

# Rearrangement and radical mediated decarboxylation of trimethylsilyl benzoates using xenon difluoride

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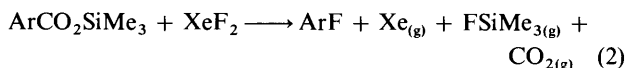
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**Treatment of trimethylsilyl benzoates **1** with xenon difluoride in CH<sub>2</sub>Cl<sub>2</sub> or C<sub>6</sub>F<sub>6</sub> results in a novel ester rearrangement and formation of aryl fluoroformates **2**: rearrangement is not observed in MeCN solution in which the main products are arenes formed via the corresponding aryl radical.**

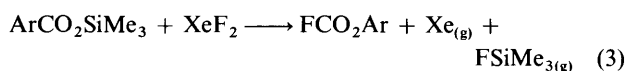
The reactions of Xe<sup>II</sup> and I<sup>III</sup> reagents are attracting increasing interest in organic synthesis but the mechanisms by which these hypervalent reagents react remain ill-defined.<sup>3</sup> We have previously described the clean formation of arylfluorides by treatment of aryltrimethylsilanes with xenon difluoride [eqn. (1)].<sup>4</sup> Attractive features of



this approach are the generation of by-products that are volatile and inert and the absence of HF in the reaction mixture. Alkanoic acids are known to react with XeF<sub>2</sub> to form alkylfluorides in good yield.<sup>1,5,6</sup> Aromatic carboxylic acids, however, do not appear to undergo a similar fluorodecarboxylation but there is limited information available on their mode of reaction with XeF<sub>2</sub>: benzoic acid has been reported to give benzoyl fluoride (20%) but no other products were identified.<sup>6</sup> We now report an investigation of trimethylsilyl benzoates **1** which was initiated in order to explore potentially useful uncatalysed (HF) fluorodecarboxylations having the stoichiometry shown in eqn. (2). We have

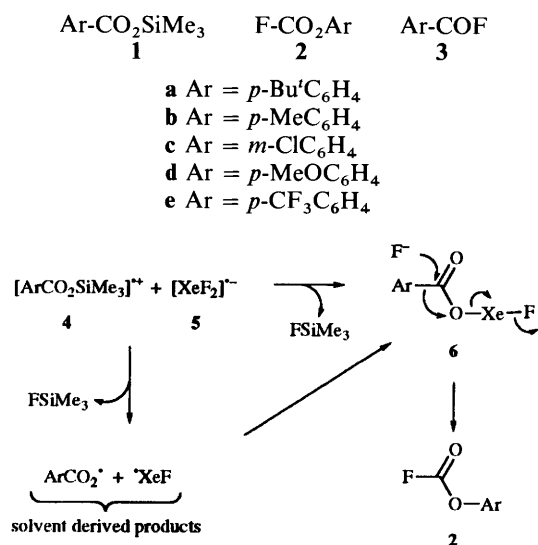


found that the course of reaction is solvent-dependent and the influence of the solvent provides further information on the mode of reaction of XeF<sub>2</sub> with organic substrates. In CH<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>F<sub>6</sub> solutions the major product is an aryl fluoroformate [eqn. (3)] and, as far as we are aware, this is the first example of



an ester rearrangement of the general type (R<sup>1</sup>CO<sub>2</sub>R<sup>2</sup> → R<sup>3</sup>CO<sub>2</sub>R<sup>1</sup>).

In a typical reaction, trimethylsilyl 4-*tert*-butylbenzoate **1a** was stirred with two equiv. of XeF<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temp. <sup>1</sup>H NMR monitoring showed quantitative formation of fluorotrimethylsilane (δ<sub>H</sub> 0.20, d, *J* 7.3 Hz) together with formation of 4-*tert*-butylphenyl fluoroformate **2a** (51%; δ<sub>H</sub> 1.33, s). GC-MS analysis of the reaction mixture confirmed the structures of the major (**2a**) and minor products (Table 1). The fluoroformate **2a** was isolated (26%) by distillation under reduced pressure and found to be identical with an authentic sample (bp 103–104 °C at 17 mmHg) prepared by reaction of 4-*tert*-butylphenyl 1-chloroethyl carbonate with potassium fluoride.<sup>7</sup> Furthermore, treatment of the crude reaction mixture with sodium methoxide in methanol gave 4-*tert*-butylphenyl methyl carbonate (38%) as a pale yellow oil, which



Scheme 1

was identical with an authentic sample prepared from methyl chloroformate and 4-*tert*-butylphenol. The constitution of the product **2a**, which requires a migration of the aryl group from C to O, is therefore firmly established.

