Radical Reactions

International Edition: DOI: 10.1002/anie.201509537
German Edition: DOI: 10.1002/ange.201509537

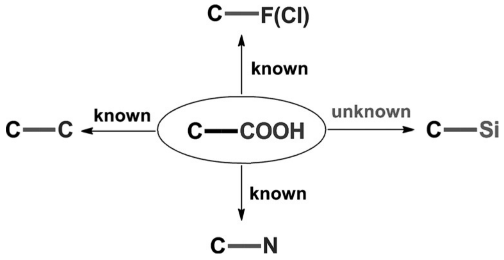
A Free-Radical-Promoted Stereospecific Decarboxylative Silylation of α,β-Unsaturated Acids with Silanes

*Lizhi Zhang, Zhaojia Hang, and Zhong-Quan Liu**

Abstract: *A stereospecific decarboxylative silylation of acrylic and propiolic acids with silanes was developed. This reaction represents the first example of decarboxylative C–Si bond formation and provides an efficient and convenient approach to various synthetically useful alkenyl and alkynyl organosilicon compounds through the reaction of α,β-unsaturated acids with silanes. Spin-trapping and EPR experiments support a radical addition/elimination process.*

Silicon-centered radicals are postulated as key intermediates in various processes in materials science, polymer science, and organic chemistry.[1] As the most successful surrogates for organotin compounds, silanes, especially tris(trimethylsilyl)silane (TTMS), have been widely applied in free-radical chemistry.[2] In the past few years, although considerable development has been achieved in transition-metal-catalyzed C–Si bond formation,[3–5] the synthesis of organosilicon compounds through an atom-transfer process remains attractive to organic chemists. For example, several efficient radical C–Si bond formation reactions with silanes have recently been explored by Studer,[6] Grubbs,[7] Yu,[8] and ourselves.[9]

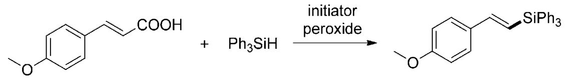
On the other hand, decarboxylative synthetic strategies are of great interest for using carboxylic acids as alternatives to halides and organometal reagents.[10] In the past decades, advances in decarboxylative bond formation (e.g., C–C, C–F (Cl), C–N) through transition-metal catalysis and/or free-radical initiation have been made (Scheme 1). For example, Pd- and/or Cu-catalyzed decarboxylative C–C bond formation has been nicely achieved by Myers,[11] Goossen,[12] Liu and Fu,[13] and others.[14] Free-radical-promoted decarboxylative transformations have also been explored in recent years.[15] For example, Li and co-workers accomplished a series of Hunsdiecker-type reactions.[16] We have also reported several C–C bond formation reactions that proceed through radical addition/elimination of cinnamic acids.[17] However, direct decarboxylative C–Si bond formation has never been realized despite its long-recognized desirability. We wondered whether combining free-radical-promoted Si–H functionalization with a decarboxylative strategy could be used to form C–Si bonds through radical-initiated decarboxylation of carboxylic acids with silanes. In this work, we successfully achieved the radical decarboxylative silylation of α,β-unsaturated acids with silanes. To the best of our knowledge, direct decarboxylative C–Si bond formation by using carboxylic acids and silanes has not yet been reported (Scheme 1).



Scheme 1. Decarboxylative CX bond formation.

Initially, (*E*)-3-(4-methoxyphenyl)acrylic acid and triphenylsilane were chosen as model compounds to optimize the reaction conditions. As depicted in Table 1, the initiator, peroxide, and solvent critically affect the efficiency of this reaction (see the Supporting Information). No reaction occurred without an initiator (Table 1, entry 1). Inspired by our previous studies on radical decarboxylative sp^{3}C–H alkenylation,[17a] Cu/*tert*-butyl hydroperoxide (TBHP, in decane) was used to trigger the reaction (Table 1, entry 2). Gratifyingly, the desired product (*E*)-(4-methoxystyryl)triphenylsilane was isolated in 37% yield. It is noteworthy that

Table 1: Optimization of the reaction.[a]



