Photochemistry of 4-Vinyl-2,5-cyclohexadien-1-ones. A Remarkable Effect of Substitution on the Type A and Dienone–Phenol Photorearrangements

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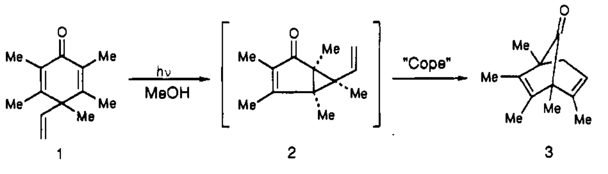
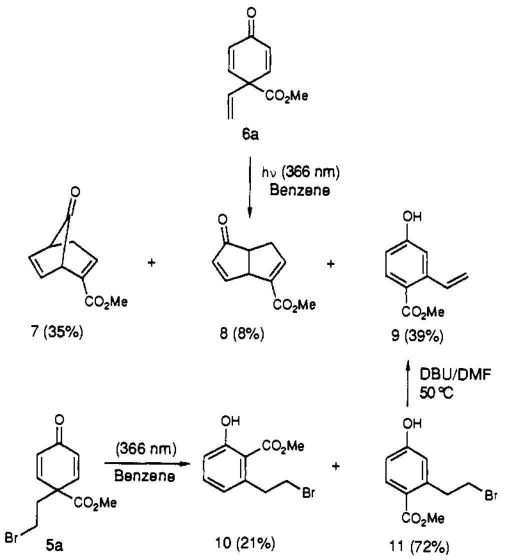
Abstract: 4-Carbomethoxy-4-vinyl-2,5-cyclohexadien-1-ones **6a** and **6b** were prepared from methyl benzoate and methyl 2-methoxybenzoate in 45% overall yields. Irradiation of **6a** in benzene solution at 366 nm gave 2-carbomethoxybicyclo-$[3^{2,3,4}.2^{6,7}.1]$-2,6-octadien-9-one (**7**, 35%), 2-carbomethoxybicyclo$[3.3.0^{1,5}]$-2,7-octadien-6-one (**8**, 8%), and 4-carbomethoxy-3-vinylphenol (**9**, 39%). The structure of phenol **9** was confirmed by irradiation of 4-(2′-bromoethyl)-2,5-cyclohexadien-1-one **5a**, which gave 3-(2′-bromoethyl)-2-carbomethoxyphenol (**10**, 21%) and 3-(2′-bromoethyl)-4-carbomethoxyphenol (**11**, 72%); dehydrobromination of **11** provided a vinylphenol that was identical to that produced from photolysis of **6a**. The *endo*-6-carbomethoxy-6-vinylbicyclohexenone **12a** was obtained from **23** and was found not to be involved in the photochemistry of **6a** at 366 nm; however, photorearrangement of **17** gave **7** in 80% yield. Irradiation of **6b** in benzene solution at 366 nm gave 4-carbomethoxy-3-methoxy-5-vinylphenol (**18**, 65%) and 4-carbomethoxy-3-methoxy-6-vinylphenol (**19**, 32%); in the presence of trifluoroacetic acid, **6b** gave 2-carbomethoxy-5-methoxy-3-vinylphenol (**20**, 5%) and 2-carbomethoxy-8-methoxybicyclo-$[3.3.0^{1,5}]$-2,7-octadien-6-one (**21**, 44%). Reduction of **21** with $NaBH_4/CeCl_3$ in ethanol followed by acid-catalyzed hydrolysis gave 2-carbomethoxybicyclo$[3.3.0^{1,5}]$-2,6-octadien-8-one (**17**, 66%), an intermediate in a previously reported total synthesis of the iridoid monoterpene, (±)-verbenalol. Irradiation of **5b** gave 6-(2′-bromoethyl)-6-*endo*-carbomethoxy-4-methoxy-bicyclo$[3.1.0^{1,5}]$hex-3-en-2-one (**22**, 70%), and dehydrobromination of **22** provided 6-*endo*-carbomethoxy-4-methoxy-6-vinylbicyclo$[3.1.0^{1,5}]$hex-3-en-2-one (**23**, 63%). It was found that **23** was not involved in the photorearrangement of **6b** to phenols **18** and **19**. **18** and **19** are suggested to arise by direct dienone–phenol photorearrangement of **6b** via an initial di-π-methane process involving the 4-vinyl substituent and the C(5)–C(6) double bond (Scheme V). Dienone–phenol photorearrangement of 4-(acetoxymethyl)-3-methoxy-4-vinyl-2,5-cyclohexadien-1-one (**34**) was completely regioselective to give 4-(acetoxymethyl)-3-methoxy-5-vinylphenol in quantitative yield.

Although there are several examples of photorearrangements of 4-vinyl-2-cyclohexen-1-ones,[1] there appears to be only one photorearrangement of a 4-vinyl-2,5-cyclohexadien-1-one recorded in the literature. Hart and Nitta found that irradiation of 2,3,4,5,6-pentamethyl-4-vinyl-2,5-cyclohexadien-1-one (**1**) in methanol gave the bicyclooctadienone **3** in excellent yield.[2] It was suggested that **3** was produced from **1** by photorearrangement to the intermediate 6-*endo*-vinylbicyclo[3.1.0]hex-3-en-2-one **2**, from which Cope rearrangement gave **3**. Neither **2** nor the corresponding 6-*exo*-vinylbicyclohexenone was detected in the study reported by Hart and Nitta.



An intriguing electronic feature of 4-vinyl-2,5-cyclohexadien-1-one **1** is that C(4) is at the center of a tri-π-methane chromophore;[3,4] however, a deuterium labeling experiment ruled out vinyl group migration[5] in the conversion of **1** into **3**. The formation of **2** from **1** appears to occur by the well-known type A photorearrangement.[6]

Scheme I



We have been involved with the development of synthetic aspects of 2,5-cyclohexadienone photochemistry, particularly with regard to the effect of substituents on product composition.[7] We now report the preparation and photochemistry of three 4-vinyl-2,5-cyclohexadien-1-ones (**6a**, **6b**, and **34**). This study has uncovered (1) the first examples of vinyl group migration occurring from photoexcited 4-vinyl-2,5-cyclohexadien-1-ones (**6a** → **9**, **6b** → **18** + **19**, and **34** → **35a**) and (2) sequential photorearrange-

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(1) For an excellent review of the photochemistry of enones, see: Schuster, D. I. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, pp 623–756.

(2) Hart, H.; Nitta, M. *Tetrahedron Lett.* **1974**, 2113.

(3) For a review of the di-π-methane and oxa–di-π-methane photorearrangements, see: Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

(4) The electronically related 4,4-diaryl-2,5-cyclohexadien-1-ones have been studied in great detail; for examples, see: (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527. (b) Zimmerman, H. E.; Keese, R.; Nasielski, J.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895. (c) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 906. (d) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4876. (e) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745.

(5) For an analogous migration of a phenyl group in the photorearrangement of 4,4-diphenyl-2-cyclohexen-1-one to 5,6-diphenylbicyclo[3.1.0]hexan-2-one, see: (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036. (b) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749. (c) Zimmerman, H. E.; Elser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 887.

(6) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.

(7) (a) Schultz, A. G. *Pure Appl. Chem.* **1988**, *60*, 981. (b) Schultz, A. G.; Plummer, M. *J. Org. Chem.* **1989**, *54*, 2112. (c) Schultz, A. G.; Geiss, W. *J. Org. Chem.* **1989**, *54*, 3158. (d) Schultz, A. G.; Hardinger, S. A. *J. Org. Chem.* **1991**, *56*, 1105. (e) Schultz, A. G.; Geiss, W. *J. Am. Chem. Soc.* **1991**, *113*, 3490.

