New Substituent Effects of the Trimethylsilyl Group: Photochemistry of 3-Trimethylsilyl-2,5-cyclohexadienones and Preparation of 4-Alkylidenecyclopentenones

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The 4-acetoxymethyl-4-alkyl-3-trimethylsilyl-2,5-cyclohexadien-1-ones **9a**−**g** were prepared from methyl 2-trimethylsilylbenzoate by the Birch reduction−alkylation reaction. Type A photorearrangements of **9a**−**g** were regiospecific to give mixtures of two diastereomers of the corresponding 5-trimethylsilylbicyclo[3.1.0]hex-3-en-2-ones **11a**−**g**. These bicyclohexenones are uniquely photostable; the diastereomers do not photointerconvert nor do they undergo the type B photorearrangement. Bicyclohexenones **11a**−**g** undergo acid-catalyzed protiodesilylative rearrangement to give the 4-alkylidene-2-cyclopenten-1-ones **25a**−**g**. It was of interest to find that the 4-(3′-butenyl)-2,5-cyclohexadienone **9e** photorearranged to the 5-trimethylsilylbicyclo[3.1.0]hex-3-en-2-one **11e** rather than undergoing the intramolecular 2 + 2 photocycloaddition. Furthermore, the 4-acetoxymethyl-3-methoxy-4-methyl-5-trimethylsilyl-2,5-cyclohexadienone **30a** did not show type A photobehavior at 366 and 300 nm, while the 4-(3′-butenyl) analogue **30b** gave the intramolecular 2 + 2 cycloadduct **31b**. The effects of the trimethylsilyl and methoxy substituents on the photochemical reactivity of 2,5-cyclohexadien-1-ones are discussed from the perspective of n → p* vs π → p* character of the triplet states of the dienones.

Intramolecular cycloadditions of reactive intermediates generated from irradiation of 2,5-cyclohexadien-1-ones have provided a wide range of novel carbocyclic and heterocyclic ring systems.[1] For example, it has been shown that the photoexcited state of 2,5-cyclohexadien-1-one **1** can be trapped by 2 + 2 cycloaddition to a tethered olefin to give the tricyclo[5.2.1.0^{5,10}]dec-2-en-4-one **4** (Scheme 1).[2] This process occurs in competition with the type A photorearrangement[3] to the bicyclo[3.1.0]-hex-3-en-2-one **2**; however, by judicious placement of substituents on **1**, the excited state of **1** can be completely diverted to the intramolecular 2 + 2 cycloadduct **4**.[2] Alternatively, it is possible to carry out a two-photon tandem rearrangement of **1** to the oxyallyl zwitterion **3**, from which intramolecular trapping with a tethered furan gives the oxyallyl zwitterion−furan cycloadduct **5**.[4] A variety of other trapping reactions have been uncovered.[1,5,6]

Substituents at C(3) of the 2,5-cyclohexadien-1-one **1** exert profound effects on the reactivity of the photoexcited state [1]* and intermediates formed by photorearrangement of [1]*. The 3-methoxy substituent has been studied in greatest detail;[3−7] the focus of the photochemical study reported in this paper, 3-trimethylsilyl substitution, has previously been examined in a single substrate, 4-carbomethoxy-4-methyl-3-trimethylsilyl-2,5-cyclohexadien-1-one (**16**).[8] Although the earlier study revealed unique potential for the 3-trimethylsilyl substituent, it appeared that the 4-carbomethoxy group was responsible for the formation of multicomponent product mixtures and, in any event, would not be compatible with anticipated intramolecular oxyallyl zwitterion cycloadditions because of the migratory aptitude of the carbomethoxy group.[4] Consequently, it was necessary to consider modifications of the substitution at C(4) to possibly control product distributions associated with the photochemistry of the 3-trimethylsilyl-2,5-cyclohexadien-1-ones. The 4-acetoxymethyl substituent is compatible with the type A photorearrangement and the intramolecular 2 + 2 photocycloaddition of 2,5-cyclohexadienones.[1] Intramolecular trapping reactions of the oxyallyl zwitterion **3** with the acetoxymethyl substituent at the quaternary center have been found to occur with high chemical efficiency.[1] We now describe the preparation and photochemistry of the 4-acetoxymethyl-4-alkyl-3-trimethylsilyl-2,5-cyclohexadien-1-ones **9a**−**g**.

* Corresponding author.
† Deceased January 20, 2000.

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(4) Schultz, A. G.; Reilly, J. *J. Am. Chem. Soc.* **1992**, *114*, 5068−5073.
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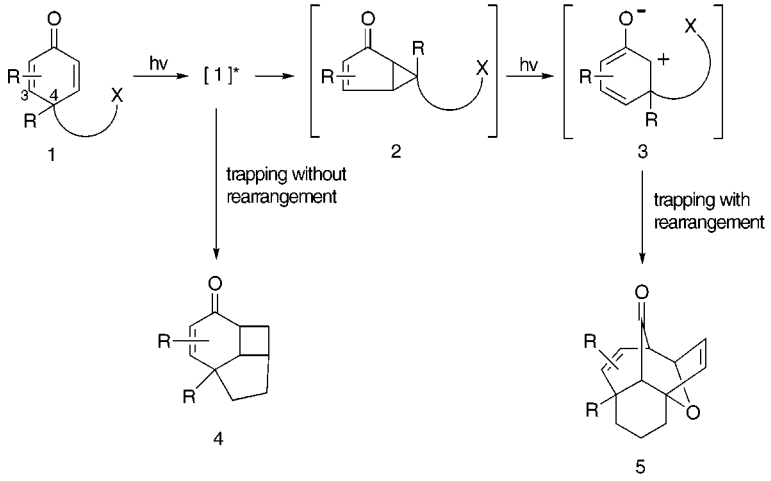
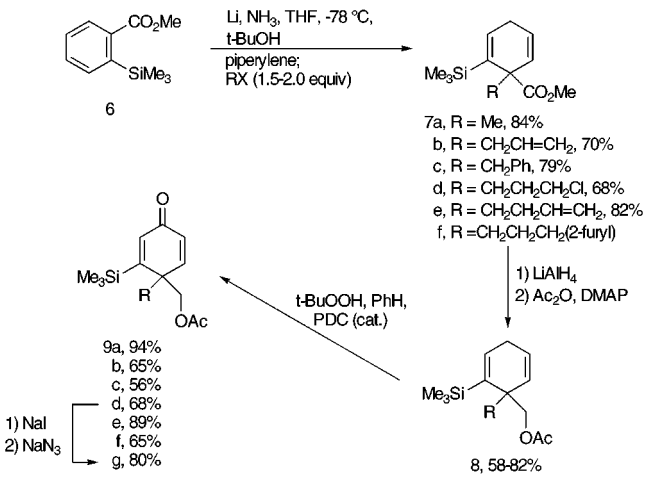
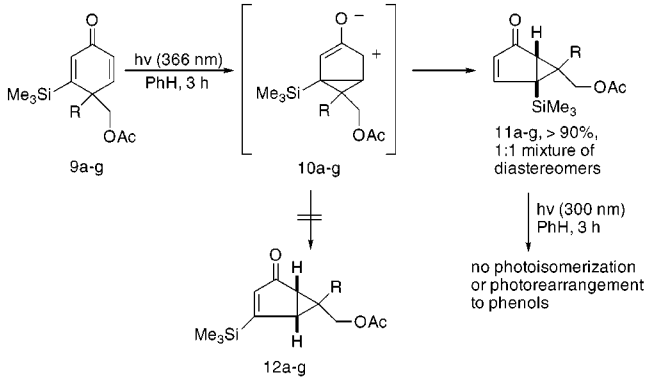
Scheme 1



Scheme 2



Scheme 3



Results and Discussion

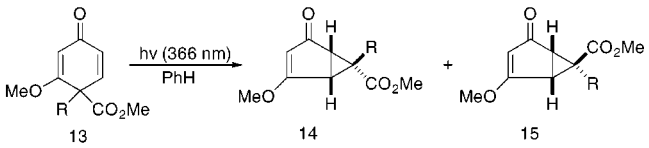
Cyclohexadienones **9a**−**g** were prepared from methyl 2-(trimethylsilyl)benzoate **6**[8] by standard procedures as shown in Scheme 2. As demonstrated by the conversions of **6** to **7a**−**f**, the Birch reduction−alkylations of **6** were carried out in good to excellent yields with a wide range of alkyl halides. The bis-allylic oxidations of **8a**−**f** to give cyclohexadienones **9a**−**f** were performed with generally high efficiency, although yields were in the 50−70% range for the allylic, benzylic, and 2-furylpropyl derivatives; however, the 4-(3′-butenyl)-2,5-cyclohexadienone was obtained in 89% yield. The 4-azidopropyl-2,5-cyclohexadien-1-one **9g** was prepared from chloride **9d** by substitution of the intermediate iodide with NaN_3.

