JOC The Journal of Organic Chemistry
Cite This: J. Org. Chem. 2019, 84, 14461−14468
Article
pubs.acs.org/joc

Lewis Acid-Activated Reactions of Silyl Ketenes for the Preparation of α-Silyl Carbonyl Compounds

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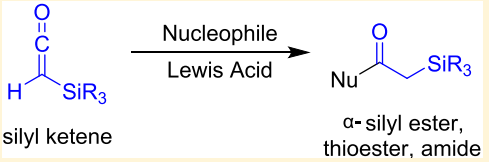
Supporting Information

ABSTRACT: Silyl-substituted ketenes are attractive molecular building blocks due to their stability and ease of storage, as opposed to unstable alkyl and aryl ketenes. To better understand the reactivity of silyl ketenes and, in turn, their use in the preparation of highly functionalized small molecules, the reaction of silyl ketenes with different nucleophiles was studied. The addition of alcohol, amine, or thiol nucleophiles to the central carbon of silyl ketene, followed by proton transfer afforded α-silyl ester, amide, or thio-ester, respectively. Catalytic amounts of Lewis acid greatly increase the rate of the reaction, and the impact of nucleophile, Lewis acid, and silyl substituent are evaluated. The small molecules produced from these reactions give insight into the use of silyl ketenes as building blocks for complex molecular structures.



INTRODUCTION

Ketenes have two, nonconjugated double bonds sharing a central carbon, of the general form $R_2C{=}C{=}O$. These double bonds provide units of unsaturation that can be used in subsequent reactions, including polymerizations.[1] The polymerization of ketenes was first reported in 1925 by Staudinger, who used amines to initiate the polymerization.[2,3] The unique reactivity of ketenes allows for three possible polymeric backbone functionalities: polyketone, polyester, and polyketene acetal.[4,5] Aryl and alkyl ketenes are difficult to work with because of their tendency to self-react in [2+2] cycloadditions as well as the ability to react with a variety of compounds including both nucleophiles and electrophiles.[6,7] Leibfarth et al. used the [2+2] cycloaddition of alkyl ketenes to crosslink polymer films by polymerizing styrenic monomers bearing pendant-protected ketenes, followed by deprotection.[8] In contrast to aryl and alkyl ketenes, silyl ketenes are significantly more stable due to the β-silicon effect, making them easier to store and prepare in large quantities.[1,9] As such, silyl ketenes are more attractive for widespread use and application.

Our group is interested in the chain-growth polymerization of silyl ketenes. We recently illustrated the reaction of silyl ketenes with anionic initiators and detailed the formation of both oligomers and highly functionalized 2-pyranone small molecules.[10,11] We found that the identity of the silyl substituents and counter ion dictated the reaction pathway and, thus, the product distribution. The polymerization of silyl ketenes initiated by an alkoxide was uncontrolled, resulting in a mixture of functional groups in the polymer backbone (acetal, ester, and ketone). Moreover, intrachain backbiting by deprotonation and nucleophilic addition of the propagating enolate led to a broad-molecular-weight distribution. Thus, to fully make use of silyl ketenes as monomers and building blocks for highly functionalized small molecules, a thorough understanding of silyl ketene reactivity is required. Silyl ketenes have the potential to react under a number of conditions including group transfer polymerization (GTP) and cationic polymerization in addition to anionic polymerization.

Lewis acids (LAs) have been used to activate compounds in a variety of reactions including polymerizations.[12,13] Of particular interest, the oxygen atom of a carbonyl can coordinate to a LA, making the carbon atom more electrophilic and, therefore, more susceptible to the addition of a nucleophile.[14,15] This approach can also be applied to silyl ketenes, where the oxygen atom of the ketene can coordinate to the LA, rendering the central carbon atom more electrophilic. In general, alcohols are poor nucleophiles for silyl ketenes, but more readily add if the ketene moiety is made more electrophilic. For example, Ruden et al. used a catalytic amount of the $BF_3{\cdot}OEt_2$ to activate trimethylsilyl (TMS) ketene and illustrated the addition of *t*-butyl alcohol to the central carbon for the preparation of an α-silyl ester; the use of a LA decreased the reaction time from 48 h for the noncatalyzed reaction to only 2 min.[16] The authors also examined the addition of the secondary amine isopropylcyclohexylamine under similar LA-catalyzed conditions to produce an α-silyl amide. Alternatively, zinc halide salts and organocerium reagents have been used to catalyze the formation of α-silyl esters from silyl ketenes.[17,18] These reports illustrate the potential of LA-activation of silyl ketenes for the

Received: July 9, 2019
Published: October 23, 2019

DOI: 10.1021/acs.joc.9b01859
J. Org. Chem. 2019, 84, 14461−14468

preparation of different small molecules, but the applications of different silyl groups and nucleophiles are unknown.

α-Silyl carbonyl compounds are of interest for various further modifications. For example, α-silyl esters can undergo Peterson olefination to produce alkenes[19] or to access β-keto silanes by reaction with Grignard reagents.[20] These compounds can also be used to synthesize silyl ketene acetals,[21−23] of use for α-silyl ester initiators for GTP.[24] Of note, α-silyl esters can alternatively be prepared by the Cu-catalyzed conjugate addition of a Grignard to an ester,[25] by direct silylation of an α-bromo ester with a silyl chloride and zinc[26] or in the presence of a base.[27] These methods for the preparation of α-silyl esters require specialized reaction conditions (i.e., low temperatures) and multiple hours. As such, simpler and more straight forward routes to their preparation are attractive.

