avoid excessive self-fluorination when fluorinating less reactive substrates.

EXPERIMENTAL

All solvents were purified and dried by standard procedures. Hygroscopic materials were handled in a dry-box under a positive pressure of dry nitrogen.

Preparation of Ph_3AsCl_2 using $PhICl_2$

Phenyl iodine dichloride (5.81 m.mol.) was suspended in MeCN (15 ml.) and triphenyl arsine (5.81 m.mol.) added. Initially a colourless solution formed and then a white precipitate. A solid residue of equivalent weight 376.5 remained after evaporation in vacuo at 10^{-4} mm. Hg for 2 hr. (Mol. wt. Ph_3AsCl_2 377.1). The chlorine content of this residue, found by hydrolsis with excess NaOH and back titration with HCl, was 9.3% (Calc. 9.4%). The hydrolysed product was extracted with CH_2Cl_2 and identified as Ph_3AsO. The distillate was identified as iodobenzene by density and refractive index.

Ph_3SbCl_2 was similarly made. However, in the Ph_3PCl_2 preparation more extensive pumping was required and formation of an intermediate,

possibly $Ph_3P \to I \underset{Cl}{\overset{Ph}{\diagup}} Cl^-$, is indicated. (Note $\equiv P \to I^+$ is

isoelectronic with the ylide $\equiv P = CH_2$).

Chlorination of pentafluoroiodo-benzene

Chlorine (6.15 g.) was condensed into C_6F_5I (6.07 g.) in
MeCN (10 ml.) and sealed in a 100 ml. ampoule. After 7 days
at room temperature the C_6F_5I was recovered unchanged.

C_6F_5I (7.31 m.mol.) was mixed with $SbCl_5$ (9.53 m.mol.) and
Cl_2 (38.0 m.mol.) condensed. A yellow solid formed before the
liquid melted. After standing overnight the residue was pumped
down to a white solid. White crystals isolated from the solid
after washing with aqueous tartaric acid, melted at 229° with
sublimation and were identified as C_6Cl_6 mass spectrometrically

Reaction with metals

Reduction potentials relative to metal chloride/metal
couples were assessed by showing that iron dissolved in methyl
cyanide solutions of $ArICl_2$. The presence of ferricchloride in
solution was identified by the twin absorption bands at 316 and
364 mμ. Similarly, nickel dissolved to $NiCl_2$, copper to a
mixture of CuCl and $CuCl_2$, tin to $SnCl_4$ and mercury to $HgCl_2$.

Aryl iodonium monochloride salt formation

Numerous attempts to isolate solid salts by mixing
$FC_6H_4ICl_2$ and silver salts of strong acids CF_3COOH, CF_3SO_3H,
HPF_6 and $HReO_4$) in solution failed. In all experiments 1 mole
of silver chloride was precipitated quantitatively, but, on
evaporation of the filtrates, the solid residues liquified more
or less readily. Examination of one of these liquids by gas
chromatography showed the same product content as in the resi-
dues from thermal or photochemical decompositions of $FC_6H_4ICl_2$.

Conductometric titration of phenyl iodine dichloride

A solution of $PhICl_2$ in liquid SO_2 (0.0229 molal) was
titrated with a solution of $SbCl_5$ in SO_2 (0.0518 molal) at

-20°C to give an end-point close to the 1:1 mole ratio
(Figure 2). (Tungsten rod electrodes were used to avoid
dissolution of platinum electrodes and any conducitivity arising
from platinum chloride in solution.) The solvent conductivity
was 7 x 10^{-8} $ohm^{-1}cm^{-1}$ and the equivalent conductivity at the
end-point was 34 $ohm^{-1}cm^{2}$.

Precipitation of silver chloride from $FC_6H_4ICl_2$ solutions

A stock solution of $AgPF_6$ (0.0497 molal) was prepared by
mixing equimolecular amounts of $AgNO_3$ and KPF_6 in MeCN and
filtering off the quantitative precipitate of KNO_3. A similar
stock solution of $FC_6H_4ICl_2$ (0.0495 molal) was also made.
Aliquots from each solution were mixed and diluted to fixed
volumes. The amount of chloride precipitated after
equilibrating for at least a day is plotted as a function of
molality (Figure 3). Precipitation is incomplete in MeCN
solutions stronger than about 0.008 molal.

Solvent oxidation by $FC_6H_4ICl^+$ ions

Silver triflate ($AgSO_3CF_3$) and FC_6H_4ICl solutions in ether
(0.065 M) were mixed and the oxidising power which remained
after fixed times was determined iodometrically after addition
of aqueous KI. The fractional oxidising power left was 0.608 at
0.33 hr, 0.509 at 0.67 hr, 0.192 at 2.33 hr, and 0.046 at
5.16 hr. The decay is approximately first order. That the
solvent was attacked without self-chlorination of the ion was
shown by the sole isolation of FC_6H_4Cl from the organic material
after titration.

A similar experiment with silver trifluoroacetate showed a
slower attack on diethyl ether as expected from the weaker
acidity of CF_3COOH compared with CF_3SO_3H.

