Fluoride Ion-Initiated Decarboxylation of Silyl Alkynoates to Alkynylsilanes

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ABSTRACT: This communication describes the development of a metal-free catalytic decarboxylation of silyl alkynoates to alkynylsilanes. Treatment of a silyl alkynoate with a catalytic amount of tetrabutylammonium difluorotriphenylsilicate (TBAT) in *N,N*-dimethylformamide at 150 °C resulted in decarboxylation to give the corresponding alkynylsilane in good to excellent yield (75 → 95%). The TBAT system was applicable to the decarboxylation of sterically demanding silyl alkynoates such as *tert*-butyldiphenylsilyl 3-phenylpropiolate. Mechanistic studies revealed that the tetrabutylammonium alkynoate derived from TBAT and the silyl alkynoate act as a catalyst for the decarboxylation.

· Transition-metal free   · Catalytic amount of fluoride
· Applicable to bulky silyl esters   · CO_2 as a co-product
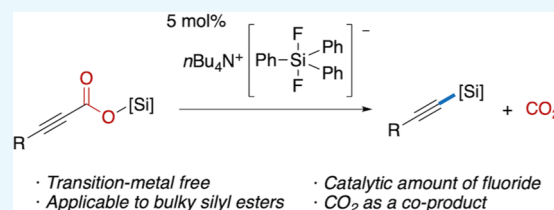
INTRODUCTION

Decarboxylative transformations are recognized as useful reactions in organic synthesis, because carboxylic acids and their ester derivatives are readily available starting materials.[1] Among them, the class of decarboxylation reactions that connect two moieties in a molecule separated by a carboxyl group, such as the protodecarboxylation of carboxylic acids and decarboxylative allylic alkylation of *β*-keto allyl esters, are operationally advantageous: the only stoichiometric coproduct is carbon dioxide, which is nontoxic, nonflammable, and readily removable from the reaction medium.[2]

Alkynylsilanes are useful building blocks in organic synthesis.[3] While the nucleophilic substitution of a halosilane with a metal acetylide prepared by deprotonating a terminal alkyne with an organometallic reagent is one of the most common methods for the synthesis of alkynylsilanes (Scheme 1a),[4] the high nucleophilicity of metal acetylides limits their functional group tolerance, and the coproducts derived from the organometallic reagents are sometimes problematic from the viewpoints of practicality and atom economy. Therefore, the catalytic Si−C cross-coupling of a terminal alkyne with a silicon electrophile has attracted increasing attention, and various silicon electrophiles such as halosilanes,[5,6] hydrosilanes,[7] and vinylsilanes[8] are now available for this purpose (Scheme 1b). On the other hand, we recently reported a catalytic decarboxylation approach for the synthesis of alkynylsilanes (Scheme 1c).[9−11] In the presence of a copper-based catalyst, a silyl alkynoate is decarboxylated to afford the corresponding alkynylsilane. Although the copper-catalyzed system has some advantages such as a low catalyst loading, mild reaction conditions, and easy-to-remove carbon dioxide as the coproduct, the steric hindrance of the silyl substituents strongly affected the reaction progress and the decarboxylation

Scheme 1. Approaches to the Synthesis of Alkynylsilanes

(a) *nucleophilic substitution*   (c) *Cu-catalyzed decarboxylation*

(b) *Si–C cross-coupling*
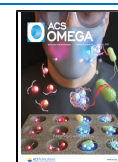
(d) *decarboxylation with F⁻*
THIS WORK
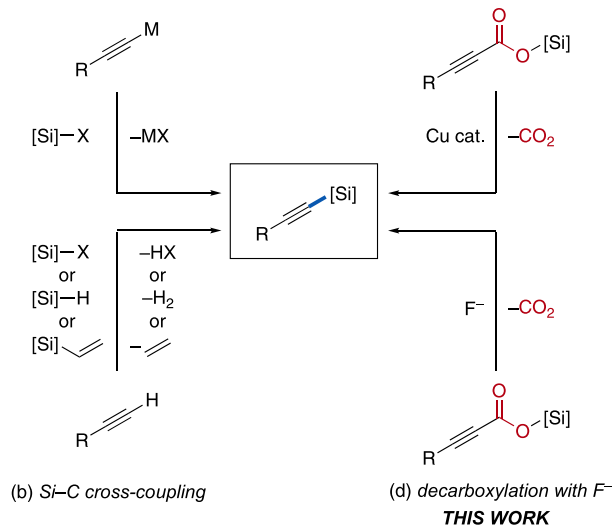
of silyl alkynoates with bulky silyl groups such as the triisopropylsilyl group was significantly impeded.

