Volume 57
Number 3
11 January 2021
Pages 261–406

ChemComm

Chemical Communications

rsc.li/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

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ChemComm

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View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2021, 57, 319

Received 5th September 2020,
Accepted 2nd December 2020

DOI: 10.1039/d0cc06004f

rsc.li/chemcomm

$TMSCFX_2$ (X = Cl, Br) as halofluorocarbene sources for the synthesis of halofluorocyclopropanes†

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$TMSCFX_2$ (X = Cl, Br; TMS = trimethylsilyl) have been developed as halofluorocarbene (CFX, X = Cl, Br) precursors for [2+1] cyclopropanation with alkenes. Structurally diverse halofluorocyclopropanes were obtained in good to excellent yields. It was found that the reactivity order of the three halofluorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$) in halofluorocyclopropanation with 1,1-diphenylethylene can be very different under different reaction conditions.

Fluorocyclopropanes have found applications in a variety of biologically active molecules and bioisosteres of natural products that were developed over the past few decades.[1] The introduction of fluorine atom(s) into constrained three-membered rings could affect the conformation and physicochemical properties of the corresponding fluorocyclopropane molecules,[2] thus allowing the discovery of novel bioactive compounds. Some bioactive molecules containing halofluorocyclopropane moieties are shown in Fig. 1. Ethyl 2-(4-(2-chloro-2-fluorocyclopropyl)phenoxy)-2-methylpropanoate (**A**) is known as a hypolipemic agent,[3] while other chlorofluoro- or bromofluorocyclopropanes (**B–D**) have shown insecticidal or acaricidal activity.[4]

Halofluorocarbenes are reactive intermediates for several types of fluorohaloalkylation reaction, among which, the [2+1] cycloaddition reaction between a halofluorocarbene and an alkene has proved to be the most straightforward method to construct halofluorocyclopropanes.[5] Because of the interaction of the electron lone pairs of fluorine with the carbenoid carbon center, halofluorocarbene tends to be a relatively stabilized species with a singlet ground state.[5a] Among all the halofluorocarbenes (:CF_2, :CFCl, :CFBr, and :CFI), difluorocarbene (:CF_2) has been the most widely studied.[5] In recent years, many convenient and efficient :CF_2 sources have been developed,[6] including $FSO_2CF_2CO_2R$ (R = $SiMe_3$, Me), $BrCF_2CO_2Na$, $TMSCF_2X$ (X = F, Cl, Br), and $Ph_3P^+CF_2CO_2^-$ reagents. By contrast, sources of :CFCl and :CFBr are limited, and most of the halofluorocarbene precursors including $CHFX_2$ (X = Cl, Br),[7] CFX_2CO_2R (X = Cl, Br, R = Me, Et),[8] and $CFCl_2C(O)CFCl_2$[9] required a strong base (*e.g.* NaOMe) to generate :CFX. Although some other reagents, such as $CFCl_3$,[10] $PhHgCFX_2$ (X = Cl, Br),[11] and $CFBr_2CO_2Na$,[10] could give access to halofluorocarbenes under base-free conditions, corrosive $TiCl_4$,[10] a toxic organomercury reagent,[11] or transition metal catalyst (NHC)AgCl (NHC = N-heterocyclic carbene)[12] was needed in the related reaction system. In this context, it is highly desirable to develop new halofluorocarbene reagents that are able to release halofluorocarbenes in a mild and efficient way.

Fluoroalkyltrimethylsilanes ($TMSR_f$) are commonly used as nucleophilic fluoroalkylating agents, among which the most well-known example is the Ruppert–Prakash reagent ($TMSCF_3$).[13] $TMSCF_3$ has been widely used for the direct trifluoromethylation of aldehydes, ketones, imines, esters, and amides, among

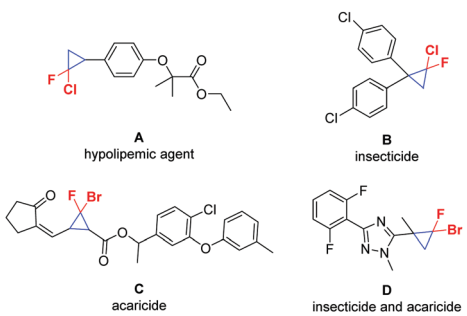

Fig. 1 Some bioactive molecules containing halofluoro-cyclopropane moieties.

