Synthesis of Arylxenon Trifluoromethanesulfonates *via* Electrophilic Substitution of F- and CF_3-substituted Aromatics

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Arylxenon trifluoromethanesulfonates are directly prepared *via* the reaction of intermediately generated xenon trifluoroacetate trifluoromethanesulfonate with fluorobenzenes or trifluoromethylbenzenes.

Several arylxenon derivatives[1,2] with xenon–carbon bonds have been prepared since the first synthesis of pentafluorophenyl xenon borates.[3] All reactions have the following in common: the primary attachment of the xenon atom to carbon proceeds *via* an exchange reaction of an arylboron derivative with xenon difluoride. The exchange reactions of the borate for the pentafluorobenzoate or trifluoromethanesulfonate group,[4] as well as the oxidation properties[5] of arylxenon derivatives as electrophilic arylation reagents, have been studied intensively.

The number of these compounds, however, is still limited, mainly because fluorine-, chlorine- or trifluoromethyl-substituted arylboron derivatives are not easily accessible in good yield. Suitable transfer reagents,[6] *e.g.* $B(2,6\text{-}F_2C_6H_3)_3$, have been unknown so far, and had to be prepared and characterized before use in exchange reactions with XeF_2.

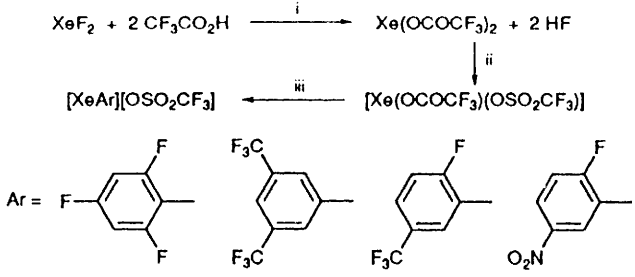
Herein we report a convenient synthesis of arylxenon trifluoromethanesulfonates by reaction of substituted benzenes with xenon bis(trifluoroacetate) in the presence of trifluoromethanesulfonic acid, which can be compared to the procedure in the syntheses of bis(fluorophenyl)iodine trifluoromethanesulfonates.[7]

Intermediately-generated xenon perfluorocarboxylates have been shown to be suitable perfluoroalkylating reagents in reactions with benzenes, although no evidence for organoxenon intermediates has been found.[8]

In the primary step, finely dispersed XeF_2 (0.6 g, 3.5 mmol) in CCl_3F (30 ml) is transformed into $Xe(OCOCF_3)_2$ by reacting the difluoride with stoichiometric amounts of trifluoroacetic acid (0.81 g, 7.1 mmol) at −20 °C. The course of the reaction can be monitored by ^{129}Xe NMR spectroscopy which, after adding some drops of MeCN to increase the solubility, allows the observation of a decrease in intensity of the XeF_2 triplet at δ 0 in favour of the $Xe(OCOCF_3)_2$ singlet at δ *ca.* −700.[9] The addition of 0.53 ml (3.5 mmol) CF_3SO_3H to the reaction mixture at −40 °C effects a downfield shift of the singlet of *ca.* 400 ppm, indicating that a new species, probably $Xe(OCOCF_3)(OSO_2CF_3)$, is formed which precipitates as a yellow solid from CCl_3F.

The ^{19}F NMR spectrum (CD_3CN–CCl_3F, −38 °C) of the intermediate shows two singlets at δ −69.1 (CF_3CO_2) and −75.6 (CF_3SO_3) in an integrative ratio of approximately 1 : 1. The ^{129}Xe NMR shift of the intermediate exhibits a considerable dependence upon solvent and concentration [δ −290, $\Delta_{1/2}$ *ca.* 10 Hz, CH_3CN–CCl_3F or CD_3CN–CCl_3F (−38 °C); δ −400, trifluoroacetic acid anhydride].

No reaction occurs using $FXeOSO_2CF_3$ as a starting material; in the absence of CF_3SO_3H, only poor spectroscopic



Scheme 1 *Reagents and conditions*: i, CCl_3F, −40 °C; ii, $+CF_3SO_3H$, $-CF_3CO_2H$; iii, +ArH, $-CF_3CO_2H$

Table 1 Compilation of NMR data of $XeAr(OSO_2CF_3)$ [Ar = $2,4,6\text{-}F_3C_6H_2$, $3,5\text{-}(CF_3)_2C_6H_3$, $2\text{-}F\text{-}5\text{-}(CF_3)C_6H_3$, $2\text{-}F\text{-}5\text{-}(NO_2)C_6H_3$, NMR spectra in CD_3CN solution, *J* in Hz]

