Novel Rearrangements of 4-Silyl-3-buten-2-ones

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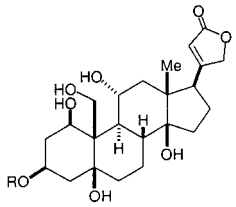
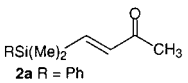
Abstract: Two 4-silyl-3-buten-2-ones, **2a** and **2c**, underwent an interesting rearrangement involving migration of the allyl or phenyl group on the silicon atom to the adjacent enone carbon when treated with various bases.

The increasing use of organosilicon compounds for the synthesis of complex organic molecules has shed new light on the chemistry of this group IV element. By means of the "temporary silicon connection", Stork et al. achieved highly regioselective formation of carbon−carbon bonds via radical, ionic, and cycloadditive processes.[1] Moreover, excellent levels of stereoselectivity have been achieved in the condensation of chiral silyl reagents with a variety of electrophiles.[2] The success of some of these strategies arises from the possibility of converting the silicon group to a hydroxy group. The oxidation of the C−Si bond[3] can be easily carried out using the procedures introduced by Tamao[4] and Fleming,[5] which display remarkable compatibility with various organic functionalities. This widely used methodology has revealed the silicon group to be a powerful tool for organic synthesis, allowing transformations that would not otherwise be possible.



1a R = L-rhamnose
1b R = H

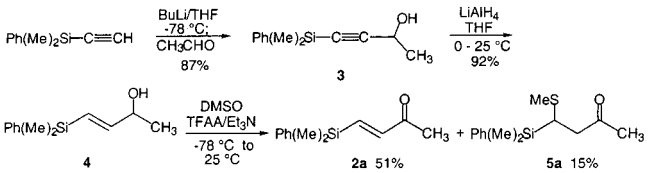


2a R = Ph
2b R = Me
2c R = CH_2-CH=CH_2

As part of our program directed toward the synthesis of the AB rings of the naturally occurring cardenolide ouabain (**1a**) and its aglycone ouabagenin (**1b**), we decided to investigate the synthesis and the potential reactivity of several 4-silyl-3-buten-2-ones, **2a**−**c**, in the hope that we might be able to use them as Michael acceptors in the Robinson annulation process as surrogates for 4-alkoxyenones to ultimately produce 5-alkoxycyclohex-2-enones. We report here some interesting rearrangements of these silyl enones.

The synthesis of 4-[dimethyl(phenyl)silyl]but-3-en-2-one (**2a**) was accomplished in three steps starting from commercially available dimethyl(phenyl)silylacetylene (Scheme 1). Two-carbon homologation of the acetylide

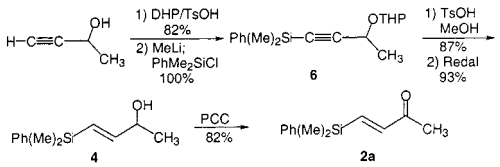
Scheme 1



anion with acetaldehyde followed by hydride reduction afforded the desired allylic alcohol **4** in high yield, as a 9:1 *E*:*Z* ratio. Subsequent Swern oxidation using trifluoroacetic anhydride afforded the desired 4-silylenone **2a** in 51% yield and the unexpected 1,4-adduct **5a** in 16% yield. The latter is formed by the 1,4-addition of dimethyl sulfide, the byproduct of the Swern oxidation, to the desired enone followed by base-promoted S-demethylation.

Alternatively, the silyl propargyl ether **6** could be prepared from 3-butyn-2-ol according to the procedure described by Woerpel et al.[6] Hydrolysis and stereoselective reduction using Redal[7] afforded exclusively the (*E*)-allylic alcohol **4** (Scheme 2). Finally, to avoid the forma-

Scheme 2



tion of undesired 1,4-adducts such as **5a**, the oxidation was carried out using PCC to furnish the desired enone **2a** in high isolated yield.

