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Photochemical and Acid-Catalyzed Rearrangements of 4-Carbomethoxy-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one[†]

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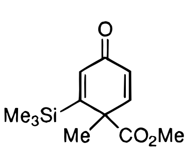
The synthesis of 4-carbomethoxy-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one (**1**) in 60% overall yield from benzaldehyde is described. Irradiation (366 nm) of **1** in benzene solution gave products of type A photorearrangement; e.g., diastereomers of the 4-(trimethylsilyl)- and 5-(trimethylsilyl)bicyclo[3.1.0]hex-3-en-2-ones **8** and **9**. Bicyclohexenones **9a** and **9b** could not be isolated, but underwent acid-catalyzed protiodesilylative rearrangements on attempted chromatography (silica gel) to give a 1:1 mixture of (*E*)- and (*Z*)-4-(carbomethoxymethylmethylene)cyclopent-2-en-1-ones **12** and **13**. Irradiation (366 nm) of either **12** or **13** resulted in photoisomerization to a photostationary state that was also a 1:1 mixture. Irradiation of **8a** or **8b** gave equivalent mixtures of phenols **14** and **15** by way of the type B oxyallyl zwitterion **17**. The available experimental evidence suggests that both **9a** and **9b** undergo regiospecific photorearrangement to phenol **16** with no trace of 3-methyl-4-carbomethoxyphenol (**19**), the product of ipso substitution of the Me_3Si group at C(4). Phenol **15** was isolated in 65% yield from the photoreaction of **1** in benzene with 20 equiv of CF_3CO_2H. The acid-catalyzed rearrangement of **1** to 3-carbomethoxy-4-methylphenol (**21**) occurs in 91% yield by way of CO_2Me group rearrangement to C(3) to give the Me_3Si-stabilized carbocation **23**.

Substituent effects on the photochemical[1] and acid-catalyzed[2] rearrangements of 2,5-cyclohexadien-1-ones are of continuing interest.[3] In this paper we report the preparation, photochemistry, and acid-catalyzed rearrangement of 4-carbomethoxy-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one (**1**).



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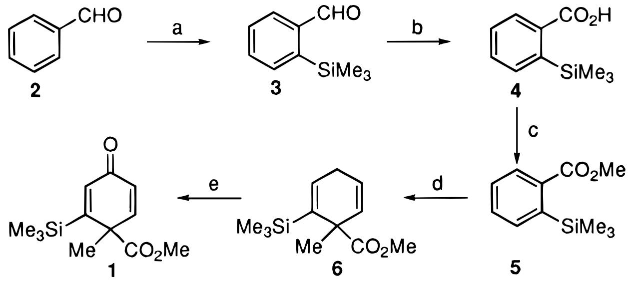
Results and Discussion

The synthesis of 4-carbomethoxy-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one (**1**) is shown in Scheme 1. Although it is possible to prepare 2-(trimethylsilyl)benzoic acid (**4**) via metal−halogen exchange from 2-bromobenzoic acid[4] or metalation of *N*,*N*-diethylbenzamide[5] or isopropyl benzoate[6a] or by other procedures,[6b−f] relatively poor yields or difficulties associated with hydrolysis of the carboxylic acid derivative necessitated development of a new procedure. Trimethylsilylation of benzaldehyde (**2**) by the method of Comins and Brown[7] provided 2-(trimethylsilyl)benzaldehyde (**3**) in 87% yield. Oxidation of **3** with $KMnO_4$ in acetone−water gave the desired carboxylic acid **4**,[8] and esterification with dimethyl sulfate/K_2CO_3 in acetone gave the desired methyl 2-(trimethylsilyl)benzoate in 93% overall yield.

Scheme 1



Reagents and conditions: (a) (i) $MeHN(CH_2)_2NMe_2$, n-BuLi, TMSCl (ii) H_3O^+; (b) $KMnO_4$, acetone/H_2O; (c) K_2CO_3,dimethylsulfate, acetone, reflux; (d) (i) THF, t-BuOH, NH_3, Li, -78°C (ii) MeI, -78°C --> rt; (e) PDC, t-BuOOH, benzene, Celite.

[†] Dedicated to Clayton H. Heathcock on the occasion of his 60th birthday.

[‡] Undergraduate research participant.

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(8) This oxidation was first performed by Aihua Wang, RPI Laboratories.

