A Convenient Route to Aryl Trifluoromethyl Sulfones by Fluoride-Catalyzed Cross-Coupling of Arenesulfonyl Fluorides with (Trifluoromethyl)trimethylsilane and (Trifluoromethyl)trimethylstannane

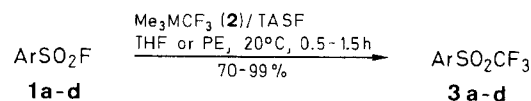A. A. Kolomeitsev, V. N. Movchun, N. V. Kondratenko, Yu. L. Yagupolski*

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Trifluoromethylsulfonyl substituted aromatic compounds 3a–d are prepared from the corresponding sulfonyl fluorides 1a–d by reacting with (trifluoromethyl)trimethylsilane (or-stannane) in the presence of a base under mild conditions in high yields.

Trifluoromethylsulfonyl substituted aromatic compounds are of potential interest as intermediates for the preparation of pharmaceuticals, agrochemicals and dyes.[1] The most widely used route to aryl trifluoromethyl sulfones is the oxidation of corresponding sulfides. The latter compounds are not easily available and are usually prepared either by ion-radical perfluoroalkylation of arylthiols[2] or from expensive reagents such as trifluoromethane sulfinyl chloride [3] or trifluoromethylthiocopper.[4]

The only known one-pot procedure for the preparation of aryl trifluoromethyl sulfones is the sulfonylation of aromatic compounds by the system trifluoromethane sulfonyl chloride/aluminum chloride, which has been successfully applied only to the benzene derivatives activated by electron-donating groups.[5] However, this reaction leads usually to a mixture of isomers. Temple has shown[6] that benzenesulfonyl fluoride reacted with tetrafluoroethylene in the presence of cesium fluoride at elevated temperature and pressure to form phenyl pentafluoroethyl sulfone. But this reaction cannot be applied to the preparation of the most practically important trifluoromethyl substituted derivatives, as it has been shown that the trifluoromethyl anion is unstable even at −100°C.[7]

In continuation of our studies on aromatic trifluoromethylthio and sulfonyl derivatives,[8] we now report a convenient one-pot and high yielding procedure for the preparation of aryl trifluoromethyl sulfones 3 from easily available arenesulfonyl fluorides 1 and (trifluoromethyl)trimethylsilane (2a) or stannane (2b), catalyzed by soluble nucleophilic agents such as tetrabutylammonium fluoride, tris(diethylamino)methylaminophosphonium difluoride and -phenolate (TAP⁺HF₂⁻ and TAP⁺PhO⁻),[9] and tris(dimethylamino)sulfonium difluorotrimethyl siliconate (TASF).

$$ArSO_2F \xrightarrow[\begin{array}{c}\text{THF or PE, } 20°C, 0.5-1.5\,h\\\hline 70-99\%\end{array}]{Me_3MCF_3 \ (2)/\,TASF} ArSO_2CF_3$$

$$\mathbf{1a-d} \qquad\qquad\qquad\qquad\qquad \mathbf{3a-d}$$

$$TASF = (Me_2N)_3S^+\ Me_3SiF_2^-$$

1, 3	Ar	2	M
a	H	a	Si
b	4-MeC₆H₄	b	Sn
c	4-ClC₆H₄		
d	3-NO₂C₆H₄		

The reaction between arenesulfonyl fluorides 1 and trifluoromethyl compounds 2 in the presence of catalytic amounts of TASF (10 mol%) is slightly exothermic. It proceeds smoothly and is completed within 0.5–1.5 h, if silane 2a or stannane 2b and arenesulfonyl fluorides 1 are used in the molar ratio of 2:1. The yields were found to be influenced by the addition modus of the reagents. The best results were obtained when silane 2a or stannane 2b were added slowly to the tetrahydrofuran or petroleum ether solution of arenesulfonyl fluorides 1 and the catalyst. Electron donating or accepting substituents in the aromatic ring of 1 do not affect the yield of sulfones (Table 1). Tetrabutylammonium fluoride, tris(diethylamino)methylaminophosphonium difluoride and -phenolate were also used as catalysts (Table 2), but TASF is favored as it can achieve the quantitative transformation of sulfonyl fluorides into aryltrifluoromethyl sulfones 3. No product was formed when the reaction was carried out without a catalyst. The formation of sulfones 3 from the silane 2a proceeds in high yield in organic solvents such as dimethylformamide, hexamethylphosphoric triamide, tetrahydrofuran or petroleum ether. The yields of sulfones 3 may vary significantly (0–100%) when the reaction is based on stannane 2b depending on the nature of the solvent used. It was shown that compound 2b is more effective in petroleum ether. It seems, that the stability of pentacoordinated anionic species,

