



Visible-Light-Induced Catalyst-Free Carboxylation of Acylsilanes with Carbon Dioxide

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photoirradiation under catalyst-free conditions. In this reaction, siloxycarbenes generated by photoisomerization of the acylsilanes added to the C=O bond of CO₂ to give α -ketocarboxylates, which underwent hydrolysis to afford α -ketocarboxylic derivatives in good yields. Control experiments suggest that the generated siloxycarbene is likely to be from the singlet state (S₁) of the acylsilane and the addition to CO₂ is not in a concerted manner.

A cylsilane derivatives, as first synthesized by Brook,¹ exhibit distinctive photochemical reactivity due to the abnormal inductive effect of the silicon atom and their long $n-\pi^*$ absorption (380–420 nm).² The acylsilanes could undergo a 1,2-silyl shift, which is similar to the well-known Brook rearrangement, to generate nucleophilic siloxycarbenes under photolysis³ or high temperature (>250 °C).⁴ The lightderived nucleophilic siloxycarbenes are capable of insertion into a wide range of X–H bonds, including O–H, halogen–H, B–H, and Si–H bonds (Scheme 1a).^{3a,5} In addition, Kusama and co-workers reported the cross-coupling between the acylsilanes and organoboronic esters through a formal B–C bond insertion intermediate and following a rearrangement to afford ketones.⁶ Recently, intra- and intermolecular addition of

Scheme 1. Photochemical Reaction Behavior of Acylsilanes



the siloxycarbene to alkynes or alkenes is reported by Bolm (Scheme 1b) to give silylated acrylic ketones.⁷ In spite of that, only limited reports have appeared, to date, utilizing the photochemically generated siloxycarbenes for C–C bond formation.⁸ To the best of our knowledge, the reaction of light-derived nucleophilic siloxycarbenes with CO₂ has not been reported (Scheme 1c).

 CO_2 is an ideal one-carbon source with a cheap, nontoxic, and abundant nature.9 Chemists have been challenged to create catalytic C-C bond-forming avenues to carboxylic acids, which are privileged motifs in a mass of molecules displaying significant biological properties.¹⁰ Although considerable advances have been realized, the catalytic synthesis of valuable carboxylic acids from CO2 remains limited to the use of either metal catalysts with stoichiometric reductants¹¹ or the use of photoredox catalysts.^{12,13} To the best of our knowledge, there are very few reports of photoinduced catalyst/reductantfree carboxylation with CO₂.¹⁴ Recently, Murakami reported a photoinduced direct carboxylation of *o*-alkylphenyl ketones with CO_{2} , which undergoes a photoenolization step and [4 + 2] cycloaddition.¹⁵ However, the employment of energetic UV light is almost compulsory. With our continuous interest in C-C bond construction with CO_{2i} we envisaged that the visible-

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light-generated siloxycarbene could capture CO_2 , which is more challenging than reacting with ketone and aldehyde to afford carboxylic acids.^{8b,c} Herein, we would like to report the first visible-light-induced catalyst-free carboxylation of acylsilanes under atmospheric CO_2 . A series of α -ketoesters can be obtained under simple conditions in moderate to high yields after esterification.

We initiated our studies by irradiating 4-methylbenzoyl-trimethylsilane (1a) and CO_2 under irradiation with blue LEDs (Table 1). After systematic exploration of reaction



	O Cs ₂ CO ₃ TMS + CO ₂ (2.0 equiv.) TMSC (1 atm) DMSO (0.05 M) rt, blue LED, ta 24 h, then 2 N HCl	CHN2 MeOH +	ne OMe 3a
entry	deviation	yield of 2a ^b (%)	yield of 3a ^b (%)
1	None	75 (69)	6
2	MeCN instead of DMSO	49	7
3	DCE instead of DMSO	30	4
4	DMF instead of DMSO	59	9
5	DMA instead of DMSO	52	10
6 ^{<i>c</i>}	0.1 M instead of 0.05 M	50	6
7	3.0 equiv of Cs ₂ CO ₃ instead of 2.0 equiv	69	3
8	1.0 equiv of Cs ₂ CO ₃ instead of 2.0 equiv	43	10
9	1.0 equiv of CsF	68	6
10	12 h instead of 24 h	48	4
11	40 °C instead of rt	57	12
12	without light	ND	ND
13	without Cs ₂ CO ₃	49	8
14	without CO ₂	ND	48
15	1.0 equiv of CsF, without light	58	6
16	1.0 equiv of CsF, without Cs ₂ CO ₅ and light	3 52	5

