Visible-Light Induced Singlet Nucleophilic Carbenes: Rapid and Mild Access to Fluorinated Tertiary Alcohol Derivatives

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ABSTRACT: Singlet nucleophilic carbenes (SNCs) that contain only one heteroatom donor remain underexplored and underutilized in chemical synthesis. To discover new synthetic strategies that harness these SNCs as reactive intermediates, aromatic or aliphatic siloxy carbenes represent excellent model substrates as they can be readily generated photochemically from stable acyl silane precursors. We herein report the discovery that photochemically generated siloxy carbenes undergo 1,2-carbonyl addition to trifluoromethyl ketones, followed by a silyl transfer process to afford benzoin-type products. This new transformation is a rare example of the use of ketones as trapping reagents for SNC intermediates and delivers an efficient, user-friendly and scalable process to access fluorinated tertiary alcohol derivatives driven by only light, circumventing the use of catalysts or additives.

Carbenes are neutral reactive intermediates that possess six valence electrons, four of which occupy two sigma-bonding orbitals while the remaining two occupy either one or both of the non-bonding orbitals.[1] Carbenes are important reactive intermediates in organic synthesis, where triplet carbenes (unpaired non-bonding electrons) exhibit reactivity akin to radical intermediates and singlet carbenes (paired non-bonding electrons) can display either electrophilic or nucleophilic reactivity.[2]

Electrophilic singlet carbenes, typically generated from diazo precursors, have been widely exploited in organic synthesis in processes including C-H insertion and cyclopropanation reactions.[3] Highly stabilized singlet nucleophilic carbenes (exemplified by NHC-based organocatalysts and ligands) have also been extensively utilized in synthesis with chiral NHC derivatives employed to catalyse a variety of chemical reactions with high chemo- and enantioselectivity.[4] Comparatively, the application of singlet nucleophilic carbenes (SNCs) containing only one heteroatom substituent in chemical synthesis remains limited. Examples of such SNCs include cyclic oxacarbenes generated photochemically from cyclobutanone,[5] aryl alkoxy carbenes,[6] aryl amino carbenes[7] and siloxy carbenes.[8]

When considering the reaction of singlet carbenes with ketones, electrophilic carbenes undergo an *O*-insertion process whereby the oxygen atom of the carbonyl group donates electrons into vacant 2p orbital of the carbene to generate a carbonyl ylide (see Figure 1). The ylide is available to react in subsequent processes including dipolar cycloadditions to generate chemotypes including oxiranes and furans.[9] While the reactivity of nucleophilic carbenes with aldehydes, esters and acyl fluorides is well-established to generate species including Breslow, acyl azolium and diazolium enolate intermediates,[4e-h] the reaction of nucleophilic carbenes with ketones remains relatively unexplored. To date, few reports have described the reaction of stabilized singlet nucleophilic carbenes (e.g. NHCs) with