Owing to the high affinity of the fluoride ion to silicon atoms, the activation of organosilicon compounds by fluoride
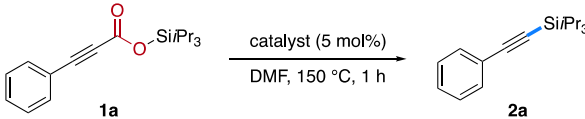
ion is a common procedure for the transformations of organosilicon compounds.[12] Indeed, alkaline metal fluorides have been applied as catalysts in the decarboxylation of trimethylsilyl perfluorobenzoates.[13] Although the applicable substrates are limited to trimethylsilyl penta- and tetrafluorobenzoates, and the applicability of the approach to the decarboxylation of other silyl esters was unclear, we expected that the small, hard fluoride ion would activate silyl alkynoates to induce decarboxylation, irrespective of the steric bulk of the silyl substituents (Scheme 1d).

■ RESULTS AND DISCUSSION

The decarboxylation of triisopropylsilyl 3-phenylpropiolate (1a) was initially investigated in the presence of 5 mol % KF in N,N-dimethylformamide (DMF) at 150 °C, and the desired alkynylsilane 2a was obtained in 42% yield after 1 h (Table 1,

Table 1. Optimization of the Reaction Conditions

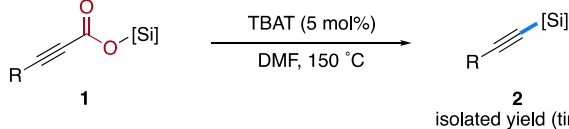| entry	catalyst	conv. (%)	yield (%)[a]
1	KF	46	42
2	KCl	23	19
3	KBr	11	2
4	KI	<5	trace
5	NaF	27	22
6	CsF	65	55
7	MgF$_2$	<5	trace
8	TBAF	>95	50
9	TBAT	94	75
10[b]	TBAT	71	65
11[b,c]	TBAT	>95	93 (89)[d]

[a]Determined by ^{1}H NMR analysis using mesitylene as internal standard. [b]PTFE vessel was used instead of glassware. [c]The reaction was carried out for 3 h. [d]Isolated yield.
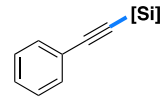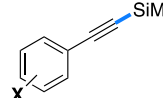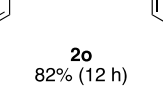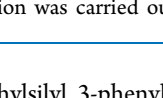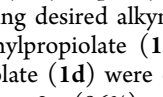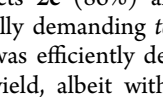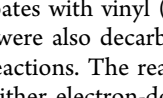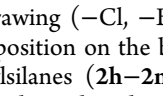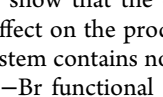
entry 1). Other potassium salts (KCl, KBr, and KI) showed remarkably diminished catalytic performance, demonstrating the importance of fluoride ion (entries 2−4). While NaF gave an inferior result (entry 5), a higher yield of 55% was observed in the decarboxylation with CsF (entry 6). An alkaline earth metal fluoride, MgF$_2$, was also examined, but only a trace amount of alkynylsilane 2a was produced (entry 7). Next, we investigated organic fluorides instead of metal fluorides. When tetrabutylammonium fluoride (TBAF) was used as a catalyst, the yield of 2a was 50%, even though 1a was completely consumed (entry 8). The major byproduct was the corresponding alkynoic acid, which was generated by hydrolysis of 1a with the water contained in TBAF.[14] Therefore, we focused on anhydrous organic fluoride sources, and found that tetrabutylammonium difluorotriphenylsilicate (TBAT) gave 2a in a higher yield of 75%, albeit with 19% of the hydrolyzed byproduct, the corresponding alkynoic acid (entry 9).[15] Because the participation of water from the glassw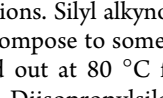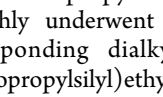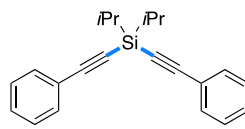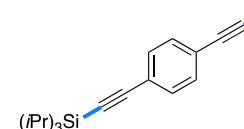are was suspected in the hydrolysis, the decarboxylation was conducted in a poly(tetrafluoroethylene) (PTFE) vessel, which afforded the product in 65% with a negligible amount of the hydrolyzed byproduct (entry 10). Finally, when the reaction was carried out for 3 h, silyl alkynoate 1a was

completely consumed, yielding the desired alkynylsilane 2a in 93% (entry 11).