Herein, we report the preparation of α-silyl esters, α-silyl amides, and α-silyl thioesters from silyl ketenes using a variety of nucleophiles and a catalytic amount of a LA. These reactions are performed at room temperature, and the reaction is complete in <5 min. First, we optimize LA identity, investigating boranes, metal triflates, and an aluminum alkoxide for the activation of the ketene moiety, thereby facilitating nucleophilic addition to the central carbon. We detail the use of primary, secondary, and tertiary alcohols as nucleophiles as well as examine phenol derivatives bearing electron-donating or -withdrawing groups at various positions. We then evaluate the addition of amine and thiol-based nucleophiles, which yielded the corresponding α-silyl amides and α-silyl thioesters, respectively. We illustrate the usefulness of this approach to a variety of silyl-substituted ketenes, examining how the steric bulk and electronics of the silyl substituent impact the reaction. All small molecule products were isolated and characterized by Fourier-transform infrared spectroscopy (FTIR), ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, ^{29}Si NMR, and gas chromatography−mass spectrometry (GC−MS). This work gives a better understanding of how silyl ketenes can be used as building blocks for α-silyl carbonyl functionalities (Figure 1) as well as provides a foundation for developing the silyl ketenes as monomers.

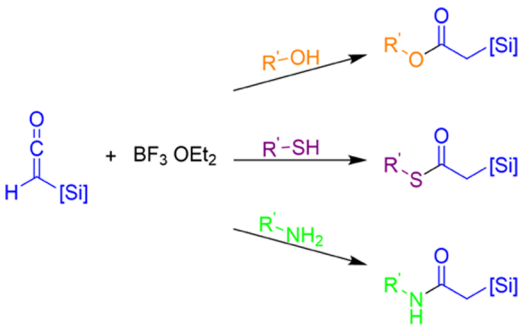


Figure 1. Lewis acid-activated reactions of silyl ketenes for forming α-silyl, esters, thioesters, and amides.

RESULTS AND DISCUSSION

All silyl ketenes were synthesized through a previously reported method and the product identity and purity characterized by NMR, FTIR, and MS (Supporting Information).[28,29] Initially, we evaluated the reaction of methyldiphenyl silyl (MDPhS) ketene with benzyl alcohol in dichloromethane (DCM) to understand the noncatalyzed reaction. Monitoring the reaction by FTIR spectroscopy revealed full ketene consumption only after 4 days of stirring at room temperature (Figure S1). The characteristic ketene stretching frequency in the FTIR spectrum at ∼2100 cm^{-1} disappeared and was accompanied by the appearance of a stretching frequency at ∼1700 cm^{-1} indicating the presence of a carbonyl. The reaction yielded the corresponding α-silyl ester in ∼50% isolated yield.

Given the sluggish nature of the reaction, we investigated the use of various LAs to activate the silyl ketene. The oxygen atom of the silyl ketene is expected to coordinate to the LA, rendering the central carbon more electrophilic and, therefore, more susceptible to nucleophilic attack. We evaluated the readily available LAs $BF_3{\cdot}OEt_2$, $Al(O^iPr)_3$, $B(C_6F_5)_3$, $La(OTf)_3$, and $Mg(OTf)_2$ with 0.2 and 1.2 equiv for the activation of triisopropylsilyl (TIPS) ketene and triethylsilyl (TES) ketene toward reaction with benzyl alcohol (Table S1). Of the LAs examined, $BF_3{\cdot}OEt_2$ produced the highest isolated yield of the α-silyl ester product, even when a substoichiometric amount was used. As such, $BF_3{\cdot}OEt_2$ was chosen as the LA to explore the preparation of other α-silyl esters as well as α-silyl amides and α-silyl thioesters.

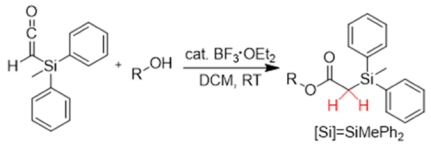
With the LA identified, the reaction of 11 different alcohols with MDPhS ketene was explored. The alcohols investigated included primary, secondary, and tertiary aliphatic alcohols as well as phenols with electron-withdrawing and -donating groups at various positions (Table 1, compounds **1**−**11**). Of the alcohols examined, all produced the corresponding α-silyl ester in good isolated yield (>60%) in less than 5 min. Figure 2 shows the ^{1}H, ^{13}C, and ^{29}Si NMR spectra, FTIR spectrum, and mass spectrum of ethyl α-methyldiphenylsilyl acetate (compound **1**). There was no significant difference in yield or reaction time between the primary, secondary, and tertiary aliphatic alcohols or phenols, although phenols with electron-donating substituents gave slightly higher isolated yields than those with electron-withdrawing groups. No significant trend was observed by varying the position of the substituents. The spectra of all products were similar (Figures S6−S15), with a little difference in the chemical shift of the $C\mathbf{H}_2SiR_3$ peak in ^{1}H NMR nor the C═O stretch in FTIR (Table 1).

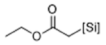
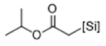
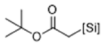
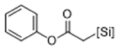
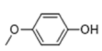
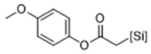
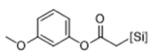
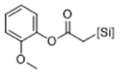
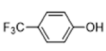
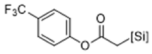
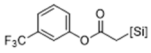
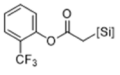
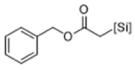
We then expanded the protocol of activating MDPhS ketene with BF_3 for the preparation of α-silyl amides and α-silyl thioesters by using amine (Table 2, compounds **12**−**14**) and thiol (Table 2, compounds **15**−**21**) nucleophiles, respectively. Primary and secondary amines as well as aniline gave α-silyl amides in higher yields than the corresponding α-silyl esters. For example, the use of aniline as a nucleophile gave the corresponding amide in 92% isolated yield (compound **14**) versus the use of phenol, which gave an isolated yield of only 61% (compound **4**). The α-silyl amides were characterized by the same methods as the α-silyl esters (Figures S16−S18), and all had high purity. The use of alkyl and aryl thiols as nucleophiles did lead to the production of the corresponding α-silyl thioesters, though at significantly lower isolated yields and no significant trend was observed for the thiol nucleophiles. Of note, the α-silyl amides were much easier to purify by column chromatography than the α-silyl thioesters (Figures S19−S25 for spectra).

