

Silylacylation of Alkenes through N-Heterocyclic Carbene Catalysis

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Cite This: *Org. Lett.* 2023, 25, 5579–5584



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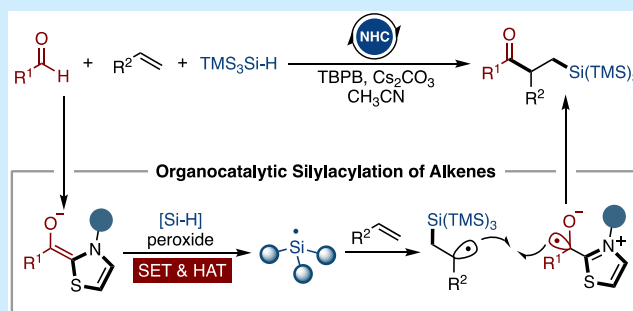
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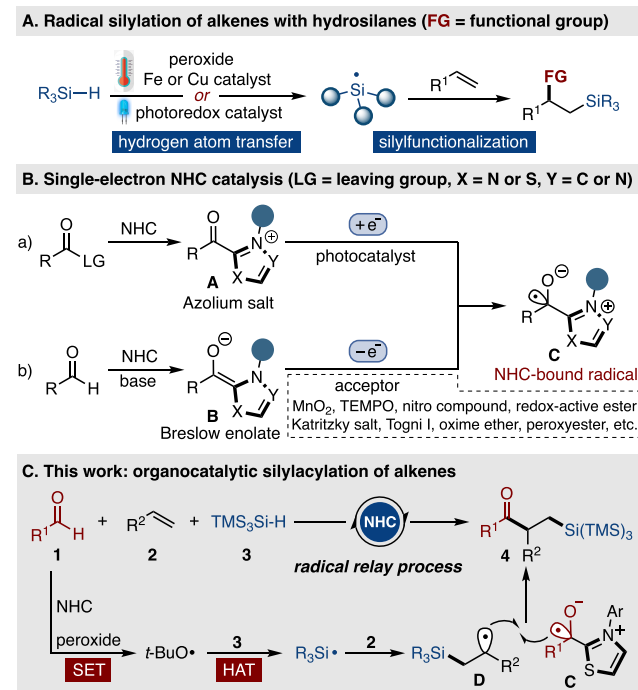
ABSTRACT: The construction of silicon-containing molecules has received increasing attention in recent years. Herein, we report the generation of silyl radicals through NHC catalysis under mild reaction conditions. This methodology offers a novel and convenient route to a diverse range of β -silyl ketones with a broad substrate scope and good functional group compatibility. Both the radical clock and electrochemical studies are consistent with the hypothesis of ground-state SET, and a plausible mechanism for the organocatalytic transformation is proposed.



Organosilanes are of significant importance in broad areas including materials science, organic synthesis, and drug discovery.¹ While a number of approaches have been developed to construct valuable C–Si bonds,^{2,3} radical silylations of carbon–carbon double bonds represent one of the most effective strategies for the formation of these silicon-containing molecules.³ Silyl radicals are normally generated from abundant hydrosilanes, using peroxides as hydrogen acceptor precursors (Scheme 1A).^{3–5} However, conventional approaches required high temperatures or transition-metal initiators.⁴ Recent developments in the field of photoredox catalysis provided an attractive protocol to access silyl radicals under mild conditions.^{3,5} For instance, the Wu^{5c,d} and Xu^{5e} groups reported elegant methods for the silylation of alkenes through synergistic photoredox and hydrogen atom transfer (HAT) catalysis. Moreover, Wu and co-workers innovatively realized the selective functionalization of Si–H bonds, utilizing neutral eosin Y as an effective HAT photocatalyst.^{5j} On the other hand, organocatalysis offers many advantages, such as easy availability, low toxicity, and excellent compatibility.⁶ However, the generation of silicon-centered radicals via organocatalytic HAT still remains underexplored.