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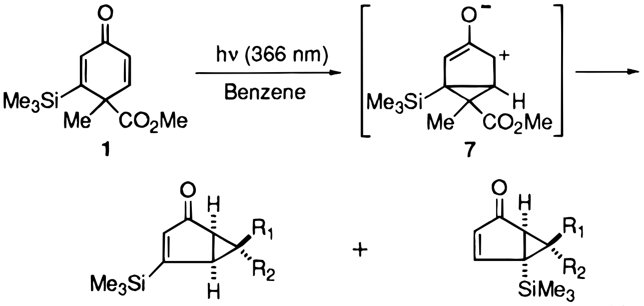
The Birch reduction−methylation of 2-(trimethylsilyl)benzoic acid has been mentioned in two review articles concerned with the Birch reduction of aromatic compounds;[9] to our knowledge, this reaction has never been described in the primary chemical literature. Birch reduction of methyl 2-(trimethylsilyl)benzoate with lithium in NH_3−THF in the presence of 1 equiv of *tert*-butyl alcohol at −78 °C, followed by addition of piperylene to consume excess metal and alkylation with methyl iodide gave diene **6** in 89% yield. The outstanding directive effects of trialkylsilyl substituents[10] together with the potential for absolute stereocontrol by way of the asymmetric analogue of the conversion **5** → **6**[11] suggest that this variant of the Birch reduction−alkylation will find important synthetic application. Allylic oxidation of **6** with *t*-BuOOH and pyridinium dichromate (catalytic) provided **1** in 86% yield (~60% overall from benzaldehyde).

Irradiation of a solution of **1** in benzene (0.02 M) through uranyl glass provided a complicated mixture of products as described in the Experimental Section. The primary photoproducts were produced by way of the type A rearrangement[1a] involving oxyallyl zwitterion **7** to give diastereomers of the 4-(trimethylsilyl)- and 5-(trimethylsilyl)bicyclo[3.1.0]hex-3-en-2-ones **8** and **9**.

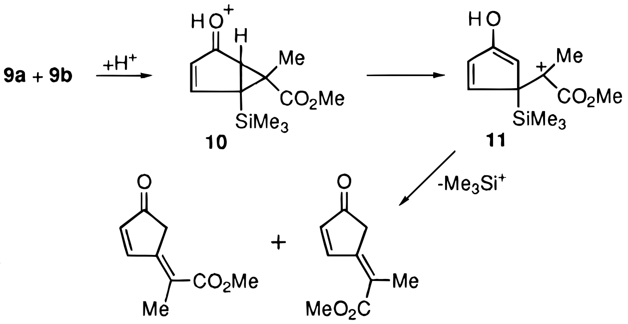


1 **7**

8a $R_1 = CO_2Me$; $R_2 = Me$
8b $R_1 = Me$; $R_2 = CO_2Me$
9a $R_1 = CO_2Me$; $R_2 = Me$
9b $R_1 = Me$; $R_2 = CO_2Me$

The absence of regioselectivity for photorearrangement of **1** to **8** and **9** is striking when compared to the regioselectivity for photorearrangement of the 3-methoxy-2,5-cyclohexadien-1-ones which give only the 4-methoxybicyclo[3.1.0]hex-3-en-2-ones corresponding to **8**.[12] Indirect trapping studies have shown that selective product formation is not the result of a regioselective rearrangement of the type A oxyallyl zwitterion corresponding to **7**.[13] Rather, both 5-methoxy- and 4-methoxybicyclo[3.1.0]hexenones are produced; however, in the absence of trapping agents, 5-methoxybicyclo[3.1.0]hexenones photorearrange to the 4-methoxy regioisomers.

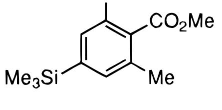
The production of 5-(trimethylsilyl)bicyclohexenones **9a** and **9b** presented a unique opportunity to examine the viability of photorearrangement to the 4-trimethylsilyl regioisomers **8a** and **8b**. Unfortunately, attempted chromatographic isolation of **9a** and **9b** resulted in protiodesilylative rearrangements to give a 1:1 mixture of (*E*)- and (*Z*)-4-(carbomethoxymethylmethylene)cyclopent-2-en-1-ones **12** and **13**. Irradiation (366 nm) of either **12** or **13** in benzene solution resulted in isomerization to a photostationary state that was the same 1:1 composition of **12** and **13** obtained from protiodesilylative rearrangement of **9a** and **9b**.



10 **11** **12** **13**

The rearrangement of **9** to **12** and **13** is related to the acid-catalyzed rearrangement of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one to 4-(diphenylmethylene)cyclopent-2-en-1-one, reported to occur in a mixture of 1 M HCl in 70% dioxane at reflux.[14] The considerably more facile acid-catalyzed rearrangement of **9** is a result of the stabilizing effect of the β-trimethylsilyl substituent **10** in carbocation **11**.