^{*a*}Reaction conditions: 1a (0.1 mmol), DMSO (2.0 mL), 1 atm of CO₂, 5 W blue LED, rt, 24 h, workup, then TMSCHN₂ (2.0 equiv in 0.5 mL of MeOH/Et₂O, v/v = 1:1). ^{*b*}Yields determined by crude ¹H NMR using CH₂Br₂ as internal standard, isolated yield in parentheses. ^{*c*}Diphenylethanedione was observed. ND = not detected.

conditions, compound 2a was detected in 75% yield in the presence of 2 equiv of Cs₂CO₃ within 0.05 M DMSO (dimethyl sulfoxide) at room temperature for 24 h (entry 1). Screening of other solvents such as acetonitrile (MeCN), 1,2dichloroethane (DCE), N,N-dimethylformamide (DMF), and N,N-dimethylacetamide (DMA) suggested that DMSO is the optimal solvent (entries 1-5). Increasing the concentration to 0.1 M resulted in a decreased yield of 2a. In this case, diphenylethanedione was observed (entry 6). The amount of additive also has a non-negligible effect on the reaction. The yield of 2a was not further increased with the addition of 3 equiv of Cs_2CO_3 (entry 7), while reducing it to 1 equiv also led to inferior yield (entry 8). Considering that fluoride may facilitate the removal of the trimethylsilyl group (-TMS), CsF was chosen as a coadditive, but the yield of 2a was not improved (entry 9). Although the fade of solution color was detectable after the reaction proceeding in 30 min, shortening the reaction time to 12 h led to 48% yield (entry 10), indicating that the addition of the siloxycarbene to CO_2 might be the rate-determining step. Elevating the temperature to 40 °C gave the desired product 2a in 57% yield (entry 11). No

detection of **2a** or **3a** without illumination proves the indispensable role of light (entry 12). A decreased yield was observed without Cs_2CO_3 (entry 13), and no **2a** was obtained when the reaction was carried out without CO_2 , ruling out the possibility of Cs_2CO_3 as additional C1 source (entry 14). The reaction was also viable in the presence of CsF without illumination (entry 15) and removal of Cs_2CO_3 hardly affected the yield, which suggests that the phototransformation of acylsilane undergoes a different route from F-mediated thermal protocol (entry 16).¹⁶

With the optimal conditions in hand, we subsequently commenced the evaluation of substrate generality. As is shown in Scheme 2, a number of *para*-substituted electron-rich and



^{*a*}Reaction conditions: **1a** (0.2 mmol), Cs_2CO_3 (2.0 equiv), DMSO (4.0 mL), 1 atm of CO_2 , 5 W blue LED, rt, 24 h, quenched by HCl (2 N), workup, then TMSCHN₂ (2.0 equiv in 1.0 mL of MeOH/Et₂O, v/v = 1:1). Isolated yield. ^{*b*}-SiPh₂Me instead of -TMS in acylsilane.

electron-neutral benzoyl trimethylsilanes gave the desired products (2a-2g) in good yields. When -TMS is replaced by more sterically hindered –SiPh₂Me in the acylsilane 1b, the yield of 2b drops significantly, which indicates that the steric effect is obvious in the 1,2-silyl shift process. Then examination of substrates bearing halides (1h, 1i, and 1j) proved that fluorine and chlorine are well-tolerated in the protocol, indicating their potential in late-stage functionalization. However, strong electron-withdrawing groups, such as $-CO_2Me$ and $-CF_3$, failed to afford the desired products, in which the corresponding benzaldehydes and benzoates were detected as byproducts. This observation manifests that the reactivity of substrates is strongly influenced by the nucleophilicity of the in situ generated siloxycarbenes. We then turned our attention to other sites of the aryl motif. Substrates with methyl (1k) and methoxy (1l) group on orthoposition of the benzene ring exhibited moderate reactivity. The

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lower yield of 2l agreed with the conclusion that a larger substituted group may impede the rearrangement of the silyl group, despite its stronger electron-donating ability. Meanwhile, we found that acylsilanes containing functional groups at *meta*-position (1m and 1n) also proceed smoothly under the protocol. Afterward, we examined disubstituted acylsilanes, such as (3,5-dimethylphenyl)(trimethylsilyl)methanone (10) and (3-fluoro-4-methylphenyl)(trimethylsilyl)methanone (1p), and the corresponding carboxylic esters were isolated in 80% (for 20) and 76% yields (for 2p), respectively. What's more, α - and β -substituted naphthalene derivatives (1g and 1r) were well-accommodated where no discrepancy in siteactivity was observed. Lastly, we replaced the benzene ring with other electron-rich heterocycles, such as thiophene and furan, and the desired carboxylated product (2s) was acquired in 38% yield while methyl 2-(furan-2-yl)-2-oxoacetate (2t) was obtained in 18% yield. When an alkyl acylsilane was applied, such as 3-phenylpropanoyltrimethylsilane, a complex mixture was observed, which may due to the less stability of the formed alkylsiloxycarbene than arylsiloxycarbene.