Type A Photorearrangements of 4-Acetoxymethyl-4-alkyl-3-trimethylsilyl-2,5-cyclohexadien-1-ones. The photochemistry of 2,5-cyclohexadien-1-ones **9a**−**g** in degassed benzene solution is outlined in Scheme 3. In contrast to the photochemistry of the 4-carbomethoxy analogue, which gave a complicated mixture of products under similar conditions,[8] irradiation of **9a**−**g** through uranyl glass provided mixtures of two diastereomers of the corresponding 5-trimethylsilylbicyclo[3.1.0]-hex-3-en-2-ones **11a**−**g**. These bicyclohexenones were stable to neutral conditions (bicyclohexenones **11a** and **11f** were recovered unchanged from refluxing benzene) but underwent protiodesilylative rearrangement to 4-alkylidene-2-cyclopenten-1-ones **25a**−**g** during attempted chromatographic separation of diastereomers. Inspection of product mixtures immediately after photolysis by ^1H NMR spectroscopy indicated that bicyclohexenones had formed in yields >90%. There was no evidence for formation of the regioisomeric 4-trimethylsilylbicyclohexenones **12a**−**g** during irradiations of **9a**−**g** at 366 nm or during irradiations of **11a**−**g** through Pyrex glass (>300 nm).

Irradiation of the ∼1:1 mixtures of **11a**−**g** at 300 nm did not result in an observable change in the diastereomer ratio. Other workers have found that 6,6-diaryl- and 6,6-dialkyl-substituted bicyclohexenone epimers do not photointerconvert under a variety of photochemical conditions.[9] However, 6-alkyl-6-carbomethoxy-4-methoxybicyclohexenones **14** and **15**, initially obtained from photolyses of 4-alkyl-4-carbomethoxy-3-methoxycyclohexadienones **13** at 366 nm as ∼1:1 mixtures, were found to undergo photoequilibration to ∼9:1 mixtures favoring the *endo*-carbomethoxy epimer **14**.[10] An investigation of the mechanism of photoequilibration for one case (R = Me) revealed that **14** and **15** interconverted by reversible cleavage of the cyclopropane bonds exocyclic to the cyclopentenone ring. Photointerconversions of bicyclohexenone epimers appear to be associated with the presence of electron-withdrawing substituents at C(6), the carbomethoxy group in **14** and **15**, and the cyano substituent in an analogous series.[4,10]

There are several unique features of the photochemistry outlined in Scheme 3. It is obvious that there is a complete shift in regiocontrol for the type A photorearrangement of **9a**−**g** to give **11a**−**g** compared to that for the conversion of **13** to **14** and **15** (Scheme 4); however,

Scheme 4



the regiospecificity for formation of the 5-substituted bicyclohexenones **11a**−**g** is a result of not only a change from the methoxy to a trimethylsilyl group, but also a change from a carbomethoxy to an acetoxymethyl substituent. The second substituent effect is revealed by comparing the photochemistry shown in Scheme 3 with that shown in Scheme 5. Notably, the 4-carbomethoxy-4-methyl-3-trimethylsilyl-2,5-cyclohexadien-1-one (**16**) has been found to photorearrange to 4-trimethylsilylbicyclohexenone **17** and 5-trimethylsilylbicyclohexenone **18**. Both **17** and **18** undergo the type B photorearrangement[11] at 366 nm to give the intermediate oxyallyl zwitterions **19** and **20**, from which 1,2-carbomethoxy group migrations give phenols **21**−**23**.[8]

Thus, the type A photorearrangements of 3-trimethylsilyl-2,5-cyclohexadienones **9a**−**g** are not only regiospecific, but the photoproducts, bicyclohexenones **11a**−**g**, also are uniquely photostable at 366 nm and even 300 nm. These observations have important synthetic consequences; however, there is a mechanistic question to consider: are reversible type B photorearrangements of **11** and even **12** to zwitterions corresponding to **19** and **20** (Scheme 5) occurring under the photolysis conditions shown in Scheme 2? This possibility must be considered in light of the reversible type B oxyallyl zwitterion formation discovered during an investigation of the photochemistry of 4-methoxy- and 5-methoxybicyclo-[3.1.0]hex-3-en-2-ones.[4] Reversible type B zwitterion formation was demonstrated in the previous study[4] by inter- and intramolecular trapping reactions of the zwitterions. The absence of any trapping products from the irradiation of the 4-[3′-(2-furyl)propyl]-2,5-cyclohexadienone **9f** or the corresponding 3′-azidopropyl derivative **9g**[12] or from photolysis of **9a** in the presence of furan suggests that two reversible type B zwitterion formation does not occur on photoexcitation possibilities of bicyclohexenones **11a**−**g** or that the lifetime of the intermediate zwitterions is not sufficiently long for the standard trapping processes to take place.

The apparent absence of a pathway for interconversion of 5-trimethylsilylbicyclohexenones **11a**−**g** with the 4-trimethylsilyl isomers **12a**−**g** suggests that bicyclohexenones **11a**−**g** are formed as kinetic products in the type A photorearrangements of 2,5-cyclohexadienones **9a**−**g**. Unlike the 6-carbomethoxy-substituted bicyclohexenones **14** and **15** and analogues,[4] there is no evidence for reversible photocleavage of the C(1)−C(6) bond in **11a**−**g**. This means that there is a kinetic preference for the thermal 1,4-sigmatropic rearrangement of the least substituted cyclopropane bond in the intermediate oxyallyl zwitterion **10**. This interesting effect of silicon appears to be related to the rate retardation of a silyl group compared to hydrogen in the thermal vinylcyclopropane to cyclopentene rearrangement.[13] The rate retardation presumably is a result of the electropositive character of silicon.

Acid-Catalyzed Rearrangements of 5-Trimethylsilylbicyclo[3.1.0]hex-3-en-2-ones to 4-Alkylidene-2-cyclopenten-1-ones. As already noted, attempted isolation of bicyclohexenones **11a**−**g** by chromatographic methods resulted in protiodesilylative rearrangement to 4-alkylidene-2-cyclopenten-1-ones **25a**−**g** as ∼1:1 mixtures of *E*- and *Z*-isomers. 4-Alkylidene-2-cyclopenten-1-ones have been prepared by Friedel−Crafts type cyclizations,[14] by $Rh(CO)_2Cl_2$-catalyzed cyclization of 3,4-diacetoxy-1,5-diynes,[15] and by the metal-catalyzed coupling of allenes and alkynes in the presence of CO.[16,17] Because these dienones have become rather valuable intermediates in organic synthesis, we decided to develop a more convenient conversion of 3-trimethylsilyl-2,5-cyclohexadienones **9a**−**g** to 4-alkylidene-2-cyclopenten-1-ones **25a**−**g** (Scheme 6).

Irradiation of **9a**−**f** in the presence of CF_3CO_2H provided **25a**−**f** as ∼1:1 mixtures of *E*- and *Z*-isomers in yields ranging from 73 to 94%. The direct procedure for the photorearrangement of the 3′-azidopropyl derivative **9g** gave **25g** in only 30% yield; in this case it was better to perform the conversion **9g** → **11g** → **25g** in a stepwise manner to give **25g** in 70% yield. The acid-catalyzed conversions of **11a**−**g** to **25a**−**g** are explained by protonation of the ketone carbonyl group in **11** followed by cleavage of the C(1)−C(6) bond to give carbocation **24**. Selective cleavage of the C(1)−C(6) bond in **11** is a result of carbocation stabilization by the β effect of silicon.[18] Loss of the trimethylsilyl group and enolization results in formation of **25**.