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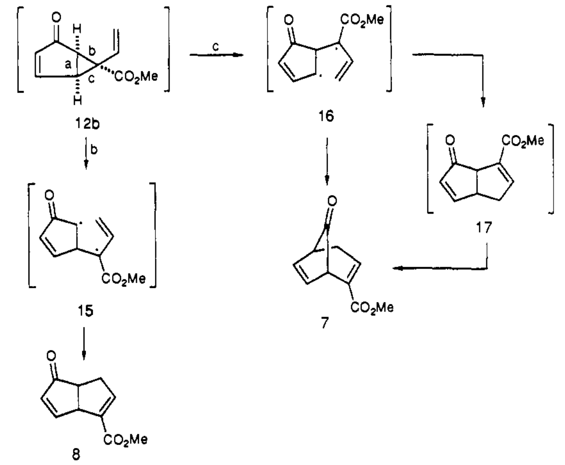
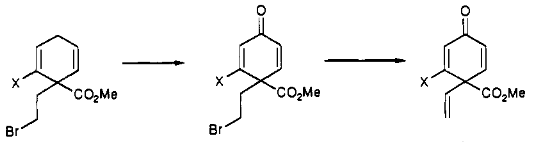
Scheme II



ments of 4-vinyl-2,5-cyclohexadien-1-ones to a bicyclo[3.2.1]-2,6-octadien-9-one (**6a** → **7**) and to bicyclo[3.3.0]-2,7-octadien-6-ones (**6a** → **8** and **6b** → **21**). A formal total synthesis of the iridoid monoterpene (±)-verbenalol also is described.

Results and Discussion

Birch reduction of methyl benzoate and alkylation with 1,2-dibromoethane gave the 1,4-cyclohexadiene **4a**, which was converted to 2,5-cyclohexadien-1-one **5a** by bis-allylic oxidation with pyridinium dichromate (PDC) and *tert*-butyl hydroperoxide (75% overall yield).[8] Conversion of **5a** to the phenyl selenide and oxidation–elimination of the selenide gave 4-carbomethoxy-4-vinyl-2,5-cyclohexadien-1-one (**6a**) in 60% yield. In an analogous manner, methyl 2-methoxybenzoate was converted to the crystalline 4-carbomethoxy-3-methoxy-4-vinyl-2,5-cyclohexadien-1-one (**6b**) in 45% overall yield.



4a, X = H b, X = OMe

5a, X = H b, X = OMe

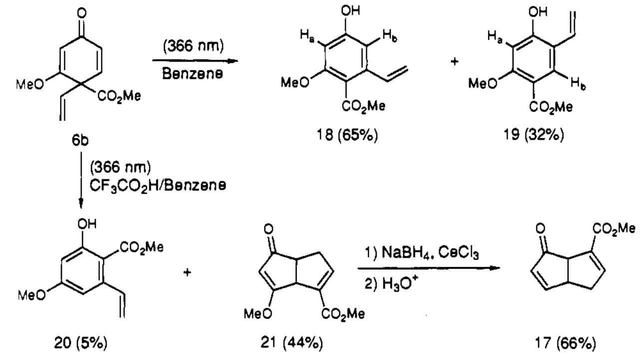
6a, X = H b, X = OMe

Irradiation of **6a** in benzene solution at 366 nm for 4 h gave three photoproducts (Scheme I). Phenol **9** was obtained in 39% isolated yield by extraction of the photoreaction mixture with 1 M potassium hydroxide solution followed by acidification with hydrochloric acid. Flash chromatography of the material in the organic layer provided 2-carbomethoxybicyclo$[3^{2,3,4}.2^{6,7}.1]$-2,6-octadien-9-one (**7**) and 2-carbomethoxybicyclo$[3.3.0^{1,5}]$-2,7-octadien-6-one (**8**).

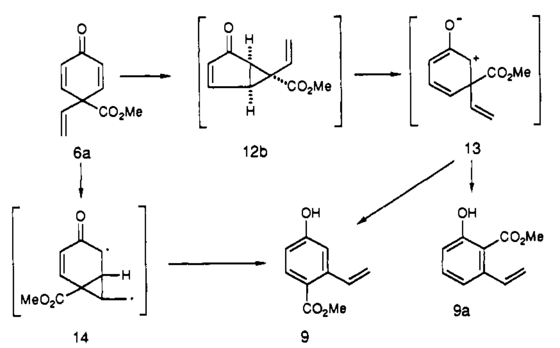
To confirm the structure of phenol **9**, the 4-(2′-bromoethyl)-2,5-cyclohexadien-1-one **5a** was photorearranged to the expected[9a] mixture of phenols **10** and **11**; separation of the phenols and treatment of **11** with diazabicycloundecane (DBU) in warm DMF solution gave a 3-vinylphenol that was identical to that produced from photolysis of **6a**. Dehydrobromination of **10** gave the regioisomeric phenol **9a**.

In analogy with earlier studies,[2,9a] intermediate bicyclo[3.1.0]hex-3-en-2-ones could not be isolated from photorearrangements of **6a**. The *endo*-6-carbomethoxy-6-vinylbicyclohexenone **12a** was prepared by alternative methods (vide infra; Scheme IV) and was found not to be an observable constituent of photoreaction mixtures obtained from **6a** (^{1}H NMR spectroscopy, $\sim$2% limit of detection). Furthermore, **12a** was stable to irradiation at 366 nm for periods that resulted in near-complete photoconversion of **6a** to **7–9**; irradiation of **12a** through Pyrex glassware resulted in decomposition to a complex mixture of products.

Scheme III



There is considerable precedent for the type B photorearrangement of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones to phenols,[10] and 6-alkyl-6-carbomethoxybicyclo[3.1.0]hex-3-en-2-ones have been proposed to be intermediates in photorearrangements of 4-alkyl-4-carbomethoxy-2,5-cyclohexadien-1-ones to phenols.[2,9a] It is remarkable, therefore, that **12a** does not photorearrange at 366 nm to phenol **9** (and **9a**); the 6-vinyl substituent in **12a** appears to "protect" the internal cyclopropane bond from photocleavage. Related substituent effects pertaining to bicyclo[3.1.0]hexenone photostabilization have been observed for the 6-cyano[9a] and the 6-methoxy[9b] groups.



Although it is possible that **9** is generated from **6a** by type B photorearrangement[10] of the diastereoisomeric bicyclohexenone **12b**, it is surprising that a competing rearrangement of the intermediate zwitterion **13** to phenol **9a** is not observed.[2,9a] A mechanism compatible with the exclusive formation of phenol **9** involves di-π-methane photorearrangement of **6a** to biradical **14**. Subsequent cleavage of the cyclopropane bond originally at C(4) in **6a** and hydrogen migration would transform **14** into **9**. A distinction between these mechanistic possibilities will have to await the completion of experiments involving isotopic labeling of **6a** at C(4).

It is possible that **7** and **8** both arise from the intermediate 6-*endo*-vinyl-6-carbomethoxybicyclo[3.1.0]hex-3-en-2-one (**12b**). **12b** might undergo Cope rearrangement[2] to **7**; however, formation of bicyclooctadienone **8** from **12b** by a thermal vinylcyclopropane to cyclopentene rearrangement is precluded because of the high activation energy for this process.[11] It seems reasonable to suggest that **7** and **8** are produced by photorearrangements of **12b** (Scheme II). Photochemical vinylcyclopropane rearrangement[12] by bond "b" cleavage to give biradical **15** followed by radical recombination would give **8**. Cyclopropane bond "c" cleavage would generate

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(8) Schultz, A. G.; Taveras, A. G.; Harrington, R. E. *Tetrahedron Lett.* **1988**, *29*, 3907.

(9) (a) Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991. (b) Schultz, A. G.; Harrington, R. E. *J. Org. Chem.* **1991**, *56*, 6391.