N-Heterocyclic carbenes (NHCs) are well-known as nucleophilic organocatalysts for the umpolung of aldehydes via Breslow intermediates.^{7,8} Moving from traditional ionic logic to a radical approach, the combination of NHC catalysis with photoredox catalysis has become a valuable strategy for the acylation of alkenes, which involves the single-electron reduction of azolium salts A (Scheme 1B, path a).^{9,10} On the other hand, electrochemical studies indicated that the Breslow enolate B processes strong reducing ability ($E_{1/2} = -1.32$ to -1.70 V vs SCE),¹¹ which may facilitate ground-state SET with a series of acceptors (Scheme 1B, path b).^{12,13} Pioneering work of the Ohmiya group demonstrated the radical cross-coupling of the resultant NHC-bound ketyl radical C.^{13a–g}

Scheme 1. Synthesis of Organosilanes and NHC Catalysis



Received: June 5, 2023

Published: July 24, 2023



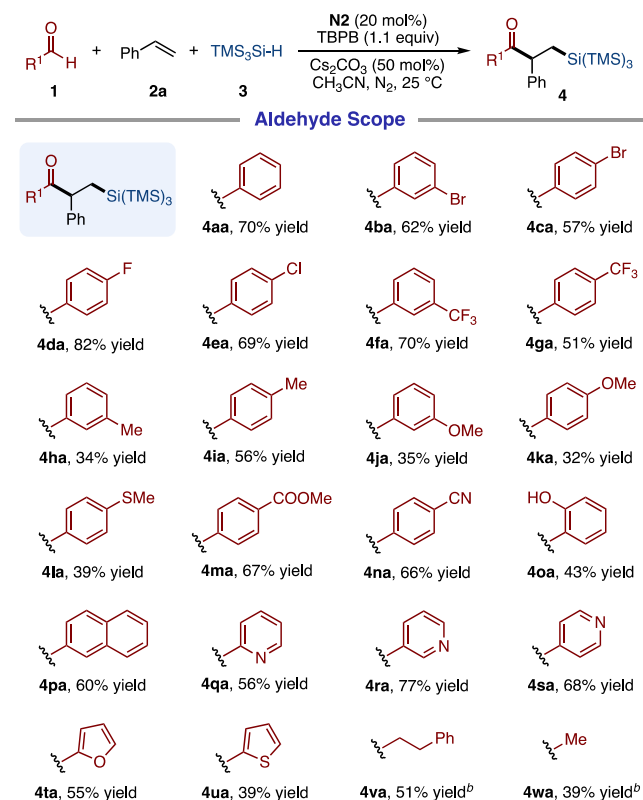
This strategy opens a new realm of chemical space for the construction of sterically hindered ketones. In 2022, Li et al. reported the SET reduction of aryl-substituted peroxyesters in the presence of a thiazolium NHC catalyst and aldehydes.^{13k} The resultant *O*-radical facilitated the intermolecular HAT to form an acyl radical, enabling the diacylation of alkenes. More recently, our group achieved the aminoacylation of trisubstituted alkenes, which involved diastereoselective radical–radical cross-coupling under covalent-based NHC radical catalysis.^{13l} In contrast to the SET oxidation pathway, the Ohmiya group reported three-component coupling of alkenes, acyl imidazoles, and silylboronates to access β -silyl ketones via cooperative NHC/photoredox catalysis.⁵ⁱ Inspired by these results, we envisioned that the radical organocatalytic system would readily reduce peroxides to generate *tert*-butoxy radicals, of which the subsequent HAT with hydrosilanes **3** would generate silyl radicals under mild conditions (Scheme 1C). Herein, we report the successful implementation of this process and the following reactions with NHC-bound ketyl radical **C** that realized silylacylation of alkenes under transition-metal- and light-free conditions. Preliminary mechanistic studies supported the involvement of C-centered radical **D** in the reaction.