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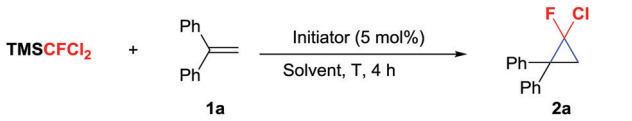
† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cc06004f

others.[14] Fluoroalkylated organosilanes can also participate in radical reactions *via* fluoroalkyl radicals.[15] Recently, our group and others reported that fluoroalkylsilanes, such as $TMSCF_2Cl$ and $TMSCF_2Br$, can act as difluorocarbene reagents.[16] These reagents require only mild nucleophiles to achieve C–Si bond cleavage and generate the desired difluorocarbene intermediates. Inspired by the $TMSCF_2X$ reagents, we envisaged that $TMSCFX_2$ (X = Cl, Br) could also act as new halofluorocarbene reagents, in which the silicon center is attacked by a nucleophile to produce CFX_2^-, followed by α-elimination of X^- to give :CFCl or :CFBr species. Herein, we report the [2+1] cycloaddition reactions of $TMSCFX_2$ (X = Cl and Br) with alkenes to give halofluorocyclopropanes, and compare the reactivity difference among the three fluorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$).

Our investigation began with the [2+1] chlorofluorocyclopropanation using fluorodichlorotrimethylsilane ($TMSCFCl_2$) as the chlorofluorocarbene source and 1,1-diphenylethylene (**1a**) as the model substrate. Reaction parameters including the solvent, initiator, and temperature were carefully screened, and the results are shown in Table 1. When the reaction was carried out in THF at 110 °C in the presence of 5 mol% of *n*-Bu_4NBr (TBAB) in a sealed pressure tube, no product **2a** was formed (Table 1, entry 1). Other polar solvents were also unfavorable to this transformation since very low yield of **2a** was obtained in the presence of CH_3CN or DMF (entries 2 and 3). The less polar solvent toluene proved to be the optimal solvent which allowed the formation of **2a** in 98% yield (entry 4). In addition to *n*-Bu_4NBr, *n*-Bu_4NCl (TBAC), *n*-Bu_4NF (TBAF), Et_3BnNCl, and *n*-$C_{18}H_{37}Me_3NBr$ were further examined as initiators, and in all cases product **2a** was formed in excellent yield (89–99%; entries 5–8). Decrease of the reaction temperature to 80 °C gave a comparable yield, but no reaction occurred at room temperature (entries 9 and 10). It is worth noting that an initiator was critical for this chemistry because no desired product was formed in the absence of a quaternary ammonium salt (entry 11). Finally, the optimized reaction conditions were obtained as follows: **1a** (1.0 equiv.), $TMSCFCl_2$ (1.5 equiv.), *n*-Bu_4NBr or *n*-Bu_4NCl (5 mol%), 110 °C, 4 h (entries 4 or 5).

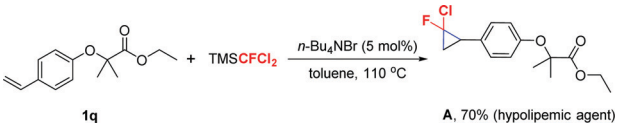
Table 1 Optimization of the reaction conditions using $TMSCFCl_2$ and 1,1-diphenylethylene (**1a**)[a]



Entry	Solvent	*T* (°C)	Initiator[b] (5 mol%)	Yield of **2a**[c] (%)
1	THF	110	*n*-Bu_4NBr	0
2	CH_3CN	110	*n*-Bu_4NBr	16
3	DMF	110	*n*-Bu_4NBr	Trace
4	Toluene	110	*n*-Bu_4NBr	98
5	Toluene	110	*n*-Bu_4NCl	>99
6	Toluene	110	*n*-Bu_4NF	93
7	Toluene	110	Et_3BnNCl	91
8	Toluene	110	*n*-$C_{18}H_{37}Me_3NBr$	89
9	Toluene	80	*n*-Bu_4NBr	94
10	Toluene	r.t.	*n*-Bu_4NBr	0
11	Toluene	110	None	0

[a] $TMSCFCl_2$ (0.3 mmol, 1.5 equiv.) and **1a** (0.2 mmol, 1.0 equiv.) were used. [b] The amount of initiator was calculated on the basis of the amount of reactant **1a** used. [c] All yields were determined using ^{19}F NMR spectroscopy with $PhCF_3$ as an internal standard.