We then evaluated the substrate scope of the LA-activated reaction of silyl ketenes. Figure 3 shows the silyl substituents that were investigated: TES, TIPS, di methyl phenyl silyl (DMPhS), and triphenylsilyl (TPhS). These silyl substituents were selected to assess how the steric bulk and electron-

DOI: 10.1021/acs.joc.9b01859
J. Org. Chem. 2019, 84, 14461−14468

Table 1. Evaluation of Nucleophile Scope by the Reaction of Alcohol and Phenol Nucleophiles with MDPhS Ketene, Catalyzed by BF_3[a]



Compound	Nucleophile	Product	% yield*	C=O (cm^{-1})	δ_{CH2} (ppm)
1			61	1717	2.42
2			78	1709	2.40
3			79	1704	2.34
4			61	1734	2.66
5			80	1732	2.64
6			75	1735	2.65
7			69	1735	2.69
8			61	1743	2.68
9			78	1737	2.67
10			70	1749	2.71
11			75	1713	2.48

[a]Isolated yield.

withdrawing capabilities of the silyl substituent impact reactivity and product formation. The use of TIPS and TES ketene allows us to evaluate the impact of steric demands of the substituent, with a little change in the electronic structure of the ketene; the TIPS group is much bulkier and sterically demanding than TES. Alternatively, comparing DMPhS and TPhS ketenes allows for comparison of the electronic demands of the silyl substituent, with limited change in the steric bulk (see Figure S2 for space-filled models). The ^1H NMR chemical shift of the terminal proton of DMPhS ketene is 2.23 ppm and that of TPhS ketene is 2.48 ppm (the chemical shifts of the terminal proton for TIPS and TES ketene are 1.64 and 1.69 ppm, respectively). By varying the silyl substituent of the monomer, different polymeric backbone orientations can be obtained.

Again, BF_3 was used as the LA in a catalytic amount to activate the different silyl ketenes, and 4-methoxy phenol, 4-methoxythiophenol, and aniline were used as nucleophiles (Figure 3). For all silyl groups, the corresponding α-silyl esters and amides were readily prepared and easily purified. Full consumption of all ketenes was realized in >5 min, regardless of the steric demands or electronic properties of the silyl group. The peaks corresponding to the CH_2SiR_3 in ^1H NMR shifted downfield with an increasing number of phenyl rings on the silyl group (Table 3). However, the silyl substituent identity had no impact on the C═O stretching frequency in the FTIR spectra (all ∼1735 cm^{-1}). In general, the α-silyl thio-ester products were obtained in lower yield than the ester and amide analogues (∼25% vs >60%), with the exception of the **TIPS 2** derivative, which was obtained in 81% yield (Table 3).

CONCLUSIONS

In summary, the activation of silyl ketenes with the LA BF_3 to produce α-silyl esters, α-silyl amides, and α-silyl thioesters is applicable to a wide scope of nucleophiles and silyl substituents. These products can be formed under mild reaction conditions by activating silyl ketenes with a catalytic amount of the LA and adding the corresponding nucleophile. Among different LAs examined, $BF_3{\cdot}OEt_2$ was identified as the best, as it can be used in substoichiometric amounts and leads to complete silyl ketene consumption in >5 min. A broad range of nucleophiles was used to prepare the corresponding α-silyl carbonyl compounds, including primary, secondary, and tertiary alcohols; phenols; primary and secondary amines; aniline; and primary, secondary, and tertiary thiols. Alcohol and amine-based nucleophiles led to better-isolated yields than sulfur-based nucleophiles, and all products were readily purified. The LA-activated reaction of silyl ketenes is applicable to all silyl substituents evaluated, with similar reaction time and yield regardless of steric demands or electronic considerations of the silyl group. Ongoing studies focus on using LAs to activate silyl ketenes toward reaction with other nucleophiles and the cationic polymerization of silyl ketenes.

EXPERIMENTAL SECTION

General Information. All purchased chemicals were used directly as received, unless otherwise stated. All reactions were performed under an inert atmosphere. DCM and THF were obtained by passing the commercial grade solvent through a column of activated neutral alumina in a Dow-Grubbs solvent system from Pure Process Technology (Nashua, NH). All ^1H, ^{13}C, ^{29}Si NMR were collected on a Bruker Ascend III HD 500 MHz NMR instrument equipped with prodigy probe and shifts are reported relative to the residual solvent peak, as noted. All NMR spectra were collected using $CDCl_3$ as the solvent unless otherwise noted. FTIR spectra were acquired using an Aglient Cary 630 FTIR in the ATR mode. ESI spectra were obtained on a THERMO Finniagn LCQ DECA ion trap mass spectrometer equipped with an external AP ESI ion source (only triphenylsilyl TPhS ketenes). THERMO DSQ II Series Single Quadrupole GC/MS.

General Procedure for Silyl Ketene Synthesis. (*Z*)-1-Bromo-2-*tert*-butoxylethene (A) was prepared using a previously reported method.[10,11,28,29] In an oven-dried round-bottom flask, 2 equiv of LDA (48 mL, 0.096 mol LDA, 2 mol/L in THF/ethylbenzene/hexane) and dry THF (48 mL) were cooled to −78 °C with a dry ice/acetone bath under N_2 (g). A mixture of A (7.08, 0.04 mol) and dry THF (16 mL) was prepared in an addition funnel and added dropwise to the LDA/THF solution. After addition, the reaction was warmed to room temperature and stirred for 3 h. After 3 h, the reaction mixture was cooled to 0 °C using an ice water bath. The corresponding silyl chloride was added (0.048 mol). The reaction was warmed to room temperature and stirred for 4 h. The mixture was

