RSC Advances

PAPER

View Article Online
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Cite this: *RSC Adv.*, 2017, **7**, 47

Synthesis of aryl triflones by insertion of arynes into C–SO_2CF_3 bonds†

Xian Zhao,[a] Yangen Huang,[a] Feng-Ling Qing[ab] and Xiu-Hua Xu*[b]

Received 7th November 2016
Accepted 22nd November 2016

DOI: 10.1039/c6ra26429h

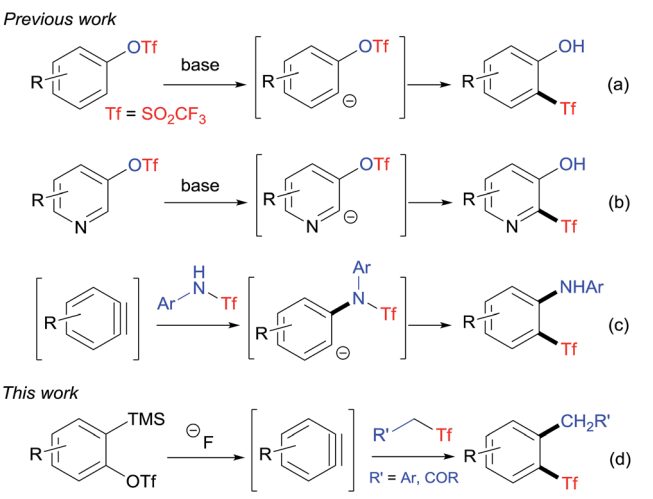
www.rsc.org/advances

A new approach toward the synthesis of aryl triflones was achieved by the formal insertion of arynes into C–SO_2CF_3 bonds. This reaction proceeds through addition of CF_3SO_2-containing nucleophiles to the *in situ* generated arynes and subsequent intramolecular rearrangement.

Largely as a result of their unique biological properties, fluorinated compounds have found wide applications in pharmaceuticals, agrochemicals, and materials.[1] Compounds containing a trifluoromethanesulfonyl (triflyl, SO_2CF_3, Tf) group have received increasing interest due to the strong electron-withdrawing ability and high lipophilicity of SO_2CF_3.[2] In particular, aryl triflones ($ArSO_2CF_3$) are frequently used as structural units in bioactive compounds,[3] catalysts or ligands,[4] and advanced functional materials.[5] Consequently, a number of methods have been developed for the preparation of aryl triflones. The general methods include oxidation of aryl trifluoromethyl sulfides,[6] trifluoromethylation of aryl sulfonyl fluorides or aryl sulfinates,[7] and triflylation of aromatic compounds.[8]

In 2003, Lloyd-Jones and co-workers reported an unprecedented method for the preparation of aryl triflones by anionic thia-Fries rearrangement of aryl triflates (Scheme 1a).[9a] Since then, Lloyd-Jones' group and Butenschön's group have applied this rearrangement reaction to the synthesis of various *o*-hydroxyaryl triflones.[4d,9] Recently, one of the present authors together with collaborators synthesized a series of heteroaryl triflones with the same methodology (Scheme 1b).[10] In these anionic thia-Fries rearrangement reactions, the carbanion intermediates are generated *via* directed *ortho*-metalation with organolithium reagents, which are not tolerant of a range of functional groups. We wondered if it was possible to develop new methods to generate carbanions under mild conditions. Considering that the addition of a nucleophile to the aryne is a general method to generate a transient aryl anion intermediate,[11] we reasoned that the reaction of a Tf-containing nucleophile and the aryne would give the Tf-containing carbanion intermediate, which may subsequently undergo anionic thia-Fries rearrangement to afford the corresponding aryl triflone. Interestingly, during the investigation of our idea, Li and co-workers reported a novel synthesis of *o*-aminoaryl triflones from *N*-triflylated anilines and arynes by adopting a similar strategy (Scheme 1c).[12] As a continuation of our research interest in triflyl chemistry,[10,13] we herein disclose the first example of preparation of *o*-alkylaryl triflones by the insertion of arynes into C–SO_2CF_3 bond through the tandem nucleophilic attack/intramolecular rearrangement (Scheme 1d).

The insertion of arynes into element–element bonds, such as carbon–carbon,[14] carbon–heteroatom,[15] and heteroatom–heteroatom[16] bonds, provides a convenient method for direct access to 1,2-disubstituted aromatics. However, this method has rarely been applied to synthesize SO_2CF_3-containing aromatics.[12,17] Thus, we chose 2-(trimethylsilyl)phenyltriflate (**1a**) and 4-(((trifluoromethyl)sulfonyl)methyl)benzonitrile (**2a**) as the model substrates to explore the alkylation–triflylation of



Scheme 1 Preparation of (hetero)aryl triflones through anionic thia-Fries rearrangement.