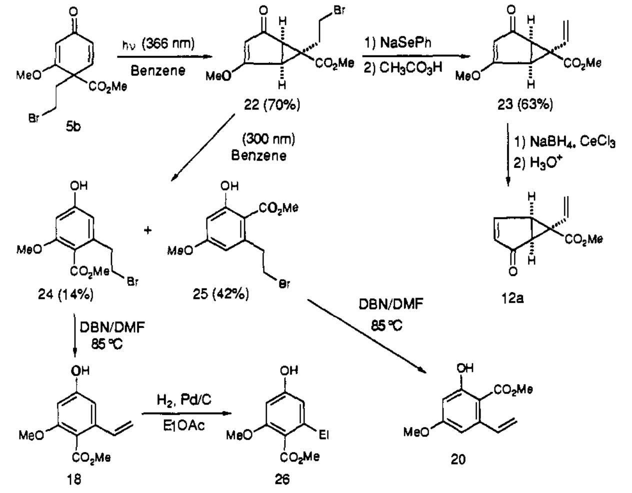
(10) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 7806.

(11) For examples of thermal Cope and vinylcyclopropane to cyclopentene rearrangements of 6-vinylbicyclo[3.1.0]hexan-2-ones, see: (a) Fleming, A.; Sinai-Zingde, G.; Natchus, M.; Hudlikcy, T. *Tetrahedron Lett.* **1987**, *28*, 167. (b) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691.

(12) The α,β-enone group has been found to be an effective chromophore for photoinitiation of the vinylcyclopropane to cyclopentene rearrangement; for examples, see: (a) Schultz, A. G.; Dittami, J. P. *Tetrahedron Lett.* **1984**, *25*, 1255. (b) Schultz, A. G.; Puig, S. *J. Org. Chem.* **1985**, *50*, 915.

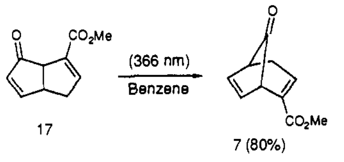
(13) Gemal, A. L.; Luche, J.-L. *J. Org. Chem.* **1979**, *44*, 4187.

Scheme IV



biradical **16**, which would give bicyclooctadienone **7** by radical recombination.

It was of interest to find that 2-carbomethoxybicyclo[3.3.0^{1,5}]-2,6-octadien-8-one (**17**) was not observed in photoreactions of **6a**. The presence of **17** would be indicative of a second vinylcyclopropane to cyclopentene rearrangement (**12b** → **16** → **17**) in competition with that of **12b** → **15** → **8** (Scheme II). Bicyclooctadienone **17** was available from parallel studies of the photochemistry of **6b** (Scheme III). Irradiation of **17** at 366 nm provided the bridged β,γ-enone **7** in 80% isolated yield. Thus, if **17** is formed by photorearrangement of **6a**, then it must undergo a secondary [1,3]-photorearrangement to **7**.

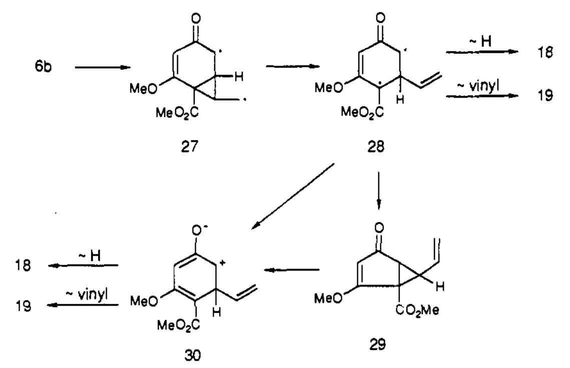


Photorearrangements of 4-alkyl-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-ones at 366 nm give diastereoisomeric 6-alkyl-6-carbomethoxybicyclo[3.1.0]hex-3-en-2-ones in good to excellent yields. Continued irradiation at 366 nm results in bicyclohexenone interconversion to give mainly the 6-*endo*-carbomethoxybicyclohexenone.[9a] Irradiation of the 3-methoxy-2,5-cyclohexadienone **6b** in benzene solution at 366 nm gave a mixture of two phenols (Scheme III). Flash chromatography on silica gel provided 4-carbomethoxy-3-methoxy-5-vinylphenol (**18**) (65% isolated yield) and 4-carbomethoxy-3-methoxy-6-vinylphenol (**19**) (32%).

The structure of **18** was suggested by its ^{1}H NMR spectrum, which showed one-proton doublets for H_a and H_b (J_{ab} = 2.3 Hz; meta coupling) at δ 6.61 and 6.37 and a broad resonance at 5.75 (exchangeable with D_2O) belonging to the phenolic proton. Hydrogenation of **18** with Pd/C in ethyl acetate gave the crystalline, previously reported 4-carbomethoxy-3-ethyl-5-methoxyphenol (**26**) (Scheme IV).[14]

Resonances for H_a and H_b in **19** appeared as sharp one-proton singlets indicative of para substitution at δ 6.45 and 7.92, respectively. The low-field resonance for H_b is consistent with its assigned position ortho to the carbomethoxy group. The phenolic proton resonance appeared at 6.05 ($CDCl_3$), in accord with its location para to the carbomethoxy group; an ortho relationship would require a phenolic proton resonance at ~11 ppm.[9a]

Scheme V



A change in the photoreaction medium for **6b** from a hydrocarbon solvent to a strong protic acid resulted in a dramatic change in product composition. Thus, irradiation of **6b** in benzene/trifluoroacetic acid gave phenol **20** (5%), 2-carbomethoxy-8-methoxybicyclo[3.3.0^{1,5}]-2,7-octadien-6-one (**21**, 44%), and a small amount of a substance subsequently identified as 6-*endo*-carbomethoxy-4-methoxy-6-vinylbicyclo[3.1.0^{1,5}]hex-3-en-2-one (**23**) (vide infra).

The structure of **20** was determined by ^{1}H NMR methods (see the Experimental Section) and synthesis. Irradiation of **5b** in benzene solution at 366 nm gave 6-(2′-bromoethyl)-6-*endo*-carbomethoxy-4-methoxybicyclo[3.1.0^{1,5}]hex-3-en-2-one (**22**) in 70% isolated yield. Trace amounts of phenolic products also were produced, but the 6-*exo*-carbomethoxybicyclohexenone was not observed under these photoreaction conditions. Photorearrangement of **22** at 300 nm produced a mixture of phenols **24** and **25**. Dehydrobromination of **24** and **25** gave phenols **18** and **20**, respectively.

Reduction of **21** with $NaBH_4/CeCl_3$ in methanol[13] followed by acid-catalyzed hydrolysis gave 2-carbomethoxybicyclo[3.3.0^{1,5}]-2,6-octadien-8-one (**17**) in 66% overall yield. Inasmuch as bicyclooctadienone **17** has been converted to (±)-verbenalol,[15] the preparation of **17** just described constitutes a formal total synthesis of this iridoid monoterpene. The conversion of methyl 2-methoxybenzoate to **17** requires seven steps and is carried out in an unoptimized 16% overall yield. By contrast, the literature method requires twelve steps from 2-cyclopentene-1-acetic acid and is reported to proceed in 9% overall yield.

Dehydrobromination of **22** provided 6-*endo*-carbomethoxy-4-methoxy-6-vinylbicyclo[3.1.0^{1,5}]hex-3-en-2-one (**23**). The photochemistry of **23** at 366 nm was found to be quite complex. Without going into great detail at this time, two important observations can be made: (1) phenols **18** and **19** were not detected in any of the photoreactions of **23**, and (2) phenol **20** and bicyclooctadienone **21** were both formed by photorearrangements of **23**.

