Organic LETTERS

Letter

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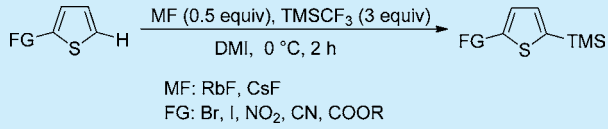
Deprotonative C−H Silylation of Functionalized Arenes and Heteroarenes Using Trifluoromethyltrialkylsilane with Fluoride

Midori Sasaki and Yoshinori Kondo*

Graduate School of Pharmaceutical Sciences, Tohoku University, Aramaki Aza Aoba 6-3, Sendai 980-8578 Japan

Supporting Information

ABSTRACT: A highly selective C−H silylation reaction of functionalized arenes and heteroarenes was developed using Ruppert−Prakash reagent ($TMSCF_3$) activated by alkali metal fluoride. $TMSCF_3$ is considered to play dual roles as a precursor of a mild base and also as a silicon electrophile. The silylation is compatible with sensitive functional groups such as halogen and nitro groups.



The selective functionalization of aromatic C−H bonds under mild and environmentally benign conditions is an important subject in organic synthesis in fields ranging from material science to medicinal chemistry.[1] Arylsilanes have been widely studied in material science for their unique properties, and they are important and versatile intermediates in the synthesis of various functional molecules or biologically attractive molecules.[2] Selective functionalization of arylsilane derivatives has attracted the interest of many synthetic chemists and diverse methodologies have been developed.[2,3] Classically, arylsilanes have been synthesized from the reaction of aryllithium or arylmagnesium compounds with silicon electrophiles. This method, however, is not suitable for arenes with sensitive functional groups. As another C−H functionalization approach, the synthesis of arylsilanes by coupling aryl bromides, aryl iodides, aryl nitriles, or aryl chlorides with disilanes or hydrosilanes using transition-metal catalysis, has been well investigated.[4] Another recent approach involves transition-metal-catalyzed direct C−H functionalization, which has been regarded as a powerful methodology for the direct silylation of arenes.[5] In recent years, a variety of directing groups (imine, oxazoline, pyridine, pyrazole, and tertiary amine functionalities) have been used to control the regioselectivity of C−H bond silylation. On the other hand, deprotonation is considered to be one of the effective methodologies for arene C−H functionalization, and the combination of LiTMP/TMSCl has been used for the deprotonative arylsilylation, but strictly regulated reaction conditions are required for the successful transformation due to the high reactivity of aryllithium species.[6] As for the recent deprotonative functionalization of arenes, Daugulis et al. reported an attractive in situ generation and trapping of aryl carbanion for halogenation.[7] In connection with our recent studies on C−H functionalization using in situ generated reactive base from silylated base precursors and fluoride,[8] we focused our interest in deprotonative C−H arylsilylation using silylated bases and fluorides under mild reaction conditions. Our working hypothesis for aromatic C−H silylation is described in Figure 1, and we designed a catalytic process using dual roles of organosilane as a silylated base precursor and also as a silylating agent.

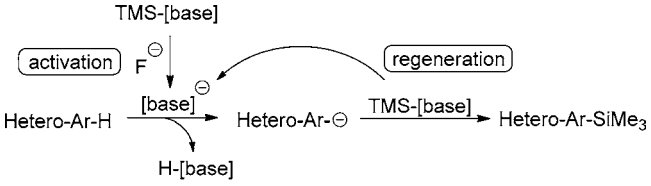


Figure 1. Working hypothesis of the new deprotonative silylation.

Initially, the C−H silylation was examined for the optimization of reaction parameters using benzothiophene (**1a**) as a model substrate. The results are summalized in Table 1. We first screened organosilanes for the aryl C−H silylation under the conditions at room temperature using KF as an activator and DMI as a solvent, which solvent was found to be a suitable solvent in our preliminary experiments.

