JOC The Journal of Organic Chemistry

Article

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Silicon Acceleration of a Tandem Alkene Isomerization/Electrocyclic Ring-opening of 2-Methyleneoxetanes to α,β-Unsaturated Methylketones

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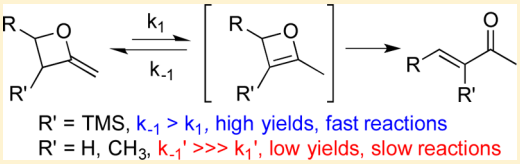
Supporting Information

ABSTRACT: The first rearrangement of 2-methyleneoxetanes to α,β-unsaturated methylketones is reported. It is proposed that when these substrates are heated, the corresponding oxetenes are formed and subsequently undergo electrocyclic ring-opening to methyl vinylketones. In particular, α-silyl-α,β-unsaturated methylketones were isolated in moderate to high yields and with high stereoselectivities. Based on the proposed mechanism, density functional theory explains the differential kinetics and stereoselectivities among substrates.



INTRODUCTION

We report an unexpected conversion of 2-methyleneoxetanes **1** to α,β-unsaturated methylketones **3** (Figure 1). Moreover, a

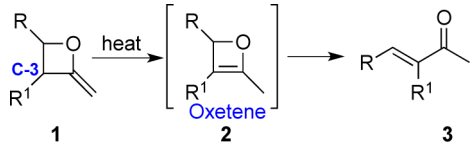


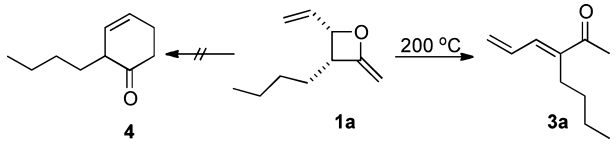
Figure 1. Enone formation from 2-methyleneoxetanes.

silyl substituent at C-3 greatly enhanced the yields and rates of these reactions. α-Silyl-α,β-unsaturated methylketones were obtained in moderate to high yields with excellent stereoselectivities. This outcome suggests a tandem alkene isomerization/four π-electron electrocyclic ring-opening pathway involving initial transformation to 2-methyloxetenes **2**, which undergo a well-precedented electrocyclic ring-opening. To our knowledge there are no reports of such a tandem reaction involving oxetanes.

We have been interested in the reactivity of 2-methyleneoxetanes **1**. These compounds are attractive intermediates due to their strained ring and electron rich exocyclic double bond. Examples of the utility of these oxetanes include their transformation to homopropargylic alcohols,[1] α-substituted ketones,[2] functionalized ketones,[3] and 1,4-dioxaspiro[2.3]-hexanes.[4]

As part of our effort to explore the reactivity of 2-methyleneoxetanes, **1a** was synthesized as a substrate for an expected Claisen rearrangement to cyclohexenone **4** (Scheme 1), since related reactions are known with the corresponding furans and pyrans.[5] However, when **1a** was heated to 200 °C, dienone **3a** (but no **4**) was observed in ^{1}H and ^{13}C NMR spectra of the reaction mixture. In addition to peaks

Scheme 1. Unexpected Outcome upon Heating 1a



characteristic of **3a**, a number of other signals, along with baseline broadening, were seen. Presumably the broad peaks were due to the formation of polymers, which would not be surprising considering the reactivity of enones. We decided to see if enone formation was a general outcome when 2-methyleneoxetanes were heated.

RESULTS AND DISCUSSION

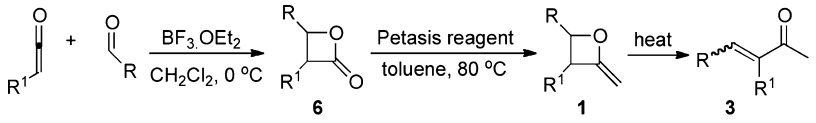
To investigate whether other 2-methyleneoxetanes would lead to the corresponding methyl vinylketones, **1b**[6] and **1c**[6] were heated to 200 °C (Table 1). Methylenones **3b** and **3c** were isolated in ∼30% yield, and the reactions were cleaner than the isomerization of **1a**. No byproducts were isolated, and the low yield was again attributed to polymerization. There was no reaction at less than 200 °C. Although the isolated yields of **3b** and **3c** were low, we were interested in the mechanism of the transformation and in seeing whether the yields could be improved.

Based on the outcome, our assumption was that the first step was isomerization of the exocyclic double bond to the endocyclic one, since it has been well-documented that exocyclic alkenes[7] are converted to endocyclic alkenes upon heating or in the presence of acid/base catalysts.[8] These bond migrations are attributed to the greater stability of the isomers

Received: July 22, 2013
Published: October 10, 2013

   dx.doi.org/10.1021/jo4014645 | J. Org. Chem. 2013, 78, 11213−11220

Table 1. Syntheses of 2-Methyleneoxetanes 1 and Methylenones 3



entry	compd	R	R^1	yield (%) of **6** (*cis*/*trans*)	stereochem. of **6** used	yield (%) of **1**	temp (°C)	time (min)	yield (%) of **3**	stereochem. of **3**
1	**b**	$CH_2OTBDPS$	Me			*a*	200	90	33	*E*
2	**c**	*c*-Hex	H			*a*	200	75	29	*E*
3	**d**	*c*-Hex	TMS	72 (2:3)	*trans*	55	160	10	80	*Z*
4	**e**	*c*-Hex	TMS		*cis*	43[b]	160	10	63	*Z*
5	**f**	*c*-Hex	TBS	79 (1:2)	*trans*	68	110	30	94	*Z*
6	**g**	*n*-C_7H_{15}	TMS	68 (5:2)	*trans*	34	160	10	89	*Z*
7	**h**	n-C_7H_{15}	TMS		*cis*	31[c]	160	10	70	*Z*
8	**i**	*t*-Butyl	TMS	67	*trans*	50[d]	110	50	33[e]	*Z*
9	**j**	Ph	TMS	60	*cis*	64	110	35	64	*Z*
10	**k**	*p*-CF_3Ph	TMS	64 (3:1)	*cis*	42	110	35	71	*Z*/*E*, 92:8
11	**l**	CH_2OBn	TMS	26 (7:3)	*cis*	40	110	15	99	*Z*

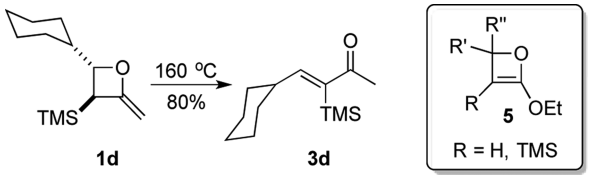
[a]See ref 6. [b]An inseparable mixture of 2-methyleneoxetane/enone (10:1) was isolated. [c]An inseparable mixture of 2-methyleneoxetane/enone (5:1) was isolated. [d]An inseparable mixture of 2-methyleneoxetane/enone (>9:1) was isolated. [e]Based on recovered starting material.

with the endocyclic double bond.[9] The isomerization of methylenecyclobutane to 1-methylcyclobutene has also been reported.[10] However, we did not find examples of the isomerization of 2-methyleneoxetanes **1** to the corresponding 2-methyloxetenes **2**.