ketones.[10] For nucleophilic carbenes containing one heteroatom donor, there exists only two single examples from 1971 (Figure 1), where Brook and co-workers reported that a siloxy carbene reacted with acetone to afford an oxirane or with cyclohexanone to afford a silyl enol ether derivative (Figure 1).[11]
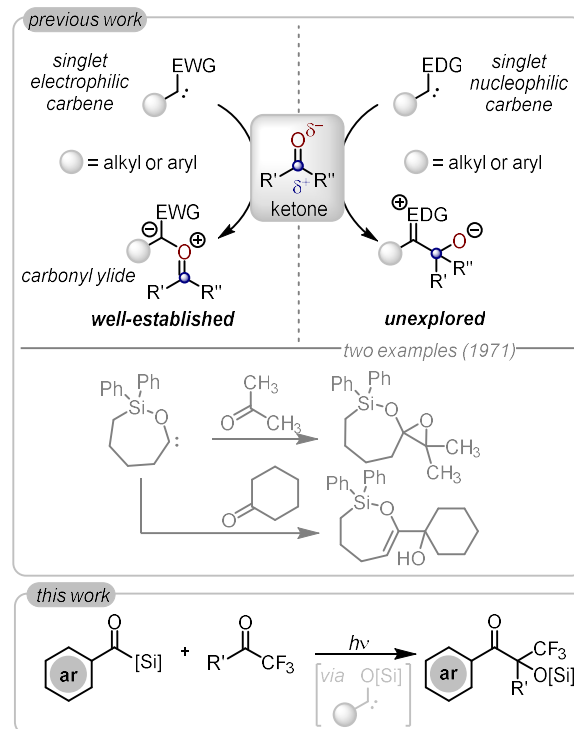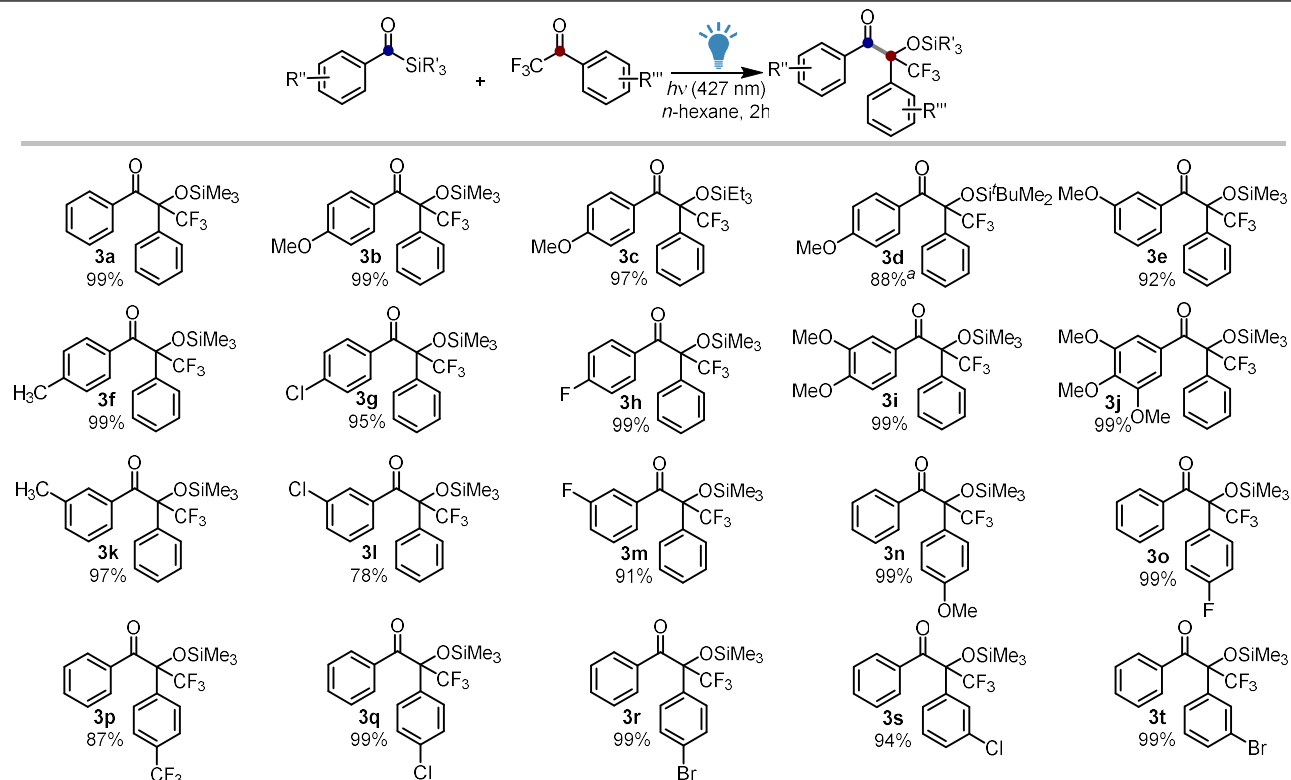

Figure 1. The reactivity of electrophilic carbenes with ketones is well-established whereas the reactivity of nucleophilic carbene intermediates with ketones is relatively unexplored.

Scheme 1. Photochemical reaction of aryl siloxy carbenes with 2,2,2-trifluoroacetophenone derivatives. *Reaction conditions:* acyl silane (0.25 mmol), 2,2,2-trifluoroacetophenone (0.50 mmol), *n*-hexane (1.0 mL), 4Å MS (~250 mg) irradiated at 427 nm for 2h. [a] reaction time of 6h required.

To gain new insight into this underexplored mode of reactivity for carbene intermediates, we set out to conduct a detailed investigation into the reaction of SNC intermediates with ketones. While oxacarbenes, aryl alkoxy carbenes, and aryl amino carbenes would all be suitable SNCs for such a study, we focused on siloxy carbenes as model substrates for studying partially stabilized SNCs as these intermediates can be readily generated from stable acyl silane precursors via irradiation with visible light, circumventing the inclusion of catalysts or additives in the reaction mixture.[1d,12] We envisaged that if successful, the photochemical addition of singlet nucleophilic carbene intermediates to ketones would deliver a new metal-free approach to the synthesis of tertiary alcohol derivatives, an important chemotype in organic synthesis and pharmaceutical sciences.[13]