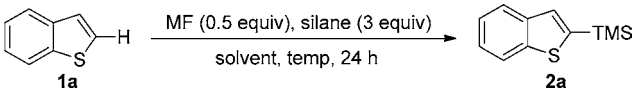
Although the use of aminosilanes gave no silylated product, the use of trifluorotrimethylsilane ($TMSCF_3$) was found to give the desired silylated product **2a** in 14% yield (Table1, entries 1−4). The elevation of the reaction temperature was found to lower the yield, and the reaction at 0 °C gave a better result. The product **2a** was obtained in 51% yield (Table 1, entry 5). The use of other amide solvents such as DMPU or NMP was not effective and gave the product **2a** in low yields (Table 1, entries 6 and 7). The use of RbF or CsF showed excellent performance, and the product **2a** was obtained in high yields (Table 1, entries 8−10), but the use of TMAF gave only a trace amount of the product **2a** (Table 1, entry 11). In the absence of fluoride source, the C−H siylation reaction did not proceed at all (Table 1, entry 12).

$TMSCF_3$ (Ruppert−Prakash reagent) is a commercially available reagent which has been known as a useful precursor for CF_3 carbanion.[9] In general, perfluoroalkylsilanes are relatively stable to acid and water, which is a considerable advantage of perfluoroalkylsilanes over related organometallic

Received: December 19, 2014
Published: January 30, 2015

DOI: 10.1021/ol503671b
Org. Lett. 2015, 17, 848−851

Table 1. Optimization of Reaction Parameters for Benzothiophene Silylation



1a 2a

entry	MF	silane	solvent	temp (°C)	yield[a] (%)
1	KF	$TMSNMe_2$	DMI	rt	0
2	KF	$TMSNEt_2$	DMI	rt	0
3	KF	$(TMS)_3N$	DMI	rt	0
4	KF	$TMSCF_3$	DMI	rt	14
5	KF	$TMSCF_3$	DMI	0	51(41)[b]
6	KF	$TMSCF_3$	DMPU	0	6
7	KF	$TMSCF_3$	NMP	0	14
8	RbF	$TMSCF_3$	DMI	0	86 (83)[b]
9	CsF	$TMSCF_3$	DMI	0	83 (82)[b]
10[c]	CsF	$TMSCF_3$	DMI	0	97 (94)[b]
11	TMAF	$TMSCF_3$	DMI	0	trace
12	none	$TMSCF_3$	DMI	0	0

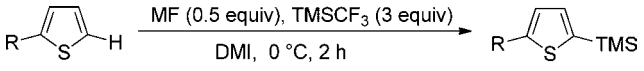
[a]Yields are determined by ^{1}H NMR. [b]Isolated yields are shown. [c]The reaction time is 2 h.

compounds. In the first preparation of $TMSCF_3$ by Ruppert and co-workers in 1984, the ozone-depleting CF_3Br was used with TMSCl mediated by $(Et_2N)_3P$.[10a] But more recently, $TMSCF_3$ has been successfully prepared in high yield by Prakash and co-workers through the reaction of nonozone depleting CF_3H with TMSCl using potassium hexamethyldisilazide (KHMDS).[10b] $TMSCF_3$ has been widely used for introducing CF_3 group in various molecules, but the use of CF_3 carbanion as a base for aromatic C−H deprotonation has not well explored in spite of a suggestive example of 1,3-dinitrobenzene deprotonation by CF_3 carbanion leading to a mixture of many products.[11] The pK_a value of CF_3H is reported to be around 30,[12] and its conjugate base CF_3 carbanion is considered to have enough basicity to deprotonate activated aromatic ring protons.

Using the optimized reaction conditions in Table 1, various functionalized benzothiophenes were examined for the deprotonative C−H silylation (Table 2). It was found that the suitable metal fluoride depends on the substrates in some cases. For the silylation of 5-methylbenzothiophene (**1b**), the use of CsF was superior to RbF. The best result was obtained when the reaction was carried out for 24 h and the product **2b** was obtained in 83% yield (Table 2, entries 1−3). In the case of 5-cyanobenzothiophene (**1c**), RbF showed better performance in short reaction time to give the product **2c** in 93% yield (Table 2, entries 4 and 5). When 5-bromobenzothiophene (**1d**) was used as a substrate, both of RbF and CsF gave excellent results and high yield of the silylated product was obtained (Table 2, entries 6 and 7). 3-Bromobenzothiophene (**1e**) can also be used as a substrate and 2-silylated product **2e** was obtained in good yield without affecting bromo substituent (Table 2, entries 8−10). The silylation reaction of benzofuran (**1f**) was found to proceed using CsF and the 2-silylated product **2f** was obtained in 51% yield.