Continued irradiation of the photolysis mixture from **1** resulted in the type B photorearrangement[15] of **8** and **9** to give phenols **14**, **15**, and **16** in a ratio of 2:4:1. The structures of phenols **14**−**16** were assigned on the basis of ^1H NMR spectral data. Resonances for aromatic protons in **14** appeared as a pair of doublets at δ 6.98 and 6.82 ($J = 0.5$ Hz). A sharp one-proton singlet for the phenolic OH group appeared at δ 11.17 (exchangeable with D_2O). The considerable downfield resonance for this proton is characteristic of phenols with an adjacent carboalkoxy group.[12] Phenol **15** displayed one-proton doublets at δ 6.86 and 6.64 ($J = 2.4$ Hz) and a broad resonance at δ 5.91 (exchangeable with D_2O) for the phenolic OH group. Phenol **16** displayed sharp one-proton doublets at δ 7.46 and 6.81 ($J = 8.5$ Hz) and a sharp one-proton singlet at δ 10.89 for the phenolic OH group, in accord with its location adjacent to the carbomethoxy substituent.



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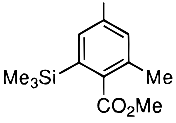

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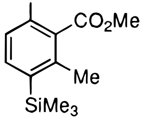

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Bicyclohexenones **8a** and **8b** were isolated and irradiated individually to give equivalent mixtures of phenols **14** and **15** (Scheme 2). Although **9a** and **9b** could not be isolated and fully characterized, the available experimental evidence (*vide supra*) suggests that both diastereomers photorearrange to phenol **16** via the type B oxyallyl zwitterion **18**. Whether **9a** and **9b** also photorearrange to **8a** and **8b** remains open to question. As recorded in the previous study of 4-methoxybicyclo[3.1.0]-

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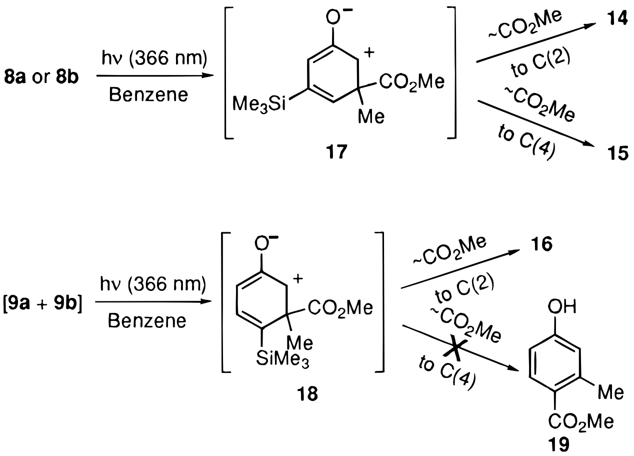
Scheme 2



hex-3-en-2-ones,[13] it is clear that the 4-substituted bicyclohexenones **8a** and **8b** do not photorearrange to the 5-substituted isomers **9a** and **9b**.

The regioselectivity for rearrangement of the type B oxyallyl zwitterion **17** to **14** and **15** is only 1:2. This is in marked contrast to the regioselectivity for rearrangement of the intermediate corresponding to **17**, wherein the Me_3Si group is replaced by MeO; rearrangement produces only the phenol resulting from migration of the CO_2Me group to C(2).[12] On the other hand, rearrangement of **18** is regiospecific within experimental error to give **16** with no trace of 3-methyl-4-carbomethoxyphenol (**19**), the product of ipso substitution at C(4).

The propensity for rearrangement of **18** is noteworthy, inasmuch as the type B intermediate with the Me_3Si group replaced by MeO failed to undergo rearrangement to generate 2-carbomethoxy-4-methoxy-3-methylphenol; trapping experiments have demonstrated that the type B oxyallyl zwitterion forms by way of a reversible photochemical process.[13] The Me_3Si compared to the MeO group at C(4) in **18** provides less stabilization of the oxyallyl zwitterion, which might enhance the migratory aptitude of the CO_2Me group.[16]

An unusual solvent effect was discovered for photoreactions of **1** in benzene in the presence of CF_3CO_2H. The addition of 1 equiv of CF_3CO_2H dramatically enhanced the rate of photorearrangement of **1** (2 h vs >20 h in benzene). Photoproduct composition was simplified to include only phenols **14** and **15** and methylenecyclopentenones **12** and **13**, suggesting that under these reaction conditions bicyclohexenones **9a** and **9b** undergo the acid-catalyzed protiodesilylative rearrangement faster than photorearrangement to phenol **16**. Furthermore, it was found that the regioselectivity of type B photorearrangements of **8a** and **8b** changes with increasing amounts of CF_3CO_2H (Table 1) from a 2:1 mixture of **15** and **14** in benzene without added acid to 32:1 in benzene with 20 equiv of CF_3CO_2H. Phenol **15** was isolated in 65% yield from the photoreaction of **1** and 20 equiv of CF_3CO_2H.