Under the optimal reaction conditions, the scope of silyl alkynoates was investigated (Table 2). The decarboxylation of

**Table 2. Scope and Limitations of Silyl Alkynoates**

[a]Reaction was carried out at 80 °C.

trimethylsilyl 3-phenylpropiolate (1b) was completed in 1 h, affording desired alkynylsilane 2b in 94% yield. Triphenylsilyl 3-phenylpropiolate (1c) and tert-butyldimethylsilyl 3-phenylpropiolate (1d) were completely consumed in 3 h, furnishing products 2c (86%) and 2d (89%), respectively. Even more sterically demanding tert-butyldiphenylsilyl 3-phenylpropiolate (1e) was efficiently decarboxylated to give alkynylsilane 2e in 76% yield, albeit with a longer reaction time of 12 h. Silyl alkynoates with vinyl (1f) and allyl (1g) groups on the silicon atom were also decarboxylated in excellent yields without any side reactions. The reactions of trimethylsilyl 3-arylpropiolates with either electron-donating (−Me and −OMe) or electron-withdrawing (−Cl, −Br, and −NO$_2$) groups at the para- and ortho-position on the benzene ring afforded the corresponding alkynylsilanes (2h−2m) in high yields (88 → 95%). These results show that the electronic nature of the aryl groups has little effect on the product yield. It is noteworthy that, because this system contains no transition metals, substrates with C−Cl and C−Br functional groups are tolerated under the reaction conditions. Silyl alkynoate 1n with an acetoxy group was found to decompose to some extent at 150 °C; thus, the reaction was carried out at 80 °C for 6 h to give alkynylsilane 2n in 94% yield. Diisopropylsilanediyl bis(3-phenylpropiolate) (1o) smoothly underwent two-fold decarboxylation to give the corresponding dialkynylsilane (2o) in 82% yield. Bis-((triisopropylsilyl)ethynyl)benzene (2p) was afforded in 75% yield by the two-fold decarboxylation of silyl alkynoate 1p.

To shed light on the reaction mechanism, the decarboxylation of **1a** was followed by ^{19}F NMR spectroscopy (Figure S1). When **1a** was reacted with 5 mol % TBAT in DMF-d_7 at room temperature, the complete consumption of TBAT and the formation of iPr$_3$SiF and Ph$_3$SiF were observed; no other compounds containing fluorine atoms were detected. The production of iPr$_3$SiF and Ph$_3$SiF was also confirmed by $^{29}Si\{^1H\}$ NMR spectroscopy (Figure S2). These observations suggest that TBAT is not the true catalyst for the decarboxylation, but rather, the tetrabutylammonium alkynoate that is produced by the reaction of the silyl alkynoate with TBAT functions catalytically. Indeed, tetrabutylammonium 3-phenylpropiolate, which was prepared from 3-phenylpropiolic acid, NaH, and tetrabutylammonium chloride, smoothly catalyzed the decarboxylation of silyl alkynoate **1a** to give alkynylsilane **2a** in 95% NMR yield under fluoride-free conditions (Scheme 2a). The clean decarboxylation of **1a** with

Scheme 2. (a) Catalytic Reaction of Silyl Alkynoate 1a with Tetrabutylammonium 3-Phenylpropiolate, (b) Catalytic Reaction of 1a with *n*Bu$_4$NOAc, (c) Stoichiometric Reaction of Tetrabutylammonium 3-Phenylpropiolate and *i*Pr$_3$SiF, and (d) Stoichiometric Reaction of 1a and TBAT
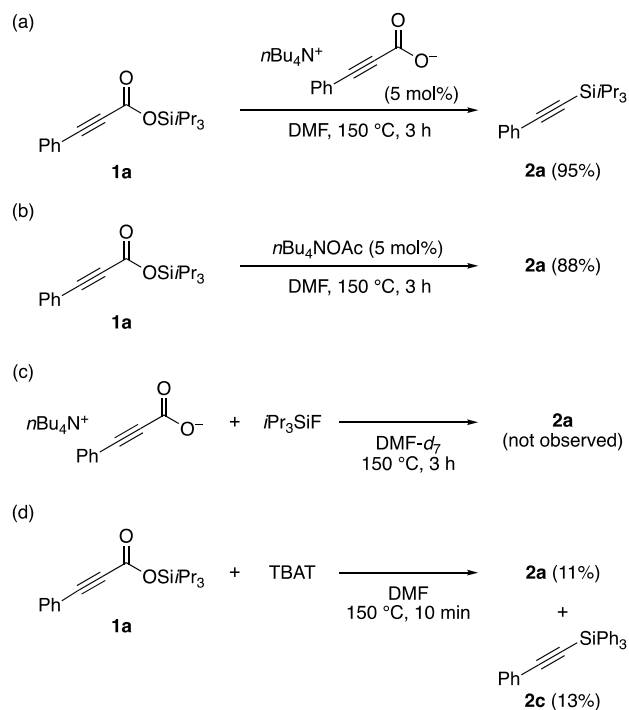
5 mol % *n*Bu$_4$NOAc also indicated that the fluoride ion is not an essential component of the catalyst, but that the carboxylate ion plays a critical role in the decarboxylation (Scheme 2b). While the formation of alkynylsilane **2a** was not observed in the stoichiometric reaction of tetrabutylammonium 3-phenylpropiolate and *i*Pr$_3$SiF (Scheme 2c and Figure S3), not only alkynytriisopropylsilane **2a** (11%) but also alkynyltriphenylsilane **2c** (13%) were produced in the stoichiometric reaction of silyl alkynoate **1a** and TBAT (Scheme 2d and Figure S4), implying that the formation of the tetrabutylammonium alkynoate is reversible.