Similar rearrangements were observed using the trimethylsilyl esters **1b–e** and the results are summarised in Table 1. By comparing yields determined by both NMR and GC-MS analysis we have found quantitative GC to be a reliable measure of the composition of the reaction mixtures. With the exception of the *m*-chloro derivative **1c**, formation of the corresponding arylfluoride **3** also occurs in low yield. Inspection of Table 1 reveals that the products **2** and **3** are always accompanied by varying yields of products formed by reaction of the solvent with either an aryl radical (Ar•) or an aryloxy radical (ArCO<sub>2</sub>•). Only low yields of arylfluorides were recorded. We have investigated a variety of solvents including C<sub>6</sub>F<sub>6</sub> and MeCN (Table 1) but an ideal solvent that does not participate in the reactions has not been found. When, for comparison, methyl 4-methylbenzoate (*p*-MeC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me) was allowed to react with XeF<sub>2</sub> in C<sub>6</sub>F<sub>6</sub> under identical conditions only methyl 3-fluoro-4-methylbenzoate (50%) was formed: the remainder of the starting material was unchanged. Rearrangement products were detected when aromatic carboxylic acids (ArCO<sub>2</sub>H) were used but the reaction mixtures were much more complex, possibly due to the presence of HF.

The pathways shown in Scheme 1 account for the observed products. One-electron oxidation of the ester **1** by XeF<sub>2</sub> leads to the radical cation **4** and the radical anion **5**. The latter can be expected to rapidly dissociate to F<sup>-</sup> and FXe• or F• + Xe. Fluorodesilylation of the radical cation **4** leads directly to an aryloxy radical (ArCO<sub>2</sub>•). The ion-pair (**4** + **5**) may collapse with loss of Me<sub>3</sub>SiF to form the fluoroxenon ester **6**, which may alternatively be formed by combination of an aryloxy radical and FXe• (Scheme 1). Fluoride substitution of the alkyl group of a fluoroxenon ester (RCO<sub>2</sub>XeF → RF) has been implicated in

**Table 1** Fluorodesilylation of trimethylsilyl benzoates **1** using xenon difluoride

Entry	Substrate	Solvent <sup>c</sup>	Product distribution (%) determined by GC-MS <sup>a,b</sup>										
			2	3	ArX					ArCO <sub>2</sub> Y			
					H	F	Cl	C <sub>6</sub> F <sub>7</sub>	C <sub>6</sub> F <sub>5</sub>	H	Ar	C <sub>6</sub> F <sub>7</sub>	CH <sub>2</sub> Cl
1	<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	50.5 <sup>d</sup>	9.9	4.7	4.6	8.1	—	—	14.7	2.6	—	4.9
2	<b>1b</b>	CH <sub>2</sub> Cl <sub>2</sub>	28.1	4.4	16.6	8.3	7.5	—	—	24.4	7.8	—	3.0
3	<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	28.0	0	27.3	0	4.2	—	—	8.5	25.2	—	2.6
4	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub>	68.3	8.9	0	4.4	0	—	—	0	0	—	0
5	<b>1e</b>	CH <sub>2</sub> Cl <sub>2</sub>	0	0	0	0	2.0	—	—	>90	0	—	0
6	<b>1a</b>	C <sub>6</sub> F <sub>6</sub>	37.5	24.5	—	0	—	9.1	0	—	0	0	—
7	<b>1b</b>	C <sub>6</sub> F <sub>6</sub>	37.1	8.8	—	0	—	3.4	5.2	—	0	0	—
8	<b>1c</b>	C <sub>6</sub> F <sub>6</sub>	37.3	0	—	0	—	14.4	6.9	—	0	3.8	—
9	<b>1d</b>	C <sub>6</sub> F <sub>6</sub>	51.8	12.9	—	0	—	0	7.8	—	0	2.3	—
10	<b>1e</b>	C <sub>6</sub> F <sub>6</sub> <sup>e</sup>	2.0	2.0	—	0	—	0	0	0	0	0	—
11	<b>1a</b>	MeCN	0	4.5	78.5	0	—	—	—	0	0	—	—
12	<b>1b</b>	MeCN	0	0	55.0	2.9	—	—	—	0	0.9	—	—
13	<b>1d</b>	MeCN	0	11.5	38.4	0	—	—	—	0	50.4	—	—
14	<b>1e</b>	MeCN	0	2.5	83.5	0	—	—	—	0	0	—	—