4-Alkylidene-2-cyclopenten-1-ones **25a**−**g** possess a dense array of functional groups that should display useful chemical reactivity. In attempts to alter the *E*:*Z*-isomer ratio, solutions of **25a** in benzene were irradiated (366 nm) in the absence or presence of Michler's ketone, but no change in isomer distribution was observed. The 1:1 ratio of isomers may represent the photostationary state for **25a** in analogy with that previously observed for a derivative of **25a**.[8] A productive process under current development is illustrated by the Baeyer−Villiger oxidation of **25a** to give the valerolactone derivative **26** (Scheme 7). Preferential migration of the vinyl group in

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(17) 4-Alkylidene-2-cyclopenten-1-ones also have been obtained as reaction byproducts; for example, see: (a) Ackroyd, J.; Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1985**, *68*, 338−344. (b) Wolff, S.; Agosta, W. *J. Org. Chem.* **1981**, *46*, 4821−4825. (c) Rizzo, C. J.; Dunlap, N. K.; Smith, A. B. *J. Org. Chem.* **1987**, *52*, 5280−5283.

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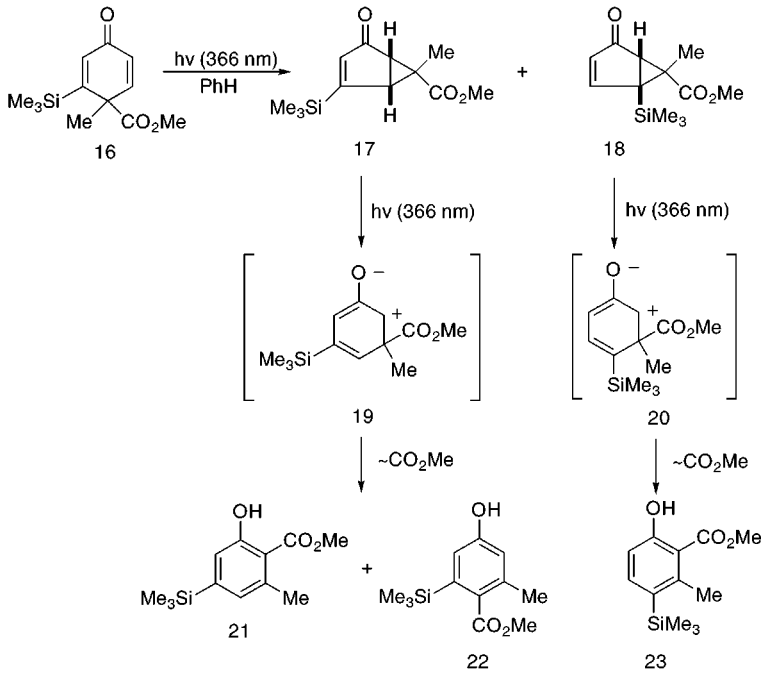
Scheme 5



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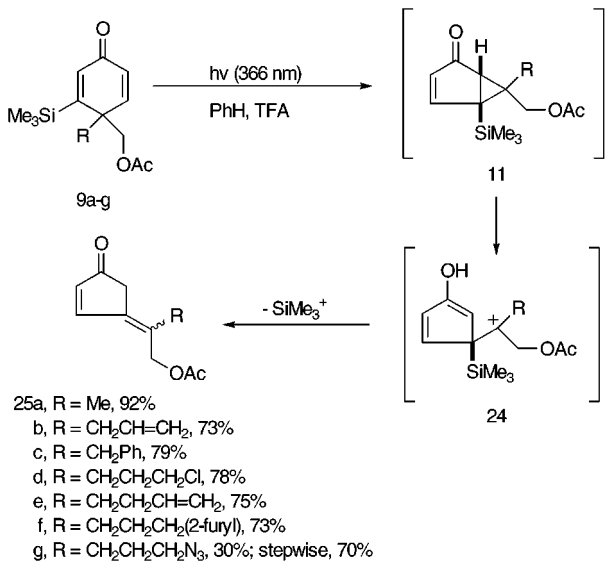
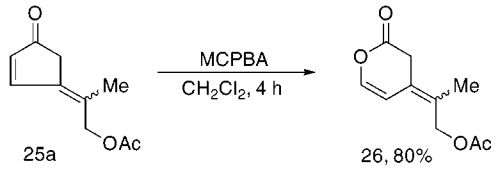


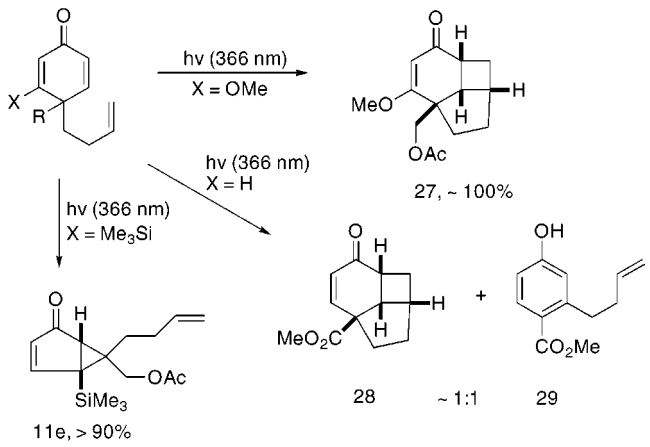
Scheme 7



α,β-unsaturated primary alkyl ketones is well-known;[19] however, it is noteworthy that the Baeyer−Villiger oxidation occurs without competing epoxidation of the tetrasubstituted double bond in both **25a** and **26**.[20]

Intramolecular 2 + 2-Cycloadditions of 4-(3′-Butenyl)-2,5-cyclohexadienones. The effect of the 3-trimethylsilyl substituent on the intramolecular 2 + 2 cycloaddition reaction of 4-(3′-butenyl)-2,5-cyclohexadienones also has been examined (Scheme 8). Remarkably, **9e** was found to undergo only the type A photorearrangement to bicyclohexenone **11e**. This result should be contrasted to the corresponding 3-methoxy analogue which gives the photocycloaddition product **27** in essentially quantitative yield.[2] The unsubstituted derivative gave both the cycloadduct **28** and phenol **29** (the product of consecutive type A and type B photorearrangements) in approximately equivalent amounts.

Scheme 8



The n → π* triplet state is generally considered to be responsible for type A photobehavior,[21] and we have suggested that the effect of the 3-methoxy substituent is to lower the energy of the π → p* triplet state to make triplet-state photocycloadditions more competitive with the type A photorearrangement.[2] Upon comparing the photoreactivity of **9e** with that of the unsubstituted analogue and the 3-methoxy variant (Scheme 8), it appears it is reasonable that the 3-trimethylsilyl group serves to enhance the n → p* reactivity of the 2,5-cyclohexadien-1-one ring system.

(19) (a) Bocecken, M.; Jacobs, R. *Recl. Trav. Chim*. **1936**, *55*, 804−814. (b) Krafft, G. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc*. **1981**, *103*, 5459−5466.

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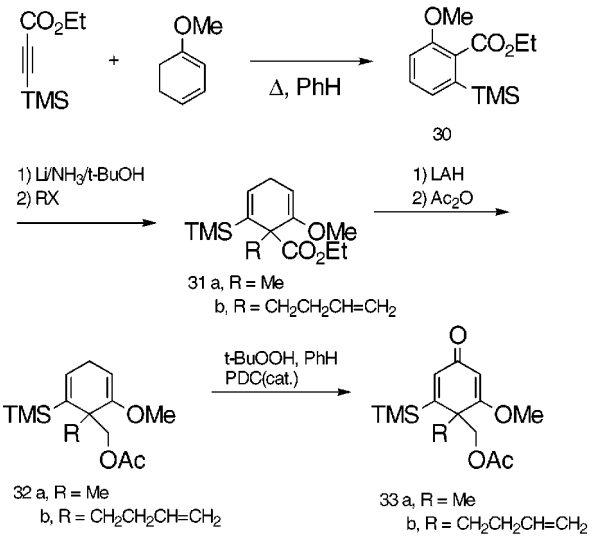
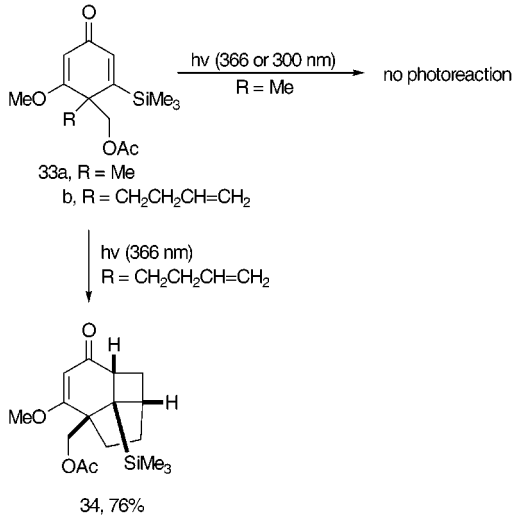
Scheme 9