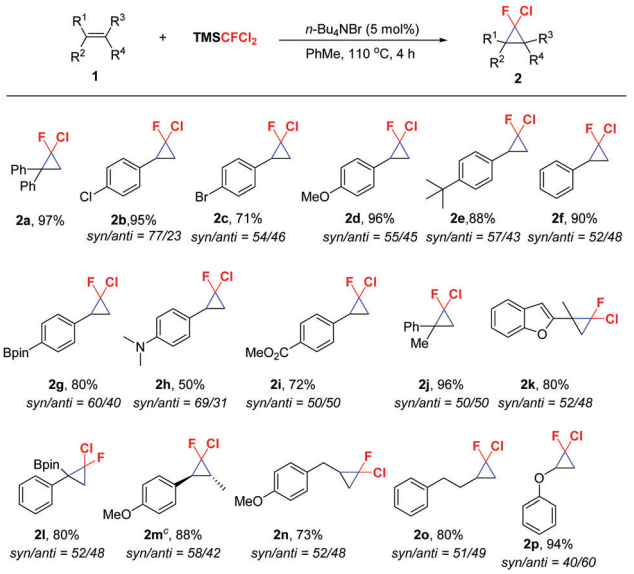
Next, we examined the substrate scope of the present [2+1] cyclopropanation between $TMSCFCl_2$ and various alkenes **1** using standard reaction conditions (as those in Table 1, entry 9).[17] As shown in Scheme 1, the reactions with most of the examined substrates **1** provided the corresponding products **2** in good to excellent yields. Most aryl-substituted alkenes bearing electron-donating or electron-withdrawing groups were able to smoothly proceed in the current chlorofluorocyclopropanation reaction (**2a–2g** and **2l–2m**) except for *N*,*N*-dimethyl-4-vinylaniline (**2h**, only in 50% yield). Aryl-substituted alkenes containing Bpin groups, reacted with $TMSCFCl_2$ to give **2g** and **2j** in 80% yield (in both cases). The reaction was also amenable to heterocycle-substituted alkene **1l**, and **2l** was formed in 80% yield. Furthermore, alkyl-substituted alkenes (such as **1n** and **1o**) are slightly less reactive than aryl-substituted ones, affording **2n** and **2o** in 73% and 80% yield, respectively. The reaction with (vinyloxy)benzene gave the product **2p** in 94% yield. Moreover, the present chlorofluorocyclopropanation was applied to synthesize compound A (see Fig. 1) from alkene **1q** in 70% yield (eqn (1)).



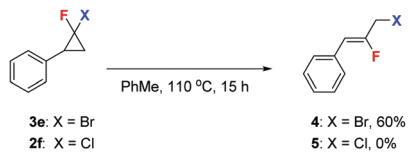
(1)

Encouraged by the success in chlorofluorocyclopropanation with $TMSCFCl_2$, we further explored the analogous bromofluorocyclopropanation with $TMSCFBr_2$ using 1,1-diphenylethylene (**1a**) as the model substrate. After a quick screening of the reaction conditions [see Table S1 in the (ESI†)], we found that under similar conditions to those used for $TMSCFCl_2$, a full conversion of alkene **1a** (8 hours) led to the desired product **3a** ((2-bromo-2-fluorocyclopropane-1,1-diyl)dibenzene) in only 62% yield (determined by ^{19}F NMR). The ^{19}F NMR spectra of **3a** showed the presence of a by-product. Indeed, we found that when fluorobromocyclopropane **3e** was heated at 110 °C for 15 hours in toluene, it underwent isomerization to give the corresponding ring-opening product **4** in 60% yield (determined by ^{19}F NMR; Scheme 1), which explains part of the reason for the low efficiency of the desired fluorobromocyclopropanation reaction at high temperature (110 °C). Interestingly, we found that the fluorochlorocyclopropane product **2f** did not undergo similar isomerization upon heating at 110 °C (Scheme 2).

