Rearrangement and radical mediated decarboxylation of trimethylsilyl benzoates using xenon difluoride

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Treatment of trimethylsilyl benzoates 1 with xenon difluoride in CH_2Cl_2 or C_6F_6 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^{II}[1] and I^{III}[2] reagents are attracting increasing interest in organic synthesis but the mechanisms by which these hypervalent reagents react remain ill-defined.[3] We have previously described the clean formation of arylfluorides by treatment of aryltrimethylsilanes with xenon difluoride [eqn. (1)].[4] Attractive features of

$$ArSiMe_3 + XeF_2 \longrightarrow ArF + Xe_{(g)} + FSiMe_{3(g)} \quad (1)$$

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_2 to form alkylfluorides in good yield.[1,5,6] 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_2: benzoic acid has been reported to give benzoyl fluoride (20%) but no other products were identified.[6] 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

$$ArCO_2SiMe_3 + XeF_2 \longrightarrow ArF + Xe_{(g)} + FSiMe_{3(g)} + CO_{2(g)} \quad (2)$$

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_2 with organic substrates. In CH_2Cl_2 and C_6F_6 solutions the major product is an aryl fluoroformate [eqn. (3)] and, as far as we are aware, this is the first example of

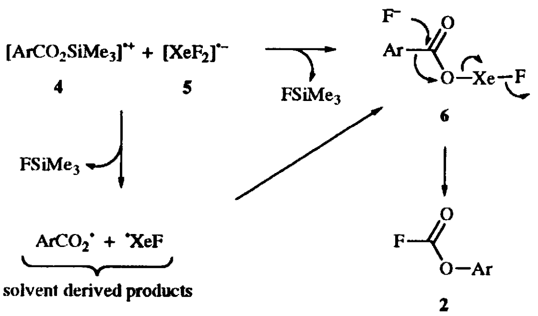
$$ArCO_2SiMe_3 + XeF_2 \longrightarrow FCO_2Ar + Xe_{(g)} + FSiMe_{3(g)} \quad (3)$$

an ester rearrangement of the general type ($R^1CO_2R^2 \longrightarrow R^3CO_2R^1$).

In a typical reaction, trimethylsilyl 4-*tert*-butylbenzoate **1a** was stirred with two equiv. of XeF_2 in CH_2Cl_2 at room temp. ^1H NMR monitoring showed quantitative formation of fluorotrimethylsilane (δ_H 0.20, d, J 7.3 Hz) together with formation of 4-*tert*-butylphenyl fluoroformate **2a** (51%; δ_H 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.[7] 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 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.

$Ar\text{-}CO_2SiMe_3$	$F\text{-}CO_2Ar$	$Ar\text{-}COF$
1	**2**	**3**

a Ar = $p\text{-}Bu^tC_6H_4$
b Ar = $p\text{-}MeC_6H_4$
c Ar = $m\text{-}ClC_6H_4$
d Ar = $p\text{-}MeOC_6H_4$
e Ar = $p\text{-}CF_3C_6H_4$



Scheme 1

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 aroylfluoride **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 aroyloxyl radical ($ArCO_2{}^\bullet$). Only low yields of arylfluorides were recorded. We have investigated a variety of solvents including C_6F_6 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 ($p\text{-}MeC_6H_4CO_2Me$) was allowed to react with XeF_2 in C_6F_6 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 ($ArCO_2H$) 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_2 leads to the radical cation **4** and the radical anion **5**. The latter can be expected to rapidly dissociate to F^- and FXe• or F• + Xe. Fluorodesilylation of the radical cation **4** leads directly to an aryloxyl radical ($ArCO_2{}^\bullet$). The ion-pair (**4** + **5**) may collapse with loss of Me_3SiF to form the fluoroxenon ester **6**, which may alternatively be formed by combination of an aroyloxyl radical and FXe• (Scheme 1). Fluoride substitution of the alkyl group of a fluoroxenon ester ($RCO_2XeF \longrightarrow RF$) has been implicated in

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

			Product distribution (%) determined by GC–MS[a,b]										
					ArX					$ArCO_2Y$			
Entry	Substrate	Solvent[c]	**2**	**3**	H	F	Cl	C_6F_7	C_6F_5	H	Ar	C_6F_7	CH_2Cl
1	**1a**	CH_2Cl_2	50.5[d]	9.9	4.7	4.6	8.1	—	—	14.7	2.6	—	4.9
2	**1b**	CH_2Cl_2	28.1	4.4	16.6	8.3	7.5	—	—	24.4	7.8	—	3.0
3	**1c**	CH_2Cl_2	28.0	0	27.3	0	4.2	—	—	8.5	25.2	—	2.6
4	**1d**	CH_2Cl_2	68.3	8.9	0	4.4	0	—	—	0	0	—	0
5	**1e**	CH_2Cl_2	0	0	0	0	2.0	—	—	> 90	0	—	0
6	**1a**	C_6F_6	37.5	24.5	—	0	—	9.1	0	—	0	0	—
7	**1b**	C_6F_6	37.1	8.8	—	0	—	3.4	5.2	—	0	0	—
8	**1c**	C_6F_6	37.3	0	—	0	—	14.4	6.9	—	0	3.8	—
9	**1d**	C_6F_6	51.8	12.9	—	0	—	0	7.8	—	0	2.3	—
10	**1e**	C_6F_6[e]	2.0	2.0	—	0	—	0	0	0	0	0	—
11	**1a**	MeCN	0	4.5	78.5	0	—	—	—	0	0	—	—
12	**1b**	MeCN	0	0	55.0	2.9	—	—	—	0	0.9	—	—
13	**1d**	MeCN	0	11.5	38.4	0	—	—	—	0	50.4	—	—
14	**1e**	MeCN	0	2.5	83.5	0	—	—	—	0	0	—	—

[a] 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. [b] Unless indicated the remaining products were formed in low yield and were of no special significance. [c] Reactions were carried out using *ca.* 0.15 mol dm^{-3} solutions of substrate under an N_2 atmosphere and at room temperature. [d] 51% by ^{1}H NMR monitoring of the reaction mixture. [e] Products were mainly of the type $(Ar–C_6F_6)_2$ and $(ArCO_2–C_6F_6)_2$.

the fluorodecarboxylation of alkanoic acids.[1] 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 aroyloxyl 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$^•$ with solvent precludes formation of the intermediate **6** (Scheme 1). In MeCN aroyl 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).[8] The closely related rearrangement reported here (**1** ⟶ **2**) using XeF_2 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_2.[9]

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_2 atmosphere) xenon difluoride (0.25 g, 1.48 mmol) was added to a solution of trimethylsilyl 4-*tert*-butylbenzoate[10] (0.19 g, 0.74 mmol) in CH_2Cl_2 (5 cm^3) 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[7] (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_2-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$^+$, 196.0895. $C_{11}H_{13}FO_2$ requires *M*, 196.0900); ν_{max}(neat)/cm^{-1} 2964, 1836 and 1236; δ_H($CDCl_3$) 1.32 [9 H, s, $C(CH_3)$], 1.32 [9 H, s, $C(CH_3)_3$], 7.17 (2 H, dd, *J* 8.8 and 1.0, ArH) and 7.44 (2 H, d, *J* 8.8 Hz, ArH); δ_C($CDCl_3$) 31.27, 34.57, 119.36, 126.74, 143.90 (d, *J* 286 Hz), 148.24 and 150.29; δ_F($CDCl_3$) −15.90; *m*/*z* 196 (M$^+$), 181 (100), 165, 153, 115, 91 and 47.

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