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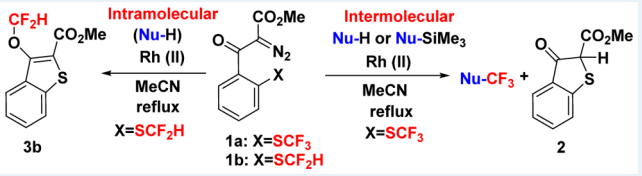
Carbene-Induced Intra- vs Intermolecular Transfer-Fluoromethylation of Aryl Fluoromethylthio Compounds under Rhodium Catalysis

Ibrayim Saidalimu, Etsuko Tokunaga, and Norio Shibata*

Department of Nanopharmaceutical Sciences, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan

Supporting Information

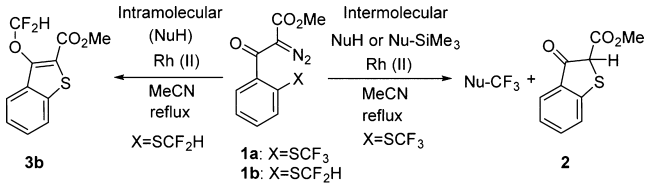
ABSTRACT: The intra- vs intermolecular transfer-fluoromethylation of aryl fluoromethylthio compounds is proposed. Finely designed $ArSCF_3$ (**1a**) nicely releases its trifluoromethyl (CF_3) group intermolecularly under rhodium catalysis, whereas a difluoromethylated analogue, $ArSCF_2H$ compound **1b** shows intramolecular reaction.



KEYWORDS: *trifluoromethylation reagent, difluoromethylation reagent, rhodium catalyst, intramolecular, intermolecular*

Notable success witnessed in recent synthetic fluorine chemistry is obviously related to the development of new fluoro-functionalization reagents, such as fluorination and trifluoromethylation reagents, and their usage under new catalytic systems supported by the meticulous work of organic chemists involved in fluorine chemistry and organometallics.[1,2] Electrophilic trifluoromethylation reagents have been one of the most awaited reagents for years.[3,4] They have been developing relatively slowly, probably due to the difficulty in generating a trifluoromethyl cation ($^+CF_3$), which is affected by its high group electronegativity (3.45).[5] Several shelf-stable reagents have been reported for this purpose: diaryl(trifluoromethyl)sulfonium salts (1984, Yagupolskii),[6] chalcogenium salts (1990, Umemoto),[7] hypervalent iodine compounds (2006, Togni),[8] (trifluoromethyl)sulfoximinium and S-thiophenium salts (2008, 2010, Shibata).[9] They are effective for the electrophilic-type trifluoromethylation of a wide range of nucleophiles, and some of them are now commercially available. It is not surprising that researchers are continuously eager for new fluoro-functionalization reagents, because new reagents often encourage an encounter with efficient synthetic methodology useful for the synthesis of sought-after organofluorine compounds on the drug market.[10] In this context, we disclose herein a different strategy based on the in situ generation of "unstable/reactive $^+CF_3$ equivalents" from a shelf-stable aryl-trifluoromethylthio compound, $ArSCF_3$, instead of "shelf-stable $^+CF_3$ equivalents". The finely designed $ArSCF_3$ compound, methyl 2-diazo-3-oxo-3-(2-((trifluoromethyl)thio)-phenyl)propanoate (**1a**), has a carbenoid generation pendant on its *ortho* position. An intermolecular transfer-trifluoromethylation from the SCF_3 moiety on **1a** to carbon nucleophiles (Nu-H, Nu-$SiMe_3$) proceeds smoothly through a tandem process consisting of a rhodium carbene intermediate[11] and a cyclized inner salt to furnish CF_3-products with the exit of methyl 3-oxo-2,3-dihydrobenzo[b]thiophene-2-carboxylate (**2**). Only a trace amount of an intramolecular transfer-trifluoromethylation product **3a**, Stevens rearrangement[12] product, was observed, even in the absence of nucleophiles. On the other hand, a difluoromethylated analogue, $ArSCF_2H$ compound **1b** behaves rather differently to **1a**. Intramolecular transfer-difluoromethylation on the oxygen atom proceeded providing O−CF_2H **3b**, even in the presence of nucleophiles (Scheme 1). Cationic, radical, and carbene mechanisms are proposed to understand the difference of the reaction pathways depend of the CF_2X based on the discussions of Stevens rearrangement.