Since the 4-silylenone **2a** should be suitable for 1,4-addition by a variety of nucleophiles and its silyl group should be easily converted into a hydroxyl group by using the above-mentioned Tamao or Fleming conditions, this compound should be a useful building block for the synthesis of our target molecule via a Robinson annulation approach. While investigating the ability of β-silyl enone **2a** to undergo Michael additions in the presence of alkoxides, we found that along with the products of presumed polymerization, an unexpected compound, the well-known 4-phenyl-2-butanone (**7**), was also formed (Table 1). Moreover, when fluoride, a well-known silicophilic anion, was used as the nucleophile, **7** was isolated in quantitative yield.

The unexpected formation of **7** can be explained by evoking an initial attack of the nucleophile on the silicon atom of the silyl enone **2a** to give the pentacovalent silicon anion **I**, which undergoes a 1,2-migration of the phenyl group from silicon to the adjacent electrophilic carbon atom to generate the enolate **II** as shown in Scheme 3. After protonation of the enolate, a second

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(2) (a) Huang, H.; Panek, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 9836. (b) Zhu, B.; Panek, J. S. *Eur. J. Org. Chem.* **2001**, 1701.
(3) For a review, see: Jones, G.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599.
(4) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120.
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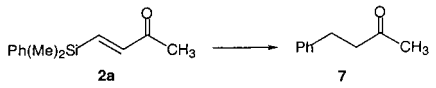
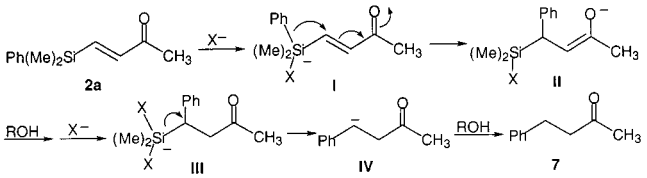
Table 1. Rearrangement of Silyl Enone 2a to Give 4-Phenylbutan-2-one 7



entry	nucleophile	conditions	yield
1	NaOMe (0.4 equiv)	MeOH, reflux, 48 h	43%
2	NaOMe (1 equiv)	MeOH, reflux, 12 h	25%
3	KO*t*Bu (0.7 equiv)	*t*BuOH, reflux, 72 h	28%
4	NaH (1 equiv)	THF, reflux, 48 h	0%
5	KF (3 equiv)	wet DMSO, 25 °C, 18 h	100%

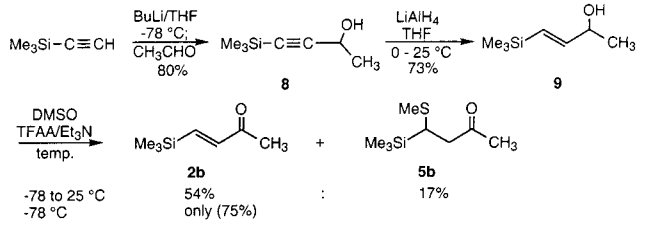
nucleophilic attack on the silicon atom generates the anion **III**, which then eliminates the neutral silicon species to afford the benzylic anion **IV**, which upon protonation gives the observed product **7**.

Scheme 3



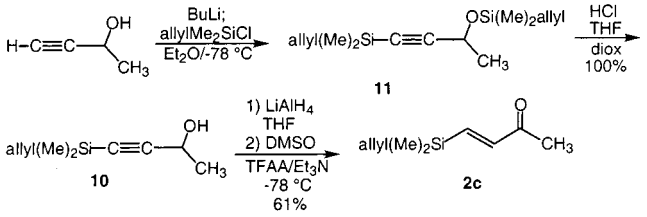
To our knowledge, the only account of such a phenyl migration, in the presence of TBAF as a fluoride source, was reported by Fleming et al.[8] Interestingly, at higher temperatures, even less efficient nucleophiles such as methoxide (Table 1, entries 1 and 2) and *t*-butoxide (entry 3) are able to promote this rearrangement. Intrigued by the unusual reactivity of silyl enone **2a** and hoping to avoid the intramolecular quenching of this class of useful Michael acceptors, we prepared two other 4-silylbutenones, **2b** and **2c**. (*E*)-4-(Trimethylsilyl)-3-buten-2-one **2b** was prepared via the same three-step sequence initially used for the synthesis of the phenyl analogue **2a** (Scheme 4). Trapping of the anion of the silyl acetylene and