Thus, **18** and **19** are generated from **6b** by a mechanistic pathway that does not involve type A photoreactivity. It is suggested that **18** and **19** arise by direct dienone–phenol photorearrangements of **6b** (Scheme V). Regioselective di-π-methane photorearrangement[3] of **6b** to biradical **27**, with preservation of the vinylogous ester chromophore,[9a] followed by additional electron reorganization would give biradical **28**. Competing hydrogen atom and vinyl group migration in **28** would give **18** and **19** directly; alternatively, radical recombination would give the expected di-π-methane product **29**. The bicyclo[3.1.0]hexenone might then undergo a type B photorearrangement[10] to zwitterion **30**, from which **18** and **19** would arise by competitive hydrogen atom and vinyl group rearrangements. It also is possible that **28** intersystem crosses to zwitterion **30** without formation of an intermediate bicyclo[3.1.0]hexenone. A more definitive statement of mechanism must await attempts to isolate potentially stable intermediates such as **29**[9a] and to intercept reactive intermediates such as **30**.[7b]

The effect of the 4-carbomethoxy group in **6b** on the regioselectivity of dienone–phenol photorearrangement was examined as shown in Scheme VI. Irradiation of 4-(acetoxymethyl)-3-methoxy-4-vinyl-2,5-cyclohexadien-1-one (**34**) in benzene solution at 366 nm gave phenol **35a** in nearly quantitative yield. This

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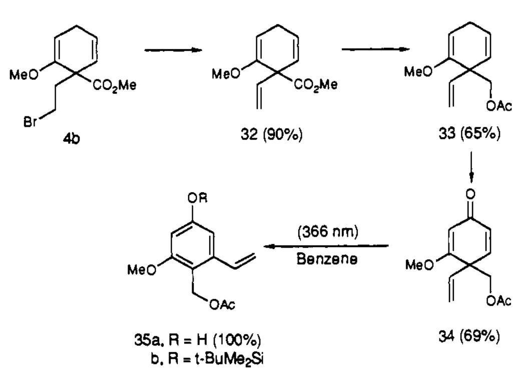
(14) Fink, M.; Gaier, H.; Gerlach, H. *Helv. Chim. Acta* **1982**, *65*, 2563.

(15) Callant, P.; Ongena, R.; Vandewalle, M. *Tetrahedron* **1981**, *37*, 2085.

Scheme VI



substance was unstable and could only be characterized completely by conversion to the corresponding *tert*-butyldimethylsilyl ether **35b**. The structure of **35b** was confirmed by preparation of **35b** from phenol **18**; see the Experimental Section.

Although we can say very little about the origin of substituent effects on the regioselectivity of the dienone–phenol photorearrangements at present, the observations recorded in Schemes III and VI do provide a foundation for future structural and kinetic studies. It is remarkable that with both **6b** and **34** the di-π-methane process occurs to the total exclusion of the normally efficient type A photorearrangement. Exclusive 1,2-aryl migration has been observed for certain 4,4-dinaphthyl-2,5-cyclohexadien-1-ones,[4e] but these rearrangements were proposed to occur from excited states of the migrating aryl groups. Obviously, photorearrangements of **6b** and **34** must occur from an excited state of the 2,5-cyclohexadien-1-one chromophore rather than the vinyl substituent.[16]

Type A photoreactivity is characteristic of the n→π^* triplet state,[6] whereas the di-π-methane reactivity of 4-vinyl-2,5-cyclohexadien-1-ones may result from mixing with the $\pi\rightarrow\pi^*$ triplet state.[17] Contrasting the photoreactivity of **6a**, which shows mixed type A and dienone–phenol reactivity, with **6b** and **34** suggests that the 3-methoxy substituent enhances di-π-methane behavior. It has already been noted that the 3-methoxy substituent lowers the energy of the $\pi\rightarrow\pi^*$ triplet state of 2,5-cyclohexadienones to such an extent that 4-aryl migration[4e] and intramolecular [2 + 2] photocycloadditions[7a,18] compete with the type A photorearrangement.

The shift in product composition as a function of solvent polarity and acidity noted for **6b** (Scheme III) has some precedent in the work of Griffiths and Hart.[19] They found that trifluoroethanol or silica gel shifts the position of the $\pi\rightarrow\pi^*$ band of the 2,4-cyclohexadien-1-one chromophore and changes photoreactivity from predominantly n→π^* to $\pi\rightarrow\pi^*$ character. Although additional studies are required to define the origin of solvent effects described in this study, it appears that trifluoroacetic acid serves to enhance the n→π^* reactivity of **6b**.

Experimental Section

General Procedures. Synthetic and photochemical procedures have been described elsewhere.[7]

6-(2′-Bromoethyl)-6-carbomethoxy-1-methoxy-1,4-cyclohexadiene (4b). Methyl 2-methoxybenzoate (0.40 g, 0.0024 mol) was dissolved in 6 mL of tetrahydrofuran (THF) containing *tert*-butyl alcohol (1 equiv). Ammonia was distilled into the solution at −78 °C. Small pieces of potassium metal were added at −78 °C until a blue coloration persisted for 10 min. 1,2-Dibromoethane (0.012 mol, 5 equiv) was added, and the solution was stirred at −78 °C for 15 min and −33 °C for 1 h. Solid ammonium chloride (NH_4Cl) was added, and the ammonia was allowed to evaporate. Water was added and the mixture was extracted with ether. After the organic layer was dried over magnesium sulfate, the solvent was removed under reduced pressure. Flash chromatography on silica gel (hexane/ethyl acetate, 13:1) gave a clear oil that solidified on standing. Crystallization from ether/hexane afforded **4b** as colorless crystals: mp 38–40 °C (0.554 g, 84%); ^{1}H NMR ($CDCl_3$) δ 5.97 (ddt, 1 H, J = 10 Hz, J = 2 Hz, J = 0.5 Hz), 5.44 (dt, 1 H, J = 10 Hz, J = 2 Hz), 4.91 (t, 1 H, J = 3.5 Hz), 3.71 (s, 3 H), 3.57 (s, 3 H), 3.18 (m, 2 H), 2.87 (m, 2 H), 2.71 (m, 2 H); IR (film) 1735 (CO_2Me), 1640 (CH=CHOMe) cm^{-1}; CIMS m/z isobutane (relative intensity) 277, 275 (100, 98), 195 (15). Anal. Calcd for $C_{11}H_{15}BrO_3$: C, 47.99; H, 5.50. Found: C, 47.79; H, 5.51.

4-(2′-Bromoethyl)-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-one (5b). To a solution of **4b** in benzene (60 mL) was added Celite (4.5 g), pyridinium dichromate (PDC, 4.5 g, 4 equiv), and *tert*-butyl hydroperoxide (1.34 mL, 90% solution, 4 equiv). The reaction mixture was stirred for 6 h at room temperature and then filtered through Celite. Evaporation of the solvent under reduced pressure and flash chromatography on silica gel (hexane/ethyl acetate, 1:1) provided **5b** (1.29 g, 76%) as a solid. An analytical sample was prepared by recrystallization from hexane/ethyl acetate/ether: mp 69–70 °C; ^{1}H NMR ($CDCl_3$) δ 6.56 (d, 1 H, J = 10 Hz), 6.40 (dd, 1 H, J = 10 Hz, J = 1.3 Hz), 5.77 (d, 1 H, J = 1.3 Hz), 3.83 (s, 3 H), 3.78 (s, 3 H), 3.12 (m, 2 H), 2.91 (m, 2 H); IR (film) 1735 (CO_2Me), 1660 (C=O), 1600 (C=C) cm^{-1}; CIMS m/z isobutane (relative intensity) 289, 291 (100, 98), 238 (5); UV (benzene) 300 nm (ϵ = 470), 366 (14). Anal. Calcd for $C_{11}H_{13}BrO_4$: C, 45.69; H, 4.53. Found: C, 45.61; H, 4.59.