Oxetenes are well-known to be unstable species, especially at high temperatures.[11,12] They usually undergo electrocyclic ring-opening, leading to *α*,*β*-unsaturated carbonyl systems. Similarly, the more stable cyclobutenes have been reported to produce dienes.[13] Friedrich et al.[14] studied the kinetics of the ring-opening of 2,3,4,4-tetramethyloxetene and compared it with that of cyclobutenes. It was found that the substitution of a methylene group from a cyclobutene with an oxygen atom accelerated the ring-opening by a factor of 10^7.

In an attempt to improve the yields for the tandem alkene isomerization/electrocyclic ring-opening of 2-methyleneoxetanes, 3-silyl-2-methyleneoxetane **1d** was prepared (Scheme 2 and Table 1). Baukov et al.[15] reported in 1981 that 2-ethoxy-3-silyloxetenes **5** (R = TMS) gave *α*-silyl-*α*,*β*-unsaturated esters in higher yields than the corresponding unsilylated systems (**5**, R = H). Compound **1d** was heated at 160 °C; after 5−10 min, it was completely isomerized to enone **3d** in an isolated yield of 80% (Scheme 2 and Table 1, entry 3). This result showed that silicon containing 2-methyleneoxetane **1d** not only provided the corresponding methylenone in higher yield but also underwent isomerization considerably faster than the unsilylated systems **1a**−**1c**.

Scheme 2. Isomerization of Silylated Methyleneoxetane 1d



Based on the result with **1d**, we decided to investigate the scope of the transformation of 3-silyl-2-methyleneoxetanes to *α*-silyl-*α*,*β*-unsaturated methylketones (Table 1). *α*-Silyl-*β*-lactones **6e**−**6l** were prepared from [2 + 2]-cycloadditions of silylketenes and a variety of aldehydes in the presence of catalytic $BF_3{\cdot}OEt_2$.[16] 2-Methyleneoxetanes **1e**−**1l** were synthesized by methylenation of *β*-lactones **6e**−**6l** using the Petasis reagent. It is noteworthy that during methylenation several of the substrates provided mixtures of 2-methyleneoxetane and *α*-silyl-*α*,*β*-unsaturated ketone (entries 4, 7, and 8). The inseparable product mixtures were heated to complete the conversion to the enones.

The reactivity of the 3-silyl-2-methyleneoxetanes **1** was investigated (Table 1). Conversions to the corresponding *α*-silylenones were complete in 10−50 min at 110−160 °C, below the temperature required for **1a**−**1c**. With the exception of **1i**, having a bulky substituent at C-4, all of the 3-silylated 2-methyleneoxetanes reacted in good to excellent yields with high stereoselectivities. The size of the silyl group (entry 5) did not affect the outcome, although the reaction was slower with TBS (entry 4 vs 5). Except for compound **1k** (entry 10), which gave a mixture of enones (92:8 *Z*/*E*), only *Z*-isomers were observed

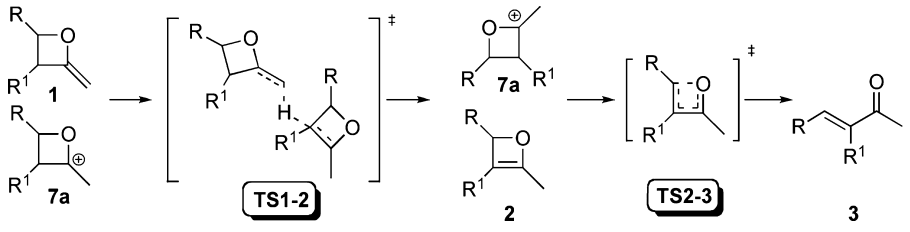


Figure 2. Proposed Mechanism for the Formation of Enones.

dx.doi.org/10.1021/jo4014645 | J. Org. Chem. 2013, 78, 11213−11220

from both *cis*- and *trans*-2-methyleneoxetanes **1**. The high *Z*-selectivity is discussed below.

Since it was assumed that oxetenes were intermediates, we tried to confirm their presence. Each reaction was monitored by NMR; no oxetene was observed. A solution of **1f** in toluene-d_8 was heated while ^{1}H and ^{13}C NMR spectra were taken every 5 min. At 90 °C, only reactant and product were observed. At lower temperatures, the reaction was very slow, and again, no oxetene was seen by NMR. The failure to observe oxetenes may be a reflection of a lack of build-up before consumption (*vide infra*). Despite the lack of spectral evidence for oxetenes, their intermediacy is logical, considering the outcome.

Based on previous literature reports on exocyclic alkene isomerization and on oxetene electrocyclic ring-opening (*vide supra*), a two-step mechanism is proposed (Figure 2). First, in the presence of a trace amount of Lewis acid, an oxocarbenium **7a** is formed from **1**. The formation of a carbocation triggers a chain reaction where **1** abstracts a proton at C-3 from **7a**, leading to oxetene **2** with regeneration of **7a**. Therefore, only a catalytic amount of **7a** would be needed to start the reaction. In the second step, **2** undergoes electrocyclic ring-opening, providing enone **3**.

In order to model the behavior of the 2-methyleneoxetanes **1** under high temperatures and explain the stereoselectivity, computational models of **1b**, **1d**, and **1e** were constructed. The results should be applicable to other 2-methyleneoxetanes.

All geometries and energies presented in this study were computed using density functional theory with the B3LYP functional[17] and basis set 6-311++G(d,p) as implemented in Gaussian 09.[18] Harmonic vibrational frequency calculations were carried out at the same level of theory in order to determine the nature of the stationary points, the zero-point energy (ZPE), and the thermal contributions to the free energy of activation. Note that entropy effects are taken into account by considering the contribution from all degrees of freedom to the partition function, which is needed in the calculation of free energies. The pathways between the transition state structures and their corresponding minima were identified by intrinsic reaction coordinate (IRC)[19] calculations.

All computed geometries of reactants, transition states, intermediates, and products, as well as rate constants, are given in the Supporting Information (Tables S1 and S2). Figure 3 shows the optimal structure for the complexation of 2-methyleneoxetane **1d** with its corresponding carbocationic species (this complex is denoted as **1d***).

To further understand the difference in reactivity between silyl- and non-silylmethyleneoxetanes, computed energy profiles of transition states and intermediates for **1c** and **1d** (Figure 4) were analyzed.[20] Since our calculations revealed that the energy profiles for **1d** and **1e** (*trans* and *cis* isomers, respectively) are identical, only the profile for **1d** is shown and analyzed. Comparing the potential energy surface (PES), we observe that the significant difference in energy between the silyl and non-silyl substrates is in the stability of the oxetene intermediates (**2c*** and **2d***). The energy barriers for the forward reactions are very similar for the conversion of each 2-methyleneoxetane to the corresponding oxetene and for the subsequent conversions to enones. Because of the high barriers (~45 kcal/mol) for the reverse reaction of the second step for either compound, this step can be considered irreversible. Moreover, for both **1c** and **1d**, the calculated rate constants for the reverse reaction of the first step (k_{-1}) are 2 orders of magnitude larger than the forward reactions of the second step (k_2). This leads to a condition of pre-equilibrium, in which the constant for the overall reaction can be expressed as

$$k = \frac{k_1}{k_{-1}} k_2$$

At 160 °C, we obtain $k_{TMS}/k_H \approx 9400$. This result explains the much faster and more facile isomerization of 3-silyl-2-methyleneoxetanes.