Scheme 1. Intra- vs Intermolecular Transfer-Fluoromethylation of $ArSCF_3$ and $ArSCF_2H$ Compounds under Rhodium Catalysis



The finely designed $ArSCF_3$ compound **1a** was easily prepared from readily available *ortho*-$ArSCF_3$ ethanone **4**[13] by the procedure shown in Scheme 2. First, **4** was treated with dimethyl carbonate under basic and reflux conditions to provide $ArSCF_3$ methyl propanoate **5** with 91% yield. The target reagent **1a** was prepared quantitatively by diazotization of **5** with 4-methylbenzenesulfonyl azide in 10 min. The reagent **1a** is stable enough at room temperature and even in MeCN under reflux for 24 h (see run 23, in Table 1).

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Scheme 2. Preparation of Designed Ar-SCF$_3$ Compound

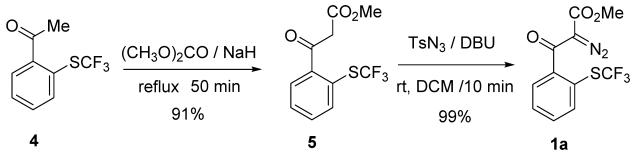
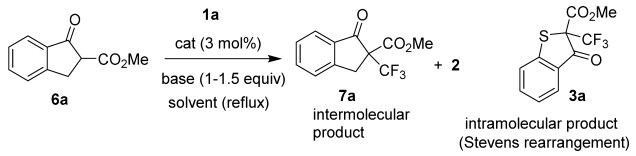


Table 1. Optimizations of Reaction Conditions[a]



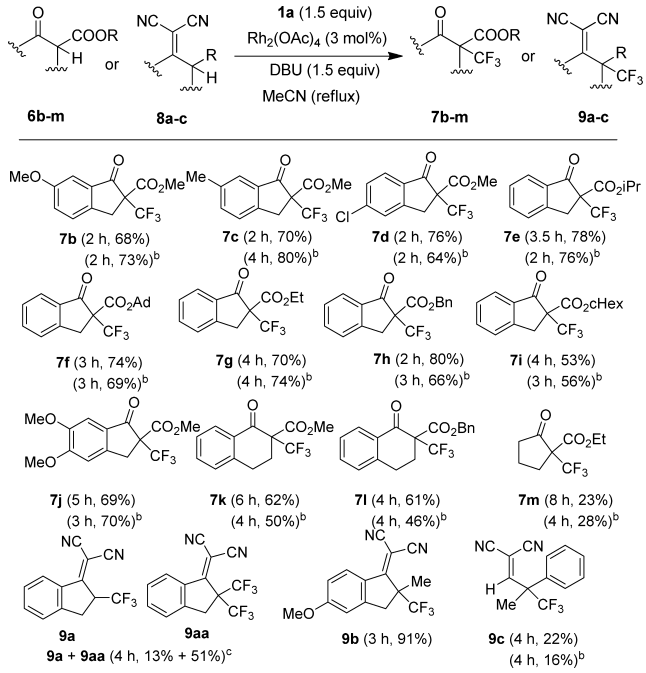
run	cat.	base	solvent	time (h)	yield (%)[b]
1	$Rh_2(OAc)_4$	DBU	DCM	5	52
2	$Rh_2(OAc)_4$	TEA	DCM	24	trace
3	$Rh_2(OAc)_4$	DABCO	DCM	24	trace
4	$Rh_2(OAc)_4$	LDA	DCM	3	trace
5	$Rh_2(OAc)_4$	K_2CO_3	DCM	24	18
6	$Rh_2(OAc)_4$	BuOK	DCM	24	9
7	CuI	DBU	DCM	24	31
8	$Pd_2(dba)_3$	DBU	DCM	24	trace
9	------	DBU	DCM	24	15
10	$Rh_2(OAc)_4$	DBU	MeCN	4	81
11	$Rh_2(OAc)_4$	DBU	MeOH	12	trace
12	$Rh_2(OAc)_4$	DBU	toluene	12	28
13	$Rh_2(OAc)_4$	DBU	DMF	12	12
14	$Rh_2(OAc)_4$	DBU	THF	12	trace
15	$Rh_2(OAc)_4$	DBU	Et_2O	12	35
16	$Rh_2(OAc)_4$	DBU	DCE	12	25
17[c]	$Rh_2(OAc)_4$	DBU	MeCN	3	76
18[d]	**$Rh_2(OAc)_4$**	**DBU**	**MeCN**	**2**	**84**
19[e]	$Rh_2(OAc)_4$	DBU	MeCN	2	83
20[f]	$Rh_2(OAc)_4$	DBU	MeCN	24	12[g]
21	$Rh_2(OAc)_4$	-----	MeCN	24	7[g]
22[h]	$Rh_2(OAc)_4$	DBU	MeCN	24	0[g]
23	-------	-----	MeCN	24	0

