Fluorine Chemistry

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Synthesis of *gem*-Difluorinated Cyclopropanes and Cyclopropenes: Trifluoromethyltrimethylsilane as a Difluorocarbene Source**

Fei Wang, Tao Luo, Jinbo Hu, Ying Wang, Hema S. Krishnan, Parag V. Jog, Somesh K. Ganesh, G. K. Surya Prakash,* and George A. Olah*

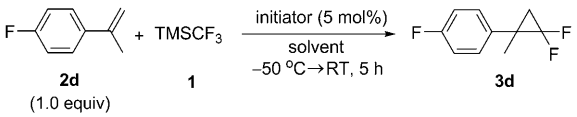
Difluorocyclopropanes and difluorocyclopropenes are becoming an important class of compounds in organofluorine chemistry. Introduction of a fluorine atom onto a cyclopropane ring is known to alter the structure and reactivity of the molecule because of the high electronegativity and small size of the fluorine atom, and consequently the increase in the C–F bond polarity.[1] Fluorine substituents also raise the biological activity, the bioavailability, and in some cases the potency of known biologically active molecules.[1] The difluoromethylene group is also considered as a bioisostere for an oxygen atom in biological studies.[2]

Recently, a unique application of difluorocyclopropanes to trap the 1,3-diradical formed during the mechanochemical activation of the polybutadiene backbone was reported.[3] Besides biological and polymeric applications, difluorocyclopropanes are synthetically useful substrates for a variety of reactions such as thermal rearrangements, bimolecular reactions, carbocation, carbanion, and radical chemistry.[4]

The synthesis of difluorocyclopropanes and difluorocyclopropenes can be achieved in various ways. However, a [2+1] cycloaddition reaction of difluorocarbene to an alkene or an alkyne has proven to be the most efficient method to date.[4,5] This result has led to considerable efforts in developing reagents that can act as a source of difluorocarbene. Owing to the interaction of the lone pairs of electrons on the fluorine substituents with the carbene center, difluorocarbene is a relatively stabilized carbene species (with a singlet ground state) and is therefore less reactive than other dihalocarbenes.[6] This could be one of the reasons why difluorocarbenes do not react well with electron-poor alkenes. Higher temperatures are often required for the generation as well as efficient reactions of difluorocarbene with alkenes. Some of the reagents used previously include sodium chlorodifluoroacetate (or sodium bromodifluoroacetate),[7] $PhHgCF_3$[8] and Me_3SnCF_3[9] (Seyferth reagents), $FSO_2CF_2CO_2SiMe_3$ (TFDA),[6h,10] and Zn/CF_2Br_2.[11] However, most of these reagents suffer from disadvantages such as harsh reaction conditions, high toxicity, lack of commercial availability, and/or low product yields. Recently, Hu and co-workers reported that $TMSCF_2Cl$ can act as an efficient difluorocarbene precursor under chloride-ion catalysis at 110 °C.[12] However, $TMSCF_2Cl$ is not commercially available and its preparation requires the use of ozone-depleting $CBrClF_2$.[13]

For substrates that are thermally unstable, the above-mentioned methods and reagents could be a serious limitation, and development of better difluorocarbene precursors that can generate difluorocarbenes at lower temperatures is required. There are only few reports[14] that discuss difluorocarbene generation at room temperature with Ph_3P/CF_2Br_2,[15] or at low temperatures (below −78 °C) with bis(trifluoromethyl) cadmium, which is a highly pyrophoric reagent, as a source. Again, the use of cadmium or phosphines and the lack of commercial availability of these reagents is a severe limitation. Trifluoromethyltrimethylsilane (Me_3SiCF_3 or $TMSCF_3$), commonly known as the Ruppert–Prakash reagent, is readily available and is the most widely used nucleophilic trifluoromethylating agent for a variety of

Table 1: Optimization of reaction conditions.



2d (1.0 equiv) **1** **3d**

Entry	**1** (equiv)	Solvent	Initiator	Yield [%][a]
1	5	THF	TBAT	82
2	5	THF	TBAF[b]	37
3	5	THF	TMAF	0
4	5	THF	TMAO	0
5	5	THF	NaI	0
6	5	monoglyme	TBAT	54
7	5	diethyl ether	TBAT	21
8	5	toluene	TBAT	0
9	5	acetonitrile	TBAT	0
10	1	THF	TBAT	40
11	2	THF	TBAT	80
12	**2.5**	**THF**	**TBAT**	**83**

[a] Yield of isolated product. [b] 1.0 M solution in THF. TBAT = tetrabutylammonium triphenyldifluorosilicate, TBAF = tetrabutylammonium fluoride, TMAF = tetramethylammonium fluoride, TMAO = trimethylamine oxide. Optimized reaction conditions (entry 12) are highlighted in bold.