Scheme 10



The ability of the trimethylsilyl substituent to promote type A photoreactivity can be completely nullified by installation of a methoxy substituent on the second dienone double bond (Scheme 9). The method of Kleschick and Thornburgh provided ethyl benzoate **30** in 75% yield.[24] In an unoptimized series of steps the previously detailed sequence was followed to provide cyclohexadienones **33**. Thus, the 4-acetoxymethyl-3-methoxy-5-trimethylsilyl-2,5-cyclohexadienone **33a** is photostable for extended periods of time at both 366 and 300 nm, but the 4-(3′-butenyl) analogue **33b** undergoes efficient intramolecular 2 + 2 photocycloaddition to give **34** (Scheme 10).

Conclusion

The trimethylsilyl group has been found to be a very effective agent of control of the photochemistry of 2,5-cyclohexadienones. Although it has not been possible to realize the tandem type A−type B photorearrangements to give oxyallyl zwitterions **3** from **9f** and **9g**, several other synthetically useful processes have evolved from a careful study of the preparation and photochemistry of the 3-trimethylsilyl-2,5-cyclohexadien-1-ones **9a**−**g**. Noteworthy discoveries include (1) the high chemical efficiencies for the Birch reduction−alkylations of methyl 2-trimethylsilyl benzoate **6**;[22] (2) the regiospecificity and high chemical efficiencies for the type A photorearrangements of the 3-trimethylsilyl-2,5-cyclohexadienones **9a**−**g** to give the 5-trimethylsilylbicyclo[3.1.0]hex-3-en-2-ones **11a**−**g**; (3) the photostability of the bicyclohexenones **11a**−**g**, especially when compared to the photoreactivity of bicyclohexenones **17** and **18** obtained from type A photorearrangements of the 4-carbomethoxy analogue **16**; (4) the generality and high chemical efficiencies for the acid-catalyzed rearrangements of 5-trimethylsilylbicyclo[3.1.0]-hex-3-en-2-ones to 4-alkylidene-2-cyclopenten-1-ones **25a**−**g**; and (5) the effect of the 3-trimethylsilyl substituent on the intramolecular 2 + 2 photocycloadditions of 4-(3′-butenyl)-2,5-cyclohexadienones.

Experimental Section

General Procedures. Tetrahydrofuran and diethyl ether were distilled from benzophenone sodium ketyl under nitrogen. Benzene was distilled from CaH_2. Analytical thin-layer chromatography was performed on 0.25 mm E. Merck silica gel (60F-254) plates using UV light and aqueous $KMnO_4/K_2CO_3$ for visualization. Flash column chromatography was carried out on Baker silica gel (40 μm). Low-resolution mass spectra were obtained by GC−MS using isobutane for chemical ionization. High-resolution mass spectra were obtained from the mass spectrometry laboratory at the University of Illinois at Urbana/Champaign. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. The light source for all photochemistry was a Hanovia 450-W medium-pressure mercury arc lamp. The lamp was placed in a water-cooled Pyrex immersion well and when necessary fitted with a uranyl glass filter to give light with wavelength mainly at 366 nm.

Birch Reduction and Alkylation of Methyl-2-trimethylsilylbenzoate (6) and Ethyl-2-methoxy-6-trimethylsilylbenzoate (30).[22] To a flame-dried three-necked flask under argon was added **6** dissolved in 10−15 mL of THF and 1.0 equiv of *t*-BuOH. The solution was cooled to −78 °C and 100 mL of twice distilled NH_3 was added. Small pieces of lithium wire (2.5−3.0 equiv) were added until the deep blue coloration persisted for 30 min. Excess metal was quenched with piperylene to give a dark orange solution, the appropriate alkylation agent (1.5−2.0 equiv) was added, and the resulting yellow solution was stirred for 1 h at −78 °C before quenching with 1−2 g of solid NH_4Cl. The solution was warmed slowly to room temperature while the NH_3 was evaporated under a stream of argon. The thick mixture was diluted with H_2O and Et_2O, the phases were separated, and the organic phase was twice extracted with Et_2O. The organic phases were combined, washed with saturated $NaHCO_3$ and saturated NaCl, and dried over $MgSO_4$. Filtration, removal of solvent in vacuo, and flash chromatography on silica gel with 5% EtOAc in hexane gave the 1,4-cyclohexadiene.[23] See ref 8 for the preparation and characterization of **7a**.

6-Carbomethoxy-6-allyl-1-(trimethylsilyl)-1,4-cyclohexadiene (7b) was prepared from **6** (1.1 g, 5.3 mmol) and allyl bromide; colorless oil (940 mg, 70%); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.13 (s, 1 H), 5.69 (m, 2 H), 5.55 (d, 1 H, J = 11 Hz), 5.06 (d, 1 H, J = 9.9 Hz), 5.04 (s, 1 H), 3.32 (s, 3 H), 2.82 (m, 2 H), 2.37 (m, 2 H), 0.17 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 175.30, 138.24, 137.36, 135.09, 129.28, 125.63, 117.88, 51.92, 51.28, 42.67, 27.85, 0.91; IR (film) 2951, 1730 cm^{-1}.

6-Carbomethoxy-6-benzyl-1-(trimethylsilyl)-1,4-cyclohexadiene (7c) was prepared from **6** (548 mg, 2.1 mmol) and

(22) The asymmetric Birch reduction−alkylations of a chiral 2-trimethylsilylbenzamide also have been reported; see: (a) Schultz, A. G.; Pettus, L. *J. Org. Chem.* **1997**, *62*, 6855−6861. (b) Schultz, A. G.; Pettus, L. *Tetrahedron Lett.* **1997**, *38*, 5433−5436.

(23) Hauser, C. R.; Hance, C. R. *J. Am. Chem. Soc.* **1951**, *73*, 5846−5848.

(24) Kleschick, W. A. and Thornburgh, S. *Synth. Commun.* **1997**, *27*, 1793−1799.

benzyl bromide; colorless oil (500 mg, 79%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 (m, 3 H), 7.16 (m, 2 H), 6.24 (s, 1 H), 5.82 (d, 1 H, J = 6.6 Hz), 5.65 (d, 1 H, J = 6.6 Hz), 3.78 (s, 3 H), 3.30 (d, 1 H, J = 6.6 Hz), 3.02 (d, 1 H, J = 6.6 Hz), 2.48 (d, 1 H, J = 11.5 Hz), 1.86 (d, 1 H, J = 11.5 Hz), 0.24 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.81, 138.33, 137.71, 137.42, 131.50, 128.39, 127.36, 126.19,126.12, 52.38, 52.28, 43.66, 27.26, 0.73; IR (film) 2952, 1731 cm^{-1}; CIMS *m*/*z* (relative intensity) 301 (M^+ + 1, 100%), 193 (68.7).

6-Carbomethoxy-6-(3′-chloropropyl)-1-(trimethylsilyl)-1,4-cyclohexadiene (7d) was prepared from **6** (1.24 g, 6 mmol) and 3-chloro-1-iodopropane; a colorless oil (1.40 g, 68%); ^{1}H NMR (C_6D_6, 500 MHz) δ 6.09 (s, 1 H), 5.62 (d, 1 H, J = 6.4 Hz), 5.39 (d, 1 H, J = 6.4 Hz), 3.31 (s, 3 H), 3.17 (m, 2 H), 2.41 (d, 1 H, J = 4.2 Hz), 2.33 (d, 1 H, J = 4.2 Hz), 1.98 (m, 2 H), 1.48 (m, 2 H), 0.15 (s, 9 H); ^{13}C NMR (C_6D_6, 125 MHz) δ 175.35, 137.95, 137.47, 129.03,126.11, 51.95, 51.05, 45.58, 44.95, 35.92, 35.32, 28.60, 27.73, 0.79; IR (film) 2955, 1735 cm^{-1}; CIMS *m*/*z* (relative intensity) 287 (M^+ + 1, 36), 271 (83), 179 (100).