Scheme 4



hydride reduction of the resulting alcohol **8** gave the allylic alcohol **9** as a 6:1 *E*:*Z* ratio. As before, the Swern oxidation of the allylic alcohol **9** yielded a 5:2 mixture of the desired enone **2b** and the product of 1,4-addition of dimethyl sulfide (**5b**). Interestingly, keeping the temperature at −78 °C throughout the oxidation gave the enone as the only product in 75% yield. 4-Allyl(dimethyl)silyl-3-buten-2 one (**2c**) was prepared by bis-silylation of 3-butyn-2-ol with 1 equiv of allyl(dimethyl)silyl chloride to give a mixture of the desired monosilylated compound **10** (49%) and the bis-silylated product **11** (19%) (Scheme 5). The bis-silylated product **11** was then hydrolyzed to the propargyl alcohol **10** in quantitative yield. Reduction

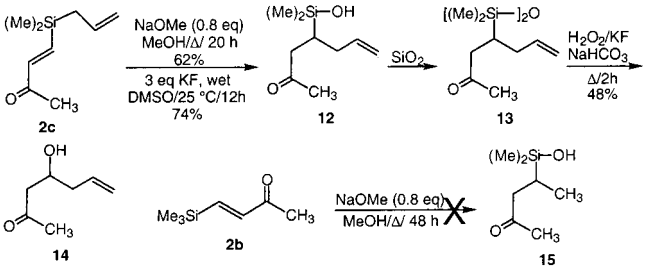
Scheme 5



and subsequent oxidation of the resulting allylic alcohol afforded the desired *β*-silyl enone **2c** in good isolated yields.

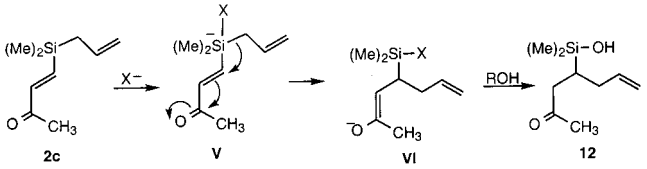
The two 4-silylbutenones **2b** and **2c** allowed us to test two possibilities, namely, (1) would the methyl and allyl groups on the silicon atom of **2b** and **2c**, respectively, migrate to the adjacent electrophilic carbon, and (2) would the rearrangement continue further with the desilylation as for the dimethyl(phenyl)silylbutenone **2a**. When the allyl(dimethyl)silyl enone **2c** was treated under the usual basic nucleophilic conditions, the starting material was converted into the rearranged silanol **12** in quantitative yields (Scheme 6). However, purification

Scheme 6



by column chromatography on silica gel afforded only the corresponding disiloxane **13.** The C−Si bond was then oxidatively cleaved using Tamao conditions[9] to yield the homoallylic alcohol **14** in 48% isolated yield. Conversely, but not surprisingly, no methyl migration was observed for the trimethylsilyl enone **2b**. This clearly suggests that for migration to occur, the migrating group must be able to stabilize a negative charge (e.g., phenyl, allyl), and thus methyl does not migrate. Furthermore, in the case of the allyl(dimethyl)silyl enone **2c**, the desilylation step observed for **2a** does not occur because this would require an unstabilized homoallylic anion intermediate.[10] Following the initial nucleophilic attack to generate the pentacovalent silicon anion **V**, a 1,2-migration of the allyl group to the enone would give the enolate **VI** and, after protonation, the observed product **12** (Scheme 7).

Scheme 7



Finally, we were interested in testing several protodesilylation conditions with the *β*-silyl enones **2a** and **2c**

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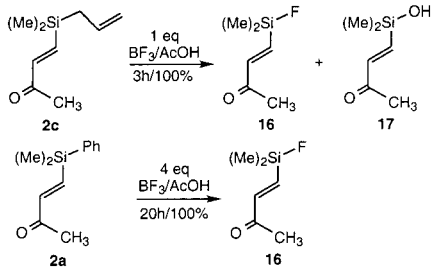
(Scheme 8). Denmark et al.[11] showed that the Si−Ar bond of β-silyl acrylates could be cleaved with dry HCl at 80

