Electrophilic Fluorination of Aryltrialkyltin Derivatives with Caesium Fluoroxysulphate

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Cleavage of aryltrialkylstannanes by caesium fluoroxysulphate provides an efficient route for selective fluorination of aromatic rings.

The reaction of fluorine with aromatic compounds is frequently non-selective and can lead to oxidation or fragmentation of the substrate,[1] therefore the development of new reagents for selective aromatic fluorination is of keen interest. Electrophilic fluorinating agents, *e.g.* CF_3OF and $MeCO_2F$, are alternatives to the classical Balz–Schiemann reaction. Rozen and co-workers have shown that fluorination with $MeCO_2F$ requires strongly electron-donating substituents on the aromatic ring.[2] Canadian workers have described the preparation of ^{18}F-labelled aryl fluorides by cleavage of aryl–metal bonds (metal = Sn, Pb, Ge, Si, Hg, and Tl) with $MeCO_2F$ and F_2, both labelled with ^{18}F.[3] Electrophilic radiofluorination with these reagents of aryltrimethylsilanes[4] and fluorination of arylmercurials with $MeCO_2F$[5] have recently been described by other groups, and we have reported fluorination of aryltin and arylmercury derivatives using CF_3OF.[6] Caesium fluoroxysulphate, $CsSO_4F$, has also been developed as a reagent for electrophilic fluorination of alkenes, enol acetates, and uracil derivatives,[7] although direct fluorination of aromatic molecules by $CsSO_4F$ tends to be non-selective.[8] We now report that $CsSO_4F$ cleaves aryltrimethylstannanes selectively to yield fluorobenzene derivatives in high yield under mild conditions. This is the first study concerned with the cleavage of aryl–metal bonds with $CsSO_4F$.

$$XC_6H_4SnR_3\text{-}p \;(\mathbf{1}) \longrightarrow XC_6H_4F\text{-}p \;(\mathbf{2})$$

			% Yield (g.c.–mass spec.)
a;	X = H;	R = Me	69
b;	X = Me;	R = Me	86
c;	X = OMe;	R = Me	79
d;	X = Cl;	R = Me	87
e;	X = OMe;	R = Bu^n	42
f;	X = Me;	R = Bu^n	11
g;	X = H;	R = C_6H_{11}	0
h;	X = OMe;	R = C_6H_{11}	0

A mixture of $CsSO_4F$ (1 mol. equiv.) and aryltrimethylstannane derivative (**1a—d**) (1.5 mol. equiv.) in acetonitrile was stirred at room temperature for 15 h; insoluble products were removed by filtration to yield a solution of the fluorocarbon product, (**2a—d**), which was characterised by comparison with authentic samples using ^{19}F n.m.r. spectroscopy and g.c.–mass spectral analysis. Cleavage of the Me_3Sn group by $CsSO_4F$ was efficient in all cases but replacement of Me_3Sn by Bu^n_3Sn, (**1e,f**) resulted in lower yields of products, while replacement by tris(cyclohexyl)tin groups (**1g,h**) led to no detectable formation of fluoroaromatic product. This may be due to the reduced solubility of the bulkier organostannane derivatives (**1e—h**), even in mixed $MeCN/CHCl_3$ solvent systems, and steric hindrance to the approach of $CsSO_4F$ could also be a relevant factor. Reactions of compounds (**1a—f**) with $CsSO_4F$ are all *regiospecific*; no difluorinated products were observed by g.l.c. under conditions where 1% would be clearly detectable.

Considering the ease with which $SnMe_3$ groups can be attached to aromatic rings and the fact that $CsSO_4F$ can be readily prepared we have described a highly efficient, regioselective approach to the synthesis of fluorobenzene derivatives.

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