6-Carbomethoxy-6-(3′-butenyl)-1-(trimethylsilyl)-1,4-cyclohexadiene (7e) was prepared from **6** (1.16 g, 5.6 mmol) and 4-bromo-1-butene; a colorless oil (1.2 g, 82%); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.14 (s, 1 H), 5.83 (m, 1 H), 5.66 (d, 1 H, J = 10.2 Hz), 5.45 (d, 1 H, J = 10.8 Hz), 5.60 (d, 1 H, J = 17 Hz), 4.96 (d, 1 H, J = 10.2), 3.32 (s, 3 H), 2.42 (d, 1 H, J = 5.4 Hz), 2.36 (d, 1 H, J = 5.4 Hz), 2.03 (m, 4 H), 0.15 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 175.46, 139.18, 138.05, 137.40, 129.22, 125.94, 114.94, 51.94, 51.43, 36.96, 29.68, 27.85, 0.829; IR (film) 2954, 1735 cm^{-1}.

6-Carbomethoxy-6-(3′-(2′-furanylpropyl))-1-(trimethylsilyl)-1,4-cyclohexadiene (7f) was prepared from **6** and 1-iodo-3-(2-furanyl)propane; flash chromatography gave a mixture of **7e** and alkylation agent that was carried to the next step.

6-Carbomethoxy-6-methyl-1-methoxy-4-trimethylsilyl-1,4-cyclohexadiene 31a was prepared from **30** (675 mg, 2.8 mmol) and iodomethane, a yellow oil that was carried to the next step.

6-Carbomethoxy-6-(3′-butenyl)-1-methoxy-4-trimethylsilyl-1,4-cyclohexadiene 31b was prepared from **30** (540 mg, 2.3 mmol) and 4-bromo-1-butene, a yellow oil that was carried to the next step.

Reduction of 7a−f and 31a−b and Acylation. To a 0.5 M solution of **7** in Et_2O at 0 °C was added 1.5 equiv of lithium aluminum hydride (1 M in Et_2O). After 30 min at 0 °C, the reaction was quenched with 1.5 equiv of H_2O, 1.5 equiv of 15% NaOH, and 3 equiv of H_2O. The mixture was filtered through Celite, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The resulting oil was redissolved in pyridine to give a 1 M solution. Then, 2 equiv of Ac_2O and 1 mg of DMAP were added and stirring at room temperature was continued for 4−6 h. The reaction mixture was diluted with H_2O and extracted three times with Et_2O. The organic phases were combined and washed successively with 5% HCl, H_2O, and saturated $NaHCO_3$. The solution was dried with $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography of the resulting oil on silica gel with 10% Et_2O in hexane gave **8**.

6-Acetoxymethyl-6-methyl-1-(trimethylsilyl)-1,4-cyclohexadiene (8a) was prepared from **7a** (5.37 g, 24 mmol); a colorless oil (4.7 g, 82%); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.13 (s, 1 H), 5.65 (d, 1 H, J = 7.5 Hz), 5.52 (d, 1 H, J = 7.5 Hz), 4.08 (d, 1 H, J = 12.1 Hz), 4.02 (d, 1 H, J = 12.1 Hz), 2.41 (s, 2 H), 1.68 (s, 3 H), 1.08 (s, 3 H), 0.165 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 170.65, 141.78, 137.68, 134.33, 124.02, 71.75, 40.67, 28.26, 25.97, 20.90, 1.73; IR (film) 2957, 1743 cm^{-1}; CIMS *m*/*z* (relative intensity) 237 (M^+ + 1, 2.5), 179 (36), 105 (100).

6-Acetoxymethyl-6-allyl-1-(trimethylsilyl)-1,4-cyclohexadiene (8b) was prepared from **7b** (700 mg, 3.3 mmol); a colorless oil (497 mg, 73%); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.15 (s, 1 H), 5.71 (m, 2 H), 5.40 (d, 1 H), 4.97 (s, 1 H), 4.92 (d, 1 H), 4.12 (d, 1 H, J = 11.0), 4.01 (d, 1 H, J = 11.0 Hz), 2.34 (m, 2 H), 2.25 (m, 1 H), 2.03 (m, 1 H), 1.65 (s, 3 H), 0.137 (s, 9 H); IR (film) 2953, 1741 cm^{-1}; CIMS *m*/*z* (relative intensity) 265 (1.5), 205 (39), 131 (100).

6-Acetoxymethyl-6-benzyl-1-(trimethylsilyl)-1,4-cyclohexadiene (8c) was prepared from **7c** (1.6 g, 5.3 mmol); a colorless oil (1.2 g, 72%); ^{1}H NMR (C_6D_6, 300 MHz) δ 7.03 (m, 5 H), 6.06 (s, 1 H), 5.58 (d, 1 H, J = 11.5 Hz), 5.46 (d, 1 H, J = 11.5 Hz), 4.27 (d, 1 H, J = 9.2 Hz), 4.16 (d, 1 H, J = 9.2 Hz), 2.63 (q, 2 H, J = 6 Hz), 2.15 (d, 1 H, J = 15 Hz), 1.76 (d, 1 H, J = 15 Hz), 1.64 (s, 3 H), 0.19 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 170.59, 140.35, 139.67, 138.04, 135.34, 131.68, 127.88, 126.59, 125.96, 71.40, 66.94, 44.15, 28.22, 20.90, 1.90; IR (film) 2953, 1737 cm^{-1}.

6-Acetoxymethyl-6-(3′-chloropropyl)-1-(trimethylsilyl)-1,4-cyclohexadiene (8d) was prepared from **7d** (1.40 g, 5.0 mmol); a colorless oil (910 mg, 60%); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.14 (s, 1 H), 5.66 (d, 1 H, J = 10.2 Hz), 5.25 (d, 1 H, J = 10.2 Hz), 4.10 (d, 1 H, J = 10.8 Hz), 3.94 (d, 1 H, J = 10.8 Hz), 3.12 (m, 2 H), 2.30 (q, 2 H, J = 3.6 Hz), 1.67 (s, 3 H), 1.49 (m, 3 H), 1.14 (m, 1 H), 0.14 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 170.63, 143.24, 139.28, 132.03, 125.55, 71.70, 45.75, 44.31, 34.87, 28.72, 28.31, 20.89, 1.72; IR (film) 2953, 1738 cm^{-1}; CIMS *m*/*z* (relative intensity) 241 (M^+ + 1, 30), 207 (22), 167 (49), 133 (100).

6-Acetoxymethyl-6-(3′-butenyl)-1-(trimethylsilyl)-1,4-cyclohexadiene (8e) was prepared from **7e** (630 mg, 2.4 mmol); a colorless oil (380 mg, 58%); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.19 (s, 1 H), 5.76 (m, 2 H), 5.34 (d, 1 H, J = 10.2 Hz), 5.03 (d, 1 H, J = 17.1 Hz), 4.96 (d, 1 H, J = 8.7 Hz), 4.08 (q, 2 H, J = 10.8), 2.37 (m, 2 H), 1.96 (m, 2 H), 1.67 (s, 3 H), 1.58 (m, 1 H), 1.32 (m, 1 H), 0.16 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 170.49, 139.75, 139.34, 132.26, 125.38, 114.74, 71.84, 44.66, 36.54, 29.89, 28.39, 20.89, 1.75; IR (film) 2953, 1744 cm^{-1}; CIMS *m*/*z* (relative intensity) 277 (M^+ + 1, 6) 233 (100).

6-Acetoxymethyl-6-(3′-(2′-furanyl)propyl)-1-(trimethylsilyl)-1,4-cyclohexadiene (8f) was prepared from **7f** (540 mg, 1.8 mmol), a light yellow oil that was carried to the next step.