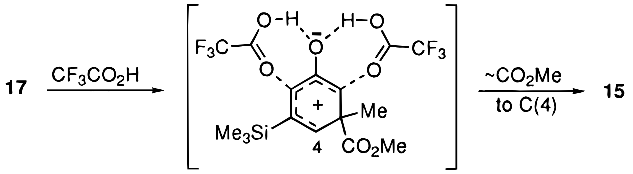
The enhanced photoreactivity of **1** in the presence of CF_3CO_2H may be connected to a shift of the position of the $\pi \rightarrow \pi^*$ band associated with **1**. The λ_{max} for **1** in benzene solution is 278 nm ($\epsilon_{max} = 200$), while the λ_{max} for **1** in benzene with 10 equiv of CF_3CO_2H is 288 nm ($\epsilon_{max} = 658$). Griffiths and Hart found that trifluoroethanol or silica gel shifts the position of the $\pi \rightarrow \pi^*$ band of the 2,4-cyclohexadien-1-one chromophore, which correlated with a change in photoreactivity.[17] Altered product distribution from photolysis of a 4-vinyl-2,5-cyclohexadien-1-one in the presence of CF_3CO_2H also has been reported.[18]

Table 1. Product Distribution[a] from Photolysis of 1 in Benzene with CF_3CO_2H

CF_3CO_2H (equiv)	product distribution			
	12	**13**	**14**	**15**
1.0	4.0	2.0	1.0	6.0
2.0	4.0	2.0	1.0	12
5.0	2.5	1.5	1.0	12
10	2.5	2.0	1.0	16
20	3.0	3.0	1.0	32[b]

[a] Product distribution determined by ^1H NMR spectral analysis of photoreaction mixtures in C_6H_6. [b] Phenol **15** was isolated (flash chromatography on silica gel) in 65% yield.

The change in regioselectivity of formation of phenols **14** and **15** might be a result of solvation effects on the type B oxyallyl zwitterion **17** as shown in structure **20**. Steric interactions between the migrating CO_2Me group and bound CF_3CO_2H might result in preferential migration to C(4) rather than C(6) of **20**. It should be noted that the Me_3Si group in **17** is at an sp^2 hybridized carbon on the cyclohexadienyl ring, not well positioned for carbocation β-stabilization[10] (*vide infra*).



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Cyclohexadienone **1** was treated with CF_3CO_2H in the dark to examine the regioselectivity of the acid-catalyzed dienone–phenol rearrangement. After 7 days at room temperature, **1** was completely converted to phenol **21**,[19] which was isolated in 91% yield (Scheme 3).

Two pathways for rearrangement of **1** to **21** are shown in Scheme 3. Protonation of the C(1) carbonyl group would generate **22**, from which migration of the CO_2Me group to C(3) would generate the Me_3Si-stabilized carbocation **23**. Loss of the Me_3Si to solvent would give phenol **21** directly. Alternatively, migration of the CO_2Me group to C(5) of **22** would give carbocation **24** in which the β-Me_3Si group is at an sp^2 hybridized carbon atom. Loss of a proton from **24** would give the 5-trimethylsilyl-substituted phenol **25**. Although **25** was never observed, it might have been generated and rapidly converted to **21** by protiodesilylation. It has been reported that 2-carbomethoxy-6-(trimethylsilyl)phenol undergoes facile protiodesilylation at room temperature in $CF_3CO_2H/CHCl_3$ solution.[20]

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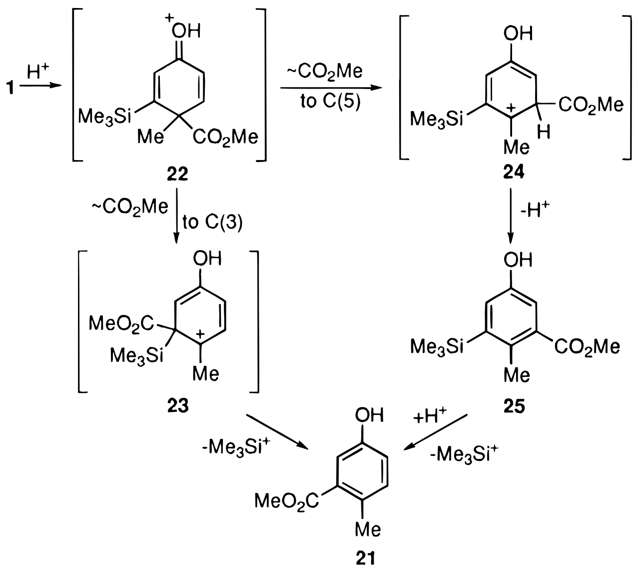
(16) (a) Hammett constants (σ_p) for MeO and Me_3Si groups have been determined: MeO (−0.27) and Me_3Si (−0.07); see: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195. (b) To the extent that the intermediate in the type B photorearrangement might be represented as a biradicaloid, it should be noted that the trimethylsilyl group has been found to exert a small destabilizing effect on adjacent radicals; see: Zhang, S.; Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1995**, *117*, 602−606.