We began our investigations by evaluating the NHC-catalyzed silylacylation of styrene **2a** with benzaldehyde and TMS₃SiH (Table 1), which contains a relatively weak Si–H bond (BDE \approx 351.5 kJ/mol).^{3c} Inspired by our previous report and after some optimization, we were pleased to find that the desired β -silyl ketones **4aa** could be isolated in 70% yield. The optimal conditions involved a solution of three reactants, NHC precatalyst **N2**, *tert*-butyl peroxybenzoate

(TBPB), and Cs₂CO₃ in CH₃CN at 25 °C for 12 h under a nitrogen atmosphere. Some variations of the reaction parameters are shown in Table 1 (for more detailed information, see Supporting Information). The reaction conducted with hexagonal ring fused thiazolium salt **N1** also occurred to form the ketone but with a lower yield (entry 2). In the case of *N*-2,6-diisopropylphenyl-substituted **N3**, no desired product was observed (entry 3). As expected, the H atom acceptor was critical for this reaction (entries 4–8). While substituted peroxyesters **P1** and **P2** still gave good yields, the replacement of TBPB with other peroxides, such as benzoyl peroxide (BPO) or di-*tert*-butyl peroxide (DTBP), failed to deliver the desired product. Further evaluation of the solvents uniformly decreased the reaction efficiency (entries 9–11). In addition, the absence of either **N2** or TBPB did not lead to formation of the desired product, indicating the essential role of these components.

With the optimized conditions in hand, we first examined the scope of aldehydes. As illustrated in Scheme 2, the

Scheme 2. Substrate Scope of Aldehyde^a



^aReaction conditions: aldehyde **1** (0.4 mmol), styrene **2a** (0.2 mmol), **3** (0.4 mmol), NHC precatalyst **N2** (20 mol %), TBPB (1.1 equiv), and Cs₂CO₃ (0.5 equiv) in CH₃CN (2.0 mL) under nitrogen at 25 °C for 12 h. Yields of isolated products. ^bReaction was performed in 4.0 mL CH₃CN.

organocatalytic system transformed an array of *meta*- and *para*-substituted benzaldehydes (**4ba**–**4ka**), while *ortho*-substituted benzaldehydes reacted less efficiently.¹⁴ In line with our previous studies, the outcome was influenced by the electronic nature of the substituents on the aromatic ring. In general, aryl aldehydes reacted more efficiently when they had electron-withdrawing groups (**4ba**–**4ga**). An array of functional groups was well-tolerated, including thioether (**4la**), ester (**4ma**),

Table 1. Effect of Reaction Parameters^a

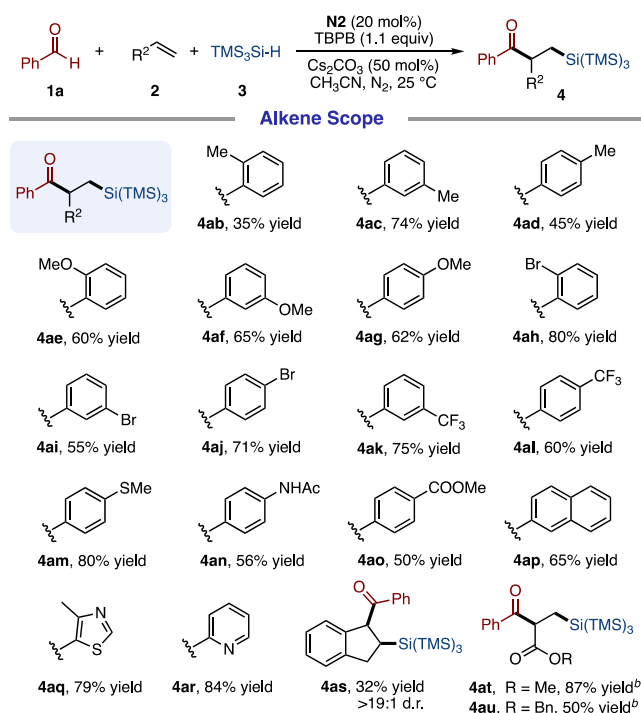
entry	Variation from above conditions	yield (%) ^b
1	none	70
2	N1 instead of N2	30
3	N3 instead of N2	N.D.
4	using 2.0 equiv of TBPB	30
5	P1 instead of TBPB	50
6	P2 instead of TBPB	46
7	BPO instead of TBPB	N.D.
8	DTBP instead of TBPB	N.D.
9	THF instead of CH ₃ CN	trace
10	CH ₂ Cl ₂ instead of CH ₃ CN	17
11	DMSO instead of CH ₃ CN	32
12	without N2 or TBPB	N.D.