To gain more insight into the mechanism, control experiments were carried out to elucidate the reaction pathway (Scheme 3). According to literature, addition of the formed

Scheme 3. Mechanistic Studies



siloxycarbene to acetaldehyde generates an oxirane, which reacted with MeMgBr to afford the corresponding carbinol.⁸⁶ Based on this result, we treated a reaction mixture generated from the reaction of 1a with CO₂ under blue LED for 12 h with 1 equiv of PhMgBr. Product 2a and 3b were obtained in 40% and 100% yield, respectively (Scheme 3a). The observation rules out the possibility of direct siloxycarbene addition to CO₂ to form a 3-membered lactone, which is not consistent with previous work.14 To further gain the intermediate of the reaction, we treated 1a with CO2 in acetonitrile under the standard conditions (Scheme 3b). After completion of the reaction, the supernatant of the crude mixture was characterized by NMR and GC-MS, and the target carboxylic acid was not observed. The residual insoluble precipitate, meanwhile, was tested by MALDI-TOF MS. The analytic results exhibit molecular weight of mono- and dicesium salt 4a as shown in Scheme 3b. Moreover, treating the precipitate with dilute HCl gave 2a', proving its role as the key intermediate. Being aware that homolytic cleavage of the C-Si bond may potentially result in an acyl radical,¹⁷ 2,2,6,6tetramethyl-1-piperidinyloxy (TEMPO) was incorporated as a radical scavenger in the reaction and the product 2a was obtained in 72% yield (Scheme 3c). This outcome manifests

that the reaction is not likely to proceed in a radical pathway. To clarify from which state of the excited acylsilane does the siloxycarbene originate, the reaction was carried out with the addition of a triplet-sensitizer, trans-stilbene (E-5). It is noteworthy that 1 equiv of E-5 ($E_{\rm T}$ = 49.3 kcal/mol) does not inhibit the reaction and only a small amount of the olefin is converted to its Z-isomer (E: Z = 12.5:1) (Scheme 3d). These results indicate that the siloxycarbene is more likely to be generated from S_1 state of $1a_1^{18}$ although minor formation of the Z-isomer suggests that the T_1 state is not totally forbidden. UV-vis spectroscopy (see the Supporting Information) shows that Cs_2CO_3 does not affect the absorption spectra of 1a. As a result, the additive mainly functions to stabilize the formed siloxycarbene and enhances its nucleophilicity. In addition, the formed cesium carboxylate also precipitates, which will push the reaction forward.

Based on the above results and previous reports, a plausible mechanism is depicted in Scheme 4. Initially, the acylsilane 1 is

Scheme 4. Proposed Mechanism



irradiated to its singlet excited state 1*, which undergoes an 1,2-silyl shift to generate the singlet siloxycarbene intermediate I and/or its resonance form I'.^{3a,8a} Subsequent nucleophilic attack to the C=O bond of CO₂ generates the cesium carboxylate 4 in the presence of Cs₂CO₃. The presence of cesium carboxylate 4 has been confirmed by MALDI-TOF MS analysis. A cation exchange between Cs⁺ and the –TMS group exists in the system. Hydrolysis of the intermediate 4 affords the desired α -keto carboxylic acid 2' and trimethylsilanol 6. The existence of 6 is verified by its condensation on GC–MS. Additionally, the formation of byproduct benzoic acid 3' can be rationalized by the insertion of residual I to water after workup.^{6a} Aldehyde 7 is generated from protonation of I' after hydrolysis, which is confirmed by deuterium-labeling experiments (50% yield, 92% D incorporation).^{16c}

In conclusion, we have developed a novel visible-lightinduced carboxylation of acylsilanes with CO_2 . The reaction provides a new reaction mode for siloxycarbene, where addition to more inert carbonyls is realized, providing 1,2dicarbonyl compounds under mild conditions. In the 1,2-silyl shift process, the siloxycarbene is more likely to occur from the S_1 state of the acylsilane. Further efforts on developing intrigue photoinduced catalyst-free carboxylation with CO_2 as a C1 source are currently in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00435.

All experimental procedures, compound characterization data, copies of spectra, UV–visible spectroscopy of 1a, and reaction setup (PDF)

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Notes

The authors declare no competing financial interest.

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