6-Acetoxymethyl-6-methyl-1-methoxy-4-trimethylsilyl-1,4-cyclohexadiene (32a) was prepared from crude **31a** (650 mg, 2.4 mmol), a light yellow oil that was carried to the next step.

6-Acetoxymethyl-6-(3′-butenyl)-1-methoxy-4-trimethylsilyl-1,4-cyclohexadiene (32b) was prepared from crude **31b** (580 mg, 2.1 mmol), a light yellow oil that was carried to the next step.

Oxidation of 8a−f and 32a−b. A 0.2 M solution of **8** or **32** in benzene was cooled to 0 °C, addition of 1 equiv by weight of Celite, 0.2 equiv of pyridinium dichromate, and 3 equiv of *tert*-butyl hydrogen peroxide in decane was followed by stirring at room temperature for 8−12 h. Filtering through Celite with EtOAc followed by concentration gave the crude oil. Flash chromatography on silica gel with 30% EtOAc in hexane yields **9**.

4-Acetoxymethyl-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one 9a was prepared from **8a** (3.15 g, 13.2 mmol) to give a yellow oil (2.8 g, 94%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.83 (d, 1 H, J = 10.3 Hz), 6.58 (s, 1 H), 6.25 (d, 1 H, J = 10.3 Hz), 4.18 (q, 2 H, J = 11 Hz), 1.93 (s, 3 H), 1.27 (s, 3 H), 0.24 (s, 9 H), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.35, 170.71, 166.96, 156.80, 142.02, 139.08, 128.78, 68.47, 45.45, 22.24, 20.78, 0.53; IR (film) 2957, 1747, 1664 cm^{-1}; CIMS *m*/*z* (relative intensity) 253 (M^+ + 1, 25.45), 193 (100). Anal. Calcd for $C_{13}H_{20}O_3Si$: C, 61.83; H, 8.01. Found: C, 61.85; H, 7.88.

4-Acetoxymethyl-4-allyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one 9b was prepared from **8b** (497 mg, 1.8 mmol) to give a yellow oil (330 mg, 65%): ^{1}H NMR (C_6D_6, 300 MHz) δ 6.84 (d, 1 H, J = 1.8 Hz), 6.36 (dd, 1 H, J = 1.8 Hz, J = 10.2 Hz), 6.12 (d, 1 H), 5.53 (m, 1 H), 4.92 (m, 2 H), 3.92 (q, 2 H, J = 11.1 Hz), 1.53 (m, 3 H), 1.51 (s, 3 H), 1.18 (m, 1 H), 0.01 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 183.67, 170.15, 163.77, 154.46, 142.11, 137.83, 131.23, 115.50, 68.68, 49.78, 34.01, 20.44, 0.57; IR (film) 2956, 1746, 1663 cm^{-1}; CIMS *m*/*z* (relative intensity) 279 (M^+ + 1, 3.6), 219 (100). Anal. Calcd for $C_{15}H_{22}O_3Si$: C, 64.70; H, 7.99. Found: C, 64.85; H, 7.82.

4-Acetoxymethyl-4-benzyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one 9c was prepared from **8c** (1.2 g, 3.8 mmol) to give a yellow oil (700 mg, 56%): ^{1}H NMR (C_6D_6, 300 MHz)

δ 7.03 (m, 3 H), 6.81 (m, 2 H), 6.76 (d, 1 H, J = 1.8 Hz), 6.37 (d, 1 H, 10.2 Hz), 6.26 (dd, 1 H, J = 1.8 Hz, J = 10.2 Hz), 4.15 (q, 2 H, J = 11.1 Hz), 2.63 (q, 2 H, J = 5.4 Hz), 1.53 (s, 3 H) 0.01 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 183.35, 170.23, 164.65, 154.04, 141.40, 135.82, 130.72, 130.66, 128.07, 127.63, 68.32, 50.05, 42.33, 20.51, 0.95; IR (film) 2956, 1744, 1662 cm^{-1}; CIMS *m*/*z* (relative intensity) 328 ($M^+ + 1$, 41), 269 (100), 179 (41). Anal. Calcd for $C_{19}H_{24}O_3Si$: C, 69.51; H, 7.39. Found: C, 69.35; H, 7.48.

4-Acetoxymethyl-4-(3′-chloropropyl)-3-(trimethylsilyl)-2,5-cyclohexadien-1-one 9d was prepared from **8d** (910 mg, 3.0 mmol) to give a yellow oil (630 mg, 68%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.79 (d, 1 H, J = 10.2 Hz), 6.69 (s, 1 H), 6.37 (d, 1 H, J = 10.2 Hz), 4.36 (d, 1 H, J = 11 Hz), 4.13 (d, 1 H, J = 11 Hz), 3.46 (m, 2 H), 2.00 (m, 1 H), 1.96 (s, 3 H), 1.74 (m, 1 H), 1.47 (m, 2 H), 0.27 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.12, 170.45, 165.34, 154.95, 140.92, 130.53, 68.12, 49.16, 44.58, 31.78, 26.94, 20.55, 0.32; IR (film) 2957, 1745, 1662 cm^{-1}. Anal. Calcd for $C_{15}H_{23}O_3ClSi$: C, 57.26; H, 7.39. Found: C, 57.15; H, 7.23.

4-Acetoxymethyl-4-(3′-butenyl)-3-(trimethylsilyl)-2,5-cyclohexadien-1-one 9e was prepared from **8e** (230 mg, 0.84 mmol) to give a yellow oil (220 mg, 89%): ^{1}H NMR (C_6D_6, 300 MHz) δ 6.85 (s, 1 H), 6.36 (dd, 1 H, J = 2.1 Hz, J = 9.9 Hz), 6.12 (dd, 1 H, J = 2.1 Hz, J = 9.9 Hz), 5.54 (m, 1 H), 4.89 (m, 2 H), 3.96 (q, 2 H, J = 10.8 Hz), 1.58 (m, 3 H), 1.52 (s, 3 H), 1.20 (m, 1 H), 0.01 (s, 9 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 183.65, 170.15, 163.76, 154.45, 142.13, 137.82, 131.23, 115.49, 68.68, 49.78, 34.01, 28.81, 20.44, 0.57; CIMS *m*/*z* (relative intensity) 319 ($M^+ + 1$, 14.63), 193 (100). Anal. Calcd for $C_{16}H_{24}O_3Si$: C, 65.75; H, 8.30. Found: C, 65.86; H, 8.33.

4-Acetoxymethyl-4-(3′-(2′-furanylpropyl))-3-(trimethylsilyl)-2,5-cyclohexadien-1-one 9f was prepared from **8f** (1.03 g, 3.1 mmol) to give a yellow oil (650 mg, 65%): ^{1}H NMR (C_6D_6, 500 MHz) δ 7.05 (s, 1 H), 6.79 (s, 1 H), 6.31 (d, 1 H, J = 10.2 Hz), 6.11 (d, 1 H, J = 10.2 Hz), 6.05 (s, 1 H), 5.75 (s, 1 H), 3.92 (q, 2 H, J = 9 Hz), 2.25 (m, 2 H), 1.47 (s, 3 H), 1.43 (m, 1 H), 1.13 (m, 3 H), −0.02 (s, 9 H); ^{13}C NMR (C_6D_6, 125 MHz) δ 183.72, 170.18, 164.19, 155.62, 154.71, 141.96, 141.62, 131.15, 110.88, 106.12, 68.69, 50.09, 34.37, 28.27, 23.36, 20.42, 0.47; IR (film) 2953, 1745, 1662 cm^{-1}. Anal. Calcd for $C_{19}H_{26}O_4Si$: C, 65.83; H, 7.58. Found: C, 65.68; H, 7.48.