DOI: 10.1021/acs.joc.9b01859
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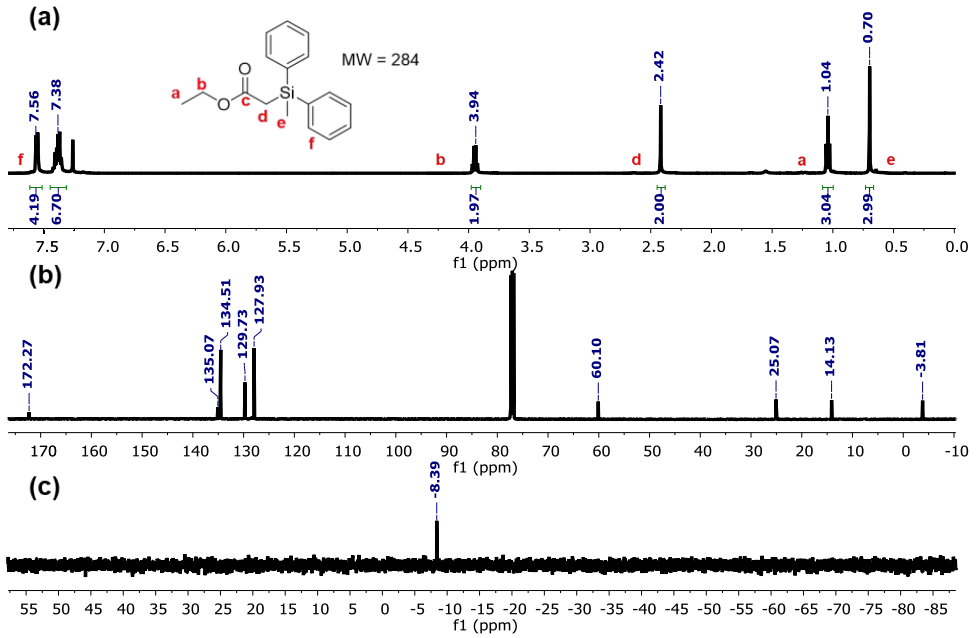


Figure 2. Characterization of compound **1**. (a) ^{1}H NMR. (b)^{13}C NMR. (c) ^{29}Si NMR.

transferred to a separation funnel and quenched with an aqueous solution of sat. $NaHCO_3$ (80 mL). The aqueous layer was washed with hexanes (2 × 20 mL). The organic layers were combined and washed with 0.5 N HCl (2 × 80 mL), H_2O (120 mL), and an aqueous solution of saturated NaCl (120 mL). The organic layer was dried with Na_2SO_4, filtered, and solvent-removed under reduced pressure. The crude alkyne product was purified through column chromatography of the silica gel. The silica gel was basified with a 2.5 vol % Et_3N in hexanes prior to loading product to the column. The product was eluted with 100% hexanes. A pale yellow oil was obtained; it was heated to 85 °C under N_2(g) for 2 h. The final ketene product was purified through vacuum distillation.

Triethylsilyl Ketene. Colorless oil, 53% yield, 6.4g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 1.69 (s, 1H), 0.96 (t, J = 7.9 Hz, 10H), 0.63 (q, J = 7.9 Hz, 7H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.0, 77.3, 77.0, 76.8, 7.1, 5.0, −4.9. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 7.49. MS: M^+ = 156, 127, 99 (m/z).

Triisopropylsilyl Ketene. Colorless oil, 75% yield, 9.7g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 1.64 (s, 1H), 1.09−1.03 (m, 27H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.0, 77.3, 18.3, 12.0, −7.3. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 10.70. MS: M^+ = 198, 113, 85 (m/z).

Dimethylphenyl Silyl Ketene. Colorless oil, 28% yield, 4.3g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59−7.56 (m, 2H), 7.39 (dd, J = 5.1, 2.0 Hz, 3H), 2.00 (s, 1H), 0.44 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.8, 138.8, 134.38, 134.2, 130.3, 128.7, 78.1, 77.8, 77.5, 0.0. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −5.77. MS: M^+ = 178, 161, 148 (m/z).

Methyldiphenylsilyl Ketene. Colorless oil, 40% yield, 6.5g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60−7.55 (m, 4H), 7.44−7.36 (m, 7H), 2.23 (s, 1H), 0.71 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.5, 137.8, 136.4, 131.8, 130.0, 79.3, 79.0, 78.8, 1.0, 0.0. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −10.19. MS: M^+ = 285, 207, 197, 165 (m/z). MS: M^+ = 238, 223, 210 (m/z).

Triphenylsilyl Ketene. Pale yellow solid, 42% yield, 4.2g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58−7.55 (m, 6H), 7.47−7.37 (m, 11H), 2.48 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.6, 136.8, 136.7, 135.3, 131.4, 131.3, 129.9, 129.2, 78.6, 78.4, 78.1, −0.0. MS: M^+ = 300, 272, 223, 104 (m/z).

General Procedure for Control Experiment (No LA). An oven-dried round-bottom flask was purged with vacuum and put under a N_2(g). Dry DCM (1 mL) was added to the round-bottom flask. Methyldiphenyl silyl ketene (1 equiv, 1.3 mmol) and the respective nucleophile (benzyl alcohol, benzyl mercaptan, or aniline) (1.2 equiv, 1.6 mmol) were then added simultaneously to the RBF. The reaction was stirred for 96, 144, or 24 h under N_2(g) at room temperature. The reaction was monitored with FTIR, till full ketene consumption was observed. The solvent was removed, and the product was purified with column chromatography. The column was built with 100% hexanes and silica gel. The product was eluted with 9:1 hexanes/ethyl acetate. The product was dried under vacuum.

General Procedure for LA Scope. An oven-dried round-bottom flask was purged with vacuum and put under a N_2(g). Dry solvent (3 mL) and the desired equivalence (0.2 or 1.2 equiv) of LA were added to the round-bottom flask. TIPS or TES ketene (1 equiv, 1.3 mmol) and the respective nucleophile (benzyl alcohol or benzyl mercaptan) (1.2 equiv, 1.6 mmol) were then added simultaneously to the RBF. The reaction was stirred under N_2(g) at room temperature until full ketene consumption was observed by FTIR. The solvent was removed, and the product was purified with column chromatography. The column was built with 100% hexanes and silica gel. The product was eluted with 9:1 hexanes/ethyl acetate. The product was dried under vacuum.

