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S Supporting Information

ABSTRACT: A visible light-promoted hydrosilylation of alkynes has been explored and achieved using 1 mol % organic dye Eosin Y as the photocatalyst and a catalytic amount of thiol as the radical quencher. The corresponding alkenylsilanes were provided with high regio- and stereoselectivites in the reactions of various terminal and internal alkynes. The experimental evidence shows that the reaction is preferentially initiated by a single electron transfer process, and a photoredox pathway is suggested.



Letter

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lkenylsilanes are widely applied as versatile silicon-Acontaining building blocks in organic synthesis and organosilicon polymer synthesis.¹ Consequently, a considerable number of protocols have been developed to access this type of silicon molecule. Among them, hydrosilylation of alkynes is the most favorable and straightforward one with perfect atom economy.² In recent decades, intensive efforts have been

devoted to the regio- and stereoselective hydrosilylation of mono- and disubstituted alkynes by tuning transition-metal complexes and coordinating ligands.³ In contrast, the radical hydrosilylation of alkynes has received less attention.⁴

Hydrogen atom transfer (HAT) was usually employed as a common strategy in silvl radical additions of carbon-carbon multiple bonds. An additional carbon- or heteroatom-centered radical is essential to ensure the formation of silvl radical(s). $^{4-6}$ Due to the hydridic property of the Si-H bond, electrophilic radicals such as ^tBuO· or RS· were preferred over nucleophilic ones. However, these reactions suffered from use of peroxidants and azo-type compounds as radical initiators. Very recently, a variety of radicals could be generated through visible light photocatalysis in a controllable catalytic manner, involving either a single electron transfer (SET) or an energy transfer process.⁷ Hence, it may be likely to access a silvl radical through an oxidative pathway based on a SET between an oxidizable hydrosilane and an excited state of photocatalyst. This may also enable a unified radical hydrosilylation for alkynes with different electronic properties and substitution patterns (Scheme 1). In





connection with our previous investigations on organic dye photocatalysis,8 we herein wish to report a visible lightpromoted transition-metal-free hydrosilylation of alkynes using Eosin Y as the photocatalyst and a catalytic amount of thiol as the radical quencher.

A survey of bond-dissociation energies and oxidation potentials of commercially available hydrosilanes confirmed that the combined use of tris(trimethylsilyl)silane (TTMS) $(E_{1/2}^{Ox} = 0.73 \text{ V vs SCE})$ and Eosin Y $(E_{1/2}^{Red} = 0.83 \text{ V vs SCE})$ for excited state of Eosin Y) may enable the oxidative scission of a Si-H bond and controllable generation of silyl radicals under proper visible-light activation conditions.⁹⁻¹² First, the hydrosilylation of but-3-ynyl acetate was examined under irradiation of 10 W white LEDs with 1 mol % of Eosin Y. To our delight, the reaction proceeded in a highly regio- and stereoselective manner in a mixed solvent of 1,4-dioxane and water (100:1, v/v), affording *anti*-Markovnikov Z-alkenylsilane 1 as a major product (Table 1, entry 1). The yield was further improved by introducing a catalytic amount of basic additives (Table 1, entries 2-4). Thiol reagents were attempted as the hydrogen donors (Table 1, entries 5-8). The combination of triisopropylsilanethiol and potassium carbonate resulted in almost quantitative yield and excellent regio- and stereoselectivity. Our experiments also revealed that (1) no hydrosilylation occurred in the absence of light; (2) poor conversion was observed when silanes (triphenylsilane and dimethylphenylsialne) with high oxidation potentials were used, instead of tris(trimethylsilyl)silane; (3) replacement of Eosin Y with other organic photocatalysts afforded inferior results; and (4) photocatalyst, thiol, and base additives are all essential for this hydrosilylation (for details, see Table S1 in the Supporting Information (SI)).