Entry	Initiator	Peroxide	Solvent	Yield[b]
1	–	TBHP	*t*BuOH	–
2	Cu	TBHP	*t*BuOH	37
3	CuI	TBHP	*t*BuOH	30
4	Cu(OAc)$_2$	TBHP	*t*BuOH	43
5	FeCl$_3$	TBHP	*t*BuOH	22
6	TBAI	TBHP	*t*BuOH	33
7	**CuCl**	**TBHP**	***t*BuOH**	**82**
8	CuCl	DCP	*t*BuOH	25
9	CuCl	TBHP[c]	*t*BuOH	65
10	CuCl	TBHP[c]	*t*BuOH/H$_2$O[d]	61
11	CuCl	TBHP[c]	Toluene	72

[a] Reaction conditions: (*E*)-3-(4-methoxyphenyl)acrylic acid (1 equiv, 0.2 mmol), triphenylsilane (5 equiv, 1.0 mmol), initiator (5 mol%), peroxide (3 equiv, 0.6 mmol), solvent (3 mL), 110°C, 24 h, unless otherwise noted. [b] Yield of isolated product. [c] TBHP (in water). [d] *t*BuOH/H$_2$O (5:1, 3.5 mL).

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201509537.

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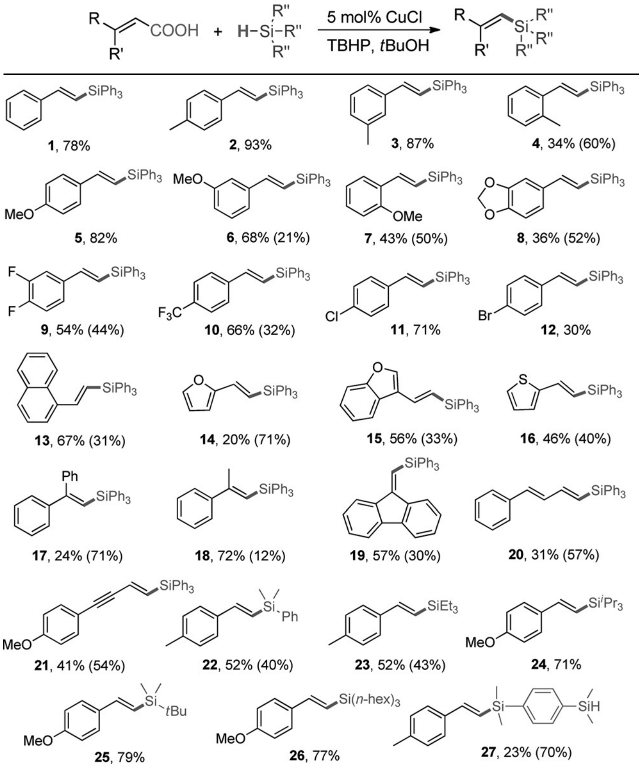
only *E*-vinyl silane was observed by ^{1}H NMR. A series of other initiators, namely CuI, $Cu(OAc)_2$, $FeCl_3$, tetrabutylammonium iodide (TBAI), and CuCl were screened (Table 1, entries 3–7). CuCl was found to be the most efficient initiator in this system (Table 1, entry 7). Various peroxides and solvents were also investigated (Table 1, entries 8–11). It is interesting that the reaction can also proceed smoothly in *t*BuOH/water (Table 1, entry 10).

With the optimized conditions in hand, we then explored the scope of this reaction (Table 2). The results show that a wide range of acrylic acids and silanes are effective substrates in this system (**1**–**27**). Although a steric effect from the aryl substituent in cinnamic acids seems apparent, the desired products can be obtained in moderate yields (**4** and **7**). Furthermore, aryl- and heteroaryl-substituted acrylic acids are amenable to this reaction (**8**–**19**). The fact that variation of the substituents on the aromatic core is tolerated indicates that there is no substantial electronic effect (**5**, **6**, and **10**). It is noteworthy that (*E*)-triphenyl(2-phenylprop-1-en-1-yl)silane was isolated as the only product in the reaction of triphenylsilane with (*E*)-3-phenylbut-2-enoic acid (**18**). No *Z*-isomer was observed, thus further suggesting stereospecific decarboxylative silylation of acrylic acids. Gratifyingly, alkenyl and alkynyl acrylic acids also gave the corresponding products in 31 % and 41 % yields, respectively (**20** and **21**). In addition, the desired alkenyl trialkyl silanes were isolated in moderate to good yields when using both arylsilanes and aliphatic silanes (**22**–**26**). Interestingly, (*E*)-(4-(dimethylsilyl)-phenyl)dimethyl(4-methylstyryl)silane was generated as the major product in the reaction of (*E*)-3-*p*-tolylacrylic acid with 1,4-bis(dimethylsilyl)benzene (**27**).