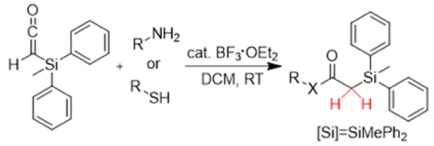
General Procedure for α-Silyl Carbonyl Compounds. An oven-dried round-bottom flask was purged with vacuum and put under N_2(g). Dry DCM (1 mL) and a catalytic amount of $BF_3{\cdot}OEt_2$ (1 drop) were added to the round-bottom flask. The desired ketene (0.3 mL, 0.0014 mmol, 1 equiv) and nucleophile (0.0017 mmol, 1.2 equiv) were then added simultaneously to the RBF. The reaction was stirred for ∼5 min under N_2(g) at room temperature. The reaction was monitored with FTIR, till full ketene consumption was observed. The solvent was removed with reduced pressure, and the product was purified with column chromatography. The column was built with 100% hexanes and silica gel. The product was eluted with 9:1 hexanes/ethyl acetate. The product was dried under vacuum.

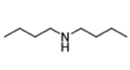
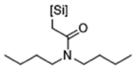
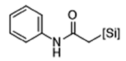
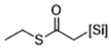
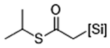
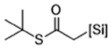
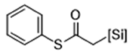
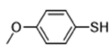
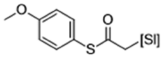
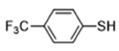
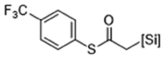
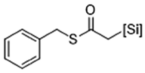
Ethyl-α-methyldiphenylsilyl Acetate (1). Colorless oil; 61% yield, 0.27g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61−7.51 (m, 4H), 7.45−7.31 (m, 7H), 3.95 (q, J = 7.1 Hz, 2H), 2.42 (s, 2H), 1.04 (t, J = 7.1 Hz, 3H), 0.70 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.3, 135.1, 134.5, 134.4, 129.8, 129.7, 128.4, 128.3, 127.9, 127.9, 60.1, 25.1, 14.1, −3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.39. MS: M^+ = 285, 207, 197, 165 (m/z).

Isopropyl-α-methyldiphenylsilyl Acetate (2). Colorless oil; 78% yield, 0.32g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59−7.53 (m, 4H), 7.43−7.34 (m, 6H), 4.83 (hept, J = 6.3 Hz, 1H), 2.40 (s, 2H), 1.02 (d, J = 6.3 Hz, 6H), 0.70 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.8, 135.2, 134.6, 129.7, 127.9, 127.8, 67.4, 25.3, 21.7,

DOI: 10.1021/acs.joc.9b01859
J. Org. Chem. 2019, 84, 14461−14468

Table 2. Nucleophilic Scope of the Reaction of Various Amine and Thiol Nucleophiles with MDPhS Ketene[a]



Compound	Nucleophile	Product	% yield*	C=O (cm^{-1})	δ_{CH2} (ppm)
12			64	1626	2.28
13			77	1622	2.44
14			92	1635	2.47
15			50	1670	2.80
16			37	1668	2.76
17			5	1667	2.70
18			40	1693	2.89
19			39	1687	2.86
20			45	1696	2.91
21			72	1674	2.82

[a]Isolated yield.

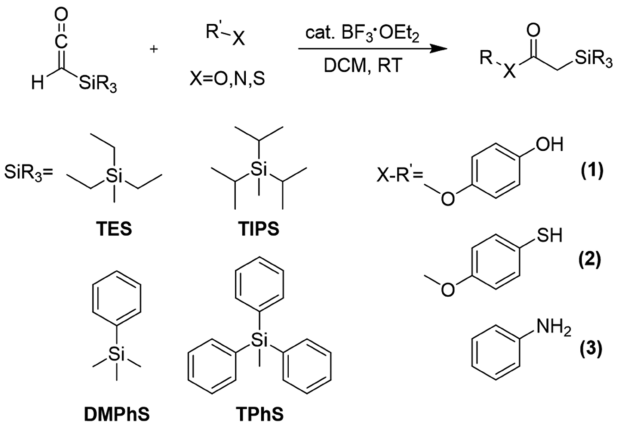
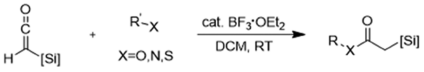
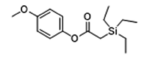
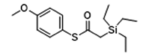
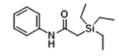
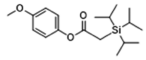
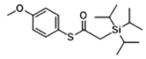
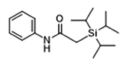
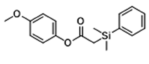
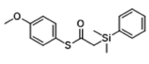


Figure 3. Evaluation of the substrate scope using silyl ketenes of various bulk and electronic demands of the silyl substituents.

−3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.43. MS: M^+ = 298, 221, 197, 137 (m/z).

Table 3. Ketene Substrate Scope, Each Silyl Ketene was Reacted with Three Choice Nucleophiles[a]



Compound	[Si]	Product	% yield*	C=O (cm^{-1})	δ_{CH2} (ppm)
TES 1			70	1735	2.10
TES 2			45	1691	2.37
TES 3			82	1642	1.94
TIPS 1			66	1735	2.16
TIPS 2			81	1694	2.42
TIPS 3			77	1642	1.96
DMPhS 1			53	1734	2.33
DMPhS 2			47	1687	2.57
DMPhS 3			71	1639	2.15
TPhS 1			74	1732	2.96
TPhS 2			24	1687	3.19
TPhS 3			58	1635	2.78

[a]Isolated yield.

tert-Butyl-α-methyldiphenylsilyl Acetate ***(3)***. Colorless oil; 79% yield, 0.34g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58−7.54 (m, 4H), 7.43−7.32 (m, 7H), 2.34 (s, 2H), 1.23 (s, 10H), 0.69 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.5, 135.4, 134.6, 134.4, 129.6, 127.9, 79.9, 27.9, 26.2, −3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.46. MS: M^+ = 312, 235, 197, 137 (m/z).

Phenyl-α-methyldiphenylsilyl Acetate ***(4)***. Colorless oil; 61% yield, 0.28g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (dt, J = 6.7, 1.6 Hz, 4H), 7.46−7.38 (m, 6H), 7.28−7.24 (m, 3H), 7.16−7.13 (m, 1H), 6.70−6.67 (m, 2H), 2.66 (s, 2H), 0.80 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.8, 150.7, 134.6, 130.0, 129.2, 128.1, 125.5, 121.6, 25.2, −3.7. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.03. MS: M^+ = 331, 290, 223, 197 (m/z).