(17) Griffiths, J.; Hart, H. *J. Am. Chem. Soc.* **1968**, *90*, 5296−5298.

(18) Schultz, A. G.; Green, N. J. *J. Am. Chem. Soc.* **1992**, *114*, 1824−1829.

(19) For previous preparations of **21**, see: Phandis, A. P.; Nanda, B.; Sarita, A.; Patwardhan, E.; Gupta, A. S. *Indian J. Chem.* **1984**, *23B*, 1098 and ref 2d.

Scheme 3



Treatment of **1** with CF_3CO_2D gave **21** with no evidence (^1H NMR) for incorporation of deuterium at C(5), thereby ruling out the intermediacy of **25** in the conversion of **1** to **21**. Acid-catalyzed dienone rearrangement to give **23** rather than **24** is, of course, consistent with the expectation of enhanced stabilization of **23** by the β-effect of the Me_3Si group.[10]

Experimental Section

General Procedures. Tetrahydrofuran (THF) was distilled from benzophenone sodium ketyl under nitrogen. Benzene was distilled from CaH_2. Analytical TLC was performed on 0.25 mm E. Merck silica gel (60F-254) plates using UV light and iodine as visualizing agents. Purifications by flash column chromatography used Baker silica gel (40 μm). Radial chromatography was performed on a Harrison Research Chromatotron, Model 7924T, using a 2 mm plate of silica gel PF. Band separation was monitored by UV. High resolution mass spectra were obtained from the mass spectrometry laboratory at the University of Illinois at Urbana/Champaign. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ, and Atlantic Microlab, 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 fitted with a uranyl glass filter to give light with wavelength mainly at 366 nm.

2-(Trimethylsilyl)benzoic Acid (4). To a solution of **3** (3.02 g, 17.0 mmol; prepared by the method of Comins and Brown in 87% yield on a 6 g scale[7]) in acetone (45 mL) and water (8 mL) was added $KMnO_4$ (3.22 g, 20.4 mmol). The solution was stirred at room temperature for 1.5 h. Solvent was evaporated under reduced pressure, and saturated Na_2SO_3 solution was added to the residue. The solution was filtered through a pad of Celite 545, and the dark brown solid was repeatedly washed with H_2O and CH_2Cl_2. The resulting colorless filtrate was acidified with 10% HCl and extracted three times with CH_2Cl_2. The combined organic extractions were dried over Na_2SO_4, and the solvent was removed *in vacuo*. **4** was obtained as white crystals (3.09 g, 94%): mp 94−95 °C (lit. 97−98.5 °C);[4] ^1H NMR ($CDCl_3$, 500 MHz) δ 8.20 (d, 1 H, $J = 7.5$ Hz), 7.75 (d, 1 H, $J = 7.3$ Hz), 7.57 (t, 1 H, $J = 7.5$ Hz), 7.48 (t, 1 H, $J = 7.5$ Hz), 0.37 (s, 9 H); CIMS *m/z* (relative intensity) 195 ($M^+ + 1$, 3%), 179 (100%), 163 (25%), 123 (80%).

Methyl 2-(Trimethylsilyl)benzoate (5). To a solution of **4** (3.00 g, 15.4 mmol) in acetone (150 mL) was added K_2CO_3 (5.33 g, 38.6 mmol) and dimethyl sulfate (3.5 mL, 39 mmol). The solution was refluxed overnight and cooled to room temperature, and then H_2O was added. Solvent was evaporated under reduced pressure, and saturated $NaHCO_3$ solution was added until the mixture tested basic. The solution was then extracted three times with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, concentrated, and purified by flash chromatography (silica gel; 2:1 hexane:EtOAc) to give **5** as a clear oil (3.16 g, 98%): ^1H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, 1 H, $J = 7.5$ Hz), 7.72 (d, 1 H, $J = 7.3$ Hz), 7.51 (t, 1 H, $J = 7.6$ Hz), 7.44 (t, 1 H, $J = 7.6$ Hz), 3.92 (s, 3 H), 0.37 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.60, 142.41, 135.52, 135.36, 131.36, 129.94, 128.74, 51.83, 0.14; IR (film) 1718 cm^{-1}; CIMS *m/z* (relative intensity) 209 ($M^+ + 1$, 2%), 193 (100%), 177 (8%), 145 (8%). Anal. Calcd for $C_{11}H_{16}O_2Si$: C, 63.42; H, 7.74. Found: C, 63.25; H, 7.81.