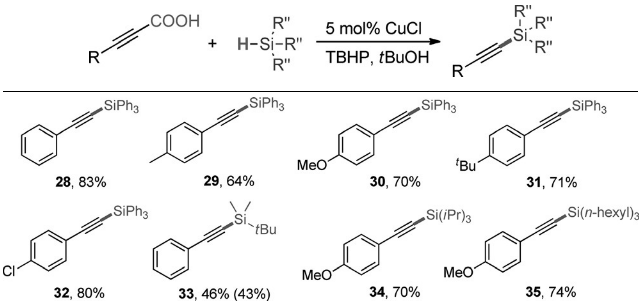
Table 2: Decarboxylative silylation of acrylic acids with R_3SiH.[a]



[a] Reaction conditions: acrylic acid (1 equiv, 0.2 mmol), silane (5 equiv, 1.0 mmol), CuCl (5 mol %), TBHP (3 equiv, 0.6 mmol), *t*BuOH (3 mL), 110 °C, 24 h. Yields of isolated product are given below the products, with recovery of starting materials in parentheses.

Encouraged by the successful decarboxylative alkenylation of Si–H bonds, we wondered whether this strategy could be applied to propiolic acids. Pleasingly, an array of alkynylsilanes could be conveniently synthesized through decarboxylative silylation of propiolic acids with silanes under the typical reaction conditions (Table 3). Various propiolic acids and silanes gave the desired products in moderate to high yields (**28**–**35**).

Table 3: Decarboxylative silylation of propiolic acids with R_3SiH.[a]



[a] Reaction conditions: propiolic acid (1 equiv, 0.2 mmol), silane (5 equiv, 1.0 mmol), CuCl (5 mol %), TBHP (3 equiv, 0.6 mmol), *t*BuOH (3 mL), 110 °C, 24 h. Yields of isolated product are given below the products, with recovery of 3-phenylpropiolic acid in parentheses.

Because of the importance of organosilicon compounds in materials science and synthetic chemistry, several alkenyl and alkynyl silane products were applied in the synthesis of valuable molecules (Figure 1).[18] Diverse transformations from organosilanes were achieved to give various useful building blocks, including allylic alcohols, indoles, naphthalenes, and stilbenes.

Next, a series of mechanistic studies involving investigation of the kinetic isotope effect (KIE), spin-trapping techniques, and electron paramagnetic resonance (EPR) were carried out (Scheme 2 and the Supporting Information). No desired alkenyl silane was observed upon addition of 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) as a radical inhibitor (Scheme 2). Similarly, no reaction occurred when using deuterated triphenyl silane (Ph_3SiD) under the typical reaction conditions, while 93 % yield of the desired product was isolated in the case of Ph_3SiH (Table 2, entry 2). Such a significant KIE suggests that cleavage of the Si–H bond is involved in the rate-determining step. The results are consistent with our previous observations for the radical addition/cyclization of *N*-arylacrylamide with silane.[9] To obtain evidence of possible radical intermediates, 2-methyl-2-nitrosopropane (MNP) was used as a radical spin trap. Mixed EPR signals were observed that might belong to Cu^{II} and a triphenylsilyl *tert*-butyl nitroxide radical or a di-*tert*-butyl nitroxide radical ($a_N = 15.88$ G, $g = 2.0063$).[19] To avoid the