[a]The reaction of **6a** with reagent **1a** (1.5 equiv) was carried out in the presence of base (1.2 equiv) in solvent at reflux temperature. For detailed reaction conditions, see the Supporting Information. [b]^{19}F NMR yield. [c]Used 1.0 equiv of DBU. [d]Used 1.5 equiv of DBU. [e]Used 2.0 equiv of DBU. [f]Used 10 mol % of DBU. [g]Intramolecular product **3a** was also obtained in 6−10% yield, based on the use of **1a**. [h]Reaction was examined in the absence of **6a**.

With the reagent **1a** in hand, we attempted the trifluoromethylation of methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**6a**) by **1a** via an intermolecular pathway. The base, metal, and solvent were varied, and the results are summarized in Table 1. Treatment of **6a** with **1a** in the presence of $Rh_2(OAc)_4$ (3 mol %) and 1.2 equiv of DBU in CH_2Cl_2 gave the trifluoromethylated product **7a** in 52% yield (Table 1, run 1). Using other organic and inorganic bases such as triethylamine (TEA), DABCO, LDA, and K_2CO_3 under the same reaction conditions led to no reaction or a low yield of desired **7a** (runs 2−6). Copper, palladium, or no-metal catalysis in the presence of DBU was also examined, but no improvement was observed (runs 7−9). Solvents were next screened under the conditions of $Rh_2(OAc)_4$ and DBU, and MeCN gave the best result of 81% (runs 10−16). Further studies focused on the amount of DBU (runs 17−21). On the basis of these results, a set of optimal reaction conditions was screened out: 1.5 equiv of **1a**, 3 mol % of $Rh_2(OAc)_4$, 1.5 equiv of DBU, and reflux temperature in MeCN (84%, run 18). In all cases, nontrifluoromethylated cyclized **2** was detected in a large quantity, and intramolecular transfer-trifluoromethylation product **3a**, i.e., Stevens rearrangement product, was observed only in a trace amount up to 10% yield (runs 20−22), even in the absence of **6a** (run 22). No reaction was observed in the absence of $Rh_2(OAc)_4$/DBU, and ArSCF$_3$ **1a** was left intact (run 23).

We proceeded to evaluate the scope of trifluoromethylation by **1a** with a wide variety of substrates **6b−m**, **8a−8c** (Table 2).

Table 2. Scope of Trifluoromethylation of 6 and 8[a]



[a]The reaction of **6** or **8** with reagent **1a** (1.5 equiv) was carried out in the presence of $Rh_2(OAc)_4$ (3 mol %) and DBU (1.5 equiv) in CH_3CN under reflux (substrate scale is 0.1 mmol). Isolated yields are indicated. For detailed reaction conditions, see the Supporting Information. [b]0.2 mmol scale of substrate was examined. [c]2.5 equiv of reagent **1a** was used.