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^{*a*}Reaction conditions: alkyne (0.3 mmol), silane (0.36 mmol), EY (1 mol %), dioxane/H₂O (100/1 v/v, 3.0 mL), 10 W white LEDs. The amount of mentioned thiol additive or base is 5 mol %. ^{*b*}NMR yield using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*}The Z/E ratios were determined by ¹H NMR analysis of the crude products.



The scope of this transition-metal-free hydrosilylation was then explored under the optimized conditions, including electron-neutral, -deficient, and -rich terminal alkynes (Scheme 2). All these reactions worked well, delivering 1,2-disubstituted alkenylsilanes 1-22 in good to excellent yields with variable Z/E selectivities. A variety of functional groups, including acetate, alkyl chloride, alcohol, N-Boc protected amine, benzaldehyde, fluorobenzene, pyridine, thiophene, acetal, carboxylate, phenoxy, phenylthio, and diphenylphosphino were tolerated. The substitution patterns on propargylic carbon were found to affect the distribution of two stereoisomers. Terminal alkynes with primary alkyl substituents gave Z-alkenylsilanes 1-4 predominantly. However, in the case of secondary and tertiary alkylsubstituted alkynes, the proportion of Z-adduct was reduced to a certain extent. A hydroxyl group at the propargylic position may cause a decreased stereoselectivity, providing alkenylsilanes 5 and 8 in a Z/E ratio lower than 15/1. It is noteworthy that Zalkenylsilanes 7-8 with a tertiary allylic carbon would isomerize to the corresponding thermodynamically more stable Estereoisomers during silica gel column purification, affording the products with an inverse Z/E ratio. Similar inversions or partial erosions of Z/E ratio were also observed in aromatic and heteroaromatic alkenylsilanes 9-16. It seems likely that electron-withdrawing groups (acetal, ester) on the alkyne terminus make Z-configuration isomers stable, and alkenylsilanes 17-19 could be isolated without any decrease of the Z/Eratio. When a divne substrate was attempted, an electrondeficient alkyne is preferred over the electron-neutral one. Furthermore, the heteroatoms attached on the alkyne terminus affected the reactivity and stereoselectivity of the hydrosilvlation, in which a longer reaction time was needed for Zalkenylsilane 20 and the formation of Z-alkenylsilanes 21-22 became unfavorable due to the increasing steric repulsion

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^aThe hydrosilylation was performed as entry 8 of Table 1. The yields and Z/E ratios out of parentheses correspond to the isolated products, while the Z/E ratios of crude products are shown inside parentheses. ^b0.3 mmol TTMSS was used. ^cThe reaction time is 24 h.

between a heteroatom-containing group and a bulky tris-(trimethylsilyl)silyl radical.

Next, the regio- and stereoselectivity of this transformation was further examined upon a range of unsymmetrical internal alkynes (Scheme 3). All the reactions of aromatic internal alkynes provided excellent regioselectivities and good yields, affording only one type of alkenylsilane regioisomers 23-26 with a tris(trimethylsilyl)silyl substituent locating at the β position toward the aromatic group. However, the stereoselectivities of the products derived from aromatic internal alkynes were poor, according to their Z/E ratios. In contrast, an α -addition of a silvl radical to electron-deficient alkynes was observed, delivering alkenylsilanes 27-31 preferentially in a stereoselective manner.¹³ The α/β selectivity varies, depending on the substituents (alkyl, aryl, trimethylsilyl) on the terminus of electron-deficient alkynes. Poor regioselectivity was observed in the presence of a methyl substituent. When primary, secondary alkyl substituents and a phenyl group are appended, the α/β selectivity increases. Perfect α/β selectivity was achieved in the case of a trimethylsilyl substituted electrondeficient alkyne. In addition, the terminal phenoxy group led to

Scheme 3. Trisubstituted Alkenylsilanes



^{*a*}50 W white LEDs were used, and the reaction time is 24 h. The yields and Z/E ratios outside of parentheses correspond to the isolated products, while the Z/E ratios of crude products are shown inside parentheses. ^{*b*}The reaction time is 60 h.

a high regio- and stereoselective formation of 32, even though the yield is moderate after extending the reaction time.

