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Sila- and Germa-Carboxylic Acids: Precursors for the Corresponding Silyl and Germyl Radicals

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Abstract: Silicon-containing compounds are widely used as synthetic building blocks, functional materials, or bioactive reagents, and silyl radicals are important intermediates for syntheses and transformations of organosilicons. Here we describe the first protocol for the generation of silyl radicals by photo-induced decarboxylation of silacarboxylic acids, which can be easily prepared in high yield on a gram scale and are very stable to air and moisture. Irradiation of silacarboxylic acids with blue LEDs (455 nm) in the presence of a commercially available photo-catalyst releases silyl radicals, which can further react with various alkenes to give corresponding silylated products in good to high yields with broad functional group compatibility. This reaction proceeds in the presence of water, enabling efficient deuterosilylation of alkenes with D₂O as the deuterium source. Germyl radicals were similarly obtained.

Efficient and robust protocols for installing hetero-elementcontaining groups are important for the design and discovery of novel functional molecules. Organosilicon compounds are versatile tools in organic synthesis,[1a-c] and their unique physicochemical properties have led to widespread application in the fields of functional materials, [1d-f] life sciences, [1g] and drug discovery.[1h] In particular, silyl radicals are key intermediates for syntheses and transformations of various organosilicon compounds and polymers.^[2] The hydrogen atom transfer (HAT) reaction of silicon hydrides (R₃SiH) has mostly been used for generating silyl radicals (R₃Si•) (Scheme 1-A), but classic protocols require the use of an excess of hydrogen acceptor precursors, such as peroxides, together with high temperature, which may result in low efficiency and poor selectivity.^[2a] In recent years, significant advances have been achieved in the area of photo-catalysis,[3] in which HAT reaction is frequently providing new methods for cleavage and involved, functionalization of X-H bonds (X = C, O, N, S, etc.).[4] In this context, photo-induced protocols incorporating a HAT process have also been established for generating R₃Si• from R₃SiH (Scheme 1-B).^[5-9] In 2015, Fagnoni and Ravelli's group demonstrated a HAT-photo-catalysis pathway for the preparation of silyl radicals, in which the photo-catalyst (PC) also acts as an H• acceptor.^[6] Meanwhile, MacMillan's groups developed a protocol that involves dual catalytic cycles (transition metal- or HAT-catalysis combined with photocatalysis).^[7] More recently, Wu's group established an elegant

catalytic protocol for the generation of various types of R₃Si•,^[8] in which the combination of HAT and photoredox reactions enabled the catalytic use of the HAT reagent, resulting in high atom-efficiency. While these reactions are synthetically useful, few alternatives are available,^[5] and R₃SiH remains the most widely used precursor of R₃Si•, despite the fact that it is readily oxidized in air (some are even combustible). Here, we describe a new method to generate silvl/germyl radicals through visiblelight-induced decarboxylation reaction of silyl/germyl carboxylic acids^[10] (Scheme 1-C). This protocol offers a number of advantages, because (1) the precursors are readily available on a gram scale in a single step without the need for column chromatography, (2) the precursors can be stored for months in an open vessel at ambient temperature without decomposition, and hence are easy to handle, and (3) the decarboxylation reaction proceeds smoothly under mild conditions, providing a versatile synthetic tool for installing silvl/germyl groups with wide substrate scope.



Scheme 1. Generation of silyl radical via HAT reaction and decarboxylation of silacarboxylic acid (this work).

Silacarboxylic acid ($R_3SiCOOH$) was identified as a "heavy" analogue of carboxylic acid in the 1950's.^[10a-c] $R_3SiCOOH$ can be readily synthesized in high yield by reaction of CO₂ with the corresponding silyl metal reagents, which are easily prepared

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from silvl chloride by treatment with Li or Na.^[10] Unlike R₃SiH, R₃SiCOOH is very stable in air, water and even strong acid solutions, and can be stored for a long period in an open vessel at room temperature. Despite the easy accessibility and excellent stability of R₃SiCOOH, its reactivity and synthetic utility have been largely ignored until recently. In the last decade, several examples of the utilization of R₃SiCOOH as a CO ¹¹CO or ¹³CO)-releasing agent (especially (through decarbonylation) have been reported,[11] and its esterification has been described.^[12] However, there have been few synthetic applications. Inspired by the recent generation of alkyl radicals from aliphatic carboxylic acids by photo-induced CO2 extrusion,^[13] we became interested in exploring new synthetic applications of silacarboxylic acids as silvl radical precursors.