6-Carbomethoxy-6-methyl-1-(trimethylsilyl)-1,4-cyclohexadiene (6). A flame-dried three-neck round bottom flask (100 mL) equipped with a dry ice condenser, magnetic stirrer, and N_2 inlet was charged with **5** (0.87 g, 4.2 mmol), dry THF (9 mL), and *t*-BuOH (0.40 mL, 4.2 mmol). The mixture was cooled to −78 °C and liquid NH_3 (~60 mL) was added. Lithium (~0.064 g, 9.2 mmol) was added in small pieces to the stirred solution and a deep blue coloration developed. 1,3-Pentadiene was added dropwise until a color change to yellow occurred. Methyl iodide (0.78 mL, 13 mmol) was added, and the solution was stirred at −78 °C for 1 h. The mixture was warmed slowly to room temperature while the ammonia was removed with a stream of N_2. Saturated NH_4Cl solution was added, and the mixture was diluted with EtOAc, extracted two times with H_2O, once with brine, and dried over Na_2SO_4. Removal of solvent *in vacuo* afforded a yellow oil. Flash chromatography (silica gel; 2:1 hexane:EtOAc) gave **6** (0.84 g, 89%) as a clear oil: ^1H NMR ($CDCl_3$, 500 MHz) δ 6.14 (m, 1 H), 5.76 (dm, 1 H), 5.52 (dt, 1 H, $J = 11.7$, 1.9 Hz), 3.60 (s, 3 H), 2.66 (q, 2 H, $J = 3.7$ Hz), 1.32 (s, 3 H), 0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.86, 139.44, 134.72, 130.44, 123.86, 51.99, 46.61, 26.85, 26.29, 0.04; IR (film) 2940, 1720 cm^{-1}; CIMS *m/z* (relative intensity) 225 ($M^+ + 1$, 100%).

4-Carbomethoxy-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one (1). To a stirred solution of **6** (3.43 g, 15.3 mmol) in benzene (200 mL) at 0 °C were added Celite 545 (3.0 g), pyridinium dichromate (1.2 g, 3.1 mmol), and 90% *t*-BuOOH (5.1 mL, 46 mmol). The resulting solution was stirred at 0 °C for 1.5 h and then allowed to warm to room temperature and stirred overnight. The reaction mixture was filtered through a pad of Celite 545, the solids were washed thoroughly with EtOAc, and the filtrate was concentrated *in vacuo* to give a yellow oil. Flash chromatography (silica gel; 2:1 hexane: EtOAc) gave **1** (3.10 g, 86%) as a pale orange oil: ^1H NMR ($CDCl_3$, 500 MHz) δ 6.79 (dt, 1 H, $J = 10$, 1.4 Hz), 6.51 (q, 1 H, $J = 1.8$ Hz), 6.22 (dq, 1 H, $J = 10$, 1.7 Hz), 3.60 (s, 3 H), 1.47 (s, 3 H), 0.11 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 183.21, 171.50, 164.69, 151.64, 137.12, 128.57, 52.68, 51.18, 23.24, −0.78; IR (film) 1730, 1660, 1625 (shoulder) cm^{-1}; CIMS *m/z* (relative intensity) 239 ($M^+ + 1$, 100%), 209 (26%), 167 (8%), 135 (64%); UV (benzene) $\lambda_{max} = 278$ nm ($\epsilon = 200$), 300 nm ($\epsilon = 67$), 366 nm ($\epsilon = 26$); UV (benzene/10 equiv of CF_3CO_2H) $\lambda_{max} = 288$ nm ($\epsilon = 658$), 300 nm ($\epsilon = 284$), 366 nm ($\epsilon = 21$). Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.47; H, 7.61. Found: C, 60.40; H, 7.70.