To explain the mechanism of this type of alkyne hydrosilylation, we designed several experiments to capture some crucial evidence (Scheme 4). When one terminal of acetylene

Scheme 4. Mechanistic Studies

I. A radical clock experiment (Me₃Si)₃S as entry 8 of Table 1 33 (Me₃Si)₃Si⊦ 99% vield, 1/1 ratio (Me₃Si)₃Si 34 II. Deuterium experiments ^{//}C₆H₁₃ (Me₃Si)₃S as entry 8 of Table 1 (Me₃Si)₃SiD ⁿC₆H₁₃ H/D (34% D) 90% vield. Z/E = 13/1 as entry 8 of Table 1 (Me₃Si)₃Si ⁿC₆H₁₃ D₂O instead of H₂O —ⁿC₆H₁₃ (Me₃Si)₃SiH . H/D (35% D) 95% yield, Z/E = 24/1 as entry 8 of Table1 D₈-dioxane instead (Me₃Si)₃Si "C6H13 (Me₃Si)₃SiH c) $\equiv {}^{n}C_{6}H_{13}$ + `н (0% D) н́ 84% yield, Z/E > 50/1 as entry 8 of Table 1 without thiol IV. 8 h (Me₃Si)₃S ⁿC₆H₁₃ d) = "C₆H₁₃ (Me₃Si)₃SiD + D/H (84% D) H 73% yield, Z/E = 12/1 as entry 8 of Table 1 (Me₃Si)₃Si ^{*n*}C₆H₁₃ without thiol IV + (Me₃Si)₃SiH e) = ⁿC₆H₁₃ D₂O instead of H₂O . H/D (< 4% D) H 83% yield, Z/E = 14/1

bears a cyclopropyl group, its reaction with tris(trimethylsilyl)silane under the standard conditions afforded a mixture of the expected product alkenylsilane 33 and allenylsilane 34 in a 1:1 ratio (Scheme 4, I). Obviously, the emergence of an allenylsilane product evidenced that a vinyl radical adjacent to the cyclopropane ring was involved in this free-radical reaction, resulting in homolytic cleavage of a carbon-carbon bond in the absence of any alkynophilic Lewis acids. To gain insight into the role of the thiol and quenching pathway of the transient vinyl radical, a variety of isotope labeling experiments were performed. When oct-1-yne was treated with deuterated tris(trimethylsilyl)silane under the standard conditions, an alkenylsilane was detected with 34% incorporation of deuterium at the C2 position (Scheme 4, IIa). A similar installation of deuterium at the same position of the product was observed when H_2O was replaced with D_2O (Scheme 4, IIb). However, no deuterium was installed in the product when 1,4-dioxane-D8 was applied as the solvent (Scheme 4, IIc). These results indicate that the new hydrogen atom in the alkenylsilane adduct originates from not only hydrosilane but also water, and it is irrelevant with the solvent 1,4-dioxane. Furthermore, in the absence of a thiol additive, 84% deuterium incorporation was observed by using deuterated silane ((TMS)₃SiD, Scheme 4, IId), while less than 4% deuterium was installed when D_2O was employed (Scheme 4, IIe). It means that two radical-quenching pathways may be involved, in which both hydrosilane and H₂O can serve as the hydrogen atom source. Most importantly, only in the presence of thiol can the hydrogen atom transfer of water be implemented. Finally, our parallel experiments revealed that the progress of the reaction was frozen after removing the light source during the reaction, while continuous irradiation gave the product in 99% yield (Figure 1). The quantum yield of the reaction was



Figure 1. Hydrosilylation of oct-1-yne with/without light.

determined to be 0.257 (for details, see the SI), which suggests that a photoredox pathway may be involved rather than a radical chain propagation.