The high *Z*-selectivity obtained from the isomerization of 3-silyloxetenes has been previously observed by Baukov et al. when α-silyl-α,β-unsaturated esters were formed.[15] Both steric and electronic effects have been shown to influence torquoselectivity in $4e^-$ electrocyclic ring-openings; however, electronic effects play a greater role.[21] Based on calculations with cyclobutenes, Houk et al.[21a] showed that an electron-donating group at C-3 or C-4 favors an outward motion, whereas electron-withdrawing substituents can also lead to inward rotation, which is consistent with entry 10 (Table 1). Recently, Shindo et al.[22] reported that oxetenes follow the same trend (Figure 5) and that the rotation is influenced by orbital interactions in the transition states. Our computational results show that the energy of the transition state leading to the *Z*-silylenones is lower than the corresponding transition state leading to *E*-isomer (see Supporting Information).

The role of silicon in the migration of the double bond is remarkable. 2-Methyleneoxetanes can be stored for long periods of time in the freezer. Occasionally, hydrolysis to β-hydroxymethylketones is seen. In contrast, the α-silylated 2-methyleneoxetanes could not be stored for extended periods. For example, 2-methyleneoxetane **1d** converted completely to the corresponding enone when stored neat in the freezer for 1 month.

α-Silyl-α,β-unsaturated ketones are useful substrates for the syntheses of α-substituted enones and their derivatives. α-Silylenones have been utilized for the preparation of α-iodo-α,β-unsaturated ketones.[23] Also, unsaturated α,γ-diketones were prepared from α-silyl-α,β-unsaturated ketones by reaction with aroyl chlorides.[24] The approach to α-silylenones described here is useful because silyl ketenes can be prepared on a large scale,[25] and *Z*-3-silyl enones can be synthesized in three steps without separating the lactone mixtures (since both isomers provide the *Z*-enone).[26] With some α-silylenone being observed during the methylenation for some of the substrates, it would seem that the methylenation and isomerization could be accomplished as a one-pot process, either by heating longer at 80 °C or by raising the bath temperature to 110 °C once the methylenation was complete. This was not the case. Although consumption of the methyleneoxetanes could be driven to completion and the enones were the only isolable products, the reactions were much slower, and the yields were much lower.

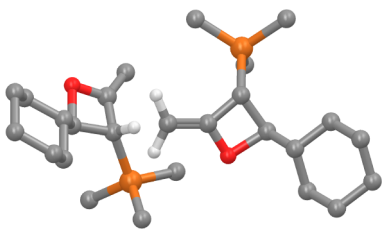


Figure 3. Graphical representation of the optimized structure of **1d*** initiating the chain reaction.

dx.doi.org/10.1021/jo4014645 | J. Org. Chem. 2013, 78, 11213−11220

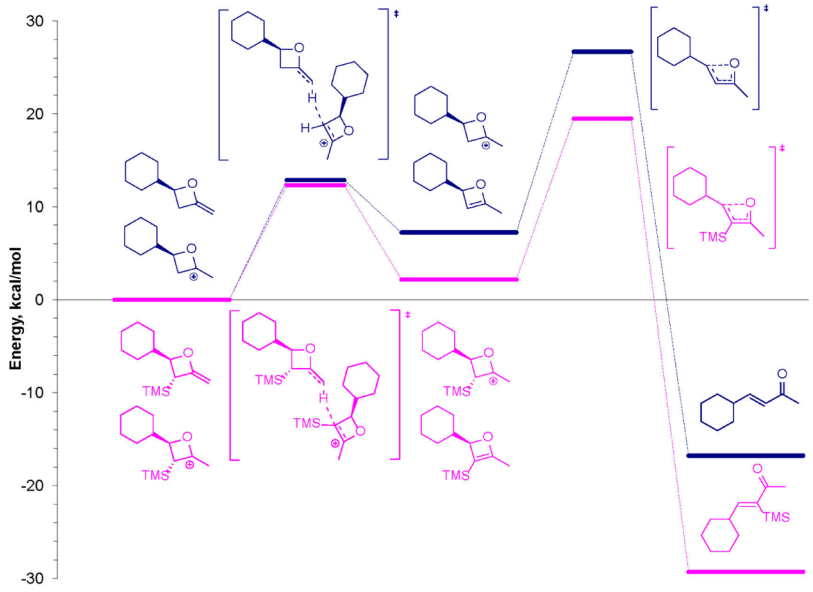


Figure 4. Potential energy surface (PES) diagrams for the stepwise production of **3c** (blue and higher set of lines) and **3d** (pink and lower set of lines).

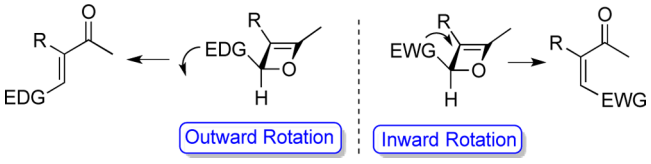


Figure 5. Electronic Effects on Torquoselectivity.

For example, after β-lactone **6j** was completely consumed, the flask was transferred to an oil bath at 110 °C. Conversion to enone **3j** was not complete even after 12 h. That the rate decrease was not a concentration effect was determined by conducting the tandem alkene isomerization/electrocyclic ring-opening at 110 °C at the same concentration as the methylenation with substrate **1j**. Only enone **3j** was present when the reaction was checked at 30 min. This suggests that either excess Petasis reagent or byproducts from the methylenation reaction compete for the catalytic carriers, slowing down the reaction. That the yield is lower if the reaction is slower is not surprising. Our earlier studies on the preparation of 2-methyleneoxetanes had shown that methylenation yields decreased if reactions were left too long, particularly if reactions were run at higher temperatures.[27]

In summary, novel tandem alkene isomerization/four π-electron electrocyclic ring-openings of 2-methyleneoxetanes to methyl vinylketones have been reported. Additionally, reactions of substituted 3-silyl-2-methyleneoxetanes are considerably faster and more efficient than the corresponding non-silicon-containing compounds. α-Silylenones were isolated in high yields and with excellent stereoselectivities, the isomerizations proceeding without solvent at moderate temperatures. DFT calculations were consistent with the experimental results and provided an explanation for the origin of differential kinetics between silyl and non-silyl substrates.