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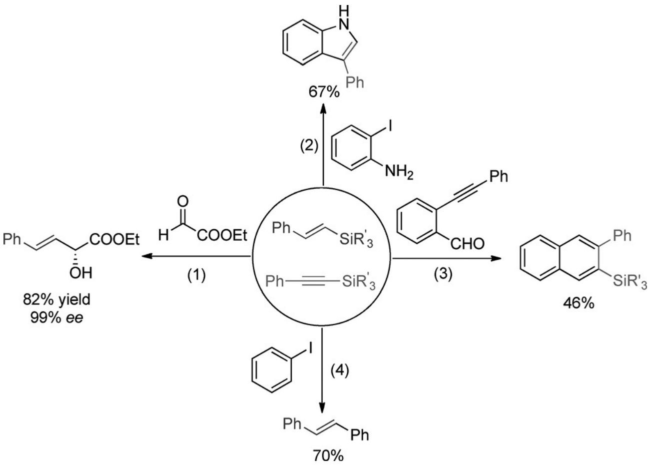
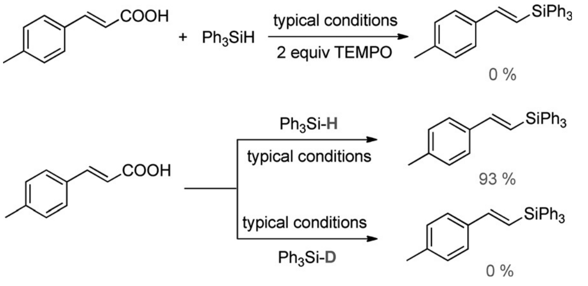


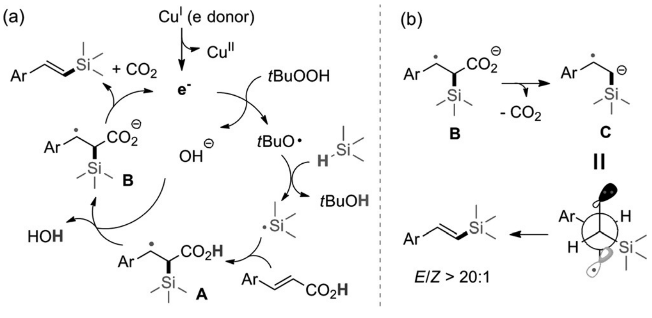
Figure 1. Application of the produced silanes in synthesis. 1) 5 mol% [$PdCl_2$((S)-BINAP)], 11 mol% $AgSbF_6$, CH_2Cl_2, −10 °C. 2) 5 mol% Pd($OAc)_2$, 5 equiv Na_2CO_3, 1 equiv nBu_4NCl, DMF, 100 °C; then nBu_4NF, THF/H_2O. 3) 5 mol% Cu($OTf)_2$, 1 equiv TFA, DCE, N_2, 100 °C. 4) 5 mol% [{PdCl(3 -allyl)}$_2$], nBu_4NF, THF, N_2, RT. BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, DMF = N,N-dimethylformamide, THF = tetrahydrofuran, DCE = 1,2-dichloroethane.



Scheme 2. The effect of TEMPO addition and investigation of the KIE.

impact of copper ions, spin-trapping experiments in the absence of copper salts were performed. A triplet signal was clearly recorded by EPR.

A suggested mechanism that is consistent with the literature precedent and experimental data is shown in Scheme 3a. As an electron donor, Cu^I injects an electron into the system.[20] A *t*BuO radical and a hydroxy anion are produced from TBHP through acceptance of the electron. Hydrogen abstraction from the silane by the *t*BuO radical gives *t*BuOH and a silyl radical, which adds to cinnamic acid to generate radical **A**. Subsequently, deprotonation of **A** by the OH anion produces H_2O and radical anion **B**. Finally, decarboxylation of **B** followed by single-electron oxidation of the radical anion affords the final product and provides an electron to reinitiate the reaction cycle.[20] As depicted in Scheme 3b, the excellent *E*/*Z* selectivity might be due to steric and stereoelectronic effects in the radical anion.[21]



Scheme 3. a) Proposed reaction mechanism. b) Origin of the E/Z selectivity.

In summary, a stereospecific decarboxylative alkenylation/alkynylation of silanes was developed, which represents the first example of decarboxylative C–Si bond formation. This strategy provides efficient and convenient access to various synthetically valuable alkenyl and alkynyl organosilicon compounds from α,β-unsaturated acids with silanes. Spin-trapping, EPR, and KIE experiments support a free-radical addition/elimination process.

Acknowledgements

This project is supported by the National Science Foundation of China (Nos. 21272096 and 21472080).

Keywords: decarboxylation · radical reactions · silanes · silylation · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 236–239
Angew. Chem. **2016**, *128*, 244–247

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Received: October 12, 2015
Published online: November 19, 2015