Owing to the undesired thermal isomerization of cyclopropanes upon heating, we further developed other reaction conditions to achieve efficient bromofluoro–cyclopropanation reactions between $TMSCFBr_2$ and alkenes at room temperature. We used an inorganic base as an activator to optimize the



Scheme 1 [2+1] Cycloaddition reaction between $TMSCFCl_2$ and alkenes.[a,b] [a] $TMSCFCl_2$ (0.75 mmol, 1.5 equiv.) and **1** (0.5 mmol, 1.0 equiv.) were used. [b] Unless otherwise mentioned, isolated yields are given. [c] *E*-1-Methyl-2-*p*-methoxyphenylethene (**1m**) was used, and the relative anti-configuration of the methyl and *p*-methoxyphenyl groups in product **2m** is shown.

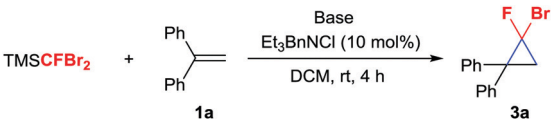


Scheme 2 Ring-opening isomerization of the bromofluoro-cyclopropane **3e** upon heating.

conditions for the reaction between $TMSCFBr_2$ and 1,1-diphenylethylene (**1a**) in dichloromethane (DCM)/water in the presence of phase-transfer catalyst Et_3BnNCl (Table 3). When 12 equivalents of KOH (aq., 20 wt%) was added dropwise to the reaction mixture, product **3a** was formed in 66% yield (Table 2, entry 1). By increasing the concentration of the KOH aqueous solution to 50 wt%, the yield of **3a** was increased to 85% (entry 2). However, 24 equivalents of KOH (aq., 50 wt%) did not improve the yield of **3a** (entry 3). The optimal yield (94%) of **3a** was obtained when 12 equivalents of NaOH (aq., 50 wt%) was used as an activator (entry 4). In contrast, the addition of weaker base Na_2CO_3 was ineffective to this reaction (entry 7).

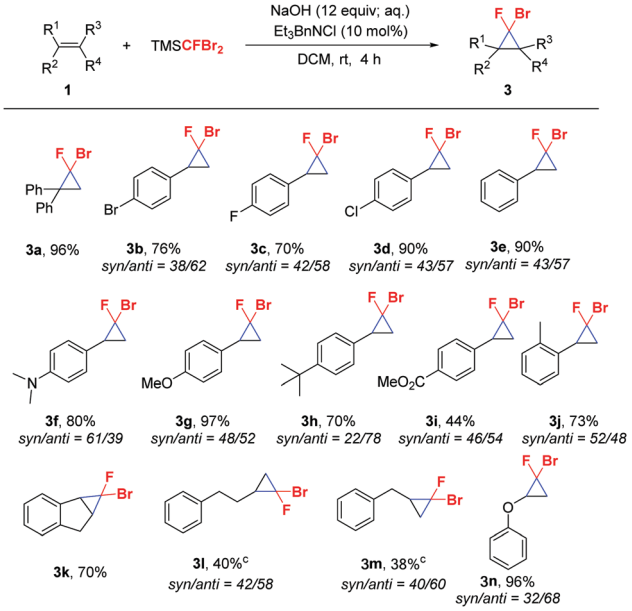
With the optimized reaction conditions in hand (Table 2, entry 4), we investigated the substrate scope of the bromofluorocyclopropanation reaction between $TMSCFBr_2$ and alkenes.[17] As shown in Scheme 3, most of the alkenes that we examined were able to undergo bromofluorocyclopropanation to provide the corresponding products in high yields. Aryl-substituted olefins bearing either electron-donating or electron-withdrawing groups were amenable to the reaction. In particular, some compounds, such as **3f** and **3k**, which were only formed in low yields using 5% TBAB in PhMe at 110 °C (as the conditions used in Scheme 1), could be obtained in good yields

Table 2 Optimization of the reaction conditions using $TMSCFBr_2$ and 1,1-diphenylethylene (**1a**) in an aqueous medium[a]