Our initial studies involved irradiation of benzoyltrimethylsilane (**1a**) with blue LEDs (427 nm, 40W) in the presence of two equivalents of various ketones including acetone, cyclobutanone, cyclohexanone, acetophenone and 2,2,2-trifluoroacetophenone in dichloromethane. Only the reaction with 2,2,2-trifluoroacetophenone led to quantifiable amounts of product, whereby after only 2 hours, complete consumption of the acyl silane was observed and trifluoromethyl alcohol derivative **3a** was isolated in 82% yield. A solvent screen was subsequently performed which revealed *n*-hexane to be the optimal solvent for this reaction (affording **3a** in near quantitative yield), however THF, diethyl ether and chloroform also proved suitable. The inclusion of 4Å molecular sieves also improved the reaction by limiting hydrolysis of the acyl silane to the corresponding aldehyde which can occur when the carbene reacts with adventitious water in the reaction mixture. Furthermore, experimental controls revealed that in the absence of light no reaction was observed.

We subsequently investigated the UV/Vis absorption profile of both the individual reaction components and the reaction mixture (see supporting information). The trifluoromethyl ketone exhibits absorption at wavelengths below 300 nm whereas acyl silane **1a** absorbs light in the visible region (λ_{max} = 420 nm) facilitating selective excitation of the carbene precursor by irradiation at 427 nm. Due to the absence of spectral shifts in the absorbance profile of the mixture, there was also no evidence for the formation of an electron-donor acceptor (EDA) complex between the two reagents.

A key consideration when employing siloxy carbene intermediates is that following nucleophilic carbene addition to a electrophile such as a ketone, an oxonium ion is formed that contains two potential sites of subsequent reaction. Following carbene addition to the trifluoromethyl ketones, the zwitterionic species formed can react in two possible manners, either via oxyanion addition to the base of the oxonium ion to afford an oxirane (for an example see Figure 1), or the oxyanion can abstract the silyl group from the oxonium ion to regenerate the carbonyl system, the latter of which is operating during the reaction described herein.

The structure of the ketone product was confirmed by ^{13}C NMR analysis with key spectral characteristics including a resonance at δ = 192 ppm assigned to the new ketone motif, a quartet at δ = 121 ppm (*J* = 286 Hz) assigned to the CF$_3$ group, and a quartet at δ = 83 ppm (*J* = 26 Hz) assigned to the new tetrasubstituted carbon center formed which is bonded to the CF$_3$, silyl ether and ketone functional groups. A shift of the CF$_3$ resonance from δ = -69 to -74 ppm from the 2,2,2-trifluoroacetophenone starting material to the product can also be observed following analysis by ^{19}F NMR.

With high-yielding conditions in hand, the photochemical reaction process was explored using different acylsilane and trifluoromethyl ketone substrates (Scheme 1). Initially, variations in the silyl group were explored with the trimethyl, triethyl and *tert*-butyldimethyl silyl analogues all affording the product in high yield (**3b-d**), however the *tert*-butyldimethyl silyl analogue required a longer reaction time (6h) to achieve full conversion and was isolated in a reduced yield (88%). The corresponding triisopropyl silyl analogue failed to react under the standard conditions.

Variations in the aryl component of **1** were then explored with 3- and 4-monosubstituted aroyl silanes containing methyl, methoxy, chloro or fluoro substituents all performing well (Scheme 1, **3e-h**, **3k-m**, 78-99%). Di- and tri-substituted aroyl silanes also afforded the corresponding fluorinated tertiary alcohol derivatives **3i** and **3j** in excellent yield. Trifluoroacetophenone derivatives containing additional substituents in either the 3- or 4-aryl position were then subjected to reaction with acyl silane **1a** under the standard photochemical conditions to afford the corresponding benzoin-type adducts in exceptional yield (Scheme 1, **3n-3t**, 87-99% yield).

To further explore the reactivity of photochemically generated nucleophilic carbene intermediates with ketones, a series of aroyl silanes **1** were reacted with an aliphatic ketone in the form of 1,1,1-trifluoroacetone **4** (Scheme 2). This reaction also proceeded with high efficiency, affording to corresponding ketones **5a-f** in near quantitative yield. Again, diverse substitution patterns on the aromatic ring of the aroyl silanes were tolerated (Scheme 2). To this point, attempts to react the carbene intermediate generated from aliphatic acyl silanes with **2a** or **4** *via* direct irradiation (using 370, 390 and 427 nm LEDs) or triplet energy transfer (employing 2 mol% of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ at 440 nm) proved unsuccessful.[8g,h]