We next focused our interest in the silylation of functionalized thiophenes using the conditions. Gratifyingly, the presence of a variety of electrophilic functional groups on the thiophene at the 2-position did not interfere with the outcome of the C−H silylation. 2-Substituted thiophenes underwent monosilylation at the C5 position in very good yields (Table 3).

Table 3. Silylation of Functionalized Thiophenes

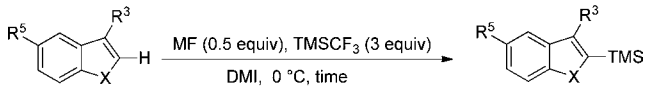


3a-e 4a-e

entry	substrate	R	MF	product	yield[a] (%)
1	**3a**	Br	RbF	**4a**	88 (71)[b]
2	**3a**	Br	CsF	**4a**	60
3	**3b**	I	RbF	**4b**	80 (72)[b]
4	**3b**	I	CsF	**4b**	46
5	**3c**	NO_2	RbF	**4c**	80 (68)[b]
6	**3c**	NO_2	CsF	**4c**	68
7	**3d**	COOEt	RbF	**4d**	40 (37)[b]
8	**3d**	COOEt	CsF	**4d**	0
9	**3e**	CN	RbF	**4e**	20 (10)[b]
10[c]	**3e**	CN	RbF	**4e**	92 (84)[b]
11	**3e**	CN	CsF	**4e**	<5

[a]Yields are determined by ^{1}H NMR. [b]Isolated yields are shown. [c]The reaction was carried out using DMI/THF(1:1) at −20 °C.

Table 2. Silylation of Functionalized Benzothiophenes and Benzofuran



1b-f 2b-f

entry	substrate	X	R^3	R^5	MF	time (h)	product	yield[a] (%)
1	**1b**	S	H	Me	RbF	2	**2b**	10
2	**1b**	S	H	Me	CsF	2	**2b**	60
3	**1b**	S	H	Me	CsF	24	**2b**	83 (81)[b]
4	**1c**	S	H	CN	RbF	2	**2c**	93 (79)[b]
5	**1c**	S	H	CN	CsF	2	**2c**	60
6	**1d**	S	H	Br	RbF	2	**2d**	100 (93)[b]
7	**1d**	S	H	Br	CsF	2	**2d**	91
8	**1e**	S	Br	H	RbF	2	**2e**	66
9	**1e**	S	Br	H	CsF	2	**2e**	77
10[c]	**1e**	S	Br	H	CsF	2	**2e**	72 (65)[b]
11	**1f**	O	H	H	RbF	2	**2f**	38
12	**1f**	O	H	H	RbF		**2f**	51 (51)[b]

[a]Yields are determined by ^{1}H NMR. [b]Isolated yields are shown. [c]$TMSCF_3$ (5 equiv) was employed.

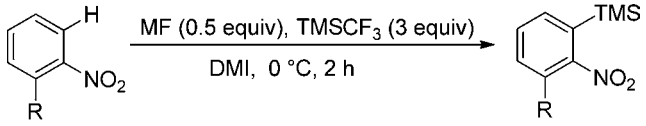
DOI: 10.1021/ol503671b
Org. Lett. 2015, 17, 848−851

For the silylation of 2-bromothiophene (**3a**), the use of RbF showed excellent performance, and 5-silylated product **4a** was obtained in 88% yield, while the use of CsF gave the product **4a** in 60% yield (Table 3, entries 1 and 2). 2-Iodothiophene (**3b**) can be used as a substrate, and the silylated product **4b** was obtained in 80% yield when RbF was used. The use of CsF in this case gave the product **4b** in lower yield (Table 3, entries 3 and 4). The silylation of 2-nitrothiophene (**3c**) proceeded smoothly using RbF to give the product **4c** in 80% yield, while the use of CsF was slightly less effective (Table 3, entries 5 and 6). In the case of ethyl 2-thiophenecarboxylate (**3d**), the silylation proceeded only when RbF was used as an activator to give the product **4d** in 40% yield and the use of CsF was not effective (Table 3, entries 7 and 8). Similarly, the silylation of 2-thiophenecarbonitrile (**4e**) proceeded smoothly only with RbF to give the product **5e** in 92% yield.