Our working hypothesis is shown in Scheme 2. First, photoredox catalyst in a photo-excited state (PC*) serves as an 1,2,3,5-tetrakis(carbazol-9-yl)-4,6oxidant [e.g., for dicyanobenzene (4CzIPN) as PC, E^{1/2}(PC*/PC*-) = +1.35V vs. SCE in MeCN]^{[14}, undergoing a single electron (SE) redox process with silacarboxylate anion A (formed by dissociation of 1) [e.g. for 1a: E^{1/2}(Ph₂MeSiCOO•/Ph₂MeSiCOO⁻) = +1.32V vs. SCE in MeCN] to give the reduced PC⁻⁻ species and silacarboxylic radical B. Decarboxylation of radical B would then take place, releasing silyl radical C and CO2. Silyl radical C would then react with alkene 2, affording alkyl radical D. Next, serving as an SE oxidant, radical D [e.g. for EtOOCCH2• radical analogue, E°(R•/R-) = -0.63V vs. SCE in MeCN, for pcyanobenzyl radical analogue, E1/2(R•/R-) = -0.77V vs. SCE in MeCNJ^[15] would react with PC⁻⁻ [E^{1/2}(PC/PC⁻⁻) = -1.21V vs. SCE in MeCN] leading to formation of anion species E concomitantly with the regeneration of PC. Finally, alkyl anion E would abstract a proton from 1 to form silacarboxylate anion A and alkylsilane 3 as the product of alkene hydrosilylation^[16] Here, the silyl radical generated directly from SE redox reaction between silacarboxylic acid 1, PC and alkyl anion E would serve as a base to facilitate the dissociation of 1, providing a short, straightforward and self-promoting reaction pathway, without the need for any other external reagent/medium.



Scheme 2. Working hypothesis (EWG: electron-withdrawing group; Ar: aryl).

To test the feasibility of this scheme, we examined the reaction of silacarboxylic acid 1a as a model Si-substrate with benzyl acrylate 2a as a representative alkene. After many attempts to optimize the conditions, we found that the reaction proceeded with the highest efficiency under visible-light irradiation (λ = 455 nm, blue LEDs) in MeCN solution with 4CzIPN as the catalyst, giving the desired silvlation product 3aa in 82% yield, as determined by NMR (Entry 1, Table 1). In contrast to the optimal conditions, we found that: I) no formation of 3aa was detected when Ir(pFppy)3, [Ir(ppy)2(bpy)]PF6, Ir[dF(t-Bu)ppy]₃, or [Ru(bpy)₃](PF₆)₂ (Entry 2) was used as the catalyst, and the yield decreased when [Ir(dFCF₃ppy)₂(dtbpy)]PF₆ was used (Entry 3); II) the reaction did not proceed in solvents other than MeCN (Entry 4); III) the reaction still took place smoothly in a diluted solution (Entry 5), but the yield decreased when the concentration of reaction solution was increased, due to oligomerization of 2a (Entry 6); IV) increasing the amount of 1a did not greatly affect the reaction (Entry 7), but lowering the PC loading reduced the yield of 3aa (Entry 8); V) no formation of 3aa was observed when the reaction was performed in the absence of light or PC (Entry 9), or in air (Entry 10). It is also noteworthy that no external additive, such as base, was needed for this reaction.[17]

Table 1. Optimization of reaction conditions.

Ph Si COOH Ph I + Ph			
entry	Char	NMR yield	
1	none		82%
2	<i>PC</i> ^[a]	Ir(pFppy) ₃ , [Ir(ppy) ₂ (bpy)]PF ₆ , Ir(dF <i>t</i> -Buppy) ₃ , [Ru(bpy) ₃](PF ₆) ₂ <i>instead of</i> 4CzIPN	0%
3	 	[Ir(dFCF ₃ ppy) ₂ (dtbpy)]PF ₆ instead of 4CzIPN	45%
4	Solvent ^[b]	DMF, DMA, THF, MeOH, CH ₂ Cl ₂ , DMSO <i>instead of</i> MeCN	<5%
5	concentration	0.02 mol/L instead of 0.10 mol/L	80%
6		0.20 mol/L instead of 0.10 mol/L	69%
7	loading	1a: 1.5 eq. instead of 1.2 eq.	82%
8		4CzIPN: 1 mol% instead of 5 mol%	52%
9	control	in the absence of light or PC	0%
10		in air <i>instead of</i> argon	0%

[b] DMF: *N*,*N*-dimethylformamide, DMA: *N*,*N*-dimethylacetamide, THF: tetrahydrofuran; DMSO: dimethyl sulfoxide.