To further probe this photochemical process a series of additional experiments were conducted (Figure 2). Aroyl silanes were reacted with 2-chloro-2,2-difluoroacetophenone to demonstrate that other halogenated ketone derivatives are applicable in this reaction process (Figure 2a). Subsequently, a competition experiment between aroyl silanes containing either electron withdrawing or electron donating substituents was conducted by irradiating a solution containing 0.25 mmol each of aroyl silanes **3g** and **3i** in the presence of 0.25 mmol of 2,2,2-trifluoroacetophenone for 2 hours at 427 nm.
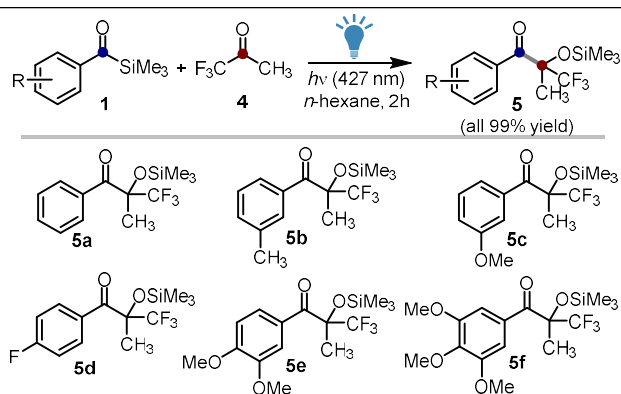
Scheme 2. Photochemical reaction of siloxy carbenes with trifluoroacetone. *Reaction conditions:* acyl silane (0.25 mmol), 1,1,1-trifluoroacetone (0.50 mmol), *n*-hexane (1.0 mL), 4Å MS (~250 mg) irradiated at 427 nm for 2h.

The conversion to the product was analyzed using ^{1}H NMR which revealed that the carbene generated from the 4-chlorophenyl acyl silane trapped 68% of the available ketone with the remaining 32% trapped by the carbene generated from the electron rich acyl silane. This result infers that either formation of the carbene from acyl silane **3i** is more facile or that the carbene generated from **3i** is in fact more reactive.

According to the Beer–Lambert law, light transmittance decreases exponentially as distance from the photon source increases. It is well established that the use of flow chemical technology (where reactions are conducted in microchannels or microtubing) can significantly increase the efficiency of photochemical processes leading to shorter reaction times and decreased by-product formation.[14] Thus, the opportunity to increase the efficiency and scalability of the process described herein was explored in flow by pumping a 0.25M solution of the reagents in *n*-hexane through a 4 mL reactor coil irradiated by 427 nm LEDs (40 W).

Initially, optimization of the reaction time was conducted with 99% and 100% conversion achieved at 15- and 20- minute reaction (residence) times, respectively. Attempts to reduce the residence time to 10 minutes led to a decreased conversion of 96%, and irradiation of the 4 mL reactor coil with two 427 nm LEDs for 10 mins failed to increase the conversion. Finally, a reaction time of 5 minutes employing two photoreactors resulted in 75% conversion of the acyl silane to the product. With optimized flow conditions in hand, a 0.25M solution of anhydrous *n*-hexane containing 7 mmol of acyl silane and two equivalents of the 2,2,2-trifluoroacetophenone was pumped in a continuous fashion through the 4 mL reactor coil employing a residence time of 15 minutes. Following the completion of this process, evaporation of the volatile components and recrystallisation from *n*-hexanes afforded 2.32 g of **3a** in 94% isolated yield (Figure 2c).

A crystal structure of **1a** confirmed the structure of the tertiary alcohol derivative generated from the photochemical bond-forming process (Figure 2f) and the fluorinated silyl ether products could be further manipulated through cleavage of the silyl group to afford the tertiary alcohol, and reduction to produce the diol (Figure 2d).

Finally, the difference in reactivity between an electrophilic carbene and nucleophilic carbene intermediate with the same trifluoromethyl ketone is depicted mechanistically in Figure 2e. In 2017, Jiang and co-workers reported that the electrophilic Pd-carbene intermediate generated from an aryl alkyl tosyl hydrazone underwent an *O*-insertion process with the carbonyl group of 2,2,2-trifluoroacetophenone to afford a carbonyl ylide which further reacted to generate the oxirane product.[15] For the new transformation described herein, reaction of the photochemically generated nucleophilic carbene intermediate occurs at the carbon-atom end of the trifluorocarbonyl group which gives rise to a zwitterionic intermediate affording the benzoin-type product after silyl transfer.