Decomp.	$2,4,6\text{-}F_3C_6H_2$ 110 °C (DTA)	$3,5\text{-}(CF_3)_2C_6H_3$ −5 to −10 °C	$2\text{-}F\text{-}5\text{-}(CF_3)C_6H_3$ 75 °C (DTA)	$2\text{-}F\text{-}5\text{-}(NO_2)C_6H_3$ 88 °C (DTA)
NMR data	−20 °C	−35 °C	−35 °C	−20 °C
δ(^{129}Xe)	−2083	−1816	−1977.8	−1950.5
$^3J(^{129}Xe\text{–}F)$	57.0		48.1	47.8
$^3J(^{129}Xe\text{–}H)$		27		
δ[F-2(,6)]	−96.2		−94.8	−91.8
δ(F-4)	−96.4			
δ(CF_3)		−61.7	−62.1	
δ(CF_3SO_3)	−77.8	−78.1	−79.0	−79.0
δ(H-2)		8.7		
δ[H-3(,5)]	7.3		7.7	7.8
δ(H-4)		8.4	8.1	8.7
δ(H-6)		8.7	8.5	9.1
δ(C-1)	84.1	117.9	103.1	102.1
$^1J(^{129}Xe\text{–}C)$	113.1	72.0	92.0	97.1
δ(C-2)	158.3	133.7	158.2	159.8
δ(C-3)	105.0	135.7	121.1	120.4
δ(C-4)	167.5	128.8	134.4	129.5
δ(C-5)	105.0	135.7	130.6	146.6
δ(C-6)	158.3	133.7	131.4	132.2
δ(CF_3)		122.5	123.0	
^1J(F–C)		273.2	272.3	
δ(CF_3SO_3)	121.4	121.2	121.5	121.5
^1J(F–C)	319.1	318.5	319.4	319.5

Table 2 Raman frequencies (cm^{-1}) and relative intensities of $Xe(2,4,6\text{-}F_3C_6H_2)(OSO_2CF_3)$, $Xe(2\text{-}F\text{-}5\text{-}CF_3C_6H_3)(OSO_2CF_3)$ and $Xe(2\text{-}F\text{-}5\text{-}NO_2C_6H_3)(OSO_2CF_3)$

$Xe(2,4,6\text{-}F_3C_6H_2)(OSO_2CF_3)$	$Xe(2\text{-}F\text{-}5\text{-}CF_3C_6H_3)(OSO_2CF_3)$	$Xe(2\text{-}F\text{-}5\text{-}NO_2C_6H_3)(OSO_2CF_3)$	assignment
3076 (1.3)			$\nu(CH)_{ring}$
		1584 (1.6)	$\nu(CF)_{ring}$
		1353 (10.0)	$\nu(NO_2)$
1242 (1.7)	1229 (2.4)		$\nu(CF_3)$
1182 (0.8)			$\nu(CC)_{ring}$
		1115 (2.1)	
1024 (6.7)	1027 (10.0)	1024 (3.5)	$\nu(SO_2)$
1008 (1.3)			
	842 (1.8)		
765 (1.1)	764 (2.5)		$\delta_{as}(CF_3)$
	664 (2.4)	666 (1.5)	$\delta(CC)_{ring}$
562 (4.1)	570 (1.1)	570 (0.3)	$\delta_s(CF_3)$
506 (1.0)			$\delta(SO_2)$
	479 (2.2)	458 (1.1)	various δ
	401 (3.3)		
356 (3.7)	352 (2.0)		
316 (1.2)	318 (2.5)	322 (1.5)	
257 (1.6)		270 (3.5)	
222 (1.4)	236 (7.3)		
203 (10.0)	194 (6.2)	203 (6.7)	$\nu(XeC)$
149 (0.7)	166 (5.2)	138 (2.7)	skeleton
	119 (6.4)	98 (2.1)	

evidence for arylxenon derivatives is found in reactions of $Xe(OCOCF_3)_2$ with $1,3,5\text{-}F_3C_6H_3$.

The benzene [$1,3,5\text{-}F_3C_6H_3$ (0.46 g, 3.5 mmol), $1,3\text{-}(CF_3)_2C_6H_4$ (0.75 g, 3.5 mmol), $1\text{-}F\text{-}4\text{-}CF_3C_6H_4$ (0.57 g, 3.5 mmol), $1\text{-}F\text{-}4\text{-}NO_2C_6H_4$ (0.49 g, 3.5 mmol)] is added dropwise to the reaction mixture. During this period the precipitate dissolves, and the initially colourless solution turns bright yellow. After a reaction time of 3 h, only the resonances of the arylxenon trifluoromethanesulfonates can be detected in the ^{129}Xe NMR spectra.

For the isolation of the arylxenon trifluoromethanesulfonates all volatile compounds are distilled off at −20 °C under reduced pressure. After treatment of the residue with 5 ml MeCN, the suspension is concentrated and washed with cold *n*-hexane (10 ml) to give a residue which is suspended overnight in 10 ml toluene at −78 °C, to which diethyl ether has been added dropwise until the toluene phase has become turbid. Low-temperature filtration and a final washing with 20 ml of cold CH_2Cl_2 gives the arylxenon compounds as colourless solids in *ca.* 15% yield with a purity better than 98%, as determined from the NMR spectra.