Irradiation of 4-Carbomethoxy-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one (1). A solution of **1** (100 mg, 0.42 mmol) in benzene (22 mL, 19 mM) was degassed with N_2 for 10 min prior to irradiation for 3 h. Concentration of the reaction mixture, flash column chromatography (silica gel; 7:3 hexane:EtOAc) to remove highly colored polar impurities, and then radial chromatography (silica gel; 2 mm; 10:1 hexane: EtOAc) gave 4-carbomethoxy-3-methyl-5-(trimethylsilyl)phenol (**15**) (14 mg, 14%) as a white solid: mp 98−99 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.87 (d, 1 H, $J = 2.4$ Hz), 6.62 (d, 1 H, $J = 2.4$ Hz), 5.91 (s, 1 H, D_2O exchangeable), 3.85 (s, 3 H), 2.30 (s, 3 H), 0.22 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.39, 156.28, 141.81, 138.74, 130.09, 119.20, 117.84, 51.73, 20.57, −0.27; IR (CH_2Cl_2) 3475−3200, 1685, 1575 cm^{-1}; CIMS, *m/z* (relative intensity) 239 ($M^+ + 1$, 3%), 223 (100%). Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.47; H, 7.61. Found: C, 60.18; H, 7.49. 2-Carbomethoxy-3-methyl-5-(trimethylsilyl)phenol (**14**) (7 mg,

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7%) was obtained as a white solid: mp 71−72 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 11.17 (s, 1 H, D_2O exchangeable), 6.98 (d, 1 H, $J = 0.5$ Hz), 6.82 (d, 1 H, $J = 0.5$ Hz), 3.94 (s, 3 H), 2.52 (s, 3 H), 0.23 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.24, 161.60, 148.84, 139.84, 127.43, 120.46, 112.31, 52.08, 23.95, −1.56; IR (CH_2Cl_2) 3670, 1655, 1605 cm^{-1}; EIMS, *m/z* (relative intensity) 238 (M^+, 40%), 223 (25%), 206 (100%), 191 (39%); HRMS (M^+) calcd for $C_{12}H_{18}O_3Si$ 238.1025, found 238.1026. 2-Carbomethoxy-3-methyl-4-(trimethylsilyl)phenol (**16**) (3 mg, 3%) was obtained as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.89 (s, 1 H), 7.46 (d, 1 H, $J = 8.5$ Hz), 6.81 (d, 1 H, $J = 8.5$ Hz), 3.95 (s, 3 H), 2.61 (s, 3 H), 0.29 (s, 9 H). Sufficient material of analytical purity could not be obtained. 6-*exo*-Carbomethoxy-6-methyl-4-(trimethylsilyl)bicyclo[3.1.0]hex-3-en-2-one (**8b**) (14 mg, 14%) was obtained as a clear oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.09 (s, 1 H), 3.70 (s, 3 H), 3.07 (d, 1 H, $J = 4.9$ Hz), 2.53 (d, 1 H, $J = 4.9$ Hz), 1.23 (s, 3 H), 0.18 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.28, 176.86, 171.58, 140.79, 52.53, 47.61, 37.78, 35.65, 8.60, −2.67; IR (film) 1700 cm^{-1}; EIMS, *m/z* (relative intensity) 238 (M^+, 22%), 223 (57%), 179 (32%), 165 (83%), 106 (100%). Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.47; H, 7.61. Found: C, 60.41; H, 7.63. (*E*)-4-(Carboxymethylmethylmethylene)cyclopent-2-en-1-one (**12**) (16 mg, 23%) was obtained as a white solid: mp 111−112 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.09 (d, 1 H, $J = 5.6$ Hz), 6.47 (d, 1 H, $J = 5.6$ Hz), 3.77 (s, 3 H), 3.33 (s, 2 H), 2.11 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.27, 167.69, 155.20, 145.48, 137.60, 123.99, 51.95, 40.94, 14.84; IR (CH_2Cl_2) 1690, 1630 (shoulder), 1545 cm^{-1}; EIMS, *m/z* (relative intensity) 166 (M^+, 100%), 138 (59%), 135 (27%), 123 (52%), 107 (33%). Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.86; H, 6.14. A positive NOESY correlation between the proton at 6.47 ppm and the methyl group protons at 2.11 ppm was observed, designating (*E*)-(**12**). A 1:4 mixture (21 mg) of 6-*endo*-carbomethoxy-6-methyl-4-(trimethylsilyl)bicyclo[3.1.0]hex-3-en-2-one (**8a**):(*Z*)-4-(carboxymethylmethylmethylene)cyclopent-2-en-1-one (**13**) was obtained. Recrystallization of the mixture using EtOAc/hexane gave pure **13** as colorless crystals: mp 70−71 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.71 (d, 1 H, $J = 5.8$ Hz), 6.41 (d, 1 H, $J = 5.8$ Hz), 3.80 (s, 3 H), 2.98 (s, 2 H), 2.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 204.07, 167.04, 156.39, 145.60, 137.56, 124.66, 51.93, 39.26, 17.32; IR (CH_2Cl_2) 1750, 1675(shoulder) cm^{-1}; EIMS *m/z* (relative intensity) 166 (M^+, 37%), 138 (27%), 123 (25%), 107 (27%); HRMS (M^+) calcd for $C_9H_{10}O_3$ 166.0630, found 166.0630. A positive NOESY correlation was observed between the protons at 2.98 ppm and the methyl group protons at 2.01 ppm, designating (*Z*)-(**13**). The resulting mother liquor contained a 1:1 mixture of **8a**:**13**: ^{1}H NMR ($CDCl_3$, 500 MHz) for **8a**: δ 5.93 (s, 1 H), 3.57 (s, 3 H), 2.66 (d, 1 H, $J = 4.4$ Hz), 2.12 (d, 1 H, $J = 4.4$ Hz), 1.41 (s, 3 H), 0.16 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.72, 174.28, 169.97, 138.88, 52.85, 52.13, 39.65, 36.42, 21.53, −2.21.