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Scheme 3. Reaction scope for decarboxylation of silacarboxylic acid and further hydrosilylation of alkenes (for 20, 2q and 2r, 2.0 eq. of 1b were used).

We next set out to examine the scope of the current reaction. Three types of silacarboxylic acid, Ph2MeSiCOOH (1a), Ph2^tBuSiCOOH (1b), and PhMe2SiCOOH (1c), were used as silyl radical sources, together with a variety of alkenes (Scheme 3). Key findings were as follows: 1) a range of acrylic acid derivatives such as 2a-e can be used in the reaction; 2) acrylates 2b-c with beta-substituents show higher reactivity than alpha-substituted 2d; 3) various styrene derivatives 2f-n are applicable, affording silvlated products in good yields; 4) reactions with 1,1-diarylalkenes 2o-s proceed efficiently, affording the corresponding products in high yields; 5) chemoselectivity is excellent: ester, amide, nitrile, CF₃, C₆F₅, borate, pyridine ring, and even free OH were tolerated, and the corresponding coupling products were obtained in good to high yields; 6) Notably, in the competitive reactions of the π -bond and the pyridine ring in **21-m**, addition of silvl radical at the alkene π bond occurred highly selectively, indicating the potential utility of this methodology for selective functionalization of the side chain of heteroaromatic compounds. Moreover, this protocol is high chemo-selective toward COOH instead of Si-H moieties. Under the current reaction conditions, silvl radicals were generated selectively through decarboxylation of 1d, leaving the Si-H bond untouched (3df) and available for further silvlation reaction (Section 2-3, supporting information). Hence, this protocol, in combination with other silyl transformation reactions, provides a potentially useful toolbox for the synthesis of multi-functionalized organosilicon and/or poly-silicon compounds.

When alkene 2 contains an electron-donating substituent, the reaction with 1 becomes very sluggish. This is probably because of the lower oxidizing ability of the electron-rich radical **D**, which is less able to receive a single electron from PC^{-} .^[Bd] To solve

this problem, we tried adding an external oxidant. Thiols have been used as radical polarity reversal catalysts to facilitate some HAT processes.^[18] Recently, Wu's group reported that silylthiol (^{*i*}Pr₃SiSH) could undergo HAT with an alkyl radical-releasing thiyl radical (^{*i*}Pr₃SiS^{*}), which would be an SE oxidant.^[8d] Thus,



Scheme 4. Combination of decarboxylation of silacarboxylic acid and a HAT process enables the hydrosilylation of electron-rich alkenes. Reaction conditions: 1a (3.0 eq.), 2t-w (1.0 eq.), 4CzIPN (5 mol%), ⁱPr₃SiSH (5 mol%), MeCN (0.1 mol/L), rt, 12 h, blue LED illumination (455 nm), under argon. Yields are calculated based on NMR analysis or isolation (in parentheses).

we considered that a plausible expanded catalytic cycle would be as shown in Scheme 4. In this route, radical **D** would be directly quenched by 'Pr₃SiSH to give product **3** through a HAT process. The resulting thiyl radical 'Pr₃SiS' would oxidize PC⁻⁻ to regenerate PC, affording the thiyl anion 'Pr₃SiS⁻. Proton exchange of 'Pr₃SiS⁻ as a base with acid **1** would then close the cycle. Indeed, the reaction of **1** with several electron-rich alkenes successfully took place in the presence of 'Pr₃SiSH, providing the desired silylated products in moderate to good yields. Here, the combination of ET and HAT enables the use of 'Pr₃SiSH in only a catalytic amount. This result indicates that the current decarboxylating protocol should also be available for combining with other reaction pathways, leading to more complex and diverse synthetic transformations.

To acquire mechanistic insights into the current reaction, firstly, the time profile of the reaction between **1a** and **2f** clearly reveals an induction period in the initial stage (Scheme 5). Due to the weak acidity of **1**,^[10f] the concentration of silacarboxylate anion **A** would initially be very low and therefore interaction between 4CzIPN* and **A** would be rather weak.^[19] With the formation of anion intermediate **E** that can exchange a proton with **1**, the reaction then self-accelerates and proceeds rapidly after the induction period.