A mechanism was thus proposed based on the above experimental evidence (Scheme 5). Under the irradiation of white LEDs, a single electron transfer (SET) occurs between the excited state EY* ($E_{1/2}^{\text{Red}} = 0.83 \text{ V}$ vs SCE) and tris(trimethylsilyl)silane ($E_{1/2}^{\text{Cx}} = 0.73 \text{ V}$ vs SCE), affording silyl radical cation **A** and reduced EY. The radical cation was converted to silyl radical **B** through deprotonation promoted by a base or water. A subsequent intermolecular addition of a silyl radical across a triple bond takes place, resulting in the



H₃O⁴ formation of interconvertible vinyl radicals C and D.14 After a hydrogen atom abstraction from thiol, the Z- and Ealkenylsilane adducts will be vielded accompanied by thiol radical E. A single electron transfer between thivl radical E and reduced EY will complete the catalytic cycle, affording the photocatalyst and a thiol anion F, the latter of which is prone to recombine with a proton to regenerate thiol. The following should be noted: (1) The relative reactivity of the intermolecular HAT and thermodynamic stability of silvlated vinyl radicals C and D are pivotal factors controlling the final distribution of regioisomers and stereoisomers. For terminal alkynes $(R_1 = H)$, anti-Markovnikov Z-alkenylsilanes derived from radical C were isolated as a major product, even though radical D is thermodynamically more stable than C. The quenching of radical **D** should be slower than that of **C**, oweing to the bulky steric hindrance of the silyl group, which makes the abstraction of hydrogen atom disadvantageous. The excellent Z-slectivity was also observed in trisubstituted alkenylsilane 32. However, in the case of trisubstituted aromatic alkenylsilanes (R² = Ar), poor stereoselectivities were encountered, which indicates that the quenching of radical D is competitive. Furthermore, the introduction of an electron-deficient group $(R^1 = CO_2Me)$ on the internal alkyne might facilitate the quenching of radical **D**, providing the *E*-alkenylsilane as a major product. (2) From the point of view of polar effect, the thiol might be preferred as a major hydrogen contributor of a nucleophilic vinyl radical rather than the silane, even though a hydrogen atom transfer from the silane to vinyl radical is practical, especially in the absence of a thiol additive, as evidenced by our deuterium experiments. (3) An alternative chain-process mechanism, in which the thiol behaves as a polarity-reversal catalyst in both the silyl-radical-initiation step and vinyl-radical-quenching step,6c,15 is not supported by the quantum-yield calculations (see SI for more details). Poor hydrosilylation was observed when triphenyl silane ($E_{1/2}^{O_x}$ = 0.81 V vs SCE) or dimethylphenylsilane $(E_{1/2}^{Ox} = 0.91^{-7})^{1/2}$ V vs

SCE) with higher oxidation potential was used, though a HAT

between this kind of silane and the thiyl radical is feasible.^{6g}

Based on our current experimental evidence, the distinguishing

reactivity between the corresponding silylated vinyl radical and

the silvlated alkyl radical may be a determinant leading to

different mechanisms, which involve either a single electron transfer or a hydrogen atom transfer in the radical-initiation step and radical-quenching step. At this stage, the thiol in this reaction is preferred to serve as a hydrogen donor in the radical-quenching step rather than a hydrogen abstractor of hydrosilane in the radical-initiation step.

In conclusion, visible-light-promoted metal-free hydrosilylation of alkynes has been developed by using catalytic amounts of Eosin Y as a photocatalyst, thiol as a radical quencher, and potassium carbonate as a base additive. A variety of terminal and internal alkynes with different electronic properties were successfully transformed to the corresponding di- and trisubstituted alkenylsilanes with good functional group tolerance. Control experiments indicate that the hydrosilylation is initiated preferentially by a SET between hydrosilane and excited Eosin Y, and a photoredox mechanism is preferred.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b00909.

Experimental procedures, characterizations, and copies of ¹H and ¹³C NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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