EXPERIMENTAL SECTION

Preparation of *cis*-3-Butyl-4-vinyloxetan-2-one (6a) from Methyl 2-Butyl-3-hydroxypent-4-enoate. *Methyl 2-Butyl-3-hydroxypent-4-enoate.*[28] A 500 mL 3-neck round-bottom flask under N_2 was charged with dry THF (270 mL) and diisopropylamine (8.40 mL, 59.2 mmol). The resulting solution was cooled to −78 °C, and *n*-BuLi (29.5 mL, 59.2 mmol, 2 M in hexane) was added dropwise through an addition funnel. The resulting solution was stirred for 1 h at −78 °C. Then, methylhexanoate (7.90 mL, 53.8 mmol) was added dropwise. The resulting dark yellow solution was stirred at −78 °C for 1.5 h. Then, acrolein (5.40 mL, 80.7 mmol) was added. After 15−20 min, the reaction was quenched with 1 M aqueous HCl solution (10 mL) at −78 °C, and the solution was allowed to warm to rt. The aqueous layer was separated and extracted with Et_2O (2 × 15 mL). The combined organic extracts were washed with brine (15 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 9:1) to give methyl (3*R**,4*R**)-2-butyl-3-hydroxypent-4-enoate (4.3 g, 43%) as a yellow oil and methyl (3*S**,4*R**)-2-butyl-3-hydroxypent-4-enoate (4.3 g, 43%) as a yellow oil. Methyl (3*R**,4*R**)-2-butyl-3-hydroxypent-4-enoate: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (ddd, J = 16.7, 10.5, 6.1 Hz, 1H), 5.25 (d, J = 17.1 Hz, 1H) 5.14 (d, J = 10.5 Hz, 1H), 4.26 (m, 1H), 3.65 (s, 3H), 2.58 (m, 1H), 2.50 (ddd, J = 9.8, 5.0, 5.0 Hz, 1H), 1.71−1.55 (m, 2H), 1.33−1.19 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 137.9, 116.6, 73.5, 51.8, 51.4, 30.0, 27.2, 22.8, 14.0. Methyl (3*S**,4*R**)-2-butyl-3-hydroxypent-4-enoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (ddd, J = 17.0, 10.4, 6.4 Hz, 1H), 5.15 (d, J = 17.2 Hz, 1H), 5.04 (d, J = 10.4 Hz, 1H), 4.06 (dd, J = 12.5, 6.5 Hz, 1H), 3.56 (s, 3H), 3.01 (d, J = 5.1 Hz, 1H), 2.35 (ddd, J = 9.7, 6.9, 5.1 Hz, 1H), 1.54−1.36 (m, 2H), 1.23−1.08 (m, 4H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8, 138.8, 116.6, 73.8, 51.9, 51.4, 29.6, 29.0, 22.6, 14.0.

(3S,4R*)-2-Butyl-3-hydroxy-4-pentenoic acid.* Aqueous NaOH (23 mL, 2 M) was added to a solution of methyl (3*S**,4*R**)-2-butyl-3-hydroxypent-4-enoate (1.2 g, 6.3 mmol) in THF/MeOH (215 mL, 1:2) at rt. The resulting mixture was stirred at 50 °C in a pre-equilibrated oil bath overnight. The solution was cooled to rt, and aqueous HCl (1 M) was added to pH = 3−4. MeOH and THF were removed under reduced pressure, and EtOAc (60 mL) was added to the residue. The two layers were separated, and the aqueous layer was extracted with EtOAc (4 × 40 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give (2*R**,3*S**)-2-butyl-3-hydroxy-4-pentenoic acid (1.02 g, quant.) as a brown oil. The crude product was utilized in the next reaction without purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddd, J = 17.0, 10.4, 6.5 Hz, 1H), 5.24 (d, J = 17.1 Hz, 1H), 5.14 (d, J = 10.4 Hz, 1H), 4.17 (dd, J = 6.7, 6.7 Hz, 1H), 2.42 (ddd, J = 9.4, 7.0, 5.1 Hz, 1H), 1.84 (m, 1H). 1.63−1.47 (m, 2H), 1.31−1.22 (m, 4H), 0.82 (t, J = 7.0 Hz, 3H);

dx.doi.org/10.1021/jo4014645 | J. Org. Chem. 2013, 78, 11213−11220

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 138.2, 117.1, 73.8, 51.4, 29.4, 28.8, 22.6, 13.9.

*cis-3-Butyl-4-vinyloxetan-2-one (**6a**).* Benzenesulfonyl chloride (1.85 g, 10.5 mmol) was added dropwise to a solution of (2*R**,3*S**)-2-butyl-3-hydroxy-4-pentenoic acid (0.60 g, 3.5 mmol) in dry pyridine (72 mL) at 0−5 °C under N_2. The resulting solution was stirred at 0−5 °C overnight. Then, it was poured onto crushed ice (100 mL) and stirred for 15 min. Et_2O (50 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 70 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (2 × 50 mL), 10% aqueous $CuSO_4$ (8 × 100 mL), and H_2O (1 × 50 mL), dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 95:5) to provide *cis*-3-butyl-4-vinyloxetan-2-one (**6a**) (0.38 g, 38%) as a clear oil: IR (neat) 2959, 2933, 2863, 1826, 1116, 857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (ddd, *J* = 17.2, 10.4, 7.0 Hz, 1H), 5.43 (d, *J* = 17.1 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 4.59 (dd, *J* = 5.4, 5.4 Hz, 1H), 3.30 (m, 1H), 1.87−1.69 (m, 2H), 1.43−1.25 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 134.3, 120.0, 77.6, 57.6, 29.0, 27.4, 22.4, 13.9; HRMS (TOF) calcd for $C_9H_{15}O_2$ (M^+ + H) *m*/*z* 155.1067, found 155.1056.

***t*-Butyldimethylsilylketene.**[29] Ethylmagnesium chloride (79 mL, 157 mmol, 2 M in THF) was added dropwise to a solution of ethoxyacetylene (10 g, 143 mmol) in dry THF (320 mL) at 0 °C under N_2. The resulting solution was stirred for 3 h while warming to rt. Then, *t*-butyldimethylsilyl chloride (24.0 g, 157 mmol) was slowly added, and the solution was stirred overnight (16 h) and then concentrated *in vacuo*. The magnesium salts precipitated upon the addition of petroleum ether, and the resulting slurry was filtered through a pad of Celite, washing with petroleum ether. The filtrate was concentrated *in vacuo* and carefully distilled under high vacuum to provide *t*-butyldimethylsilylethoxyacetylene (6.5 g, 25%) as a clear, colorless oil. It was then slowly distilled (140−180 °C bath temperature, 1 atm) to give *t*-butyldimethylsilylketene (4.4 g, 20%) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (s, 1H), 0.96 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 26.1, 17.8, −3.0, −4.3.

Typical Procedure for the Syntheses of β-Lactones 6b−6l. *4-Cyclohexyl-3-trimethylsilyloxetan-2-one (**6d/6e**).*[30] $BF_3{\cdot}OEt_2$ (3.7 μL, 0.030 mmol) was added dropwise to a solution of trimethylsilylketene[31] (0.46 mL, 3.2 mmol), cyclohexylcarboxaldehyde (0.32 mL, 2.7 mmol), and dry CH_2Cl_2 (2.5 mL) at 0 °C under N_2. The resulting solution was stirred at 0 °C until the aldehyde was consumed (reaction monitored by TLC). Then, pH 7 buffer solution (2.5 mL) was added. The two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 96:4) to give *trans*-4-cyclohexyl-3-trimethylsilyloxetan-2-one (**6d**) (0.26 g, 43%) as a white solid and *cis*-4-cyclohexyl-3-trimethylsilyloxetan-2-one (**6e**) (0.18 g, 29%) as a white solid. Trans diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (dd, *J* = 7.8, 3.9 Hz, 1H), 2.92 (d, *J* = 3.8 Hz, 1 H), 1.92 (m, 1H), 1.75−1.65 (m, 3H), 1.56−1.49 (m, 2H), 1.25−1.10 (m, 3H), 1.00−0.83 (m, 2H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 76.6, 46.5, 43.0, 28.7, 27.5, 26.1, 25.6, 25.3, −2.8. Cis diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (dd, *J* = 10.4, 5.9 Hz, 1H), 3.23 (d, *J* = 5.9 Hz, 1H), 1.92 (m, 1H), 1.73−1.67 (m, 2H), 1.65−1.57 (m, 3H), 1.23−1.11 (m, 3H), 0.97−0.82 (m, 2H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 78.0, 46.0, 40.8, 29.0, 28.7, 26.0, 25.2, 25.1, −0.8.