4-Methoxybenzyl-α-methyldiphenylsilyl Acetate ***(5)***. White solid; 80% yield, 0.40g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (dt, J =

DOI: 10.1021/acs.joc.9b01859
J. Org. Chem. 2019, 84, 14461−14468

6.6, 1.6 Hz, 4H), 7.46−7.38 (m, 6H), 6.79−6.75 (m, 2H), 6.60−6.57 (m, 2H), 3.75 (s, 3H), 2.64 (s, 2H), 0.79 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 171.2, 157.0, 144.3, 134.7, 134.6, 134.0, 129.9, 128.1, 128.1, 127.9, 122.3, 114.3, 55.6, 25.1, −3.7. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.06. MS: M^+ = 362, 223, 197, 124 (m/z).

3-Methoxybenzyl-α-methyldiphenylsilyl Acetate ***(6)***. Pale yellow oil; 75% yield, 0.38g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65−7.60 (m, 4H), 7.46−7.38 (m, 6H), 7.15 (t, J = 8.2 Hz, 1H), 6.70 (ddd, J = 8.3, 2.5, 0.9 Hz, 1H), 6.32 (ddd, J = 8.1, 2.1, 0.9 Hz, 1H), 6.18 (t, J = 2.3 Hz, 1H), 3.70 (s, 3H), 2.65 (s, 2H), 0.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.7, 160.3, 151.7, 134.6, 134.6, 134.5, 130.0, 129.6, 128.4, 128.3, 128.1, 128.1, 113.9, 111.6, 107.4, 77.3, 77.0, 76.8, 55.4, 25.1, −3.7. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.02. MS: M^+ = 362, 223, 197, 124 (m/z).

2-Methoxybenzyl-α-methyldiphenylsilyl Acetate ***(7)***. Colorless oil; 79% yield, 0.35g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68−7.59 (m, 4H), 7.40 (tt, J = 8.3, 4.4 Hz, 6H), 7.13 (td, J = 7.9, 1.7 Hz, 1H), 6.97−6.81 (m, 4H), 6.61 (dd, J = 7.9, 1.8 Hz, 1H), 3.67 (s, 3H), 2.69 (s, 2H), 0.82 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.2, 151.3, 139.9, 134.6, 129.8, 128.0, 126.6, 122.8, 120.6, 112.2, 55.5, 24.8, −3.9. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.07. MS: M^+ = 362, 223, 197, 124 (m/z).

4-(Trifluoromethyl)benzyl-α-methyldiphenylsilyl Acetate ***(8)***. Pale yellow oil; 61% yield, 0.34g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63−7.60 (m, 4H), 7.51 (d, J = 8.4 Hz, 2H), 7.47−7.38 (m, 6H), 6.73 (d, J = 8.3 Hz, 2H), 2.67 (s, 2H), 0.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.3, 153.2, 134.6, 134.3, 130.1, 128.2, 126.6, 126.5, 122.1, 25.2, −3.7. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −7.89. MS: M^+ = 358, 239, 223, 197 (m/z).

3-(Trifluoromethyl)benzyl-α-methyldiphenylsilyl Acetate ***(9)***. Colorless oil; 78% yield, 0.43g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64−7.61 (m, 4H), 7.48−7.34 (m, 8H), 6.86 (dt, J = 7.9, 1.7 Hz, 1H), 6.74 (s, 1H), 2.67 (s, 2H), 0.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.4, 150.7, 134.6, 134.2, 130.2, 129.7, 128.2, 125.3, 122.3, 25.2, −3.6. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −7.88. MS: M^+ = 358, 23, 223, 197 (m/z).

2-(Trifluoromethyl)benzyl-α-methyldiphenylsilyl Acetate ***(10)***. Colorless oil; 70% yield, 0.39g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65−7.58 (m, 5H), 7.47−7.37 (m, 7H), 6.48 (d, J = 8.2 Hz, 1H), 2.71 (s, 2H), 0.82 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.2, 134.6, 134.5, 132.8, 130.0, 128.1, 126.7, 125.5, 124.2, 24.7, −3.7. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.09. MS: M^+ = 358, 239, 223, 197 (m/z).

Benzyl α-Methyldiphenyl Silyl Acetate ***(11)***. Pale yellow oil; 75% yield, 0.36g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55−7.51 (m, 4H), 7.42−7.33 (m, 6H), 7.30−7.27 (m, 3H), 7.12 (dd, J = 6.6, 2.9 Hz, 2H), 4.92 (s, 2H), 2.48 (s, 2H), 0.66 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 172.1, 136.0, 134.9, 134.5, 129.8, 128.4, 128.3, 128.0, 66.2, 25.1, −3.9. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.29. MS: M^+ = 346, 227, 197, 91 (m/z).

α-Methyldiphenylsilyl-N-propylacetamide ***(12)***. White solid; 64% yield, 0.26g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (dt, J = 6.6, 1.6 Hz, 4H), 7.43−7.35 (m, 6H), 3.02 (td, J = 7.3, 5.9 Hz, 2H), 2.29 (s, 2H), 1.23 (h, J = 7.4 Hz, 2H), 0.74−0.68 (m, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.9, 135.4, 134.5, 129.8, 128.1, 41.3, 27.3, 22.8, 11.3, −4.2. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.57. MS: M^+ = 291, 232, 217 (m/z).

N,N-Dibutyl-α-methyldiphenylsilyl Acetamide ***(13)***. Pale yellow oil; 77% yield, 0.39g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59−7.55 (m, 4H), 7.41−7.33 (m, 6H), 3.22−3.15 (m, 2H), 2.84 (dd, J = 8.9, 6.8 Hz, 2H), 2.44 (s, 2H), 1.40−1.28 (m, 5H), 1.26−1.10 (m, 5H), 0.86 (dt, J = 19.7, 7.3 Hz, 7H), 0.71 (s, 3H).$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 171.0, 136.0, 134.6, 129.6, 127.9, 48.6, 45.8, 30.9, 30.0, 23.6, 20.3, 20.1, 14.0, 13.8, −3.6. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −9.05. MS: M^+ = 367, 281, 207 (m/z).