[a]*College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China*

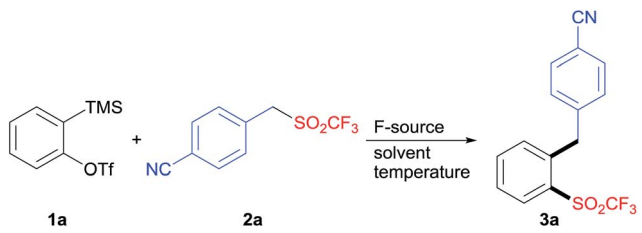
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 345 Lingling Lu, Shanghai 200032, China. E-mail: xuxiuhua@sioc.ac.cn*

† Electronic supplementary information (ESI) available. CCDC 1509106. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ra26429h

arynes for the preparation of *o*-alkylaryl triflones (Table 1). Initially, different fluoride sources, including CsF, KF, tetrabutylammonium fluoride (TBAF), and KF/18-crown-6, were explored employing THF as the solvent (entries 1–4). Among them, KF/18-crown-6 proved to be the optimal fluoride source, leading to desired product **3a** in 60% yield (entry 4). In the subsequent solvent screen, we found that the use of other solvents such as MeCN, toluene, dioxane, and Et_2O diminished the yield of **3a** (entries 5–8). Furthermore, increasing the temperature to 50 °C could slightly improve the yield to 75% (entry 9). However, when the reaction was performed at 70 °C, lower yield was obtained (entry 10). Additional surveys of the reaction stoichiometry (entries 11–14) revealed that the instance with **1a** as the limiting reagent, 1.0 equivalent of **2a**, 2.0 equivalents of KF, and 2.0 equivalents of 18-crown-6 afforded the highest yield of **3a** (entry 12). Finally, increasing or reducing the concentration of this reaction had no positive effects on the yield (entries 15 and 16).

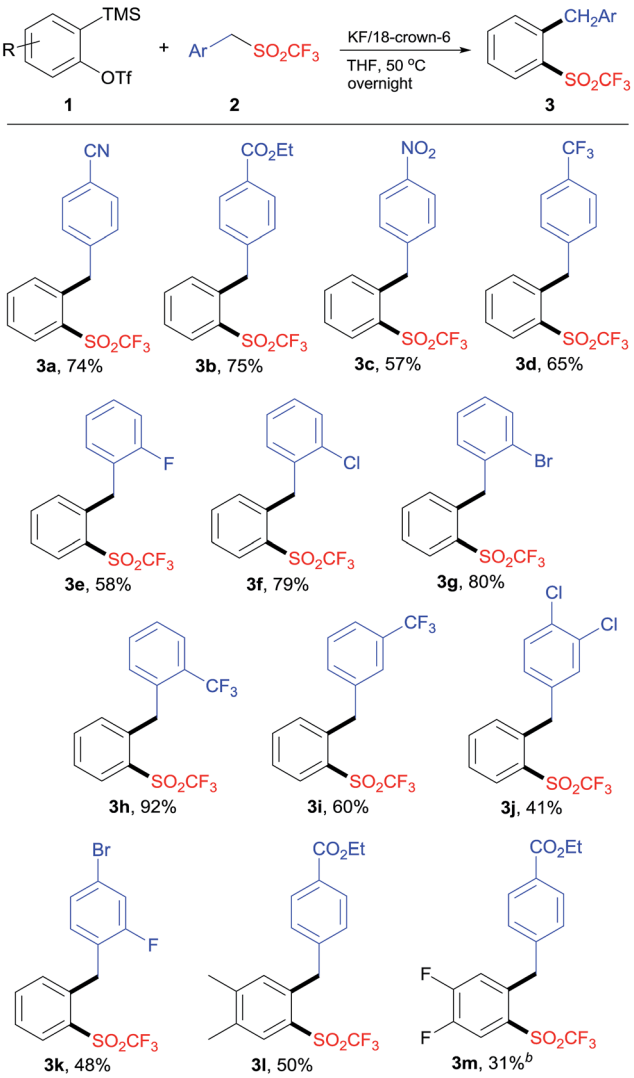
With the optimized reaction conditions (Table 1, entry 12) in hand, we then investigated the substrate scope of this reaction. The reaction of aryne precursor **1a** with substituted benzyl triflones **2** carried out effectively to give the corresponding *o*-alkylaryl triflones **3a–k** in moderate to excellent yields

Table 1 Optimization of reaction conditions[a]



Entry	F-Source	Solvent	Temperature	Yield[b] (%)
1	CsF	THF	rt	Trace
2	KF	THF	rt	10
3	TBAF	THF	rt	49
4	KF/18-crown-6	THF	rt	60
5	KF/18-crown-6	MeCN	rt	24
6	KF/18-crown-6	Toluene	rt	5
7	KF/18-crown-6	Dioxane	rt	45
8	KF/18-crown-6	Et_2O	rt	51
9	KF/18-crown-6	THF	50 °C	75
10	KF/18-crown-6	THF	70 °C	54
11[c]	KF/18-crown-6	THF	50 °C	73
12[d]	KF/18-crown-6	THF	50 °C	85
13[e]	KF/18-crown-6	THF	50 °C	30
14[f]	KF/18-crown-6	THF	50 °C	60
15[g]	KF/18-crown-6	THF	50 °C	69
16[h]	KF/18-crown-6	THF	50 °C	78