Preparation of Ph_3AF_2 (A=As,Sb)

Triphenyl arsine (6 g. 0.02 moles) was stirred with H_2O_2
(20 ml. of 30% w/v) and HF (20 ml. of 40% w/v) in a covered
P.T.F.E. beaker held just below boiling for a few hours or over-
night. Initially the arsine liquefied under the water and then

deposited a solid. This was filtered through a polythene
sinter after cooling to room temperature, washed with water and
dried in vacuo. Consistent yields of 98% were obtained, m.pt.
135.5^{o}C. The oxidising power was found from the iodine
liberated on adding acidified KI to the sample in CH_2Cl_2 (Found
1.99 e mol.$^{-1}$). The presence of two fluorines in the compound
was confirmed mass spectrometrically by the successive loss of
two 19 masses from the parent ion $Ph_3AsF_2^+$ and fragment ions
$Ph_2AsF_2^+$, $PhAsF_2^+$ and AsF_2^+.

Triphenyl antimony difluoride (m.pt. 117°C) was made in an
analogous fashion in 97% yields on the 1-10 g. scale. This
compound did not oxidise KI. It was analysed for fluorine by
heating with aqueous NaOH at 130° and titrating fluoride with
cerous nitrate (Found F 9.8%; calc. 9.7%). Its mass spectrum
was similar to that from Ph_3AsF_2 except for extra lines of
antimony isotopes. Tris (pentafluorobenzene) arsine cannot be
fluorinated by this technique because it is not oxidised with
this strength of peroxide.

Fluorine transfer reactions

Equi-molar amounts of the two substances were sealed in
glass tubes, held at 130°C overnight and then cooled at room
temperature until solid. I.r. spectra (KBr discs) showed no
reaction between $Ph_3AsF_2+Ph_2Sb$, $Ph_3SbF_2+Ph_3As$, and $Ph_3SbF_2+SbF_3$.
The reaction $Ph_3AsF_2+Ph_3P{\rightarrow}Ph_3As+Ph_3PF_2$ was confirmed by the
appearance of characteristic i.r. peaks at 310, 470 and 476 for
Ph_3As and the disappearance of peaks at 490 and 510 for Ph_3P
and 273, 294, 323, 364, 373 and 516 cm^{-1} for Ph_3AsF_2. New
peaks at 542, 561 and 722 cm^{-1} were presumably due to Ph_3PF_2.

Conductivity measurements

Melt conductivities were made in a miniature cell (0.4 ml.
capacity with tungsten electrodes) in which the solid was melted
in vacuo and then held under dry nitrogen. All conductivities
were measured on a Wayne-Kerr auto-transformer bridge (B641)
Ph_3AsF_2 and Ph_3SbF_2 had conductivities at their melting points
of 6.8 x 10^{-5} and 8.2 x 10^{-9} ohm^{-1}cm^{-1} respectively with posi-
tive temperature coefficients. The former is about ten times

as conducting as AsF_3 at $25^\circ C$. The stability of the difluorides was checked by holding them molten in a P.T.F.E. vessel with limited access to atmosphere at $150^\circ C$ for 10 hours. No weight change or alteration in i.r. spectra was observed.

The conductivities in different solvents are compared in

TABLE 3

Molar conductivities (Λ) of Ph_3AsF_2 solutions at $25^\circ C/ohm^{-1}cm^2mol^{-1}$

Solvent	Molarity	Λ
SO_2	0.0119	0.42
	0.0207	0.63
*MeCN	0.01	0.3
**AsF_3	0.0064	17.5
	0.0145	12.8
	0.0286	9.4
	0.0541	6.9
	0.0805	5.7

*Ref [29]
**Solvent conductivity 7.9×10^{-6} $ohm^{-1}cm^{-1}$
 is less than reported previously [31]

Conductimetric titration of Ph_3AsF_2

A solution of Ph_3AsF_2 in AsF_3 (8.51 ml. of 0.0805 M) was titrated with a solution of SbF_5 in AsF_3 (1.62 M) by adding 0.100 ml. increments of the latter under dry nitrogen. The corrected curve has been adjusted by a factor $(8.51 + V)/8.51$ where V is the volume of SbF_5 solution added (Figure 4).

Ph_3AsF_2 - Lewis acid adducts

Ph_3AsF_2 (1 g.) was exposed to a five fold excess of PF_5 or BF_3 (5-10 atmos.) at room temperature. The excess gas was removed in vacuo (0.01 torr.). With PF_5 the mole ratio reached 0.75 in 16 hr. and 1.00 in 5 days; with BF_3 the 1:1 ratio was reached in 16 hr. The PF_5 adduct had the same oxidising power as Ph_3AsF_2 towards KI. The i.r. spectrum had new peaks at 560 and 840 (broad) (cf. 560 and 830 in KPF_6) and broad peaks at 2270, 2760 and 2900 cm^{-1}. The 516 cm^{-1} peak in Ph_3AsF_2 was absent (ν As-F). Only minor changes occurred in the rest of the spectrum.

Reactions with olefins

A slight excess of olefin was added to 30 mg. of reagent in 0.3 ml. of CD_2Cl_2 or CH_2Cl_2 in the n.m.r. tube and the ^{19}F or ^1H spectra, p.p.m. relative to CF_3COOH and T.M.S. respectively, observed with time.

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