The reaction was performed under 0.1 mmol and/or 0.2 mmol scales. Indanone carboxylates **6b−i** reacted with **1a** smoothly under the optimized conditions, independent of the electronic nature of the substitution on the benzene ring (MeO, Me, Cl) or the size of the ester moiety (Me, Et, *i*Pr, Ad, Bn, *c*Hex) to provide corresponding products **7b−i** in good to excellent yields. Notably, electron-rich dimethoxy-indanone carboxylate **6j** also underwent the trifluoromethylation reaction to give the corresponding product in moderate yield (**7j**, 69−70%). Tetralone carboxylates **6k−l** were also good substrates for the trifluoromethylation reaction to furnish desired products **7k−l** in 46−62% yields. The yield of **7m** was 23−28% when methyl 2-cyclopentanonecarboxylate **6m** was used as substrate. It is noteworthy that dicyanoalkylidenes **8a−c** reacted nicely with **1a** to provide the desired products **9a−c** in moderate to good yields independent of the cyclic and acyclic structures, whereas the bis-trifluoromethylated compound **9aa** was predominantly obtained (51%) instead of **9a** (13%) with the 2.5 equiv of **1a**. The ArSCF$_3$ reagent **1a** was found to be effective for

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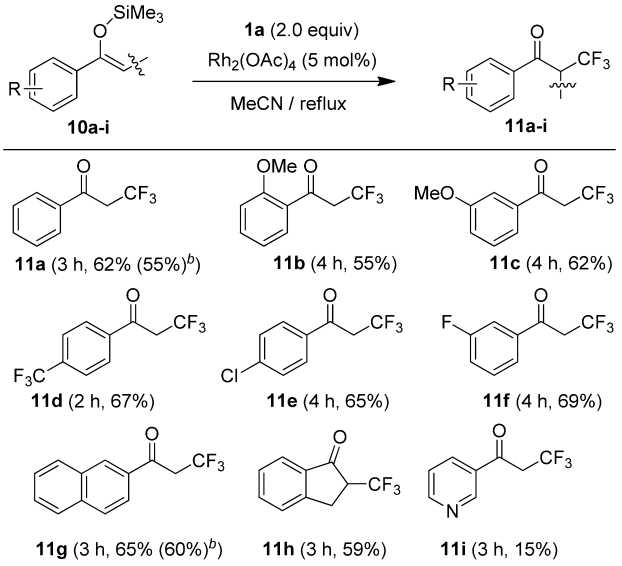
intermolecular transfer trifluoromethylation independent of the substrate family **6** and **8** under the same reaction conditions to provide the desired CF_3-products **7** and **9** within several hours in good to excellent yields.

The scope of rhodium-catalyzed transfer-trifluoromethylation from **1a** to substrates was next extended to silyl enol ethers **10**. The results are summarized in Table 3. The silyl enol ethers

Table 3. Substrate Scope of Trifluoromethylation of 10[a]



[a]The reaction of **10a–i** with reagent **1a** (2.0 equiv) was carried out in the presence of $Rh_2(OAc)_4$ (5 mol %) in MeCN at reflux temperature. For detailed reaction conditions, see SI. [19]F NMR yield. [b]Isolated yield.

10a–f with various substituents on the aromatic ring, including electron-donating (OMe) and electron-withdrawing groups (Cl, CF_3, F) reacted smoothly and led to the corresponding trifluoromethylation product **11a–f** in moderate to good yields. The sterically demanding naphtyl substrate **10g** and indanone trimethylsilyl ether **10h** were also compatible with this transformation, providing desired α-CF_3-ketones **11g** and **11h** in 65% and 59% yield, respectively. Pyridine derivative **10i** was tolerated under the same reaction conditions to provide **10i** in 15% yield. All the reactions of silyl enol ethers **10** proceeded nicely, and the yields of products **11** were moderate to good. Competitive intramolecular Stevens rearrangement providing **3a** was observed only in 5–10% yield (Table 3).