[*] F. Wang, T. Luo, Prof. Dr. J. Hu
Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Ling-Ling Road, Shanghai, 200032 (China)
Fax: (+86) 21-6416-6128
E-mail: jinbohu@sioc.ac.cn
Dr. Y. Wang, H. S. Krishnan, Dr. P. V. Jog, Dr. S. K. Ganesh, Prof. Dr. G. K. S. Prakash, Prof. Dr. G. A. Olah
Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California
University Park, Los Angeles, CA 90089-1661 (USA)
Fax: (+1) 213-740-6679
E-mail: gprakash@usc.edu

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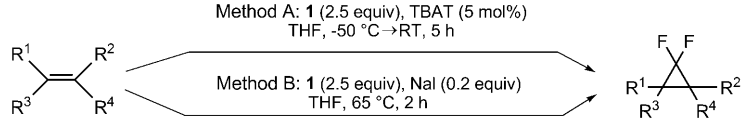
applications.[16] Silicon-based systems have been increasingly used for transition-metal-based (Cu, Pd, Ni) trifluoromethyl-group transfer.[17] Importantly, $TMSCF_3$ can be used as a trifluoromethyl anion source at low temperatures, and the decomposition of the trifluoromethyl anion to difluorocarbene and a fluoride ion at low temperatures was recognized as a side decomposition reaction.[18] Based on this background, we studied the cyclopropanation reaction of alkenes with $TMSCF_3$ at low temperatures using nonmetallic fluoride sources as initiators. Additionally, we found that $TMSCF_3$ can be easily activated even at room and/or higher temperatures, and we explored reactions of this reagent with alkenes and even alkynes at 65 °C under iodide-based activation. Herein, we report our efforts toward the synthesis of *gem*-difluorocyclopropanes and *gem*-difluorocyclopropenes by using $TMSCF_3$ as a novel difluorocarbene source.

We have previously reported that by using anhydrous nonmetallic fluoride sources such as tetramethylammonium fluoride (TMAF) or tetrabutylammonium triphenyldifluorosilicate (TBAT), $TMSCF_3$ can be employed as a difluorocarbene source that reacts at low temperatures (−50 to 25 °C) with electron-rich alkenes to give *gem*-difluorocyclopropanes.[19] During optimization of the reaction conditions, we observed a marked effect of the initiator that was used to activate $TMSCF_3$ (used in excess, 5 equiv), and TBAT, which is a nonmetallic initiator, proved to be the best in THF (Table 1, entries 1–5). Better yields tend to be obtained in etheral solvents, and THF proved to be the ideal solvent (Table 1, entries 1 and 6–9). Optimization of the amount of $TMSCF_3$ (Table 1, entries 1 and 10–12) showed that 2.5 equivalents gave the best results and we chose these conditions (Table 1, entry 12) to perform all further reactions (Table 2).

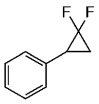
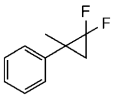
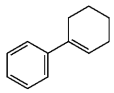
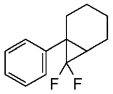
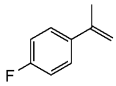
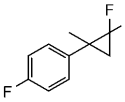
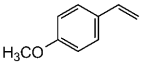
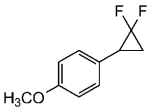
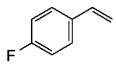
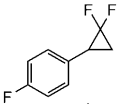
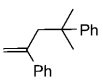
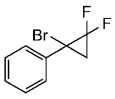
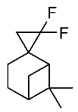
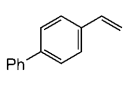
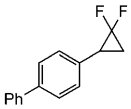
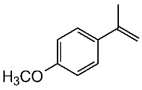
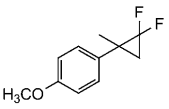
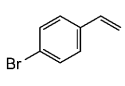
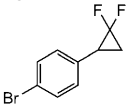
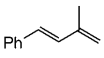
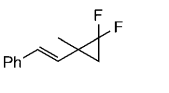
Both aryl- and alkyl-substituted alkenes gave the desired cyclopropanes in good yields. As expected for the electron-deficient singlet difluorocarbene (:CF_2), electron-rich alkenes gave better yields than electron-poor alkenes (Table 2, entries 5, 6, 8, and 9; method A). The isolation of some of the cyclopropane products was difficult using standard column chromatographic techniques, and distillation was used as the purification method of choice (Table 2, entries 5, 9, 10, 12, and 14). Unfortunately, some alkenes either did not react or gave poor yields under these low-temperature reaction conditions.