Scheme 8



°C in high yield. Sieburth et al.[12] accomplished the same goal using triflic acid. Unfortunately, the β-silyl enones **2a** and **2c** proved to be unstable to strongly acidic electrophilic conditions. Attempted bromodesilylation of **2c** with Br_2 at −78 °C proved to be unsuccessful, giving only decomposition of the starting enone. Moreover, treatment of the enone **2a** with dry HCl, BBr_3/AcOH, HBF_4−Et_2O, or triflic acid, also resulted in decomposition. Ultimately, the protodesilylation of the allylsilane **2c** was achieved using an excess of boron trifluoride−acetic acid complex to give the desired fluorosilane **16** with still some of the hydrolysis product **17** (here 1:1) (Scheme 8).[13] The phenylsilane was converted into the fluorosilane **16** in quantitative yield by this process. Interestingly, under these protic, mildly nucleophilic conditions, no allyl or phenyl migration was observed. Presumably, even if the initial protonation of the carbonyl group can promote the intramolecular shift, the formation of the pentacovalent silicon anionic intermediate (such as **I** or **V**), which is needed to trigger the rearrangement, does not occur under these conditions.

In summary, we have shown that 4-silylbutenones bearing a phenyl (**2a**) or allyl group (**2c**) on the silicon atom undergo an intramolecular Michael addition under mildly nucleophilic conditions. The process can stop at the corresponding β-silyl ketone or continue further depending upon the extent of stabilization of the anion intermediate. Enones such as **2a** and **2b** can be useful Michael acceptors for organic synthesis. However, our results showed that their use may be limited to soft, nonsilicophilic anions or to acidic conditions.

Experimental Section

General. ^{1}H NMR spectra were obtained at 200.132, 400.132, or 500.132 MHz as indicated. ^{13}C NMR spectra were recorded at 100.625 or 125.773 MHz as indicated. ^{1}H NMR and ^{13}C NMR data are reported in parts per million (δ) downfield from tetramethylsilane. Resonance patterns are reported with the following notations: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Second-order spectra in which coupling cannot be obtained by inspection are reported as multiplets, with the center of the signal indicated by the δ value given. Infrared spectra were recorded as neat liquid films, and only the most significant absorption bands are reported in cm^{-1}. Thin-layer chromatography (TLC) was carried out by the use of silica gel 60 F254 0.2 mm alumina-backed plates. Visual detection was performed with ultraviolet light or using phosphomolybdic acid or permanganate stain. Flash column chromatography was performed using silica gel 60 (230−400 mesh) using compressed air. All solvents/reagents were purified using literature procedures. All reactions were performed under an atmosphere of argon unless otherwise noted.

4-Phenylbutan-2-one (7). The starting enone **2a** (16 mg, 0.078 mmol) was dissolved in dimethylformamide (DMF, 5 mL) and treated with water (5 drops) and potassium fluoride (13 mg, 0.235 mmol). The resulting mixture was stirred for 18 h at 20 °C. Then, the solvent was removed under vacuum and the residue dissolved in dichloromethane (10 mL) and washed with water (2 mL). The aqueous layer was extracted with dichloromethane (2 × 20 mL), and the combined organic phases were dried over $MgSO_4$. The solvent was removed under vacuum to afford the phenyl ketone **7** (11 mg, quantitative) as a colorless oil that did not require further purification. The spectroscopic properties of this compound were consistent with those reported in the Aldrich catalog. The same compound was also obtained using sodium methoxide or potassium *t*-butoxide with the appropriate solvent under reflux, as shown in Table 1.

(±)-4-(Trimethylsilyl)-but-3-yn-2-ol (8). Trimethylsilylacetylene (2.0 mL, 14.15 mmol) was dissolved in THF (20 mL) at −78 °C and treated with *n*-butyllithium (6.8 mL, 16.98 mmol) over 4 min. After the reaction was stirred for 15 min, acetaldehyde (1.6 mL, 28.3 mmol) was added and the yellow solution turned colorless immediately. After the mixture was stirred for 2 h at −78 °C, the reaction was quenched with aqueous saturated NH_4Cl (10 mL) and extracted with ethyl acetate (4 × 50 mL). The organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum to afford a pale yellow oil. Flash column chromatography (4:1 hexanes/ethyl acetate) afforded the desired compound **8** (1.6 g, 80%). The ^{1}H NMR spectrum of **8** was consistent with the that reported in the literature.[17] ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 107.6, 88.4, 58.8, 24.2, −0.14. IR (neat): 3331, 2175, 1371, 1251, 1118, 1047, 839 cm^{-1}.