The proposed reaction mechanism is shown in Figure 1. $ArSCF_3$ **1a** initially reacts with $Rh_2(OAc)_4$ providing a rhodium carbene intermediate **A**, which cyclizes into a reactive inner salt **B**.[11] An intermolecular transfer-trifluoromethylation predominantly proceeds from the salt **B** to NuH or Nu-$SiMe_3$ as outlined in the figure to provide CF_3-products, Nu-CF_3 with **2** after a workup process. Intramolecular Stevens rearrangement of the CF_3 group in **B** furnishing **3a** is considerably inferior relative to the desired intermolecular transfer-trifluoromethylation, even in the absence of nucleophiles (up to 10%).

It should be mentioned that the present system displays very different reactivity from the established Stevens rearrangement using thioethers with rhodium carbenoids furnishing intramolecular 1,2-migration products.[12c,d,14] The fact of the preference of unprecedented intermolecular trifluoromethyl transfer to carbon nucleophiles **6**, **8**, and **10** over an

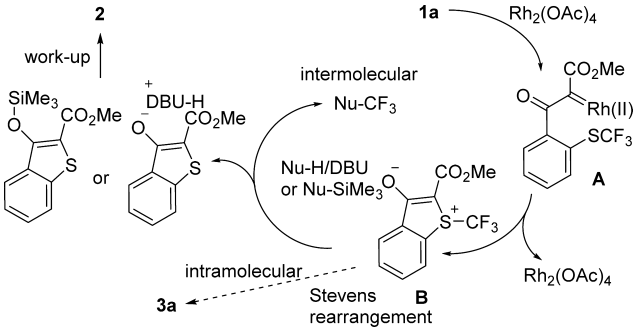


Figure 1. Proposed reaction mechanism I: Intra- vs intermolecular transfer-trifluoromethylation from $ArSCF_3$ **1a** via a tandem process consisting of a rhodium carbene intermediate **A** and a cyclized inner salt **B**.

intramolecular Stevens rearrangement to form **3a** should support a concerted or stepwise cationic reaction pathway for electrophilic trifluoromethylation via $^+CF_3$ (Figure 2a), which is

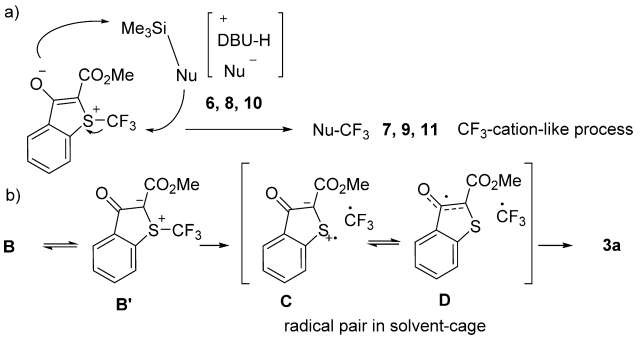


Figure 2. Proposed reaction mechanism II: (a) Cationic process providing intermolecular products. (b) Stevens 1,2-migration process involving radical pair in a solvent-cage providing intramolecular product **3a**.

still one of the matter of debates in fluorine chemistry over decades.[15] The mechanism of Stevens 1,2-rearrangement of stabilized ammonium ylides and sulfonium ylides is proposed to occur via an intramolecular homolytic dissociation-recombination processes involving radical pair in a solvent-cage, by crossover experiments and stereochemical investigations.[14] If the transfer trifluoromethylation in this system involves a radical related process, the intramolecular Stevens 1,2-migration should predominantly be observed to form **3a** over intermolecular reaction (Figure 2b).