To extend the scope of the Rupert–Prakash reagent **1**, we decided to use a different initiator (NaI) and higher temperatures to achieve a more efficient synthesis of the corresponding difluorocyclopropanes (Table 2; method B). Our initial efforts were directed toward increasing the yield of the

Table 2: [2+1] Cycloaddition between difluorocarbene (generated from **1**) and alkenes (**2**).



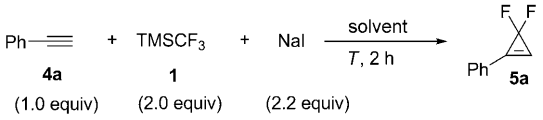
2 **3**

Entry[a]	Substrate	Product	Yield [%]	Entry	Substrate	Product	Yield [%]
1			82[a] 85[b]	9			20[a] (33)[c] 81[b]
	2a	**3a**			**2i**	**3i**	
2			83[a] 85[b]	10			80[a] 82[b]
	2b	**3b**			**2j**	**3j**	
3			83[a] 82[b]	11			10[a,c] 83[b]
	2c	**3c**			**2k**	**3k**	
4			82[a] 85[b]	12			80[a] 82[b]
	2d	**3d**			**2l**	**3l**	
5			23[a] (38)[c] 78[b]	13			78[a] 83[b]
	2e	**3e**			**2m**	**3m**	
6			0[a] 79[b] (97)[c]	14			79[a] 88[b]
	2f	**3f**			**2n**	**3n**	
7			– 83[d]	15			– 94[d]
	2g	**3g**			**2o**	**3o**	
8			26[a,c] 83[d]	16			– 90[d]
	2h	**3h**			**2p**	**3p**	

[a] Method A was used. [b] Method B was used. [c] Yield was determined by ^{19}F NMR spectroscopy using C_6F_6 as an internal standard. [d] Reaction was carried out in CH_3CN at 110 °C for 2 h.

product, and hence we chose acetonitrile as the solvent, a greater than stoichiometric amount of NaI (2.2 equiv), and high temperatures (110 °C; Table 2, entries 7, 8, 15 and 16). However, further optimization of the reaction conditions led us to use 0.2 equivalents of NaI in THF at 65 °C to achieve greater conversions to the corresponding difluorocyclopropanes. Under these reaction conditions, not only electron-rich alkenes but even electron-poor alkenes gave excellent yields of the corresponding difluorocyclopropanes (Table 2, entries 4, 6, 7, and 11; method B). This result could be due to the thermal activation of the parent difluorocarbene and/or alkene under the chosen reaction conditions. Encouraged by our results with alkenes, we also examined the NaI-promoted [2+1] thermal cycloaddition reactions between difluorocarbene (generated from **1**) and alkynes **4**, by using ethynylbenzene **4a** as a model substrate (Table 3). The reaction was

Table 3: Optimization of reaction conditions.



Entry[a]	Solvent	*T* [°C]	Yield [%][b]
1	DME	110	37
2	**THF**	**110**	**99**
3	acetonitrile	110	73
4	toluene	110	0
5	THF	80	82
6	THF	110	83[c]
7	THF	110	71[d]
8	THF	110	0[e]

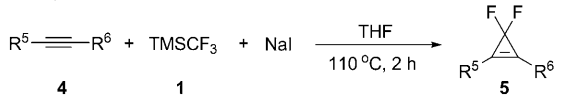
[a] Typical reaction conditions: **2a** (1 mmol), **1** (2 mmol), NaI (2.2 mmol) and solvent (3 mL) were added to a pressure tube equipped with a magnetic stirrer and the tube was sealed. The reaction mixture was vigorously stirred at the indicated temperature for 2 h. [b] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [c] 1.6 equiv of $TMSCF_3$ were used. [d] 1.0 equiv of NaI was used. [e] NaBr was used instead of NaI. DME = 1,2-dimethoxyethane. Optimized reaction conditions (entry 2) are highlighted in bold.

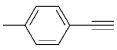
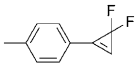
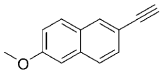
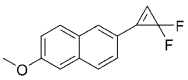
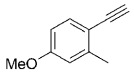
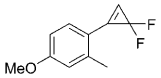
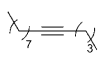
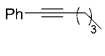
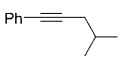
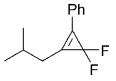
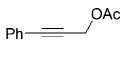
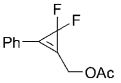
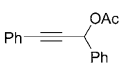
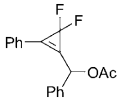
typically performed in a sealed reaction tube at 110 °C for 2 h. It turned out that the product yield was sensitive to the solvent that was used; THF was found to be a better solvent for this reaction than DME or acetonitrile (Table 3, entries 1–3).