*4-Cyclohexyl-3-t-butyldimethylsilyloxetan-2-one (**6f**, Cis Isomer).*[27] Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 97:3) provided *trans*-4-cyclohexyl-3-*t*-butyldimethylsilyloxetan-2-one (**6f**) (0.73 g, 53%) as a white solid and *cis*-4-cyclohexyl-3-*t*-butyldimethylsilyloxetan-2-one (0.37 g, 26%) as a white solid. Trans diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (dd, *J* = 7.6, 4.1 Hz, 1H), 3.00 (d, *J* = 4.1 Hz, 1H), 1.95 (m, 1H), 1.78−1.74 (m, 2H), 1.69−1.66 (m, 1H), 1.60−1.51 (m, 2H), 1.30−1.09 (m, 3H), 1.04−0.8 (m, 2H), 0.93 (s, 9H), 0.11 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 76.6, 43.7, 43.3, 28.6, 28.2, 26.6, 26.2, 25.8, 25.5, 17.0, −6.6, −7.5. Cis diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.39 (d, *J* = 6.1 Hz, 1H), 1.97−1.93 (m, 1H), 1.78−1.58 (m, 5H), 1.26−1.16 (m, 3H), 1.09−0.93 (m, 2H), 0.94 (s, 9H), 0.18 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 76.8, 42.8, 40.5, 29.6, 28.5, 26.6, 26.0, 25.3, 25.1, 17.0, −4.7, −5.5.

*4-Heptyl-3-trimethylsilyloxetan-2-one (**6g** and **6h**).* Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 98:2) provided *trans*-4-heptyl-3-trimethylsilyloxetan-2-one (**6g**) (0.10 g, 19%) as a clear oil and *cis*-4-heptyl-3-trimethylsilyloxetan-2-one (**6h**) (0.26 g, 49%) as a clear oil. Trans diastereomer: IR (neat) 2956, 2928, 2858, 1808, 1253 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.21 (ddd, *J* = 6.5, 6.5, 4.2 Hz, 1H), 2.87 (d, *J* = 4.1 Hz, 1H), 1.93−1.81 (m, 1H), 1.72−1.61 (m, 1H), 1.30−1.25 (m, 10H), 0.85 (t, *J* = 6.8 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 72.9, 48.5, 35.9, 31.9, 29.4, 29.3, 25.3, 22.8, 14.2, −2.8; HRMS (TOF) calcd for $C_{13}H_{27}O_2Si$ (M^+ + H) *m*/*z* 243.1780, found 243.1759. Cis diastereomer: IR (neat) 2928, 2857, 1803, 1253, 1123 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.52 (ddd, *J* = 9.8, 6.0, 4.6 Hz, 1H), 3.28 (d, *J* = 6.0 Hz, 1H), 1.77−1.68 (m, 2H), 1.53−1.44 (m, 1H), 1.34−1.21 (m, 9 H), 0.83 (t, *J* = 6.9 Hz, 3 H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 74.2, 46.5, 33.7, 31.8, 29.3, 29.2, 26.4, 22.7, 14.2, −1.0; HRMS (TOF) calcd for $C_{13}H_{26}NaO_2Si$ (M^+ + Na) *m*/*z* 265.1594, found 265.1610.

*trans-4-t-Butyl-3-trimethylsilyloxetan-2-one (**6i**).*[27] No purification was needed. The desired *trans*-4-*t*-butyl-3-trimethylsilyloxetan-2-one (**6i**) (0.49 g, 67%) was isolated as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (d, *J* = 4.2 Hz, 1H), 2.91 (d, *J* = 4.1 Hz, 1H), 0.88 (s, 9H), 0.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 79.7, 43.1, 33.3, 24.3, −3.0.

*cis-4-Phenyl-3-trimethylsilyloxetan-2-one (**6j**).*[32] Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 98:4) provided *cis*-4-phenyl-3-trimethylsilyloxetan-2-one (**6j**) (0.48 g, 60%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 5H), 5.66 (d, *J* = 6.6 Hz, 1H), 3.69 (d, *J* = 6.4 Hz, 1H), −0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 137.1, 128.7, 128.5, 125.6, 72.8, 49.9, −1.7.

*4-(p-Trifluoromethylphenyl)-3-trimethylsilyloxetan-2-one (**6k**, Trans Isomer).* Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 9:1) provided *cis*-4-(*p*-trifluoromethylphenyl)-3-trimethylsilyloxetan-2-one (**6k**) (0.69 g, 47%) as a white solid and *trans*-4-(*p*-trifluoromethylphenyl)-3-trimethylsilyloxetan-2-one (0.25 g, 17%) as a clear oil. Trans diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 5.26 (bs, 1H), 3.22 (bs, 1H), 0.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 142.8, 131.2 (q, $^2J_{C-F}$ = 32.4 Hz), 126.2 (q, $^1J_{C-F}$ = 4.2 Hz), 126.1, 125.6, 124.0 (q, $^3J_{C-F}$ = 272.2 Hz), 71.4, 53.2, −2.7. Cis diastereomer: mp 78−82 °C; IR (neat) 2964, 2918, 1797, 1324 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 5.70 (d, *J* = 6.5 Hz, 1H), 3.75 (d, *J* = 6.5 Hz, 1H), −0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 141.3, 131.0 (q, $^2J_{C-F}$ = 33.0 Hz), 126.2, 125.6 (q, $^1J_{C-F}$ = 3.7 Hz), 124.0 (q, $^3J_{C-F}$ = 270.7 Hz), 72.1, 50.4, −1.7; HRMS (TOF) calcd for $C_{13}H_{16}F_3O_2Si$ (M^+ + H) *m*/*z* 289.0866, found 289.0862.

*4-Benzyloxymethyl-3-trimethylsilyloxetan-2-one (**6l**, Trans Isomer).* Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 9:1) provided *cis*-4-benzyloxymethyl-3-trimethylsilyloxetan-2-one (**6l**) (0.17 g, 19%) as a clear oil and *trans*-4-benzyloxymethyl-3-trimethylsilyloxetan-2-one (0.077 g, 6%) as a clear oil. Trans diastereomer: IR (neat) 2956, 2898, 2862, 1804, 1454, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.36−7.27 (m, 5H), 4.59 (s, 2H), 4.41 (ddd, *J* = 4.9, 4.2, 3.7 Hz, 1H), 3.75 (dd, *J* = 11.4, 3.5 Hz, 1H), 3.69 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.16 (d, *J* = 4.2 Hz, 1H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 137.7, 128.7, 128.1, 127.8, 73.9, 71.0, 70.9, 45.3, −2.7; HRMS (TOF) calcd for $C_{14}H_{21}O_3Si$ (M^+ + H) *m*/*z* 265.1254, found 265.1247. Cis diastereomer:[33] ^{1}H NMR (400 MHz, $CDCl_3$) 7.36−7.29 (m, 5H), 4.74 (ddd, *J* = 6.0, 6.0, 6.0 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 3.75 (m, 2H), 3.37 (d, *J* = 6.5 Hz, 1H), 0.16 (s, 9H);

dx.doi.org/10.1021/jo4014645 | J. Org. Chem. 2013, 78, 11213−11220

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 137.4, 128.7, 128.2, 128.2, 73.8, 72.0, 69.9, 45.6, −0.9.