^aReactions were carried out with benzaldehyde **1a** (0.4 mmol), styrene **2a** (0.2 mmol), **3** (0.4 mmol), NHC precatalyst (20 mol %), TBPB (1.1 equiv), and Cs₂CO₃ (0.5 equiv) in CH₃CN (2.0 mL) under N₂ at 25 °C for 12 h. ^bYields of isolated products. TBPB, *tert*-butyl peroxybenzoate; BPO, dibenzoyl peroxide; DTBP, di-*tert*-butyl peroxide; and N.D., not detected.

nitrile (**4na**), and hydroxy groups (**4oa**). The β -silyl ketone **4oa** was isolated in 43% yield, and X-ray diffraction analysis of its single crystal confirmed the expected structure (CCDC 2235279). Furthermore, the silylacylation reaction proceeded smoothly with naphthyl (**4pa**) and various heteroaromatic aldehydes, such as substituted pyridine (**4qa–4sa**), furan (**4ta**), and thiophene (**4ua**). In addition to aromatic aldehydes, we found that the strategy was also compatible with aliphatic aldehydes under identical conditions. This is fortunate, as the NHC-bound ketyl radical from aliphatic aldehyde is more congested and usually leads to unsuccessful radical–radical coupling.^{13c}

Having established a broad scope for aldehydes, we turned our attention to the scope with respect to the alkenes (Scheme 3). Styrene and its analogues with various substituents at

Scheme 3. Substrate Scope of Alkene^a

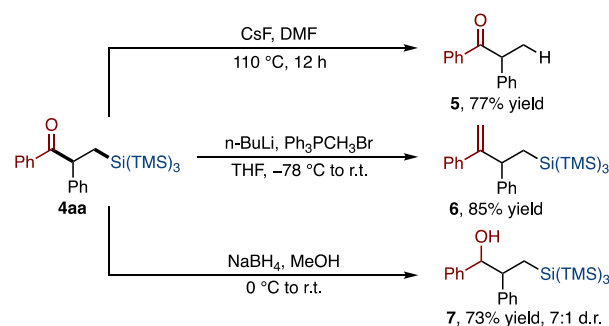


^aReaction conditions: benzaldehyde **1a** (0.4 mmol), alkene **2** (0.2 mmol), **3** (0.4 mmol), NHC precatalyst **N2** (20 mol %), TBPB (1.1 equiv), and Cs₂CO₃ (0.5 equiv) in CH₃CN (2.0 mL) under nitrogen at 25 °C for 12 h. Yields of isolated products. ^bReaction was performed in 4.0 mL of CH₃CN.

different positions (*ortho*, *meta*, or *para*) generally exhibited a high reaction efficiency. The arenes could be substituted with both electron-donating and -withdrawing groups, delivering the β -silyl ketones in high yields (**4ab–4aj**). In addition, functionalized vinyl arenes with trifluoromethyl, thioether, ester, or amino substituents were compatible with the reaction conditions (**4ak–4ao**). Fused-ring and pyridine-substituted alkenes also performed well to give the desired products **4ap–4ar** in moderate to good yields. Notably, the indene could engage in the silylacylation reaction, providing the corresponding cyclic product **4as** with excellent diastereoselectivity. We were delighted to find that the reaction was compatible with electron-deficient acrylates (**4at**, **4au**), affording multifunctionalized organosilanes in good yields.