We were next interested in a difluoromethylated analogue, $ArSCF_2H$ **1b**, because a difluoromethyl group is also important in medicinal chemistry, due to the isosteric relation between CF_2H group and OH and NH groups through hydrogen bonding.[16,17] The $ArSCF_2H$ **1b** was prepared according to the modified procedure based on Scheme 2 (see, Supporting Information for details), and the reaction was examined. Interestingly, the reactivity of **1b** was rather different from **1a**: the intramolecular reaction of **1b** predominantly proceeded to complete the O–CF_2H product **3b** in 48–56% yield, even in the presence of nucleophile **6a**. Neither intramolecular C–CF_2H products like **3a** nor intermolecular products **12a, b** were observed (Scheme 3a). To see the generality of this reactivity pattern, the reaction of **1b** with other nucleophiles (**6b**, 4-hydroxybenzenesulfonic acid) was also attempted, and similar

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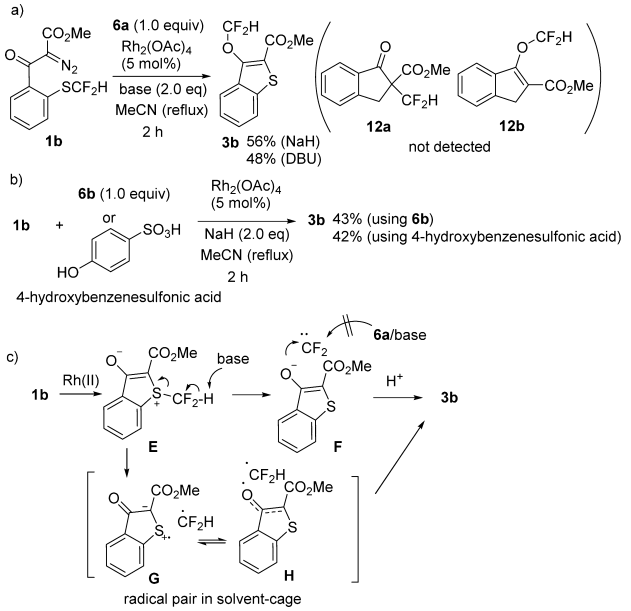
Scheme 3. Reaction of $ArSCF_2H$ 1b under Rhodium Catalysis (a, b) and Its Proposed Mechanism (c)



results were obtained to provide **3b** in 42−43% yields. The formation of O−CF_2H product **3b** rather than C−CF_2H is an additional difference stemming from the reaction of CF_3-reagent **1a**. The reason for these phenomena is not clear, and it could be explained on the basis of the generation of a CF_2 carbene intermediate **F** from a CF_2H salt **E**, as shown in Scheme 3b. In our previous paper, the reaction of 1,3-diketones with CF_2 carbene selectively furnishes O-regioselective difluoromethylation products.[15a] Another possibility is the homolytic cleavage-radical pair recombination process via **G** and **H** as established conventional Stevens 1,2-rearengement in a solvent cage[14] (Scheme 3c). Indeed, we have already hypothesized that O-fluoromethylation might proceed via radical process.[15b,c] Hence, an intramolecular rearrangement to the O-anion or O-radical is superior than the intramolecular C-alkylation and intermolecular C and O-alkylation reactions, although it is still a matter of debate.[15a−c]

In summary, we have demonstrated the intra- vs intermolecular transfer-fluoromethylation (CF_3, CF_2H) of $ArSCF_2X$ (X = F, H) compounds via a carbenoid generation/cyclization tandem process under mild conditions. The $ArSCF_3$ compound **1a**, having a carbenoid generation pendant on the *ortho* position, is thermally stable and can be easily prepared in three steps from commercially and readily available *ortho*-$ArSCF_3$ ethanone **4**. A tandem cyclization and unprecedented intermolecular transfer-trifluoromethylation of **1a** is observed under rhodium catalysis in the presence of nucleophiles, NuH and Nu-$SiMe_3$, giving Nu-CF_3 compounds. On the other hand, the difluoromethylated analogue $ArSCF_2H$ **1b** performs an intramolecular reaction under rhodium catalysis to provide migration CF_2H product. Hence, compound **1a** acts as an electrophilic trifluoromethylation reagent, whereas **1b** can be used as a difluoromethyl building block. Further applications of this methodology are under investigation.[18]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00853.

Experimental procedures and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nozshiba@nitech.ac.jp.

Notes

The authors declare no competing financial interest.

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