4-Acetoxymethyl-4-(3′-azidopropyl)-3-(trimethylsilyl)-2,5-cyclohexadien-1-one 9g was prepared by stirring a 1 M solution of **8d** (214 mg, 0.7 mmol) in acetone with 4 equiv of sodium iodide for 48 h. The solution was filtered and concentrated in vacuo. Redissolving the oil in EtOAc and washing with saturated $Na_2S_2O_5$ and saturated NaCl followed by drying with $MgSO_4$, filtration, concentration in vacuo, and flash chromatography with 30% EtOAc in hexane yields the iodide as a yellow oil (260 mg, 90%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.80 (d, 1 H, J = 10 Hz), 6.70 (s, 1 H), 6.38 (d, 1 H, J = 10 Hz), 4.36 (d, 1 H, J = 10.7 Hz), 4.14 (d, 1 H, J = 10.7 Hz), 3.10 (m, 2 H), 1.97 (s, 3 H), 1.92 (m, 1 H), 1.73 (m, 1 H), 1.52 (m, 2 H), 0.28 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.35, 170.72, 165.69, 155.22, 141.14, 130.82, 68.29, 50.15, 49.35, 35.64, 27.80, 20.83, 0.68; IR (film) 2955, 1745, 1660 cm^{-1}. Anal. Calcd for $C_{15}H_{23}O_3ISi$: C, 44.31; H, 5.72. Found: C, 44.60; H, 5.75.

The iodide was then dissolved in 2 mL of DMF before adding 3 equiv of sodium azide and stirring for 3 h at room temperature. The reaction mixture was diluted with Et_2O and water, and the aqueous phase was extracted twice with Et_2O. The organic phases were combined and washed with water, saturated $Na_2S_2O_5$, and saturated NaCl, and dried over $MgSO_4$. Filtration and concentration in vacuo followed by flash chromatography with 30% EtOAc in hexane yields a yellow oil (165 mg, 80%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.79 (d, 1 H, J = 10 Hz), 6.70 (s, 1 H), 6.38 (d, 1 H, J = 10 Hz), 4.35 (d, 1 H, J = 11 Hz), 4.12 (d, 1 H, J = 11 Hz), 3.25 (m, 2 H), 1.97 (s, 3 H), 1.66 (m, 1 H), 1.24 (m, 2 H), 0.27 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.42, 170.74, 165.45, 155.15, 141.26, 130.86, 68.43, 49.57, 31.87, 24.00, 20.83, 0.57; IR (film) 2959, 2098, 1744, 1660 cm^{-1}. Anal. Calcd for $C_{15}H_{23}O_3N_3Si$: C, 56.02; H, 7.24. Found: C, 55.88; H, 7.18.

4-Acetoxymethyl-3-methoxy-4-methyl-5-trimethylsilyl-2,5-cyclohexadien-1-one 33a was prepared from **32a** (547 mg, 2.3 mmol) to give a yellow oil (375 mg, 65%): ^{1}H NMR ($CDCl_3$, 300 MHz) 7.15 (s, 1 H), 6.78 (s, 1 H), 4.37 (d, 1 H, J = 11.0 Hz), 4.18 (d, 1 H, J = 11.0 Hz), 2.99 (s, 3 H), 1.51 (s, 3 H), 1.03 (s, 3 H), 0.06 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 186.82, 178.95, 170.60, 162.80, 138.30, 102.94, 67.34, 55.95, 47.42, 21.55, 20.77, 0.87. Anal. Calcd for $C_{14}H_{22}O_4Si$: C, 59.50; H, 7.87. Found: C, 59.65; H, 7.77.

4-Acetoxymethyl-4-(3′-butenyl)-3-methoxy-5-trimethylsilyl-2,5-cyclohexadien-1-one 33b was prepared from **32b** (547 mg, 2.3 mmol) to give a yellow oil (375 mg, 65%): ^{1}H NMR ($CDCl_3$, 300 MHz) 7.15 (s, 1 H), 6.87 (d, 1 H, J = 1.4 Hz), 5.72 (s, 1 H), 5.56 (m, 1 H), 4.93 (d, 1 H, J = 1.7 Hz), 4.87 (s, 1 H), 4.44 (d, 1 H, J = 10.6 Hz), 4.18 (d, 1 H, J = 10.6 Hz), 2.97 (s, 3 H), 1.71 (m, 3 H), 1.50 (m, 4 H), 0.07 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz), 186.88, 177.07, 170.54, 161.24, 140.45, 137.06, 115.41, 104.83, 67.38, 55.88, 51.78, 32.36, 27.97, 20.69, 0.83. Anal. Calcd for $C_{17}H_{26}O_4Si$: C, 63.29; H, 8.15. Found: C, 63.33; H, 8.00.

Intermolecular Trapping with Furan. Compound **9a** (50 mg) in 5 mL of benzene and 3 equiv of furan was degassed by bubbling argon into the solution for 15 min and then irradiated through uranyl glass for 3 h. Concentration in vacuo and crude ^{1}H NMR showed only the bicyclohexenone mixture **11a**.

General Procedure for Preparation and Crude Analysis of 11a−g. A 0.06−0.08 M solution of **9** in benzene-d_6 was degassed by bubbling argon through the solution for 15 min. Irradiation through uranyl glass for 3 h was followed by ^{1}H NMR analysis.

General Procedure for Direct Preparation of 25a−f. A 0.06−0.08 M solution of **9** in benzene with 2 equiv of trifluoroacetic acid was degassed by bubbling argon into the solution for 15 min. Irradiation through uranyl glass for 3 h is followed by washing the organic phase with H_2O, saturated $NaHCO_3$, and saturated NaCl and drying over $MgSO_4$. After filtration and concentration in vacuo the oil was flash chromatographed with 40% EtOAc in hexane to yield a 1:1 mixture of E/Z isomers **25a−e**.

General Procedure for Stepwise Preparation of 25a−g. A 0.06−0.08 M solution of **9** in benzene was degassed by bubbling argon through the solution for 15 min and irradiated through uranyl glass for 3 h. To the photolysis mixture was added 1.1 equiv of TFA at room temperature and the solution was stirred for 30 min. The organic phase was washed with water, saturated $NaHCO_3$, and saturated NaCl and dried over $MgSO_4$. After filtration and concentration in vacuo the oil was flash chromatographed on silica gel with 40% EtOAc in hexane to yield a 1:1 mixture of E/Z isomers.

4-(Acetoxymethylmethylmethylene)cyclopent-2-en-1-one 25a was prepared from **9a** (530 mg, 2.1 mmol) to yield a pale yellow oil (350 mg, 92%): ^{1}H NMR (C_6D_6, 300 MHz) δ major isomer, 7.36 (d, 1 H, J = 5.7 Hz), 5.93 (d, 1 H, J = 5.6 Hz), 4.38 (s, 2 H), 2.36 (s, 2 H), 1.64 (s, 3 H), 1.32 (s, 3 H); δ minor isomer, 7.14 (d, 1 H, J = 5.6 Hz), 5.96 (d, 1 H, J = 5.6 Hz), 4.19 (s, 2 H), 2.59 (s, 2 H), 1.61 (s, 3 H), 1.44 (s, 3 H); IR (film) 2921, 1738, 1708 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.62; H, 6.73. Found: C, 66.87; H, 6.59.

4-(Acetoxymethylallylmethylene)cyclopent-2-en-1-one 25b was prepared from **9b** (200 mg, 0.7 mmol) to yield a pale yellow oil (100 mg, 73%): ^{1}H NMR (C_6D_6, 300 MHz) δ major isomer, 7.48 (d, 1 H, J = 5.9 Hz), 5.97 (t, 1 H, J = 4.2 Hz), 5.50 (m, 1 H), 4.87 (m, 2 H), 4.51 (s, 2 H), 2.55 (d, 2 H, J = 6.4 Hz), 2.49 (s, 2 H), 1.66 (s, 3 H); δ minor isomer, 7.23 (d, 1 H, J = 5.8 Hz), 5.97 (t, 1 H, J = 4.2 Hz) 5.50 (m, 1 H), 4.87 (m, 2 H), 4.34 (s, 2 H), 2.71 (d, 2 H, J = 6.4 Hz), 2.66 (s, 2 H), 1.63 (s, 3 H); IR (film) 2978, 1739, 1712 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.86; H, 6.86. Found: C, 70.10; H, 6.91.