Typical Procedure for the Preparation of 2-Methyleneoxetanes (1). *trans-4-Cyclohexyl-2-methylene-3-trimethylsilyloxetane (1d).* Dimethyltitanocene[34] (4.0 mL, 2.0 mmol, 0.50 M in toluene) and *trans*-4-cyclohexyl-3-trimethylsilyloxetan-2-one (**6d**) (0.22 g, 1.0 mmol) were stirred at 80 °C under N_2 in the dark for 2 h. Additional dimethyltitanocene (1−6 equiv) was added until complete consumption of **6d** was observed by TLC (petroleum ether/EtOAc/Et_3N). The solution was cooled to rt, and petroleum ether (8 mL) was added, at which point a yellow precipitate formed. The resulting mixture was stirred for 18 h at rt. The solid residue was filtered through a pad of Celite, rinsing with petroleum ether. The solvent was removed under reduced pressure to 5 mL (approximate volume), and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) to give *trans*-4-cyclohexyl-2-methylene-3-trimethylsilyloxetane (**1d**) (127 mg, 55%) as a clear oil: IR (neat) 2927, 2853, 1678, 1451, 1249 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (dd, J = 8.1, 5.0 Hz, 1H), 3.95 (m, 1H), 3.49 (m, 1H), 2.63 (m, 1H), 1.91 (m, 1H), 1.75−1.60 (m, 4H), 1.55 (m, 1H), 1.30−1.08 (m, 3H), 0.93−0.77 (m, 2H), 0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 84.9, 77.2, 44.1, 36.5, 28.3, 26.9, 26.5, 25.8, 25.5, −3.3; HRMS (TOF) calcd for $C_{13}H_{25}OSi$ (M^+ + H) m/z 225.1669, found 225.1675.

cis-3-Butyl-2-methylene-4-vinyloxetane (1a). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 98:1.5:0.5) provided *cis*-3-butyl-4-vinyl-2-methyleneoxetane (**1a**) (50 mg, 36%) as a yellow oil: IR (neat) 2959, 2930, 2874, 2859, 1662, 1178 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (ddd, J = 17.1, 10.4, 6.7 Hz, 1H), 5.33 (d, J = 17.1 Hz, 1H), 5.22 (d, J = 10.4 Hz, 1H), 4.78 (dd, J = 5.8, 5.8 Hz, 1H), 4.09 (dd, J = 3.3, 2.4 Hz, 1H), 3.74 (dd, J = 3.4, 1.7 Hz, 1H), 3.11−3.06 (m, 1H), 1.72−1.67 (m, 2H), 1.32−1.26 (m, 4H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 137.0, 117.7, 85.7, 78.9, 48.7, 31.7, 29.0, 22.7, 14.1; HRMS (TOF) calcd for $C_{10}H_{17}O$ (M^+ + H) m/z 153.1274, found 153.1236.

cis-4-Cyclohexyl-2-methylene-3-trimethylsilyloxetane (1e). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) provided a mixture of *cis*-4-cyclohexyl-2-methylene-3-(trimethylsilyl)oxetane (**1e**) and (*Z*)-4-cyclohexyl-3-trimethylsilylbut-3-en-2-one (**3e**) (10:1, 97 mg, 43%) as a yellow oil. *cis*-4-Cyclohexyl-2-methylene-3-(trimethylsilyl)oxetane (**1e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (dd, J = 10.5, 6.9 Hz, 1H), 3.99 (dd, J = 2.8, 2.8 Hz, 1H), 3.56 (dd, J = 3.0, 1.8 Hz, 1H), 2.96 (ddd, J = 6.8, 1.9, 1.9 Hz, 1H), 1.93 (m, 1H), 1.77−1.58 (m, 5H), 1.28−1.09 (m, 3H), 0.88−0.73 (m, 2H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 85.9, 77.1, 41.8, 37.3, 28.3, 26.5, 25.5, 25.3, −0.9.

trans-3-t-Butyldimethylsilyl-4-cyclohexyl-2-methyleneoxetane (1f). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) provided *trans*-3-*t*-butyldimethylsilyl-4-cyclohexyl-2-methyleneoxetane (**1f**) (110 mg, 68%) as a yellow oil: IR (neat) 2927, 2855, 1812, 1676, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (dd, J = 7.2, 4.9 Hz, 1H), 3.99 (dd, J = 2.8, 2.8 Hz, 1H), 3.54 (dd, J = 3.2, 1.9 Hz, 1H), 2.77 (ddd, J = 4.3, 1.9, 1.9 Hz, 1H), 1.93 (m, 1H), 1.77−1.74 (m, 2H), 1.69−1.57 (m, 3H), 1.29−1.09 (m, 3H), 1.01−0.87 (m, 2H), 0.90 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 84.9, 78.2, 44.2, 33.4, 27.9, 27.8, 27.1, 26.5, 26.1, 25.7, 17.2, −7.4, −7.5; HRMS (TOF) calcd for $C_{16}H_{31}OSi$ (M^+ + H) m/z 267.2144, found 267.2131.

trans-4-Heptyl-2-methylene-3-trimethylsilyloxetane (1g). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) provided *trans*-4-heptyl-2-methylene-3-trimethylsilyloxetane (**1g**) (30 mg, 34%) as a clear oil: IR (neat) 2956, 2929, 2857, 1678, 1251 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (ddd, J = 6.1, 6.1, 6.1 Hz, 1H), 3.97 (m, 1H), 3.51 (m, 1H), 2.57 (m, 1H), 1.85 (m, 1H), 1.66 (m, 1H), 1.27 (m, 10H), 0.86 (t, J = 6.8 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 81.2, 77.5, 38.6, 37.4, 32.0, 29.6, 29.4, 24.7, 22.8, 14.3, −3.3. HRMS (TOF) calcd for $C_{14}H_{29}OSi$ (M^+ + H) m/z 241.1982, found 241.1973.

cis-4-Heptyl-2-methylene-3-trimethylsilyloxetane (1h). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) provided a mixture of *cis*-4-heptyl-2-methylene-3-trimethylsilyloxetane (**1h**) and (*Z*)-4-heptyl-3-trimethylsilylbut-3-en-2-one (**3h**) (5:1, 50 mg, 31%) as a clear oil: IR (neat) 2956, 2926, 2856, 1678, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (m, 1H), 3.98 (m, 1H), 3.53 (m, 1H), 3.03 (m, 1H), 2.54 (m, 1H), 2.25 (m, 1H) 1.84 (m, 1H), 1.59 (m, 1H), 1.49−1.37 (m, 2H), 1.25 (m, 6H), 0.84 (t, J = 7.3 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 82.4, 77.0, 37.2, 35.1, 32.0, 29.6, 29.4, 26.0, 22.8, 14.3, −1.1.