Intrigued by the high compatibility with sensitive functional groups such as halogen and nitro groups, our next interest was focused on the silylation of functionalized nitrobenzenes. Nitrobenzenes are versatile synthetic intermediates due to their ease of synthesis, their ability to activate leaving groups in nucleophilic substitution, and their ready reduction to versatile amine derivatives. The selective C−H functionalization chemistry compatible with nitro functionality is considered to be a great advantage. The nitro group is expected to enhance the acidity of adjacent aromatic ring protons significantly, allowing the use of a mild base for deprotonation.

2-Bromonitrobenzene (**5a**) was examined for the silylation, and the silylation occurred at C6 position using RbF or CsF to give the product **6a** in 37 or 28% yield (Table 4, entries 1 and 3). The yield was improved up to 50% yield when excess RbF and $TMSCF_3$ were employed (Table 4, entry 2). 2-Iodonitrobenzene (**5b**) was also silylated using RbF to give the product **6b**, and the use of CsF gave no silylated product (Table 4, entries 4 and 5). The silylation of 1,2-dinitrobenzene **5c** proceeded with CsF to give the product **6c** in 40% yield, and the use of RbF was less effective in this case (Table 4, entries 6−8). The C−Si functionalization of trimethylsilylated nitroarenes has been investigated using electrophiles with fluoride catalysts and these products could be useful intermediates in the synthesis of polyfunctionalized nitroarenes.[13]

Table 4. Silylation of Functionalized Nitrobenzenes



5a-c **6a-c**

entry	substrate	R	MF	product	yield[a] (%)
1	**5a**	Br	RbF	**6a**	37 (35)[b]
2[c]	**5a**	Br	RbF	**6a**	50 (49)[b]
3	**5a**	Br	CsF	**6a**	28 (24)[b]
4	**5b**	I	RbF	**6b**	20 (17)[b]
5	**5b**	I	CsF	**6b**	0
6	**5c**	NO_2	RbF	**6c**	14
7	**5c**	NO_2	CsF	**6c**	28
8[d]	**5c**	NO_2	CsF	**6c**	40 (33)[b]

[a]Yields are determined by ^{1}H NMR. [b]Isolated yields are shown. [c]RbF (2.4 equiv) and $TMSCF_3$ (6 equiv) were employed for the reaction. [d]The reaction was carried out using DMI/THF (1:1) at −20 °C for 24 h.

The CF_3 carbanion generated in situ is considered to function as a base to deprotonate aromatic ring proton. The aryl carbanion reacts with $TMSCF_3$ to give the arylsilane and regenerates CF_3 carbanion which deprotonates another substrate molecule to form a catalytic cycle releasing trifluoromethane CF_3H (HFC-23, bp −82 °C) as a side product of silylation.[14] Whereas the mechanistic details have yet to be elucidated, the observed regioselectivity is considered to be consistent with the acidity of ring protons of arenes and heteroarenes suggesting the ring C−H deprotonation is a key step.[15] Very recently, an important report on the nature of CF_3 carbanion appeared and the discussions on the stability is considered be supportive for the function of CF_3 carbanion as a deprotonating base.[11b,16,17]

In conclusion, we have developed a new selective deprotonative C−H silylation of functionalized arenes and heteroarenes using a combination of Ruppert−Prakash reagent and metal fluoride. Further investigations on the scope, mechanism, and synthetic application of the deprotonative C−H silylation are underway.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedure and characterization data for each compound. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ykondo@mail.pharm.tohoku.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support by a Grant-in-Aid for Scientific Research (B) (No. 23390002), a Grant-in-Aid for Challenging Exploratory Research (No. 25670002) from Japan Society for the promotion of Science, a Grant-in-Aid for Scientific Research on Innovative Areas "Advanced Molecular Transformations by Organocatalysis" (No. 23105009), and the project "Platform for Drug Discovery, Informatics, and Structural Life Science" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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DOI: 10.1021/ol503671b
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DOI: 10.1021/ol503671b
Org. Lett. 2015, 17, 848−851