4-Carbomethoxy-3-methoxy-4-vinyl-2,5-cyclohexadien-1-one (6b). To a solution of **5b** (3.20 g, 0.011 mol) in absolute ethanol (120 mL) was added diphenyl diselenide (3.83 g, 0.012 mol). Sodium borohydride (0.464 g, 0.012 mol) was added, and the mixture was heated at 50 °C for 5 h. After the reaction was cooled to room temperature, a 10% solution of hydrochloric acid (10 mL) was added, and the solvent was removed under reduced pressure. The residue containing the crude selenide was dissolved in 50 mL of chloroform, and peracetic acid (32% in acetic acid, 6 mL) was slowly added. After stirring at room temperature for 20 min, the clear solution was carefully washed twice with a saturated solution of aqueous sodium bicarbonate and once with brine. The chloroform layer was heated to reflux for 15 min and then cooled to room temperature. The yellow solution was dried over magnesium sulfate, and the solvent was removed under reduced pressure. Flash chromatography of the crude product (hexanes/ethyl acetate, 2:1) and crystallization from hexane/ethanol gave **6b** (1.7 g, 71%) as colorless crystals: mp 94–95 °C; ^{1}H NMR ($CDCl_3$) δ 6.62 (d, 1 H, J = 9.8 Hz), 6.44 (m, 1 H) overlapped by 6.35 (d, 1 H, J = 9.8 Hz), 5.67 (s, 1 H), 5.33 (d, 1 H, J = 10.5 Hz), 5.19 (d, 1 H, J = 17.6 Hz), 3.79 (s, 3 H), 3.77 (s, 3 H); IR (film) 1740 (CO_2Me), 1660 (C=O), 1600 (C=C) cm^{-1}; CIMS m/z isobutane (relative intensity) 209 (100); UV (MeOH) 300 nm (ϵ = 1250), 366 (2.8), (benzene) 300 nm (508), 366 (3.4). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.39; H, 5.72.

4-Carbomethoxy-3-methoxy-5-vinylphenol (18) and 4-Carbomethoxy-3-methoxy-6-vinylphenol (19). A solution of **6b** (150 mg) in benzene (20 mL) was irradiated at 366 nm for 4 h. A white precipitate suspended in the reaction mixture was observed. The benzene was decanted, and the white solid was washed with cold benzene/hexane. The solid material was saved; evaporation of the combined solvent layers and flash chromatography (hexanes/ethyl acetate, 2:1) provided **18** as colorless crystals (98 mg, 65%): mp 117–118 °C; ^{1}H NMR ($CDCl_3$) δ 6.66 (dd, 1 H, J = 17.5 Hz, J = 10.9 Hz) overlapped by 6.61 (d, 1 H, J = 2.3 Hz), 6.37 (d, 1 H, J = 2.3 Hz), 5.8 (br s, 1 H, exchangeable with D_2O), 5.68 (dd, 1 H, J = 17.5 Hz, J = 1 Hz), 5.33 (dd, 1 H, J = 10.9 Hz, J = 1 Hz), 3.93 (s, 3 H), 3.78 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 169 (e), 159 (e), 158 (e), 138 (e), 134 (o), 114 (e), 107 (e), 104 (o), 99 (o), 56 (o), 52 (o); IR ($CHCl_3$), 3540 (OH), 3370 (OH), 1720 (CO_2Me), 1590 (C=C) cm^{-1}; CIMS m/z isobutane (relative intensity) 209 (100), 177 (5); UV (benzene) 300 (ϵ = 1800), 366 (4.7). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.34; H, 5.72.

Another fraction contained material identical (TLC) to the white precipitate filtered from the crude reaction mixture. The combined solid material (sparingly soluble in ethyl acetate, methylene chloride, ether, or methanol) was chromatographed on silica gel (hexanes/acetonitrile, 3:1) to provide **19** as colorless crystals (48 mg, 32%): mp 161–162 °C; ^{1}H NMR (THF-d_8) δ 9.11 (s, 1 H, exchangeable with D_2O), 7.93 (s, 1 H), 6.88 (dd, 1 H, J = 17.5 Hz, J = 11.3 Hz), 6.39 (s, 1 H), 5.68 (dd, 1 H, J = 17.5 Hz, J = 1.7 Hz), 5.09 (dd, 1 H, J = 11.3 Hz, J = 1.7 Hz), 3.78 (s, 3 H), 3.73 (s, 3 H); ^{13}C NMR (THF-d_8) δ 168 (e), 163 (e), 161 (e), 134 (o), 133 (o), 119 (e), 115 (e), 113 (e), 101 (o), 57 (o), 52 (o); IR (THF) 3545, 3330 (OH), 1735 (CO_2Me), 1595 (C=C) cm^{-1}; CIMS m/z isobutane (relative intensity) 209 (100); UV (benzene) 300 (ϵ =

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(16) For examples of possible intramolecular energy transfer from an excited 2,5-cyclohexadien-1-one to a 4-(4′-phenyl-3′-butenyl) group, see ref 7e.

(17) It has been shown that the reactive triplet state of ketones undergoing the oxa-di-π-methane photorearrangement are of a $\pi\rightarrow\pi^*$ configuration; see: Hancock, K. G.; Grider, R. O. *J. Chem. Soc., Chem. Commun.* **1972**, 580.

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347), 366 (2.8). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.46; H, 5.81. Found: C, 63.04; H, 5.81.

6-(2′-Bromoethyl)-6-*endo*-carbomethoxy-4-methoxybicyclo[3.1.0^{1,5}]hex-3-en-2-one (22). A solution of **5b** (1.0 g) in 400 mL of benzene was irradiated at 366 nm for 17 h. The residue was chromatographed (hexanes/ethyl acetate, 1:1) to give 0.71 g (70%) of **22** as a yellow tinted oil and 11% of **25**. An analytical sample of **22** was prepared by crystallization (hexanes/ethanol): mp 80–82 °C; ^{1}H NMR ($CDCl_3$) δ 4.74 (s, 1 H), 3.79 (s, 3 H), 3.63 (s, 3 H), 3.36 (dt, 2 H, J = 7.7 Hz, J = 1.8 Hz), 2.50 (d, 1 H, J = 5.2 Hz), 2.26 (d, 1 H, J = 5.2 Hz), 2.16 (dt, 2 H, J = 7.7 Hz, J = 1.8 Hz); IR (film) 1725 (CO_2Me), 1680 (C=O), 1590 (HC=COMe); CIMS m/z (relative intensity) 291, 289 (100). Anal. Calcd for $C_{11}H_{13}BrO_4$: C, 45.69; H, 4.53. Found: C, 45.81; H, 4.64.

6-*endo*-Carbomethoxy-4-methoxy-6-vinylbicyclo[3.1.0^{1,5}]hex-3-en-2-one (23). Dehydrobromination of **22** (0.79 g, 0.0027 mol) by the procedure described for **6b** and chromatography of the product mixture (hexanes/ethyl acetate, 1:1) gave 0.353 g (63%) of **23** as a colorless solid. An analytical sample was prepared by recrystallization from hexanes/ethanol (short white needles, mp 97–98 °C): ^{1}H NMR ($CDCl_3$) δ 5.71 (dd, 1 H, J = 17.5 Hz, J = 10 Hz), 5.21 (d, 1 H, J = 17.5 Hz), 5.23 (d, 1 H, J = 10 Hz), 4.82 (s, 1 H), 3.82 (s, 3 H), 3.71 (s, 3 H), 2.64 (dd, 1 H, J = 6 Hz, J = 1.1 Hz), 2.48 (dd, 1 H, J = 6 Hz, J = 1.1 Hz); ^{13}C NMR ($CDCl_3$) δ 197 (e), 185 (e), 168 (e), 134 (o), 116 (e), 97 (o), 58 (o), 55 (e), 53 (o), 34 (o), 31 (o); IR (film) 1725 (CO_2Me), 1680 (C=O), 1585 (C=C) cm^{-1}; CIMS m/z isobutane (relative intensity) 209 (100); UV (benzene) 300 nm (ε = 294), 366 (5.5), (MeOH) 300 nm (2250), 366 (5.8). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.63; H, 6.00.