α-Methyldiphenylsilyl-N-phenylacetamide ***(14)***. Pale yellow solid; 92% yield, 0.42g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62−7.58 (m, 4H), 7.48−7.38 (m, 6H), 7.21 (dd, J = 8.5, 7.3 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.49 (s, 1H), 2.47 (s, 2H), 0.72 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 169.3, 135.0, 134.6, 130.1, 128.8, 128.3, 123.9, 119.6, 28.9, −4.3. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.38. MS: M^+ = 331, 254, 118 (m/z).

S-Ethyl-α-methyldiphenylsilyl Ethanethioate ***(15)***. Colorless oil; 50% yield, 0.21g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56−7.53 (m, 4H), 7.42−7.35 (m, 7H), 2.80 (s, 2H), 2.80−2.73 (m, 2H), 1.11 (t, J = 7.4 Hz, 2H), 0.71 (s, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 196.3, 134.8, 134.6, 129.8, 128.0, 36.0, 23.8, 14.9, −3.9. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −9.21. MS: M^+ = 281, 238, 197 (m/z).

S-Isopropyl-α-methyldiphenylsilyl Ethanethioate ***(16)***. Colorless oil; 37% yield, 0.16g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (dt, J = 6.6, 1.6 Hz, 4H), 7.42−7.35 (m, 7H), 3.51 (p, J = 6.9 Hz, 1H), 2.76 (s, 2H), 1.17 (d, J = 6.9 Hz, 6H), 0.71 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 196.4, 134.9, 134.6, 129.8, 127.9, 36.0, 34.9, 22.9, −3.9. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −9.21. MS: M^+ = 314, 239, 197 (m/z).

S-tert-Butyl-α-methyldiphenylsilyl Ethanethioate ***(17)***. Colorless oil; 5% yield, 0.05g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (dt, J = 6.6, 1.6 Hz, 6H), 7.41−7.36 (m, 9H), 2.70 (s, 2H), 1.33 (s, 10H), 0.72 (s, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 197.3, 134.5, 129.7, 128.1, 127.9, 47.9, 36.3, 29.7, −3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −9.14. MS: M^+ = 286, 239, 197 (m/z).

S-Phenyl-α-methyldiphenylsilyl Ethanethioate ***(18)***. Pale yellow oil; 40% yield, 0.19g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60−7.57 (m, 4H), 7.41 (ddd, J = 14.0, 7.7, 6.1 Hz, 6H), 7.35−7.33 (m, 2H), 7.19−7.17 (m, 2H), 2.89 (s, 2H), 0.76 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 194.4, 134.7, 134.5, 129.9, 129.2, 129.2, 129.1, 129.0, 128.0, 125.6, 35.6, −3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.87. MS: M^+ = 348, 281, 207, 197 (m/z).

S-4-Methoyphenol-α-methyldiphenylsilyl Ethanethioate ***(19)***. Colorless oil; 39% yield, 0.20g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59−7.56 (m, 4H), 7.43−7.37 (m, 6H), 7.09−7.06 (m, 2H), 6.87−6.84 (m, 2H), 3.80 (s, 3H), 2.86 (s, 2H), 0.75 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 195.5, 160.5, 136.1, 134.7, 132.4, 129.9, 128.00, 119.3, 114.7, 55.3, 35.3, −3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.94. MS: M^+ = 378, 291, 227, 197 (m/z).

S-4-Trifluoromethyl Phenyl-α-methyldiphenylsilyl Ethanethioate ***(20)***. Colorless oil; 45% yield, 0.26g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61−7.55 (m, 7H), 7.49−7.36 (m, 8H), 2.91 (s, 2H), 0.77 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 193.1, 134.7, 134.5, 130.0, 128.1, 125.8, 36.0, −3.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.73. MS: M^+ = 416, 223, 207, 197 (m/z).

S-Benzyl-α-methyldiphenylsilyl Ethanethioate ***(21)***. Colorless oil; 72% yield, 0.36g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53−7.50 (m, 4H), 7.43−7.34 (m, 6H), 7.25−7.20 (m, 2H), 7.17−7.14 (m, 2H), 4.01 (s, 2H), 2.82 (s, 2H), 0.68 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 195.3, 137.9, 134.6, 129.8, 128.8, 128.5, 128.0, 127.0, 35.9, 33.6, −4.0. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −9.01. MS: M^+ = 362, 271, 197, 91 (m/z).

4-Methoxybenzyl-α-triethylsilyl Acetate ***(TES 1)***. Colorless oil; 70% yield, 0.32g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.99−6.96 (m, 2H), 6.89−6.86 (m, 2H), 3.79 (s, 3H), 2.10 (s, 2H), 1.02 (t, J = 7.9 Hz, 9H), 0.72 (q, J = 7.9 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 172.1, 157.0, 144.5, 122.4, 114.4, 55.6, 22.0, 7.1, 3.7. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 9.22. MS: M^+ = 280, 209, 124 (m/z).

S-4-Methoyphenol-α-triethylsilyl Ethanethioate ***(TES 2)***. Pale yellow oil; 45% yield, 0.22g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31−7.28 (m, 2H), 6.94−6.91 (m, 2H), 3.82 (s, 3H), 2.37 (s, 2H), 1.00 (t, J = 7.9 Hz, 10H), 0.69 (q, J = 7.9 Hz, 7H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 195.7, 160.5, 136.1, 132.7, 119.7, 114.7, 114.6, 77.2, 55.3, 32.7, 7.2, 3.5. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 8.44. MS: M^+ = 296, 157, 140, 115 (m/z).

α-Triethylsilyl-N-phenylacetamide ***(TES 3)***. Pale yellow solid; 82% yield, 0.34g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.93 (s, 1H), 1.94 (s, 2H), 1.00 (t, J = 8.0 Hz, 9H), 0.69 (q, J = 7.6 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 170.6, 138.3, 129.0, 123.9, 119.7, 25.7, 7.3, 3.6. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 8.15. MS: M^+ = 249, 220, 157, 118 (m/z).