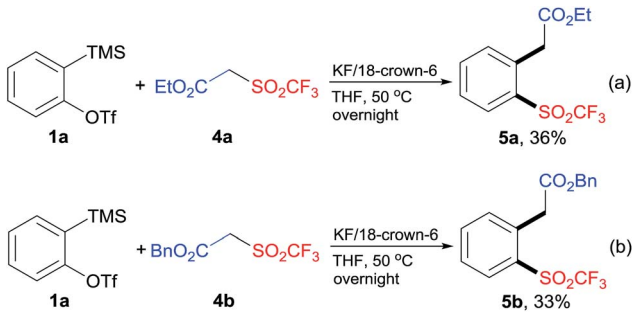
[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), fluoride source (0.20 mmol), solvent (3.0 mL), under N_2, temperature, overnight. [b] Yields determined by ^{19}F NMR spectroscopy using trifluoromethoxybenzene as an internal standard. [c] **2a** (0.12 mmol). [d] **2a** (0.10 mmol). [e] KF (0.10 mmol), 18-crown-6 (0.10 mmol). [f] KF (0.30 mmol), 18-crown-6 (0.30 mmol). [g] THF (1.5 mL). [h] THF (5.0 mL).



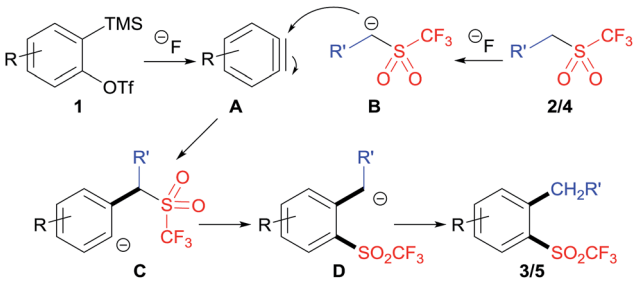
Scheme 2 The reaction of 2-(trimethylsilyl)aryl triflates and benzyl triflones.[a] [a]Reaction conditions: **1** (0.30 mmol), **2** (0.30 mmol), KF (0.60 mmol), 18-crown-6 (0.60 mmol), THF (9.0 mL), under N_2, 50 °C, overnight, isolated yields. [b]Yield determined by ^{19}F NMR spectroscopy using trifluoromethoxybenzene as an internal standard.

(Scheme 2). In general, the electron-withdrawing substituent on benzyl triflones was essential for this transformation. Benzyl triflones bearing fluoro (**2e**), chloro (**2f**), and bromo (**2g**) groups were suitable substrates, providing products **3e–g** in good yields. The steric hindrance had no obvious effect on the yield, as benzyl triflone **2h** proceeded well to afford **3h** in high yield. Benzyl triflone **2i** with a substituent into the *meta* position of the benzyl scaffold was also effective. In addition, disubstituted triflones **2j** and **2k** underwent this reaction smoothly. It was noteworthy that benzyl triflone **2b** reacted with aryne precursors **1b** and **1c** to produce the corresponding insertion products **3l** and **3m**. The structure of product **3** was confirmed by X-ray crystallographic analysis of compound **3a** (see the ESI†).

To extend the scope of this protocol, we further examined other CF_3SO_2-containing substrates. In a similar manner, the reaction of **1a** with β-triflyl esters **4a** or **4b** gave the desired



Scheme 3 The reaction of **1a** and β-triflyl esters.



Scheme 4 Proposed reaction mechanism.

products **5a** and **5b**, albeit in low yields (Scheme 3). Some unknown byproducts (<10% yield) were also obtained. In the cases of β-triflyl amides, the yields of the desired products were even lower. Furthermore, when β-triflyl ketones were subjected to the standard reaction conditions, the insertion of arynes into C–SO_2CF_3 bond did not happen. Instead, the insertion of arynes into C(active methylene)–C(ketone) bond was detected.

A plausible mechanism of this reaction is proposed in Scheme 4. The substrates 2-(trimethylsilyl)aryltriflate **1** and CF_3SO_2-containing nucleophile **2**/**4** were respectively converted to aryne **A** and carbanion **B** under the treatment of fluoride anion. Then, the addition of **B** to **A** afforded intermediate **C**, which underwent intramolecular migration of the triflyl group to give intermediate **D**. Finally, protonation of intermediate **D** gave the target product **3**/**5**. It should be noted that the triflyl group plays an important role in this reaction. The analogous reaction of aryne precursors with substituted benzyl methanesulfones could not give the desired aryl methanesulfones.

In conclusion, we have developed a new access to aryl triflones starting from aryne precursors and CF_3SO_2-containing nucleophiles. This protocol proceeds through the tandem nucleophilic attack/intramolecular rearrangement to give the formal insertion products. Further exploration of this insertion reaction in the preparation of bioactive fluorinated compounds is in progress.

Acknowledgements

We are grateful for the financial support from National Natural Science Foundation of China (21502215, 21421002, 21332010, 21272036), Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20020000), Youth Innovation Promotion Association CAS (2016234), and Shanghai Pujiang Program (15PJ1410300).

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