To further demonstrate the synthetic potential of this catalytic system, conversions of product **4aa** were performed. As shown in Scheme 4, treatment of the β -silyl ketone with

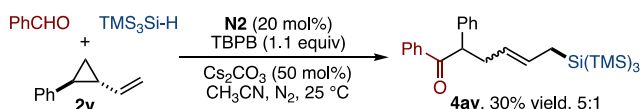
Scheme 4. Transformation of the Product



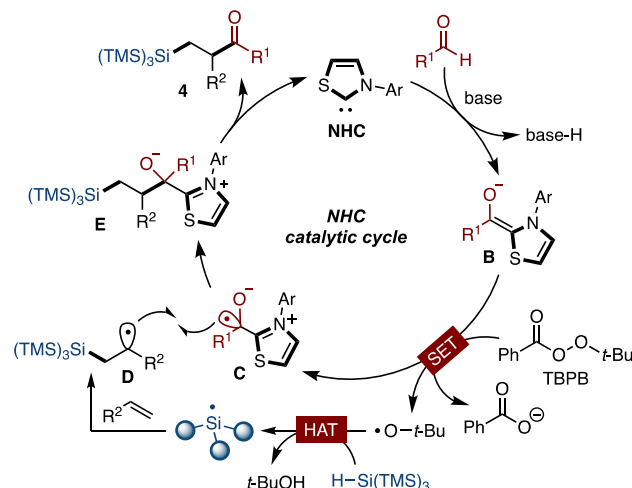
CsF in DMF afforded the corresponding desilylated product **5** in 77% yield. Meanwhile, the silicon-containing molecule could further participate in several carbonyl-based transformations, such as the Wittig reaction to provide alkene **6** and reduction to give γ -silyl alcohol **7** in good diastereoselectivity. To gain further insight into the organocatalytic cycle, the mechanism of the silylacylation reaction was investigated by a radical clock experiment (Scheme 5A). It was found that cyclopropyl-

Scheme 5. Mechanistic Insight

A. Radical clock experiment



B. Proposed mechanism



containing alkene **2v** underwent a smooth ring opening of the cyclopropyl ring under standard reaction conditions, producing **4av** as a mixture of diastereomers. This result provided strong support for the formation of benzyl radical **D**. On the basis of our experimental observations as well as previous studies,^{11,13} a mechanism for the silylacylation reaction is proposed in Scheme 5B. The catalytic cycle is initiated by the nucleophilic addition of NHC to the aldehyde in the presence of a base. Subsequent single-electron reduction of TBPB ($E_{1/2} = -1.12$ V vs SCE)¹⁵ by the Breslow enolate **B** ($E_{1/2}[\text{C/B}] \approx -1.32$ V vs SCE)^{11b,13i} generated the *tert*-butoxyl radical and the NHC-

bound ketyl radical C. Intermolecular HAT between TMS₃SiH and *t*-BuO• delivers the silicon-centered radical, which underwent facile radical addition onto the double bond. Finally, radical–radical coupling between the benzyl radical D and ketyl radical C, followed by the elimination of the NHC catalyst, afforded the desired β -silyl ketone 4 and closed the catalytic cycle.

In summary, we developed an NHC-catalyzed method for the generation of silyl radicals from hydrosilanes¹⁶ under ambient temperature. The transition-metal-free method allowed the preparation of a variety of β -silyl ketones with good tolerance of both electron-rich and electron-deficient alkenes. The radical clock and electrochemical studies supported the generation of silyl radicals via ground-state SET and HAT. We believe that further advances can be expected by applying this organocatalytic strategy to other valuable radical-involved transformations.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its [Supporting Information](#).

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.3c01840>.

General procedure, optimization details, characterization data, cyclic voltammetry experiments, crystallographic data, and NMR spectra for all compounds (PDF)

Accession Codes

CCDC 2235279 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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<https://pubs.acs.org/doi/10.1021/acs.orglett.3c01840>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the assistance of Dr. Huihui Wan in DUT Instrumental Analysis Center for her help with HRMS analysis. We are grateful for the financial support provided by the National Natural Science Foundation of China (No. 21901030), the Fundamental Research Funds for the Central Universities (No. DUT22LK25) and Open Sharing Fund for the Large-scale Instruments and Equipment of Dalian University of Technology.

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(14) See the [Supporting Information](#) for details.

(15) For the reduction potential of the peroxyesters, see the [Supporting Information](#) for details.

(16) In addition to TMS₃SiH, we found that the strategy was also compatible with Ph₂MeSiH at 80 °C, affording the desired product in 17% yield. See the [Supporting Information](#) for detail.