Irradiation of (*E*)- and (*Z*)-4-(Carboxymethylmethylmethylene)cyclopent-2-en-1-ones (12 and 13). **12** (12 mg, 0.07 mmol) in benzene (5 mL) was irradiated for 3 h. ^{1}H NMR analysis of the reaction mixture showed a 1:1 mixture of **12** and **13**. **13** (7 mg, 0.04 mmol) in benzene (3 mL) was irradiated for 3 h. ^{1}H NMR analysis of the reaction mixture showed a 1:1 mixture of **12** and **13**.

Irradiation of 6-*endo*- and 6-*exo*-Carbomethoxy-6-methyl-4-(trimethylsilyl)bicyclo[3.1.0]hex-3-en-2-ones (8a and 8b). **8a** (7 mg, 0.03 mmol) in benzene (3 mL) was irradiated for 3 h. ^{1}H NMR analysis of the reaction mixture showed that **15** and **14** were formed in a ratio of 2:1. **8b** (6 mg, 0.03 mmol) in benzene (3 mL) was irradiated for 3 h. ^{1}H NMR analysis of the reaction mixture showed that **15** and **14** were formed in a ratio of 2:1.

3-Carbomethoxy-4-methylphenol (21). A solution of **1** (0.10 g, 0.43 mmol) in trifluoroacetic acid (2 mL) was stirred at room temperature for 7 days. Removal of the solvent *in vacuo* followed by flash chromatography (silica gel; 7:3 hexane: EtOAc) gave **21** (65 mg, 91%) as colorless crystals: mp 72−73 °C (lit. 74−75 °C);[19] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40 (d, 1 H, $J = 3$ Hz), 7.12 (d, 1 H, $J = 9$ Hz), 6.92 (dd, 1 H, $J = 9$, 3 Hz), 4.81 (s, 1 H, D_2O exchangeable), 3.89 (s, 3 H), 2.51 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.34, 153.55, 132.91, 132.06, 130.05, 119.46, 117.21, 52.04, 20.80; IR (CH_2Cl_2) 3315, 1685, 1220 cm^{-1}.

3-Carbomethoxy-4-methylphenol (21). **1** (5 mg, 0.02 mmol) was placed in an NMR tube, dissolved in CF_3CO_2D and allowed to stand in the dark for 4 days. ^{1}H NMR analysis of the reaction mixture showed complete conversion of **1** to **21** and that there was no deuterium incorporation in **21**. **21:** ^{1}H NMR (CF_3CO_2D, 500 MHz) δ 9.49 (s, 1 H), 9.22 (d, 1 H, $J = 8.6$ Hz), 9.06 (d, 1 H, $J = 8.3$ Hz), 6.03 (s, 3 H), 4.50 (s, 3 H); **1:** ^{1}H NMR (CF_3CO_2D, 500 MHz) δ 9.35 (d, 1 H, $J = 9.8$ Hz), 8.99 (s, 1 H), 8.66 (d, 1 H, $J = 9.7$ Hz), 5.83 (s, 3 H), 3.71 (s, 3 H), 2.29 (s, 9 H).

General Procedure for the Irradiation of 4-Carbomethoxy-4-methyl-3-(trimethylsilyl)-2,5-cyclohexadien-1-one (1) in Benzene Using Trifluoroacetic Acid as a Cosolvent. To a solution of **1** (28 mg, 0.12 mmol) in benzene (7 mL, 17 mM) was added 1, 2, 5, 10, or 20 equiv of trifluoroacetic acid. The solutions were degassed with N_2 prior to irradiation for 2 h. Removal of the solvent *in vacuo* was followed by ^{1}H NMR analysis. Consult Table 1 for product distributions.

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Supporting Information Available: Copies of NMR spectra of compounds **13** and **14** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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