trans-4-t-Butyl-2-methylene-3-trimethylsilyloxetane (1i). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) provided *trans*-4-*t*-butyl-2-methylene-3-trimethylsilyloxetane (**1i**) and (*Z*)-4-*t*-butyl-3-trimethylsilylbut-3-en-2-one (**3i**) (∼9:1, 136 mg, 50%) as a yellow oil: IR (neat) 2957, 2898, 1679, 1251 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (d, J = 5.1 Hz, 1H), 3.95 (dd, J = 2.8, 2.8 Hz, 1H), 3.48 (dd, J = 3.1, 1.9 Hz, 1H), 2.67 (m, 1H), 0.9 (bs, 9H), 0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 88.1, 76.7, 34.4, 33.3, 24.1, −3.2; HRMS (TOF) calcd for $C_{11}H_{23}OSi$ (M^+ + H) m/z 199.1513, found 199.1535.

cis-2-Methylene-4-phenyl-3-trimethylsilyloxetane (1j). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) provided *cis*-2-methylene-4-phenyl-3-trimethylsilyloxetane (**1j**) (210 mg, 64%) as a yellow oil: IR (neat) 3065, 3030, 2955, 2899, 1681, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.35 (m, 4H), 7.32−7.28 (m, 1H), 6.03 (d, J = 7.9 Hz, 1H), 4.23 (dd, J = 2.8, 2.8 Hz, 1H), 3.69 (dd, J = 3.3, 2.0 Hz, 1H), 3.46 (ddd, J = 7.9, 2.2, 2.2 Hz, 1H), −0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.9, 128.3, 128.1, 125.7, 81.1, 77.9, 40.3, −1.9; HRMS (TOF) calcd for $C_{13}H_{19}OSi$ (M^+ + H) m/z 219.1200, found 219.1219.

cis-2-Methylene-4-(p-trifluoromethylphenyl)-3-trimethylsilyloxetane (1k). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 94:5:1) provided *cis*-2-methylene-4-(*p*-trifluoromethylphenyl)-3-trimethylsilyloxetane (**1k**) (121 mg, 42%) as an orange oil: IR (neat) 2958, 2902, 1684, 1621, 1417, 1325 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 6.03 (d, J = 8.0 Hz, 1H), 4.22 (dd, J = 3.5, 2.7 Hz, 1H), 3.69 (dd, 3.6, 2.0 Hz, 1H), 3.47 (ddd, J = 7.9, 2.2, 2.2 Hz, 1H), −0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 144.0, 130.4 (q, $^2J_{C-F}$ = 32.4 Hz), 126.1, 125.3 ($^1J_{C-F}$ = 3.8 Hz), 124.3 ($^3J_{C-F}$ = 272.1 Hz), 80.4, 78.5, 40.2, −2.0; HRMS (TOF) calcd for $C_{14}H_{18}F_3OSi$ (M^+ + H) m/z 287.1074, found 287.1049.

cis-4-Benzyloxymethyl-2-methylene-3-trimethylsilyloxetane (1l). Purification by flash chromatography on silica gel (petroleum ether/EtOAc/Et_3N, 97.5:2:0.5) provided *cis*-4-benzyloxymethyl-2-methylene-3-trimethylsilyloxetane (**1l**) (40 mg, 40%) as a yellow oil: IR (neat) 2954, 2858, 1679, 1251 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.32 (m, 4H), 7.30−7.20 (m, 1H), 5.12 (ddd, J = 7.3, 7.3, 4.2 Hz, 1H), 4.58 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.8 Hz, 1H), 4.05 (m, 1H), 3.77 (dd, J = 10.7, 7.3 Hz, 1H), 3.68 (dd, J = 10.7, 4.3 Hz, 1H), 3.58 (dd, J = 3.5, 2.0 Hz, 1H), 3.12 (ddd, J = 7.7, 2.2, 2.2 Hz, 1H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 137.9, 128.6, 128.1, 128.0, 80.3, 77.8, 73.7, 71.6, 35.7, −1.2; HRMS (TOF) calcd for $C_{15}H_{23}O_2Si$ (M^+ + H) m/z 263.1462, found 263.1453.

Typical Procedure for the Preparation of α,β-Unsaturated Ketones 3b and 3c. *(E)-5-t-Butyldiphenylsilyloxy-3-methylpent-3-en-2-one (3b).* *trans*-4-*t*-Butyldiphenylsilyloxymethyl-3-methyl-2-methyleneoxetane (**1b**) (61 mg, 1.7 mmol; neat) was heated in a sand bath at 200 °C under N_2 until the starting material was consumed (by NMR). It was then cooled to rt and purified by flash chromatography on silica gel (petroleum ether/EtOAc, 95:5) to give (*E*)-5-*t*-butyldiphenylsilyloxy-3-methylpent-3-en-2-one (**3b**) (20 mg, 33%) as a clear oil: IR (neat) 3071, 2931, 2858, 1675, 1428 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69−7.67 (m, 4H), 7.46−7.38 (m, 6H), 6.69 (t, J = 5.3 Hz, 1H), 4.46 (d, J = 5.5 Hz, 2H), 2.25 (s, 3H), 1.53 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (400 MHz, CD_2Cl_2) δ 199.6, 142.7, 136.8, 136.1, 133.9, 130.4, 128.3, 62.2, 27.1, 25.7, 19.5, 11.5; HRMS (TOF) calcd for $C_{22}H_{28}NaO_2Si$ (M^+ + Na) m/z 375.1751, found 375.1757.

(E)-3-Cyclohexylbut-3-en-2-one (3c).[35] Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 95:5) provided (*E*)-3-cyclohexylbut-3-en-2-one (**1c**) (11 mg, 29%) as a clear oil: ^{1}H

dx.doi.org/10.1021/jo4014645 | J. Org. Chem. 2013, 78, 11213−11220

NMR (400 MHz, CD_2Cl_2) δ 6.70 (dd, J = 16.2, 6.7 Hz, 1H), 6.00 (d, J = 16.1 Hz, 1H), 2.22 (s, 3H), 2.19 (m, 1H), 1.76−1.60 (m, 5H), 1.32−1.09 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 153.6, 129.0, 40.8, 32.0, 27.1, 26.1, 25.9.

Typical Procedure for the Preparation of α,β-Unsaturated Ketones 3d and 3g. *(Z)-4-Cyclohexyl-3-trimethylsilylbut-3-en-2-one (3d).* *trans*-4-Cyclohexyl-2-methylene-3-trimethylsilyloxetane (**1d**) (56 mg, 2.5 mmol) (neat) was heated in a pre-equilibrated oil bath at 160 °C for 10 min under N_2. It was then cooled to rt and purified by flash chromatography on silica (petroleum ether/EtOAc, 97:3) to give (*Z*)-4-cyclohexyl-3-trimethylsilylbut-3-en-2-one (**3d**) (45 mg, 80%) as a clear oil: IR (neat) 2928, 2852, 1663, 1598, 1450, 1248 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, J = 10.2 Hz, 1H), 2.37 (m, 1H), 2.21 (s, 3H), 1.75−1.60 (m, 5H), 1.28−1.08 (m, 5H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 158.9, 143.8, 40.7, 32.8, 28.1, 26.0, 25.7, 1.1; HRMS (TOF) calcd for $C_{13}H_{25}OSi$ (M^+ + H) m/z 225.1669, found 225.1683.