In summary, we have discovered a new process for the formation of tertiary alcohol derivatives employing fluorinated ketone derivatives as trapping reagents in the presence of photochemically generated nucleophilic carbene intermediates. To note, the formation of related products has been achieved employing reactions that proceed via acyl anion intermediates generated from the addition of an NHC catalysts to an aldehyde or a cyanide reagent to acyl phosphonates.[16] Advantageously, the protocol described herein proceeds
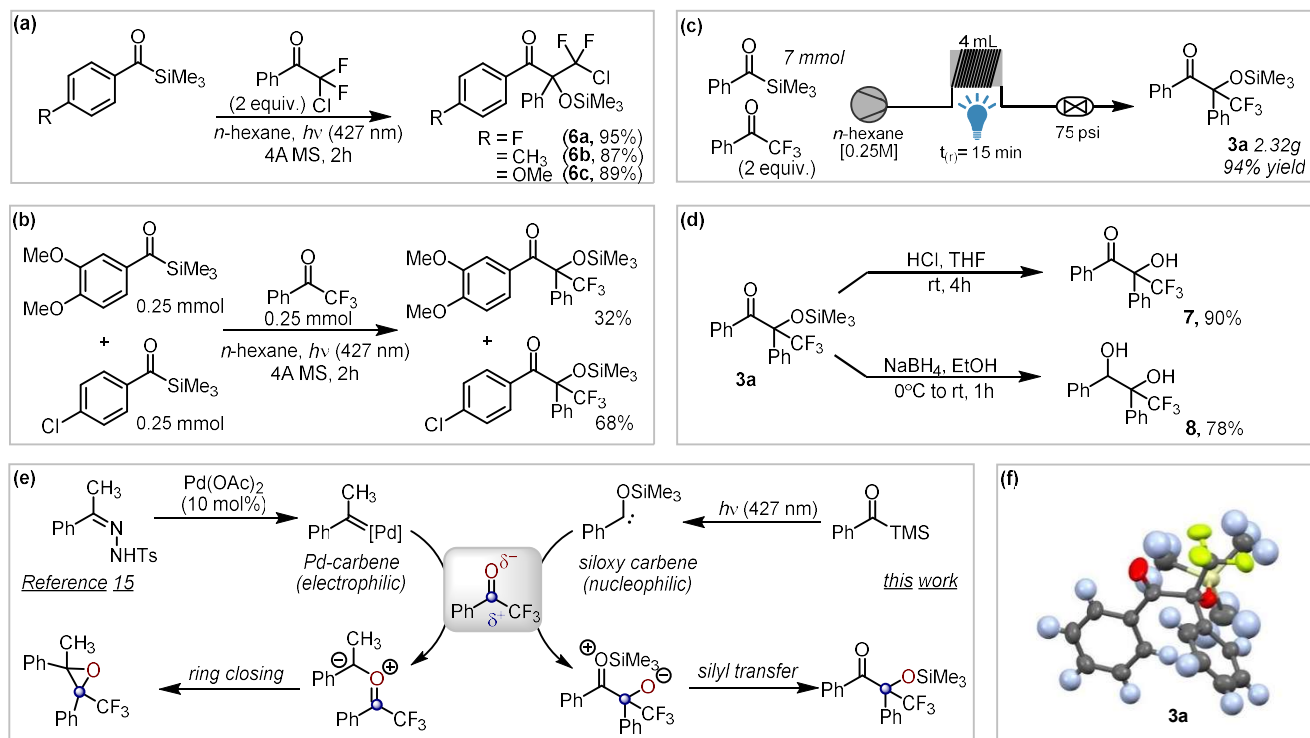
Figure 2. A summary of additional experiments to probe acyl silane photochemistry and carbene reactivity: (a) 3-chloro-3-difluoroacetophenone reacted with various acyl silanes in excellent yield; (b) a competition experiment between acyl silanes containing electron donating and electron withdrawing substituents; (c) the photochemical benzoin reaction conducted in flow; (d) additional manipulations of the fluorinated tertiary alcohol derivative; (e) a comparative mechanism highlighting the difference in reactivity between electrophilic and nucleophilic carbenes with the same ketone; (f) a crystal structure of **3a**.

with 100% atom economy and does not require the use of exogenous catalyst or additives, representing a high-yielding practical photochemical strategy towards the preparation of fluorinated tertiary alcohol derivatives.

In addition, this new transformation represents a unique example of SNCs reacting with ketones and importantly, providing additional insights into the properties and reactivity of the relatively underexplored class of singlet nucleophilic carbene intermediates that contain one-heteroatom donor.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge:
    Full experimental details including NMR spectra (PDF)
    Crystal structure (CIF)

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Author Contributions

The manuscript was written through contributions of all authors.

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Graphical Abstract:

new carbon-carbon bond formed using only light