Using this reaction pathway the new compounds $Xe(2,4,6\text{-}F_3C_6H_2)(OSO_2CF_3)$, $Xe\{3,5\text{-}(CF_3)_2C_6H_3\}(OSO_2CF_3)$, $Xe\{2\text{-}F\text{-}5\text{-}(CF_3)C_6H_3\}(OSO_2CF_3)$ and $Xe\{2\text{-}F\text{-}5\text{-}(NO_2)C_6H_3\}(OSO_2CF_3)$ have been synthesized and fully characterized by multinuclear NMR spectroscopy (Table 1) and, in part, vibrational spectroscopy (Table 2) for the first time.

Absence of any CN- and Me-bands in the IR and Raman spectra indicates that the solid compounds are not complexed with acetonitrile.

All compounds are insoluble in toluene, diethylether and CH_2Cl_2, but readily soluble in MeCN. The decomposition points and ^{129}Xe NMR shifts correspond with the series of arylxenon tetrafluoroborates described in ref. 1. Empirically, an increased thermal stability, with the exception of that of $Xe\{2\text{-}F\text{-}5\text{-}(NO_2)C_6H_3\}(OSO_2CF_3)$ is accompanied by an upfield shift of the resonance signal of the compound in the ^{129}Xe NMR spectra in CD_3CN solution.

The salt-like character of the xenon–oxygen bonds and the complete dissociation in MeCN solution into a solvent-stabilized cation and the trifluoromethanesulfonate anion can be proved by ^{129}Xe and ^{19}F NMR measurements. For example, the ^{129}Xe NMR spectrum of a mixture of equimolar amounts of $Xe(2,4,6\text{-}F_3C_6H_2)(OSO_2CF_3)$ and $Xe(2,4,6\text{-}F_3C_6H_2)[BF_4]$ exhibits only one resonance signal located at δ −2085. In the ^{19}F NMR spectrum, only the resonances of the $[Xe(2,4,6\text{-}F_3C_6H_2)]^+$ cation besides those of $CF_3SO_3^-$ and $[BF_4]^-$ can be observed. The ratio of the integrals corresponds with the chosen stoichiometry, indicating a complete dissociation of both derivatives in MeCN solution.

On the whole, the reaction sequence may be described as an electrophilic substitution of benzene, as given in Scheme 1. The orientation of substitution is basically influenced by the directing group. The reactions proceed selectively if the directing effects are uniform. Thus, the reactions with $1,3,5\text{-}F_3C_6H_3$ (*ortho*-directing substituents) and $1,3\text{-}(CF_3)_2C_6H_4$ (*meta*-directing groups) exclusively yield the compounds $Xe(2,4,6\text{-}F_3C_6H_2)(OSO_2CF_3)$ and $Xe\{3,5\text{-}(CF_3)_2C_6H_3\}(OSO_2CF_3)$, respectively. The *ortho*-directing effect of the fluorine substituent as well as the *meta*-directing effect of the CF_3 or NO_2 group in $1\text{-}F\text{-}4\text{-}(CF_3)C_6H_4$ and $1\text{-}F\text{-}4\text{-}(NO_2)C_6H_4$ both favour the 2-position of the ring for substitution, and hence yield selectively the corresponding xenon derivatives. Similar results are also obtained in reactions with C_6F_5H and $1,3,5\text{-}Cl_3C_6H_3$; products of these reactions were exclusively the derivatives $Xe(C_6F_5)(OSO_2CF_3)$ [$\delta\{^{129}Xe, -35\ °C, (CF_3CO)_2O\}$ −2093, $^3J(^{129}Xe\text{–}^{19}F) = 64$ Hz] and $Xe(2,4,6\text{-}Cl_3C_6H_2)(OSO_2CF_3)$ [$\delta\{^{129}Xe, -35\ °C, (CF_3CO)_2O\}$ −1924]. Unfortunately, these derivatives could not be obtained as analytical pure solids until now.

If, however, $1,3\text{-}F_2C_6H_4$ is used as a starting material, a product mixture of $Xe(2,4\text{-}F_2C_6H_3)(OSO_2CF_3)$ and $Xe(2,6\text{-}F_2C_6H_3)(OSO_2CF_3)$ (ratio 10:1, determined by integrating the ^{129}Xe resonances) is obtained, besides several further organoxenon derivatives as byproducts. Unspecified reactions also occur with $1\text{-}F\text{-}3\text{-}(CF_3)C_6H_4$. No reaction is observed with $1,3,5\text{-}(CF_3)_3C_6H_3$. An immediate decomposition takes place after adding the benzene to the reaction mixture in all those cases where the aromatic ring does not bear at least one fluorine, chlorine or trifluoromethyl substituent.

This novel route for the synthesis of arylxenon derivatives is advantageous above all because it uses commercially available benzenes and avoids the tedious preparation of boranes.

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