Table 1. Aryl Trifluoromethyl Sulfones 3 Prepared

Product	Reagent 2 Used[a]	Reaction Conditions Temp (°C)/Time (h)/Solvent[b]	Yield (%)	mp (°C) (pentane) or bp (°C)/mbar	Lit. mp (°C) or bp (°C)/mbar	^{19}F-NMR (acetone-d_6/CDCl$_3$) δ, CF$_3$
3a	2a	25/0.5/PE	99	118–119/20[c]	80/3[11]	78.13[d]
	2a	25/1.5/THF	96			
	2b	25/1.5/PE	96			
3b	2a	25/0.5/PE	99	34–35	31[11]	78.60
	2a	25/1/THF	96			
	2b	25/1.5/PE	96			
3c	2a	25/1/PE	96	56–57	55–56[11]	78.03
	2b	25/1.5/PE	95			
3d	2a	25/1/PE	73	56–57	56–57[12]	78.07
	2b	25/1.5/PE	70			

[a] A 100% excess of the reagent is used.
[b] PE refers to petroleum ether bp 60–80°C.

[c] $n_D^{20} = 1.4637$.
[d] ^{19}F-NMR spectrum corresponds to the literature data.[13]

Table 2. Catalytic Influence of Nucleophilic Agents on the Yield of Phenyl Trifluoromethyl Sulfone

Catalyst/Mol%	Reagent/ Molar Equiv	Reaction Temp.(°C)/ Solvent	Yield (%) of 3a in 1 h
(Et$_2$N)$_3$PNHCH$_3$HF$_2^-$/10	2a/2	25/DMF	10
	2a/2	25/THF	17
	2a/10	25/THF	60
	2b/10	25/THF	50
	2b/5	25/THF	20
(Et$_2$N)$_3$PNHCH$_3$PhO$^-$/10	2a/2	25/THF	75, 93[a]
	2b/2	25/PE	0
	2b/2	25/THF	0
Bu$_4$N$^+$F$^-$·3H$_2$O/100	2a/2	25/THF	15
	2a/5	25/THF	90
(Me$_2$N)$_3$S$^+$Me$_3$SiF$_2^-$/10	2a/2	25/THF	98
	2a/2	25/PE	100[b]
	2a/1.3	25/PE	81
	2b/2	25/PE	92

[a] Reaction carried out in 2 h.
[b] The full transformation of PhSO$_2$F into PhSO$_2$CF$_3$ is completed within 0.5 h according to GC data.

generated from stannane 2b and fluoride ion, increases in the solvent of lower polarity.

The proposed reaction provides a convenient one-pot synthetic method for the preparation of aryl trifluoromethyl sulfones 3 in high yields from easily available starting materials. The preparation of aryl perfluoroalkyl sulfones with longer perfluoroalkyl substituents are now under investigation.

Me$_3$MCF$_3$, M = Si (2a), Sn (2b) were obtained according to Marchenko–Ruppert method.[10] The starting arenesulfonyl fluorides 1 were prepared from corresponding sulfonylchlorides by usual methods. Tetrabutylammonium fluoride and TASF were purchased from Fluka AG. THF was dried by distillation over LiAlH$_4$. Petroleum ether PE, bp 60–80°C was used without purification. ^{19}F-NMR spectra were recorded on a Bruker WP-200 spectrometer in acetone-d_6 with CCl$_3$F as internal standard. GC analyses were performed on a Chrom-5 instrument fitted with a flame-ionization detector on a PEGA (polyethyleneglycol 20 M) column.

Aryl Trifluoromethyl Sulfones 3 a–d; General Procedure:

Method A, *From Me$_3$SiCF$_3$* (2a): A solution of Me$_3$SiCF$_3$ (2a; 2.84 g, 20 mmol) in THF (10 mL) is added portionwise to a stirred suspension of arenesulfonyl fluoride 1 a–d (10 mmol) and TASF (1 mmol) in THF or petroleum ether (10 mL) at 25°C during 10–15 min under Ar atmosphere. The mixture is stirred for 0.5–1.5 h, then treated with water (30 mL), and extracted with petroleum ether (30 mL). The organic phase is washed with water (4 × 50 mL), dried (MgSO$_4$) and concentrated. The products 3 a–d are distilled or recrystallized from pentane (Table 1).

Method B, *From Me$_3$SnCF$_3$* (2b): A solution of Me$_3$SnCF$_3$ (2b; 4.7 g, 20 mmol) in petroleum ether (10 mL) is added portionwise to a stirred suspension of arenesulfonyl fluoride 1 a–d (10 mmol) and TASF (1 mmol) in petroleum ether (10 mL) at 25°C during 10–15 min under Ar atmosphere. The mixture is stirred for 1–1.5 h and treated with an excess of aq KF for 1 h with vigorous stirring. The precipitated Me$_3$SnF is filtered and washed with petroleum ether (20 mL). Further workup is performed according to Method A (Table 1).

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