(±)(*E*) and (*Z*)-4-(Trimethylsilyl)-but-3-en-2-ol (9). The alkyne **8** (830 mg, 5.84 mmol) was dissolved in THF (5 mL) and added to a solution of lithium aluminum hydride (2.9 mL, 2.92 mmol) in the same solvent (10 mL) at 0 °C. After the mixture was stirred for 2 h, the cooling bath was removed and the mixture stirred at 20 °C for 18 h. The reaction was then quenched by addition of water (1 mL) at 0 °C and the mixture extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum to yield the allylic alcohol **9** as a 6:1 inseparable mixture of *E*:*Z* isomers that did not need further purification. The spectroscopic properties of **9** were consistent with those reported in the literature.[18]

(*E*)-4-(Trimethylsilyl)-but-3-en-2-one (2b) and 4-(Trimethylsilyl)-4-(methylthio)-butan-2-one (5b). A solution of dimethyl sulfoxide (0.35 mL, 4.5 mmol) in dichloromethane (30 mL) was treated with trifluoroacetic anhydride (0.48 mL, 3.37 mmol) dropwise at −78 °C. After the mixture was stirred for 10 min, a solution of the allylic alcohol **9** (162 mg, 1.16 mmol) in dichloromethane (5 mL) was added via syringe. The resulting mixture was stirred at −78 °C for 50 min, and then triethylamine (1.4 mL, 10.12 mmol) was added dropwise. After the mixture was stirred for 5 min, the cooling bath was removed and the mixture allowed to warm to 20 °C over 45 min. The clear solution was treated with water (10 mL) and extracted with

(10) One may also consider these rearrangements to be fundamentally cationic in nature or at least similar to cationic rearrangements in which the pentacovalent silicon atom provides a nucleophilic "push" for migration to a somewhat cationic center, an unusual sort of push−pull effect. Thus, phenyl and allyl are good migrating groups because they can bond easily to an adjacent partially cationic center. We thank Professor Ian Fleming for his input on the mechanism of this rearrangement.

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dichloromethane (3 × 80 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed under vacuum to yield a 5:2 mixture of **2b** and **5b**. Purification by flash column chromatography (5:1 hexanes/ethyl acetate, 1% triethylamine) afforded the pure enone **2b** (86 mg, 54%) and **5b** (34 mg, 17%). The spectroscopic properties of **2b** were consistent with those reported in the literature.[18b,19] Compound **5b**. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.76 (bd, J = 6.6 Hz, 2H), 2.34 (dt, J = 6.6, 1.0 Hz, 1H), 2.25 (s, 3H), 2.14 (s, 3H), 0.12 (s, 9H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 207.9, 45.8, 30.5, 27.3, 17.2, −2.8.[20] When the reaction was carried out keeping the temperature at −78 °C throughout, only the desired enone **2b** was isolated in 75% yield.

(±)-4-(2-Propenyldimethylsilyl)-but-3-yn-2-ol (10). 3-Butyn-2-ol (0.3 mL, 3.8 mmol) was dissolved in THF (10 mL) at −78 °C and then treated with *n*-butyllithium (3.3 mL, 8.36 mmol) dropwise. The resulting cloudy mixture was stirred for 5 min and then warmed to 20 °C for 1.5 h. The clear solution was then cooled back to −78 °C and treated with allyldimethylsilyl chloride (0.6 mL, 3.8 mmol) dropwise. After stirring for 30 min, the mixture was warmed to 20 °C and stirred for 18 h. Then, the reaction was quenched by the addition of water (20 mL) at 0 °C and extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After solvent removal under vacuum, the resulting crude oil was purified by flash column chromatography (3:1 hexanes/ethyl acetate) to afford the desired monosilylated compound **10** (314 mg, 49%) and the bis-silyl compound **11** (191 mg, 19%). Treatment of the bis-silylated compound **11** with 8 drops of concentrated HCl in a 1:1 mixture of THF and dioxane at 20 °C for 2 h afforded the desired compound **10** in quantitative yield.[20] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.80 (m, 1H), 4.90 (m, 2H), 4.53 (m, 1H), 1.80 (d, J = 5.3 Hz, 1H), 1.62 (d, J = 7.0 Hz, 2H), 1.44 (d, J = 6.6 Hz, 3H), 0.15 (s, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 133.7, 125.3, 113.8, 108.5, 86.6, 58.5, 24.1, 23.6, −2.4. IR (neat): 3343, 3078, 2963, 2175, 1630, 1251, 1045, 808 cm^{-1}.