4-Methoxybenzyl-α-triisopropylsilyl Acetate ***(TIPS 1)***. Colorless oil; 66% yield, 0.26g; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.01−

DOI: 10.1021/acs.joc.9b01859
J. Org. Chem. 2019, 84, 14461−14468

6.95 (m, 2H), 6.91−6.84 (m, 2H), 3.79 (s, 3H), 2.13 (s, 2H), 1.28−1.18 (m, 4H), 1.11 (dd, J = 19.2, 7.1 Hz, 26H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.6, 157.0, 144.5, 122.4, 114.4, 55.6, 19.04, 18.4, 11.4. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 8.92. MS: M^+ = 322, 279, 124 (m/z).

S-4-Methoyphenol-α-triisopropylsilyl Ethanethioate (TIPS 2). Pale yellow oil; 81% yield, 0.33g; ^1H NMR (500 MHz, Chloroform-d) δ 7.31−7.27 (m, 2 H), 6.94−6.90 (m, 2H), 3.81 (s, 3H), 2.39 (s, 2H), 1.24−1.16 (m, 4H), 1.10 (d, J = 7.2 Hz, 19H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 196.3, 160.5, 136.1, 132.4, 119.8, 114.8, 55.3, 29.9, 18.5, 11.3. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 8.74. MS: M^+ = 338, 199, 157 (m/z).

α-Triisopropylsilyl-N-phenylacetamide (TIPS 3). White solid; 77% yield, 0.27g; ^1H NMR (500 MHz, Chloroform-d) δ 7.45 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.98 (s, 1H), 1.97 (s, 2H), 1.25−1.16 (m, 4H), 1.11 (d, J = 7.2 Hz, 19H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.9, 138.3, 129.0, 124.0, 119.7, 22.6, 18.6, 11.3. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 7.82. MS: M^+ = 291, 248, 199, 118 (m/z).

4-Methoxybenzyl-α-dimethylphenyl Silyl Acetate (DMPhS 1). Colorless oil; 53% yield, 0.10g; ^1H NMR (500 MHz, Chloroform-d) δ 7.62−7.58 (m, 2H), 7.41 (td, J = 5.9, 2.7 Hz, 3H), 6.85−6.77 (m, 4H), 3.78 (s, 3H), 2.33 (s, 2H), 0.51 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.4, 157.0, 144.3, 136.5, 133.7, 129.7, 128.1, 122.4, 114.3, 55.6, 26.3, −2.6. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −2.28. MS: M^+ = 300, 135, 124 (m/z).

S-4-Methoyphenol-α-dimethylphenyl Silyl Ethanethioate (DMPhS 2). Pale yellow oil; 47% yield, 0.08g; ^1H NMR (500 MHz, Chloroform-d) δ 7.57−7.54 (m, 2H), 7.43−7.37 (m, 3H), 7.23−7.19 (m, 2H), 6.92−6.89 (m, 2H), 3.81 (s, 3H), 2.57 (s, 2H), 0.47 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 195.5, 160.5, 136.1, 133.7, 129.7, 128.0, 119.5, 114.7, 55.3, 36.8, −2.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −3.27. MS: M^+ = 316, 301, 165, 135 (m/z).

α-t Dimethylphenyl Silyl-N-phenylacetamide (DMPhS 3). Yellow solid; 71% yield, 0.11g; ^1H NMR (500 MHz, Chloroform-d) δ 7.62−7.58 (m, 2H), 7.46−7.41 (m, 3H), 7.27 (d, J = 7.0 Hz, 4H), 7.21−7.17 (m, 1H), 7.07 (s, 1H), 6.76−6.72 (m, 1H), 6.62 (s, 1H), 2.18 (s, 2H), 0.49 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 169.8, 138.0, 137.1, 133.6, 129.8, 128.9, 128.3, 123.9, 119.7, 118.9, 115.4, 30.3, −3.2. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −2.88. MS: M^+ = 269, 254, 192, 118 (m/z).

4-Methoxybenzyl-α-triphenylsilyl Acetate (TPhS 1). White solid; 74% yield, 0.16g; ^1H NMR (500 MHz, Chloroform-d) δ 7.64−7.61 (m, 6H), 7.49−7.44 (m, 3H), 7.43−7.38 (m, 6H), 6.74−6.70 (m, 2H), 6.42−6.38 (m, 2H), 3.73 (s, 3H), 2.96 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.1, 157.0, 144.2, 135.9, 133.0, 130.1, 128.1, 122.3, 114.2, 55.5, 24.3. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −13.17. MS: M^{+23} = 447 m/z.

S-4-Methoyphenol-α-triphenylsilyl Ethanethioate (TPhS 2). Yellow solid; 24% yield, 0.05g; ^1H NMR (500 MHz, Chloroform-d) δ 7.62−7.58 (m, 6H), 7.48−7.43 (m, 3H), 7.39 (dd, J = 7.8, 6.5 Hz, 6H), 6.95−6.92 (m, 2H), 6.83−6.80 (m, 2H), 3.78 (s, 3H), 3.17 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 195.5, 160.5, 136.1, 136.0, 132.9, 130.0, 128.0, 119.3, 114.6, 55.3, 34.2. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −13.48. MS: M^{+23} = 463 m/z.

α-Triphenylsilyl-N-phenylacetamide (TPhS 3). White solid; 58% yield, 0.12g; ^1H NMR (500 MHz, Chloroform-d) δ 7.61 (d, J = 7.1 Hz, 6H), 7.50−7.38 (m, 10H), 7.18 (t, J = 7.7 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 2.78 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.9, 135.7, 133.0, 130.3, 128.4, 123.8, 119.5, 27.9. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −13.38. MS: M^{+23} = 416 m/z.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b01859.

Control experiments, NMR spectra, FTIR spectra, MS data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (NSF 1807510) and NSF MRI-1334048 for NMR instrumentation. We acknowledge Dr Daniel Lambrecht (University of Pittsburg) for thoughtful discussions and John McCaffrey for help with the synthesis of silyl ketenes.

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