The [2+1] cycloaddition reaction could not proceed in toluene, and the two starting materials **1** and **4a** were recovered (Table 3, entry 4). Decreasing either the reaction temperature or the amount of reagent **1** led to a decrease in product yield (Table 3, entries 5 and 6). It was found that the addition of a greater than stoichiometric amount of NaI relative to **1** was necessary to obtain product **5a** in 99% yield; the addition of 0.5 equivalents of NaI relative to **1** gave **5a** in only 71% yield (Table 3, entries 2 and 7). On the other hand, the reaction did not occur when NaBr was used (Table 3, entry 8).

By using the optimized reaction conditions (Table 3, entry 2), we investigated the scope of the current NaI-promoted [2+1] cycloaddition between difluorocarbene (generated from **1**) and alkynes **4** (Table 4). It was found that by using the $TMSCF_3$/NaI reagent system, a variety of structurally diverse mono- and disubstituted alkynes **4a**–**4l** were readily converted into *gem*-difluorinated cyclopropenes **5a**–

Table 4: [2+1] Cycloaddition between difluorocarbene (generated from **1**) and alkynes **4**.

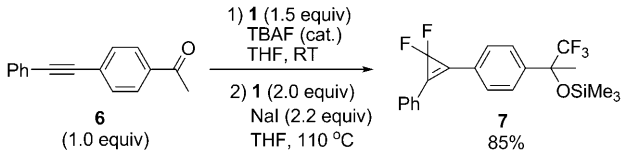


Entry[a]	Substrate	Product	Yield [%][b]
1			99[c]
	4a	**5a**	
2			73[c]
	4b	**5b**	
3			96[c]
	4c	**5c**	
4			95
	4d	**5d**	
5			94
	4e	**5e**	
6			90
	4f	**5f**	
7			99[d]
	4g	**5g**	
8			80
	4h	**5h**	
9			95
	4i	**5i**	
10			96
	4j	**5j**	
11			88
	4k	**5k**	
12			68
	4l	**5l**	

[a] For all cases, the molar ratio of reactants was **4**/**1**/NaI = 1.0:2.0:2.2. [b] Yield of isolated product. [c] Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as the internal standard. [d] The reaction temperature was 80 °C.

5l in good to excellent yields. We also found that the reaction worked well with both alkyl- and aryl-substituted alkynes. It is noteworthy that in the case of tetradec-5-yne **4g**, the reaction at 110 °C resulted in a complete decomposition of the product, however, when we performed the reaction at 80 °C for 2 h, the desired product **5g** was obtained in almost quantitative yield (Table 4, entry 7).

Considering that **1** can serve both as a nucleophilic trifluoromethylating agent[15] and as a difluorocarbene equivalent under different reaction conditions, we envisioned that the reagent might be applied in a one-pot sequential trifluoromethylation and [2+1] cycloaddition reaction. To verify this assumption, we reacted **1** with 4′-(phenylethynyl)-acetophenone (**6**), which contains both a carbonyl group and a triple bond. As shown in Scheme 1, **1** enabled both a fluoride-initiated nucleophilic trifluoromethylation on the carbonyl group and a NaI-promoted difluoromethylenation on the triple bond to give product **7** in 85% overall yield.



Scheme 1. One-pot sequential trifluoromethylation and difluoromethylenation with $TMSCF_3$ (**1**).

In conclusion, we have successfully developed an efficient method for the generation of difluorocarbene from the Ruppert–Prakash reagent (**1**). This method has enabled the synthesis of *gem*-difluorocyclopropanes and difluorocyclopropenes from alkenes and alkynes. TBAT, which is a nonmetallic fluoride compound, was able to initiate decomposition of **1** to generate difluorocarbene at low temperatures, thus giving the corresponding *gem*-difluorocyclopropane in good yields. This procedure could be a very attractive synthetic protocol for the synthesis of thermally unstable *gem*-difluorocyclopropanes. NaI was found to play a crucial role in promoting the [2+1] cycloaddition of alkenes and alkynes at higher temperatures. It was also found that **1** could be applied in one-pot sequential trifluoromethylation/difluoromethylenation reactions. Since **1** is readily available and much less toxic than the Seyferth reagents (Me_3SnCF_3 and $PhHgCF_3$), the new synthetic protocol promises to find many applications in the synthesis of difluoromethylene-containing compounds.

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