Entry	Base	Equivalents[b]	Yield of **3a**[c] (%)
1	KOH (aq., 20 wt%)	12	66
2	KOH (aq., 50 wt%)	12	85
3	KOH (aq., 50 wt%)	24	75
4	NaOH (aq., 50 wt%)	12	94
5	NaOH (aq., 50 wt%)	24	69
6	NaOH (aq., 50 wt%)	6	85
7	Na_2CO_3 (aq., 20 wt%)	12	Trace

[a] $TMSCFBr_2$ (0.50 mmol, 2.0 equiv.) and **1a** (0.25 mmol, 1.0 equiv.) were used. [b] The amount of base was calculated on the basis of the amount of alkene **1a**. [c] All yields were determined using ^{19}F NMR spectrosopy with $PhCF_3$ as an internal standard. Et_3BnNCl = benzyltriethylammonium chloride (TEBAC).

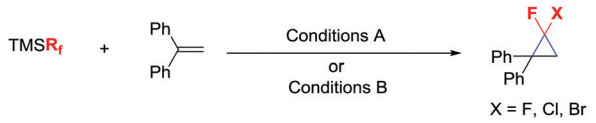


Scheme 3 [2+1] Cycloaddition reactions between $TMSCFBr_2$ and alkenes.[a,b] [a] $TMSCFBr_2$ (0.50 mmol, 2.0 equiv.), **1** (0.25 mmol, 1.0 equiv.) and NaOH (12 equiv.; as 50 wt% aqueous solution) were used. [b] Isolated yields. [c] The reaction time was 12 h.

(85% and 70%, respectively) under the present NaOH-mediated conditions. The reaction with vinyl ether **1n** gave the product **3n** in 96% yield. However, we found that the reactions with alkyl-substituted alkenes gave the corresponding products in moderate yields (such as **3l** and **3m**), although the reaction time was prolonged to 12 h. It is worthy to note that product **3a** could be readily debrominated to give 1-fluoro-2,2-diphenylcyclopropane in 75% yield (see section 6 in the ESI†).

Finally, we conducted a comparative study on the reactivity of the different halofluorochlorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$) developed by our group. As shown

Table 3 The comparison of the reactions using different halofluorocarbene reagents and 1,1-diphenylethylene



	Conditions A[a]		Conditions B[b]	
$TMSR_f$	Conversion[c] (%)	Yield[d] (%)	Conversion[c] (%)	Yield[d] (%)
$TMSCF_2Br$	100	98	0	0
$TMSCFCl_2$	95	90	90	85
$TMSCFBr_2$	70	65	100	94

[a] Conditions A: n-Bu_4NBr (5 mol%); toluene as solvent; 110 °C; 4 h. [b] Conditions B: NaOH (12 equiv.; as 50 wt% aqueous solution); Et_3BnNCl (10 mol%); DCM as solvent; r.t.; 4 h. [c] Conversion of alkene was determined by ^1H NMR spectroscopy analysis of the crude product using 1,3,5-triisopropylbenzene as an internal standard. [d] Yield of the product was determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

in Table 3, under non-aqueous conditions A [TBAB (5 mol%), PhMe as solvent, 110 °C, 4 h], both the conversion of alkene and product yield increased in the following order: $TMSCF_2Br$ > $TMSCFCl_2$ > $TMSCFBr_2$. However, under the DCM/water biphasic conditions [NaOH (aqueous solution, 12 equiv.), Et_3BnNCl (10 mol%), dichloromethane as the solvent, r.t., 4 h], the conversion of alkene and product yield increased in the following order: $TMSCF_2Br$ < $TMSCFCl_2$ < $TMSCFBr_2$. The different reactivity order of the three halofluorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$) in halofluorocyclopropanation with 1,1-diphenylethylene is mainly due to the different reaction mechanisms in the non-aqueous and aqueous medium (see section 4 in the ESI†).

This work was financially supported by the Natural Science Foundation of China (No. 21632009 and 214210025), the Key Programs of the Chinese Academy of Sciences (No. KGZD-EWT08), the Key Research Program of Frontier Sciences of CAS (No. QYZDJ-SSW-SLH049), the Shanghai Science and Technology Program (No. 18JC1410601), the Natural Science Foundation of Zhejiang Province (No. LY18B020003 and LY18B020002), and Chemical Engineering & Technology of Zhejiang Province First-Class Discipline (Taizhou University).

Conflicts of interest

There are no conflicts to declare.

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