Scheme 5. Time profile of the reaction between 1a and 2f

Secondly, the quantum yield of the reaction between 1a and 2f was determined to be ϕ = 0.04, indicating that chain propagation is not the major pathway.^[20] Thirdly, deuteration experiments were carried out to verify proton transfer between anion E and acid 1. We found that: 1) no deuterated product was observed when the reaction was performed in CD₃CN solution, indicating that the solvent did not act as the hydrogen source (Scheme 6-A); 2) when deuterated silacarboxylic acid was used, 3af-D was obtained with high D-incorporation (Scheme 6-B); 3) when D₂O was added as the deuterium source^[8b,21] (Scheme 6-C), the reaction proceeded even in the presence of water, and the deuteration ratio reached 95% when 10 eq. of D₂O was added. We then examined the reactions between 1b and several alkenes in the presence of D₂O (Scheme 6-D). To our delight, all these reactions provided the corresponding silylation products in good to high yields with high levels of D-incorporation. These results are consistent with the proposed mechanism, and furthermore provide a mild and efficient deuteration protocol employing D₂O as an inexpensive and easy-to-handle D-source for selective deuterium labelling of organic molecules.



Scheme 6. Results of deuteration experiments. Yields are calculated based on isolation. D-inc. stands for incorporation of deuterium.

Finally, we examined whether the current protocol could be extended to the generation of germyl radicals.^[22] Previously, we reported a rapid, efficient and quantitative preparation method for stannyllithium and germyllithium.^[23] Treating germyllithium with CO₂ led to the formation of germacarboxylic acids in high yields, and these products are also stable to oxygen and water. As a representative case, photo-induced decarboxylation of germacarboxylic acid **4e** took place smoothly under similar mild conditions,^[24] and the resulting germyl radical could be further trapped by alkenes **2f** or **2p** to afford germylated protect **5ef** and **5ep** in moderate to good yields (Scheme 7).





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In summary, we have developed a new protocol for efficient generation photo-induced of silyl radicals through decarboxylation of silacarboxylic acids, which can be easily prepared in high yield on a gram scale and can be stored for a long period even in air. In the presence of a commercially available photo-catalyst, decarboxylation of silacarboxylic acid proceeded smoothly under mild conditions, affording silyl radicals that can be used for silylation of alkenes with broad functional group compatibility. The current protocol can be performed with D₂O as the deuterium source even in the presence of water, enabling deuterosilylation of alkenes in high yield and with a high deuteration ratio. It is also applicable for the generation of germyl radicals with equally high efficiency. This work provides a mild, selective and synthetically useful method for the generation of reactive hetero-radical intermediates, exemplifying the value of photocatalysis for efficient synthetic transformations of functional elements. We also confirmed the feasibility of a cascade involving both decarboxylation and a HAT process. Thus, the present methodology, in combination with other types of reactions, should be useful for designing and developing complex and diverse transformation routes. Currently, efficient preparation of trialkylsilyllithium remains a big challenge in organosilicon chemistry, and this also limits the ability to synthesize trialkylsubstituted silacarboxylic acids. Work to find solutions to these problems, as well as to extend the scope of this reaction and to apply it for the synthesis of group-14-element-containing functional molecules, is in progress.

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Keywords: silyl radical • decarboxylation • photo-catalysis • deuteration • germyl radical

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silacarboxylic acid, see refs. 11-12. Indeed, addition of bases led to no improvement or even a decrease of yields: 80% with Li₂CO₃, 45% with K₂CO₃, 0% with Cs₂CO₃, 76% with NaHCO₃, 78% with pyridine.

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- [24] 4CZIPN decomposed in the reaction of 4e. After light irradiation, a clear, colorless solution was obtained, and no product was observed. We then tested several PCs and found that [lr(ppy)₂(dtbbpy)]PF₆ showed the highest catalytic reactivity.

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We describe the first protocol for the generation of silyl radicals by photo-induced decarboxylation of silacarboxylic acids, which can be easily prepared in high yield on a gram scale and are very stable to air and moisture. The reaction proceeds smoothly in the presence of a commercially available photo-catalyst with broad functional group compatibility. This reaction could also be carried out in the presence of water, enabling use of D_2O as the deuteration reagent. Germyl radicals were similarly obtained.