6-*endo*-Carbomethoxy-6-vinylbicyclo[3.1.0^{1,5}]hex-3-en-2-one (12a). To a solution of **23** (0.121 g, 0.59 mmol) in methanol (5 mL) was added cerium trichloride heptahydrate (0.23 g, 3 equiv). After 15 min, the solution was cooled to 0 °C, and sodium borohydride (0.08 g, 2 equiv) was added. After the mixture was stirred for 4 h at 0 °C and 0.5 h at room temperature, a solution of 10% hydrochloric acid (5 mL) was added. After the solution was stirred for 15 min, the solvents were removed by evaporation at reduced pressure, and the residue was extracted with ether (3 × 10 mL). The combined organic layers were washed with saturated sodium bicarbonate and brine and then dried over magnesium sulfate. Removal of the solvent under reduced pressure and flash chromatography on silica gel (hexanes/ethyl acetate, 2:1) provided **12a** (0.043 g, 41%) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.42 (dd, 1 H, J = 5.5 Hz, J = 2.6 Hz), 5.84 (d, 1 H, J = 5.5 Hz) overlapped by 5.71 (dd, 1 H, J = 17.5 Hz, J = 10.2 Hz), 5.20 (d, 1 H, J = 10.2 Hz), 5.19 (d, 1 H, J = 17.5 Hz), 3.67 (s, 3 H), 2.84 (dd, 1 H, J = 4.5 Hz, J = 2.6 Hz), 2.45 (d, 1 H, J = 4.5 Hz); IR (film) 1720 (CO_2Me), 1695 (C=O) cm^{-1}; CIMS m/z isobutane (relative intensity) 179 (100), 147 (8). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.15; H, 5.71.

2-Carbomethoxy-8-methoxybicyclo[3.3.0^{1,5}]-2,7-octadien-6-one (21). Dienone **6b** (0.10 g) was irradiated at 366 nm in a solution of benzene (20 mL) and trifluoroacetic acid (1.5 mL) for 4 h. Chromatography on silica gel (hexanes/ethyl acetate, 2:1, then 1:1, then ethyl acetate) gave **20** (0.005 g, 5%), recovered **6b** (0.01 g, 10%), **23** (0.004 g, 4%), and **21** (0.044 g, 44%) as tan needles. The analytical sample was prepared by recrystallization from ethanol/pentane to give off-white prisms: mp 111–111.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.60 (t, 1 H, J = 2.4 Hz), 5.1 (d, 1 H, J = 1 Hz), 4.11 (m, 1 H), 3.74 (s, 3 H), 3.69 (s, 3 H), 3.27 (m, 1 H), 2.63 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 191 (e), 164 (e), 144 (o), 134 (e), 102 (o), 59 (o), 52 (o), 51 (o), 48 (o), 34 (e), 30 (o); IR (film) 1720 (CO_2Me), 1690 (C=O), 1600 (C=C); CIMS m/z isobutane (relative intensity) 209 (100), 197 (10), 195 (5); UV (benzene/CF_3CO_2H, 20:1.5) 300 nm (ε = 154), 366 (11). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.46; H, 5.81. Found: C, 63.57; H, 5.64.

Determination of the Structure of 20. Dehydrobromination of 3-(2′-Bromoethyl)-2-carbomethoxy-5-methoxyphenol (25) to 2-Carbomethoxy-5-methoxy-3-vinylphenol (20). To a solution of **25** (90 mg, 0.3 mmol) in DMF (1 mL) was added diazabicyclononane (0.12 mL, 0.9 mmol), after which the mixture was heated at 85 °C for 12 h. After being cooled to room temperature, the mixture was extracted with chloroform (25 mL). The organic layer was washed with a 10% solution of hydrochloric acid (3 × 5 mL) and brine. After being dried over magnesium sulfate, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (hexanes/ethyl acetate, 4:1) to give **20** as a colorless powder (14 mg, 23%): mp 75–76 °C; ^{1}H NMR ($CDCl_3$) δ 11.0 (s, 1 H), 7.23 (dd, 1 H, J = 17.5 Hz, J = 10.2 Hz), 6.50 (d, 1 H, J = 2.8 Hz), 6.41 (d, 1 H, J = 2.8 Hz), 5.48 (dd, 1 H, J = 17.5 Hz, J = 1.4 Hz), 5.23 (dd, 1 H, J = 10.2 Hz, J = 1.4 Hz), 3.9 (s, 3 H), 3.8 (s, 3 H); IR ($CHCl_3$) 3540, 3335 (OH), 1705 (CO_2Me), 1600 (C=C); CIMS m/z isobutane (relative intensity) 209 (100). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.46; H, 5.81. Found: C, 63.47; H, 6.02. This material was found to be identical to the phenol, **20**, obtained from photolysis of **6b**.

2-Carbomethoxybicyclo[3.3.0^{1,5}]-2,6-octadien-8-one (17). To a solution of **21** (39 mg, 0.19 mmol) in methanol (3 mL) was added cerium trichloride heptahydrate (105 mg, 0.281 mmol). After being stirred at room temperature for 15 min, the mixture was cooled to 0 °C and then stirred for an additional 15 min. Sodium borohydride (21 mg, 0.56 mmol) was added, and the mixture was stirred at 0 °C for 30 min and then at room temperature for 2 h. A solution of 10% hydrochloric acid (2 mL) was added, and after 5 min, the reaction mixture was extracted with ethyl acetate (10 mL). The organic layer was washed with a saturated solution of sodium bicarbonate and brine and then was dried over magnesium sulfate. The solvent was evaporated under reduced pressure to afford a tan oil; flash chromatography on silica gel (hexanes/ethyl acetate, 1:1) provided **17** as a colorless oil (22 mg, 66%). The spectral data (^{1}H NMR, IR, CIMS) agreed with literature reports.[14]

Photorearrangement of 17 to 7. Irradiation of a solution of **17** (0.015 g) in benzene (3.0 mL) and flash chromatography on silica gel (hexanes/ethyl acetate, 4:1) gave **7** (12 mg, 80%).

3-(2′-Bromoethyl)-2-carbomethoxy-5-methoxyphenol (25) and 3-(2′-Bromoethyl)-4-carbomethoxy-5-methoxyphenol (24). Irradiation of bicyclohexenone **22** (0.13 g) in benzene (20 mL) through Pyrex glassware for 24 h and chromatography on silica gel (hexanes/ethyl acetate, 3:1) afforded **25**, mp 94–95 °C (R_f = 0.75, 0.0054 g, 42%), and **24**, mp 165 °C dec (R_f = 0.4, 0.018 g, 14%). **25**: ^{1}H NMR ($CDCl_3$) δ 11.1 (s, 1 H), 6.44 (d, 1 H, J = 2.1 Hz), 6.35 (d, 1 H, J = 2.1 Hz), 4.01 (s, 3 H), 3.82 (s, 3 H), 3.45 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 171 (e), 165 (e), 164 (e), 142 (e), 111 (o), 106 (e), 104 (e), 55 (o), 52 (o), 40 (e), 32 (e); IR ($CHCl_3$) 3600 (OH), 1665 (CO_2Me), 1610 (Ar) cm^{-1}. **24**: ^{1}H NMR ($CDCl_3$) δ 6.36 (d, 1 H, J = 1.8 Hz), 6.32 (d, 1 H, J = 1.8 Hz), 5.81 (br s, 1 H, exchangeable with D_2O), 3.95 (s, 3 H), 3.78 (s, 3 H), 3.52 (t, 2 H, J = 6.3 Hz), 3.08 (t, 2 H, J = 6.3 Hz); IR ($CHCl_3$) 3350 (OH), 1710 (CO_2Me), 1610 (Ar) cm^{-1}; CIMS m/z isobutane (relative intensity) 291, 289 (100). Anal. Calcd for $C_{11}H_{13}BrO_4$: C, 45.69; H, 4.53. Found: C, 45.55; H, 4.66.