(Z)-4-Heptyl-3-trimethylsilylbut-3-en-2-one (3g). Derived from *trans*-4-heptyl-2-methylene-3-trimethylsilyloxetane (**1g**). No purification was needed, and (*Z*)-4-heptyl-3-trimethylsilylbut-3-en-2-one (**3g**) (25 mg, 89%) was isolated as a yellow oil: IR (neat) 2956, 2926, 2856, 1663, 1599, 1247 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (t, J = 7.3 Hz, 1H), 2.24 (m, 4H), 1.41 (m, 2H), 1.26 (m, 9H), 0.86 (m, 3H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 154.4, 145.8, 32.0, 29.6, 29.4, 28.0, 22.8, 14.3, 1.0; HRMS (TOF) calcd for $C_{14}H_{29}OSi$ (M^+ + H) m/z 241.1982, found 241.1964.

Typical Procedure for the Preparation of α,β-Unsaturated Ketones 3f and 3i−3l. *(Z)-3-t-Butyldimethylsilyl-4-cyclohexylbut-3-en-2-one (3f).* A solution of *trans*-4-cyclohexyl-3-(*t*-butyldimethylsilyl)-2-methyleneoxetane (**1f**) (68 mg, 0.26 mmol) in toluene-d_8 (0.52 mL) was heated to reflux in a pre-equilibrated oil bath at 120−135 °C under N_2 until the starting material was consumed (by NMR). The solution was then cooled to rt, and the solvent removed *in vacuo*. No purification was needed. The desired (*Z*)-3-*t*-butyldimethylsilyl-4-cyclohexylbut-3-en-2-one (**3f**) (64 mg, 94%) was isolated as a yellow oil: IR (neat) 2928, 2854, 1668, 1595, 1248 cm^{-1}; ^{1}H NMR (400 MHz, toluene-d_8) δ 6.45 (d, J = 10.6 Hz, 1H), 2.32 (dtt, J = 10.6, 10.6, 3.5 Hz, 1H), 2.00 (s, 3H), 1.63−1.55 (m, 5H), 1.20−1.08 (m, 3H), 1.02 (s, 9H), 0.98−0.86 (m, 2H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, toluene-d_8) δ 206.6, 158.9, 143.8, 40.7, 32.8, 28.1, 26.0, 25.7, −1.1; HRMS (TOF) calcd for $C_{16}H_{30}NaOSi$ (M^+ + Na) m/z 289.1958, found 289.1957.

(Z)-4-t-Butyl-3-trimethylsilylbut-3-en-2-one (3i). Derived from *trans*-4-*t*-butyl-2-methylene-3-(trimethylsilyl)oxetane (**1i**). Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 96:4) provided (*Z*)-4-*t*-butyl-3-(trimethylsilyl)but-3-en-2-one (**3i**) (11 mg, 33% based on unreacted starting material) as a clear oil: IR (neat) 2959, 1675, 1585, 1251 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (s, 1H), 2.21 (s, 3H), 1.12 (s, 9H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 158.3, 145.1, 34.7, 30.8, 30.0, 2.8; HRMS (TOF) calcd for $C_{11}H_{23}OSi$ (M^+ + H) m/z 199.1513, found 199.1527.

(Z)-4-Phenyl-3-trimethylsilylbut-3-en-2-one (3j). Derived from *cis*-2-methylene-4-phenyl-3-trimethylsilyloxetane (**1j**). Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 97:3) provided (*Z*)-4-phenyl-3-trimethylsilylbut-3-en-2-one (**3j**) (35 mg, 64%) as a clear oil: IR (neat) 3026, 2953, 2898, 1665, 1587, 1588, 1227 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.23−7.20 (m, 3H), 7.15−7.13 (m, 2H), 2.28 (s, 3H), −0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 149.7, 149.1, 138.0, 128.7, 128.3, 28.1, 0.75; HRMS (TOF) calcd for $C_{13}H_{19}OSi$ (M^+ + H) m/z 219.1200, found 219.1205.

4-p-Trifluoromethylphenyl-3-trimethylsilylbut-3-en-2-one (3k). Derived from *cis*-2-methylene-4-*p*-trifluoromethylphenyl-3-trimethylsilyloxetane (**1k**). Purification by flash chromatography on silica gel (petroleum ether/EtOAc, 97:3 to 90:10) provided (*Z*)-4-*p*-trifluoromethylphenyl-3-trimethylsilylbut-3-en-2-one (**3k**) (75 mg, 65%) as a clear oil and (*E*)-4-*p*-trifluoromethylphenyl-3-trimethylsilylbut-3-en-2-one (7 mg, 6%) as a clear oil. *Z*-stereoisomer: IR (neat) 2956, 2900, 1670, 1592, 1410, 1327 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H), −0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 151.3, 147.1, 141.7, 130.6 (q, $^2J_{C-F}$ = 32.6 Hz), 128.9, 125.3 (q, $^1J_{C-F}$ = 3.6 Hz), 124.2 (q, $^3J_{C-F}$ = 272.6 Hz), 28.2, 0.65; HRMS (TOF) calcd for $C_{14}H_{18}F_3OSi$ (M^+ + H) m/z 287.1074, found 287.1095. *E*-stereoisomer: IR (neat) 2959, 2927, 1682, 1617, 1414, 1325 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 6.76 (s, 1H), 2.03 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 153.6, 140.4, 136.4, 130.4 (q, $^2J_{C-F}$ = 32.3 Hz), 128.7, 125.7 (q, $^1J_{C-F}$ = 3.7 Hz), 124.0 (q, $^3J_{C-F}$ = 272.4 Hz), 31.4, −1.5; HRMS (TOF) calcd for $C_{14}H_{18}F_3OSi$ (M^+ + H) m/z 287.1074, found 287.1084.

(Z)-4-Benzyloxymethyl-3-trimethylsilylbut-3-en-2-one (3l). Derived from *cis*-4-benzyloxymethyl-2-methylene-3-trimethylsilyloxetane (**1l**). No purification needed. (*Z*)-4-Benzyloxymethyl-3-trimethylsilylbut-3-en-2-one (**3l**) (30 mg, 99%) was isolated as a light brown oil: IR (neat) 2952, 2856, 1664, 1248 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.27 (m, 5H), 6.89 (t, J = 5.7 Hz, 1H), 4.54 (s, 2H), 4.24 (d, J = 5.7 Hz, 2 H), 2.25 (s, 3H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 149.6, 147.2, 137.8, 128.7, 128.2, 128.1, 73.3, 69.0, 27.9, 0.6; HRMS (TOF) calcd for $C_{15}H_{23}O_2Si$ (M^+ + H) m/z 263.1462, found 263.1457.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods and ^{1}H and ^{13}C NMR spectra for all new compounds, structures and relative energies of the reactants, products, and transition states in both *E*- and *Z*-isomers, tables of atom coordinates and absolute energies, and evaluation of rate constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This manuscript is based upon work partially supported by the National Science Foundation (NSF) under Grant Nos. CHE-0111522 and CHE-1048717. J.A.G. acknowledges financial support from the Camille and Henry Dreyfus foundation and NSF CAREER Award CHE-0847340.

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