Based on these findings, a possible reaction mechanism is proposed, as illustrated in Scheme 3. First, TBAT reacts with the silyl alkynoate to produce a tetrabutylammonium alkynoate

Scheme 3. Proposed Reaction Mechanism for the Catalytic Decarboxylation of Silyl Alkynoates with TBAT
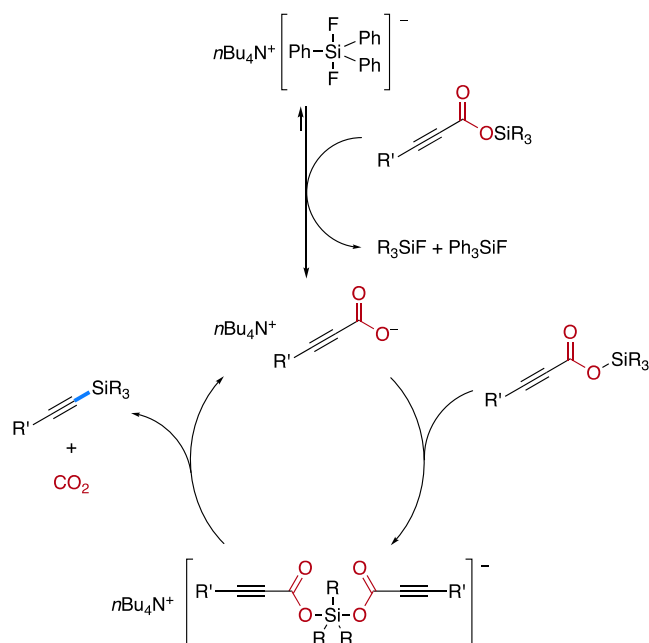
as well as two fluorosilanes (R$_3$SiF and Ph$_3$SiF) derived from the silyl alkynoate and TBAT. The thus-obtained tetrabutylammonium alkynoate reacts with the silyl alkynoate to form a pentacoordinate silicon intermediate, which undergoes decarboxylation to give the desired alkynylsilane and carbon dioxide with regeneration of the tetrabutylammonium alkynoate.

In summary, we have developed a facile method for the synthesis of alkynylsilanes by decarboxylating silyl alkynoates in the presence of a catalytic amount of commercially available TBAT. A wide variety of substrates, including those with bulky silyl groups such as the *tert*-butyldiphenylsilyl group or functional groups such as chloro, bromo, and acetoxy groups, were efficiently decarboxylated in good to excellent yields. Mechanistic studies revealed that the tetrabutylammonium alkynoate is the catalyst for the decarboxylation and TBAT acts as a precatalyst. Our group is now investigating catalytic systems for the decarboxylation of silyl esters other than silyl alkynoates.

■ EXPERIMENTAL SECTION

General Procedure for Decarboxylation of Silyl Alkynoates 1. In a PTFE vessel, a solution of silyl alkynoate **1** (0.50 mmol) and tetrabuthylammonium difluorotriphenylsilicate (5 mol %, 0.025 mmol) in DMF (1.0 mL) was stirred at 150 °C. After 1−12 h, the reaction mixture was diluted in CH$_2$Cl$_2$ (0.5 mL) and passed through a silica gel column. After evaporation, the desired alkynylsilane **2** was obtained in 75 → 95% yield.

■ ASSOCIATED CONTENT

ⓈＩ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01256.

> Experimental procedures, characterization data, and copies of NMR spectra (^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$) of the alkynylsilane products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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