<sup>a</sup> Mixtures were analysed using a Hewlett-Packard 5890 GC directly coupled to a 5970B MSD controlled by a Hewlett-Packard Series 300 computer with an HP59970c Chemstation. <sup>b</sup> Unless indicated the remaining products were formed in low yield and were of no special significance. <sup>c</sup> Reactions were carried out using ca. 0.15 mol dm<sup>-3</sup> solutions of substrate under an N<sub>2</sub> atmosphere and at room temperature. <sup>d</sup> 51% by <sup>1</sup>H NMR monitoring of the reaction mixture. <sup>e</sup> Products were mainly of the type (Ar-C<sub>6</sub>F<sub>6</sub>)<sub>2</sub> and (ArCO<sub>2</sub>-C<sub>6</sub>F<sub>6</sub>)<sub>2</sub>.

the fluorodecarboxylation of alkanolic acids.<sup>1</sup> In the case of the proposed aryl analogue **6** migration of the aryl substituent (**6** → **2**) is a plausible alternative mode of reaction. A tetrahedral intermediate [ArCF(OTMS)OXeF], analogous to the Criegee intermediate in Baeyer-Villiger oxidations, can also be envisaged. When MeCN is used as solvent the absence of rearrangement products **2** and the high yields of arenes ArH (Table 1) are significant. The arenes must result from decarboxylation of the aryloxy radicals and subsequent reaction of the resulting aryl radical with the solvent. Under these conditions we assume that a similar rapid reaction of the radical anion **5** or FXe<sup>•</sup> with solvent precludes formation of the intermediate **6** (Scheme 1). In MeCN aryl fluorides **3** continue to be formed suggesting that these products are produced *via* a different, non-radical pathway.

We have recently reported a new rearrangement of amidines using diacetoxyiodo(benzene).<sup>8</sup> The closely related rearrangement reported here (**1** → **2**) using XeF<sub>2</sub> is a further example of the ability of hypervalent reagents to induce *umpolung* behaviour, in this case the transformation of the oxygen atom of an ester carbonyl group into an electron-deficient centre. In this context it is interesting to note recently described analogous rearrangements of aldehydes and ketones using XeF<sub>2</sub>.<sup>9</sup>

## Experimental

The products described were obtained using the following typical procedures.

### 4-*tert*-Butylphenyl fluoroformate **2a**

(a) From trimethylsilyl 4-*tert*-butylbenzoate **1a**. In a glove box (dry N<sub>2</sub> atmosphere) xenon difluoride (0.25 g, 1.48 mmol) was added to a solution of trimethylsilyl 4-*tert*-butylbenzoate<sup>10</sup> (0.19 g, 0.74 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) at room temperature. The mixture was stirred for 3 h, after which the major product (51% by NMR) was isolated by evaporation and distillation of the residue under reduced pressure to yield compound **2a** (0.31 g, 26%), which was shown to be identical with an authentic sample prepared from 4-*tert*-butylphenyl 1-chloroethyl carbonate.

(b) From 4-*tert*-butylphenyl 1-chloroethyl carbonate. A mixture of 4-*tert*-butylphenyl 1-chloroethyl carbonate<sup>7</sup> (6.49 g, 25 mmol), potassium fluoride (4.40 g, 75 mmol) and 18-crown-6

(0.34 g, 5 mol%) was stirred for 2 h at 80 °C and at a pressure of 17 mmHg. Then the mixture was distilled under reduced pressure (liquid N<sub>2</sub>-cooled receiver flask) to give a colourless liquid identified as 4-*tert*-butylphenyl fluoroformate **2a** (2.0 g, 40%), bp 103–104 °C (17 mmHg). A sample was further purified by short path distillation (50 °C at 0.5 mmHg) (Found: M<sup>+</sup>, 196.0895. C<sub>11</sub>H<sub>13</sub>FO<sub>2</sub> requires M, 196.0900);  $\nu_{\max}$ (neat)/cm<sup>-1</sup> 2964, 1836 and 1236;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.32 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.32 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 7.17 (2 H, dd, *J* 8.8 and 1.0, ArH) and 7.44 (2 H, d, *J* 8.8 Hz, ArH);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 31.27, 34.57, 119.36, 126.74, 143.90 (d, *J* 286 Hz), 148.24 and 150.29;  $\delta_{\text{F}}$ (CDCl<sub>3</sub>) -15.90; *m/z* 196 (M<sup>+</sup>), 181 (100), 165, 153, 115, 91 and 47.

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