(*E*)-4-(2-Propenyldimethylsilyl)-but-3-en-2-one (2c). The alkyne **10** (300 mg, 1.78 mmol) was dissolved in THF (5 mL) and added to a suspension of lithium aluminum hydride (68 mg, 1.78 mmol) in the same solvent (10 mL) at 0 °C. After the reaction was stirred for 1.5 h, the cooling bath was removed and the mixture stirred at 20 °C for 45 min. The reaction was then quenched by addition of saturated NH_4Cl (1 mL) at 0 °C and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum to yield a 9:1 mixture of the (*E*)- and (*Z*)-allylic alcohols. The crude material was used in the following step with further purification.

A solution of dimethyl sulfoxide (0.19 mL, 2.4 mmol) in dichloromethane (15 mL) was treated with trifluoroacetic anhydride (0.26 mL, 1.84 mmol) dropwise at −78 °C. After the reaction was stirred for 10 min, a solution of the crude allylic alcohol (174 mg, 1.02 mmol) in dichloromethane (3 mL) was added via syringe. The resulting mixture was stirred at −78 °C for 50 min, and then triethylamine (0.68 mL, 4.9 mmol) was added dropwise. After the reaction was stirred for 1.5 h at −78 °C, the cooling bath was removed and the mixture allowed to warm for 5 min. Then, the clear solution was poured into a separatory funnel containing a solution of 2 M HCl (8 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum to yield a 10:1 mixture of the (*E*)-enone **2c** and its (*Z*)-isomer. Purification by flash column chromatography (4:1 hexanes/ethyl acetate) afforded the pure (*E*)-enone **2c** (122 mg, 61%) and the pure (*Z*)-isomer (10 mg, 5%).[20]

(*E*)-Isomer (2c). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 6.94 (d, J = 19.3 Hz, 1H), 6.40 (d, J = 19.3 Hz, 1H), 5.68 (m, 1H), 4.82 (m, 2H), 2.22 (s, 3H), 1.58 (d, J = 8.0 Hz, 2H), 0.09 (s, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 198.2, 145.5, 143.6, 133.4, 113.8, 26.1, 22.5, −4.1. IR (neat): 2959, 1678, 1630, 1251, 995, 844 cm^{-1}.

(*Z*)-Isomer. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 6.92 (d, J = 13.9 Hz, 1H), 6.36 (d, J = 13.9 Hz, 1H), 5.76 (m, 1H), 4.82 (m, 2H), 2.24 (s, 3H), 1.66 (d, J = 8.1 Hz, 2H), 0.14 (s, 6H).

4-(Hydroxydimethylsilyl)-6-hepten-2-one (12) and 1,1′-Bis(2-oxo-6-hepten-4-yl)tetramethyldisiloxane (13): Method A. Sodium metal (4 mg, 0.16 mmol) was dissolved in methanol (2 mL) followed by the addition of a solution of the enone **2c** (34 mg, 0.20 mmol) in the same solvent (1 mL). The resulting solution was refluxed for 20 h. After the mixture was cooled to 20 °C, the reaction was quenched by the addition of saturated NH_4Cl (2 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ followed by solvent removal under vacuum to afford the silanol **12** (23 mg, 62%).[20] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 5.75 (m, 1H), 5.05 (m, 2H), 2.74 (bs, 1H), 2.68 (dd, J = 18.4, 6.95 Hz, 1H), 2.61 (dd, J = 18.4, 5.3 Hz, 1H), 2.31 (m, 1H), 2.20 (s, 3H), 1.99 (btd, J = 14.2, 8.9 Hz, 1H), 1.20 (m, 1H), 0.17 (s, 3H), 0.15 (s, 3H).