4-(Acetoxymethylbenzylmethylene)cyclopent-2-en-1-one 25c was prepared from **9c** (230 mg, 0.7 mmol) to yield a pale yellow oil (140 mg, 79%): ^{1}H NMR (C_6D_6, 300 MHz) δ major isomer, 8.19 (d, 1 H, J = 5.6 Hz), 7.28 (m, 2 H), 7.23 (m, 1 H), 7.15 (m, 2 H), 6.37 (d, 1 H, J = 5.6 Hz), 4.74 (s, 2 H), 3.59 (s, 2 H), 3.08 (s, 2 H), 2.00 (s, 3 H); δ minor isomer, 8.16 (d, 1 H, J = 5.6 Hz), 7.28 (m, 2 H), 7.23 (m, 1 H), 7.15 (m, 2

H), 6.41 (d, 1 H, $J = 5.6$ Hz), 4.58 (s, 2 H), 3.71 (s, 2 H), 3.12 (s, 2 H), 1.95 (s, 3 H); IR (film) 2932, 1739, 1711 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_3$: C, 75.04; H, 6.32. Found: C, 72.42; H, 6.23.

4-[Acetoxymethyl(3′-chloropropyl)methylene]cyclopent-2-en-1-one 25d was prepared from **9d** (75 mg, 0.2 mmol) to yield a pale yellow oil (45 mg, 78%): ^{1}H NMR (C_6D_6, 300 MHz) δ major isomer, 7.42 (d, 1 H, $J = 5.6$ Hz), 5.98 (t, 1 H, $J = 5.6$ Hz), 4.40 (s, 2 H), 2.97 (t, 2 H, $J = 6.3$ Hz), 2.51 (s, 2 H), 1.86 (t, 2 H, $J = 6.3$ Hz), 1.66 (s, 3 H), 1.42 (m, 2 H); δ minor isomer, 7.36 (d, 1 H, $J = 5.6$ Hz), 5.98 (t, 1 H, $J = 5.6$ Hz), 4.23 (s, 2 H), 3.02 (t, 2 H, $J = 6.3$ Hz), 2.61 (s, 2 H), 2.05 (t, 2 H, $J = 6.3$ Hz), 1.63 (s, 3 H), 1.42 (m, 2 H); IR (film) 2960, 1738, 1712 cm^{-1}. Anal. Calcd for $C_{12}H_{15}O_3Cl$: C, 59.36; H, 6.24. Found: C, 59.18; H, 6.11.

4-(Acetoxymethyl(3′-(2-furanyl))methylene)cyclopent-2-en-1-one 25f was prepared from **9f** (100 mg, 0.3 mmol) to yield a pale yellow oil (60 mg, 73%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ major isomer, 8.10 (d, 1 H, $J = 5.8$ Hz), 7.31 (m, 1 H), 6.29 (m, 2 H), 5.99 (m, 1 H), 4.80 (s, 3 H), 2.89 (s, 2 H), 2.65 (m, 2 H), 2.25 (t, 2 H, $J = 7.9$ Hz), 2.07 (s, 3 H), 1.85 (m, 2 H); δ minor isomer, 7.90 (d, 1 H, $J = 5.9$ Hz), 7.31 (m, 1 H), 6.29 (m, 2 H), 5.99 (m, 1 H), 4.65 (s, 2 H), 3.01 (s, 2 H), 2.65 (m, 2 H), 2.38 (t, 2 H, $J = 7.3$ Hz), 2.07 (s, 3 H), 1.85 (m, 2 H); IR (film) 2958, 1736, 1710. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.03; H, 6.63. Found: C, 70.15; H, 6.88.

4-(Acetoxymethyl(3′-butenyl)methylene)cyclopent-2-en-1-one 25e was prepared from **9e** (200 mg, 0.5 mmol) to yield a pale yellow oil (120 mg, 80%): ^{1}H NMR (C_6D_6, 500 MHz) δ major isomer, 7.42 (d, 1 H, $J = 5.6$ Hz), 5.93 (d, 1 H, $J = 5.6$ Hz), 5.54 (m, 1 H), 4.88 (m, 2 H), 4.45 (s, 3 H), 2.45 (s, 3 H), 1.94 (q, 2 H, $J = 7.1$ Hz), 1.87 (s, 2 H), 1.60 (s, 3 H); δ minor isomer, 7.20 (d, 1 H, $J = 5.3$ Hz), 5.92 (d, 1 H, $J = 5.3$ Hz), 5.54 (m, 1 H), 4.88 (m, 2 H), 4.28 (s, 3 H), 2.59 (s, 3 H), 2.03 (t, 2 H, $J = 7$ Hz), 1.88 (s, 2 H), 1.57 (s, 3 H); IR (film) 2952, 1739, 1711 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.86; H, 7.34. Found: C, 70.69; H, 7.15.

4-(Acetoxymethyl(3′-azidopropyl)methylene)cyclopent-2-en-1-one 25 g was prepared from **9g** (20 mg, 0.1 mmol) to yield a pale yellow oil (10 mg, 70%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ major isomer, 8.10 (m, 1 H), 6.32 (d, 1 H, $J = 5.6$ Hz), 4.81 (s, 2 H), 3.32 (m, 2 H), 3.03 (s, 2 H), 2.40 (m, 1 H), 2.32 (m, 1 H), 2.08 (s, 3 H), 2.01 (m, 2 H); δ minor isomer, 8.06 (m, 1 H), 6.34 (m, 1 H), 4.66 (s, 2 H), 3.54 (m, 2 H), 2.97 (s, 3 H), 2.54 (m, 1 H), 2.44 (m, 1 H), 2.08 (s, 3 H), 1.78 (m, 2 H); IR (film) 2953, 2098, 1708, 1648 cm^{-1}. Anal. Calcd for $C_{12}H_{15}O_3N_3$: C, 57.79; H, 6.08. Found: C, 57.71; H, 6.25.

4-(Acetoxymethylmethylmethylene)-5,6-dehydrocaprolactone 26 was prepared from **25** (50 mg, 0.3 mmol) by treating a 0.1 M solution in CH_2Cl_2 at room temperature with 2 equiv of *m*-chloroperbenzoic acid for 4 h. Dilution with CH_2Cl_2 and washing the organic phase with water, 10% $NaHCO_3$ solution, and saturated NaCl solution was followed by drying with $MgSO_4$, filtration, and concentrating in vacuo. Flash chromatography with 1:1 EtOAc in hexane yields the pure lactone as a yellow oil (43 mg, 80%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ major isomer, 7.34 (d, 1 H, $J = 5.9$ Hz), 6.43 (d, 1 H, $J = 5.9$ Hz), 4.25 (q, 2 H, $J = 12.0$ Hz), 2.45 (q, 2 H, $J = 12.9$ Hz), 2.10 (s, 3 H), 1.46 (s, 3 H); δ minor isomer, 7.27 (d, 1 H, $J = 5.8$ Hz), 6.47 (d, 1 H, $J = 5.8$ Hz), 4.13 (q, 2 H, $J = 12.1$ Hz), 2.69 (t, 2 H, $J = 19.3$ Hz), 2.10 (s, 3 H), 1.50 (s, 3 H) IR (film) 2963, 1722; CIMS *m/z* (relative intensity) 197 ($M^+ + 1$, 100). Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.19; H, 6.18. Found: C, 61.28; H, 6.01.

1-Acetoxymethyl-2-methoxy-6-trimethylsilyltricyclo-[5.2.1.0]dec-2-en-4-one 34 was prepared from **33b** (50 mg) in benzene (5 mL), degassed for 15 min by bubbling argon, by irradiation for 3 h through uranyl glass. Concentration in vacuo and recrystallization from 10:1 Hex:EtOAc yields 38 mg (76%) of colorless, needlelike crystals, mp 80−82 °C: ^{1}H NMR (500 MHz) 5.41 (s, 1 H), 4.34 (d, 1 H, $J = 11.2$ Hz), 3.87 (d, 1 H, $J = 11.5$ Hz), 3.69 (s, 3 H), 2.95 (m, 1 H), 2.82 (m, 1 H), 2.64 (q, 1 H, $J = 1.0$ Hz, $J = 8.1$ Hz), 2.16 (m, 2 H), 2.01 (s, 3 H), 1.82 (m, 1 H), 1.74 (m, 1 H), 1.53 (m, 1 H), 0.09 (s, 9 H); ^{13}C NMR (125 MHz) 200.59, 182.14, 170.76, 101.47, 65.61, 56.45, 52.49, 41.98, 41.30, 39.93, 39.57, 31.45, 30.31, 21.17, −1.94. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.33; H, 8.92. Found: C, 69.21; H, 8.70.

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