Determination of the Structure of 18. Conversion to 4-Carbomethoxy-3-ethyl-5-methoxyphenol (26). A mixture of **18** (0.035 g, 0.17 mmol) and 5% palladium on carbon (~1 mg) in ethyl acetate (3 mL) was shaken on a Parr hydrogenator under a hydrogen atmosphere (24 psi) for 24 h. The suspension was filtered through Celite, and the solvent was removed under reduced pressure. Chromatography on silica gel (hexanes/ethyl acetate, 3:1) gave **26** as a colorless solid (21 mg, 60%): mp 106 °C (lit. mp 106 °C[15]); ^{1}H NMR ($CDCl_3$) δ 6.28 (s, 1 H), 6.27 (s, 1 H), 5.87 (br s, 1 H, exchangeable with D_2O), 3.9 (s, 3 H), 3.74 (s, 3 H), 2.56 (q, 2 H, J = 7.6 Hz), 1.17 (t, 3 H, J = 7.6 Hz); IR (film) 3350 (OH), 1725 (CO_2Me), 1610 (Ar) cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.73; H, 6.73.

Determination of the Structure of 24. Dehydrobromination of 24 to 4-Carbomethoxy-3-methoxy-5-vinylphenol (18). Dehydrobromination of **24** (0.13 g, 0.0004 mol) by the procedure described for the conversion of **25** to **20** and chromatography of the product mixture (hexanes/ethyl acetate, 2:1) afforded **18** as a colorless solid (0.028 g, 30%), mp 116–117 °C. Spectral data agreed with those of the product obtained from irradiation of **6b**.

3-(2′-Bromoethyl)-2-carbomethoxyphenol (10) and 3-(2′-Bromoethyl)-4-carbomethoxyphenol (11). Dienone **5a** was irradiated at 366 nm in benzene for 26 h; chromatography on silica gel (hexanes/ethyl acetate, 9:1) gave **10** (higher R_f, 7.4 mg, 21%, oil) and **11** (lower R_f, 25.8 mg, 72%, mp 109–110 °C). **10**: ^{1}H NMR ($CDCl_3$) δ 11.18 (s, 1 H), 7.39 (t, 1 H, J = 7.9 Hz), 6.96 (dd, 1 H, J = 7.9 Hz, J = 1.3 Hz), 6.79 (dd, 1 H, J = 7.9 Hz, J = 1.3 Hz), 4.04 (s, 3 H), 3.51 (m, 4 H); IR (CH_2Cl_2) 3650, 3300 (OH), 1665 (CO_2Me), 1610 (Ar) cm^{-1}; CIMS m/z isobutane (relative intensity) 259, 261 (100, 98). Anal. Calcd for $C_{10}H_{11}O_3Br$: C, 46.17; H, 4.65. Found: C, 46.26; H, 4.72. **11**: ^{1}H NMR ($CDCl_3$) δ 7.95 (dd, 1 H, J = 8.9 Hz, J = 1.2 Hz), 6.78 (dd, 1 H, J = 8.9 Hz, J = 1.2 Hz) overlapped by 6.76 (d, 1 H, J = 1.2 Hz), 5.66 (s, 1 H), 3.88 (s, 3 H), 3.66 (dt, 2 H, J = 6.7 Hz, J = 1.7 Hz), 3.51 (dt, 2 H, J = 6.7 Hz, J = 1.7 Hz); IR (film) 3250 (OH), 1710 (CO_2Me), 1605 (Ar) cm^{-1}; CIMS m/z isobutane (relative intensity) 259, 261 (100, 95), 179 (10). Anal. Calcd for $C_{10}H_{11}O_3Br$: C, 46.17; H, 4.65. Found: C, 46.16; H, 4.51.

4-(2′-Bromoethyl)-4-carbomethoxy-2,5-cyclohexadien-1-one (5a). Birch reduction of methyl benzoate and alkylation with 1,2-dibromoethane as described for the preparation of **4b** gave **4a**, which was used without purification: ^{1}H NMR ($CDCl_3$) δ 5.97 (dt, 2 H, J = 10.3 Hz, J = 3.3 Hz), 5.71 (dt, 2 H, J = 10.3 Hz, J = 1.9 Hz), 3.72 (s, 3 H), 3.15 (dt, 2 H, J = 8.6 Hz, J = 2.3 Hz), 2.65 (m, 2 H), 2.30 (dt, 2 H, J = 8.6 Hz, J = 2.3 Hz); IR (film) 1725 (CO_2Me), 1600 (CH=CH) cm^{-1}; CIMS m/z isobutane (relative intensity) 247, 245 (98, 100), 165 (15). Oxidation by the procedure described for the preparation of **5b** and chromatography on silica gel (hexanes/ethyl acetate, 3:1) provided **5a** as a yellow tinted oil (1.59 g, 75%): ^{1}H NMR (CDCl$_3$) δ 7.03 (d, 2 H, J = 10.4 Hz), 6.43 (d, 2 H, J = 10.4 Hz), 3.79 (s, 3 H), 3.21 (t, 2 H, J = 8.2 Hz), 2.60 (t, 2 H, J = 8.2 Hz); IR (film) 1735 (CO$_2$Me), 1665 (C=O), 1630 (C=C); CIMS m/z isobutane (relative intensity) 259 (100), 261 (98), 179 (10); UV (benzene) 300 nm (ϵ = 54), 366 (14). Anal. Calcd for $C_9H_{11}OBr$: C, 46.17; H, 4.65. Found: C, 46.19; H, 4.59.

4-Carbomethoxy-4-vinyl-2,5-cyclohexadien-1-one (6a). The procedure described for the conversion of **5b** to **6b** was carried out with **5a**. Chromatography of the product on silica gel (hexanes/ethyl acetate, 5:1) gave **6a** as a pink oil (0.542 g, 60%): ^{1}H NMR (CDCl$_3$) δ 7.11 (dd, 2 H, J = 8.4 Hz, J = 1.9 Hz), 6.36 (dd, 2 H, J = 8.4 Hz, J = 1.9 Hz), 6.06 (dd, 1 H, J = 17.3 Hz, J = 10.3 Hz), 5.29 (d, 1 H, J = 10.3 Hz), 5.24 (d, 1 H, J = 17.3 Hz), 3.79 (s, 3 H); IR (film) 1735 (CO$_2$Me), 1665 (C=O), 1630 (C=C); CIMS m/z isobutane (relative intensity) 179 (100); UV (benzene) 300 nm (ϵ = 59), 366 (16). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.06; H, 5.63.