Method B. The starting enone **2c** (10 mg, 0.059 mmol) was dissolved in DMF (2 mL) and treated with water (5 drops) and potassium fluoride (3 mg, 0.059 mmol). The resulting mixture was stirred for 12 h at 20 °C. Then, the solvent was removed under vacuum and the residue dissolved in dichloromethane (10 mL) and washed with water (2 mL). The aqueous layer was extracted with dichloromethane (2 × 20 mL), and the combined organic phases were dried over $MgSO_4$. The solvent was removed under vacuum to afford the silanol **12** (8 mg, 74%). Purification by flash column chromatography (4:1 hexanes/ethyl acetate) afforded exclusively the dimer **13** (7 mg, 64%).[20] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 5.68 (m, 2H), 4.94 (m, 4H), 2.38 (m, 4H), 2.24 (m, 2H), 2.11 (s, 6H), 1.91 (m, 2H), 1.33 (m, 2H), 0.05 (s, 12H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 208.7, 138.2, 115.5, 42.5, 33.9, 30.1, 21.8, 21.7, −0.5, −0.7. IR (neat): 3074, 2957, 1716, 1637, 1255, 1051, 835, 781 cm^{-1}.

4-Hydroxy-6-hepten-2-one (14). The dimer **13** (18 mg, 0.051 mmol) was dissolved in a 1:1 mixture of methanol and THF (6 mL) and treated with potassium fluoride (23 mg, 0.406 mmol), sodium bicarbonate (42 mg, 0.508 mmol), and 30% H_2O_2 (0.2 mL, 1.01 mmol). The resulting mixture was stirred at 20 °C for 6 h and then refluxed for 2 h. The cloudy mixture was allowed to cool to 20 °C and the reaction quenched by the addition of saturated $Na_2S_2O_3$ (5 mL). After stirring for 30 min, the mixture was poured into a separatory funnel and extracted with ethyl acetate (4 × 30 mL). The combined organic layers were dried under $MgSO_4$, and solvent removal under vacuum yielded a crude oil. Purification by flash column chromatography (2:1 hexanes/ethyl acetate) afforded the alcohol **14** (6 mg, 48%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 5.80 (m, 1H), 5.12 (m, 2H), 4.11 (m, 1H), 2.93 (bs, 1H), 2.63 (dd, J = 17.6, 3.0 Hz, 1H), 2.55 (dd, J = 17.6, 8.9 Hz, 1H), 2.24 (m, 2H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 209.4, 134.0, 117.9, 66.7, 49.0, 40.72, 30.65. IR (neat): 3404, 2922, 1716 cm^{-1}.

(*E*)-4-(Fluorodimethylsilyl)-but-3-en-2-one (16). The enone **2a** (37 mg, 0.184 mmol) was dissolved in dichloromethane (2 mL) and treated with boron trifluoride−acetic acid complex (0.1 mL, 0.725 mmol), and the resulting deep-yellow solution was stirred for 20 h at 20 °C. Then, the dark-red mixture was poured into a separatory funnel containing saturated $NaHCO_3$ (5 mL) and extracted with dichloromethane (3 × 20 mL). The combined (bright-green) organic layers were dried over $MgSO_4$, and solvent removal yielded **16** (23 mg, quantitative) as a brown-green oil. Attempted purification by flash column chromatography afforded the correspondent silanol **17** exclusively.[20] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 6.88 (dd, J = 19.5, 3.8 Hz, 1H), 6.58 (d, J = 19.3 Hz, 1H), 2.30 (s, 3H), 0.37 (d, J = 0.37, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 198.1, 144.4 (d, J = 12.5 Hz), 140.7 (d, J = 67.5 Hz), 26.5, −1.48 (d, J = 60 Hz). ^{19}F NMR ($CDCl_3$, 500 MHz) δ: −163.

Supporting Information Available: Spectra for compounds mentioned and text providing experimental procedures for compounds **3**, **4**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The structure was assigned by high-field proton and carbon NMR. We did not obtain HRMS data due to the instability of this material.