2-Carbomethoxybicyclo[$3^{2,3,4}.2^{6,7}$.1]-2,6-octadien-9-one (7), 2-Carbomethoxybicyclo[3.3.$0^{1,5}$]-2,7-octadien-6-one (8), and 4-Carbomethoxy-3-vinylphenol (9). Dienone **6a** (0.80 g) was irradiated at 366 nm for 4 h in benzene (300 mL). After rotary evaporation of the benzene and addition of chloroform (100 mL), the mixture was extracted with aqueous potassium hydroxide (1 M, 5 × 15 mL). The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give an oil. Chromatography on silica gel (hexanes/ethyl acetate, 4:1) gave **7** (higher R_f, 0.28 g, 35%, oil) and **8** (lower R_f, 0.065 g, 8%, oil). **7**: ^{1}H NMR (CDCl$_3$) δ 6.70 (m, 2 H), 6.21 (dd, 1 H, J = 6.7 Hz, J = 2.9 Hz), 3.76 (s, 3 H), 3.44 (d, 1 H, J = 2.9 Hz), 2.72 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 210 (e), 165 (e), 139 (o), 137 (o), 136 (e), 130 (o), 51 (o), 46 (o), 45 (o), 31 (e); IR (film) 1765 (C=O), 1710 (CO$_2$Me), 1620 (C=C) cm^{-1}; CIMS m/z isobutane (relative intensity) 179 (100). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.28; H, 5.74. **8**: ^{1}H NMR (CDCl$_3$) δ 8.02 (dd, 1 H, J = 5.7 Hz, J = 2.6 Hz), 6.66 (dd, 1 H, J = 4.4 Hz, J = 2.6 Hz), 6.12 (dd, 1 H, J = 5.7 Hz, J = 1.9 Hz), 4.25 (m, 1 H), 3.79 (s, 3 H), 3.15 (m, 1 H), 2.96 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 211 (e), 166 (o), 164 (e), 143 (o), 135 (e), 133 (o), 54 (o), 51 (o), 47 (o), 34 (e); IR (film) 1700 (CO$_2$Me and C=O), 1620 (C=C); CIMS m/z isobutane (relative intensity) 179 (100). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.29; H, 5.46. The basic layer was acidified with concentrated hydrochloric acid and extracted with chloroform (4 × 150 mL). The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give **9** as a colorless solid (0.31 g, 39%, mp 105–106 °C): ^{1}H NMR (CDCl$_3$) δ 7.85 (d, 1 H, J = 8.6 Hz), 7.61 (dd, 1 H, J = 17.5 Hz, J = 10.9 Hz), 7.01 (d, 1 H, J = 2.5 Hz), 6.77 (dd, 1 H, J = 8.6 Hz, J = 2.5 Hz), 5.59 (dd, 1 H, J = 17.5 Hz, J = 1.4 Hz), 5.26 (dd, 1 H, J = 10.9 Hz, J = 1.4 Hz), 3.81 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 168 (e), 160 (e), 143 (e), 136 (o), 133 (o), 120 (e), 116 (e), 115 (o), 114 (o), 52 (o); IR (CHCl$_3$) 3650, 3350 (OH), 1690 (CO$_2$Me), 1600 (Ar); CIMS m/z isobutane (relative intensity) 179 (100). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.48; H, 5.60.

Determination of the Structure of 9. Dehydrobromination of 3-(2′-Bromoethyl)-4-carbomethoxyphenol (11) to 4-Carbomethoxy-3-vinylphenol (9). To a solution of **11** (13 mg, 0.65 mol) in DMF (3 mL) was added diazabicycloundecane (2 equiv), and the mixture was heated at 50 °C for 48 h. Ether was added, and the organic layer was washed three times with 10% hydrochloric acid solution and brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (hexanes/ethyl acetate, 7.5:1) to give **9** (4.2 mg, 32%). This material was found to be identical to the phenol, **9**, obtained from photolysis of **6a**.

4-(Acetoxymethyl)-3-methoxy-4-vinyl-2,5-cyclohexadien-1-one (34). By the utilization of well-documented experimental procedures,[7] **4b** was converted to **34** as shown in Scheme VI; chromatography of the product mixture on silica gel (hexanes/ethyl acetate, 3:1) gave **34** as colorless crystals: mp 71–72 °C; ^{1}H NMR (CDCl$_3$) δ 6.66 (d, 1 H, J = 10 Hz), 6.31 (dd, 1 H, J = 10 Hz, J = 1.5 Hz), 5.84 (dd, 1 H, J = 17.5 Hz, J = 10.6 Hz), 5.63 (d, 1 H, J = 1.5 Hz), 5.30 (d, 1 H, J = 10.6 Hz), 5.21 (d, 1 H, J = 17.5 Hz), 4.41 (d, 2 H, J = 2.4 Hz), 3.77 (s, 3 H), 2.0 (s, 3 H); IR (film) 1740 (OAc), 1655 (C=O), 1625 (C=C); CIMS m/z isobutane (relative intensity) 223 (100), 193 (14), 163 (5), 150 (2); UV (benzene) 300 nm (ϵ = 302), 366 (11). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.87; H, 6.32.

4-(Acetoxymethyl)-3-methoxy-5-vinylphenol (35a). Dienone **34** (0.10 g) was irradiated at 366 nm in benzene (20 mL) for 4 h. Evaporation of the solvent under reduced pressure gave **35a** as a colorless solid that slowly decomposed to a pink oil with a faint smell of acetic acid. A ^{1}H NMR spectrum recorded immediately after photolysis indicated that **35a** had been produced in approximately quantitative yield: ^{1}H NMR (CDCl$_3$) δ 6.91 (dd, 1 H, J = 17.5 Hz, J = 10.9 Hz), 6.61 (d, 1 H, J = 2.3 Hz), 6.4 (d, 1 H, J = 2.3 Hz), 5.67 (dd, 1 H, J = 17.5 Hz, J = 1.3 Hz), 5.34 (dd, 1 H, J = 10.9 Hz, J = 1.3 Hz), 5.21 (s, 2 H), 3.81 (s, 3 H), 2.07 (s, 3 H). Phenol **35a** was fully characterized as its *tert*-butyldimethylsilyl ether **35b**.

4-(Acetoxymethyl)-5-methoxy-3-vinyl-1-(*tert*-butyldimethylsiloxy)benzene (35b). Phenol **35a** (0.10 g) was dissolved in DMF (0.7 mL) and methylene chloride (0.2 mL). To this solution was added *tert*-butyldimethylsilyl chloride (0.135 g, 0.0089 mol), imidazole (0.09 g, 0.0135 mol), and 3 crystals of 4-(*N*,*N*-dimethylamino)pyridine. The mixture was stirred at room temperature overnight, diluted with methylene chloride (30 mL), and washed with a 10% solution of hydrochloric acid (3 × 10 mL), a saturated solution of sodium bicarbonate (10 mL), and then brine. After the solution was dried over magnesium sulfate, the solvent was removed under reduced pressure, and the residue was chromatographed (hexanes/ethyl acetate, 10:1) to give **35b** as a clear, colorless oil (0.84 g, 56% from **34**): ^{1}H NMR (CDCl$_3$) δ 6.91 (dd, 1 H, J = 17.5 Hz, J = 10.9 Hz), 6.61 (d, 1 H, J = 2.2 Hz), 6.35 (d, 1 H, J = 2.2 Hz), 5.62 (dd, 1 H, J = 17.5 Hz, J = 1.3 Hz), 5.34 (dd, 1 H, J = 10.9 Hz, J = 1.3 Hz), 5.2 (s, 2 H), 3.80 (s, 3 H), 2.06 (s, 3 H), 0.9 (s, 9 H), 0.2 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 171 (e), 159 (e), 157 (e), 140 (e), 134 (o), 117 (e), 114 (e), 109 (o), 103 (o), 57 (e), 55 (o), 25 (o), 21 (o), 19 (e), −4 (o); IR (film) 1745 (OAc), 1605 (C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_4Si$: C, 64.64; H, 7.84. Found: C, 64.72; H, 8.06.

Determination of the Structure of 35b. Conversion of 18 to 35b. Phenol **18** was converted to its *tert*-butyldimethylsilyl ether in quantitative yield: ^{1}H NMR (CDCl$_3$) δ 6.69 (dd, 1 H, J = 17.5 Hz, J = 10.3 Hz), 6.60 (d, 1 H, J = 2.2 Hz), 6.33 (d, 1 H, J = 2.2 Hz), 5.69 (dd, 1 H, J = 17.5 Hz, J = 1.3 Hz), 5.30 (dd, 1 H, J = 10.3 Hz, J = 1.3 Hz), 3.89 (s, 3 H), 3.78 (s, 3 H), 1.1 (s, 9 H), 0.01 (s, 6 H); IR (film) 1730 (CO$_2$Me), 1595 (C=C) cm^{-1}; CIMS m/z isobutane (relative intensity) 323 (100), 291 (8), 265 (5). Anal. Calcd for $C_{17}H_{26}O_4Si$: C, 63.31; H, 8.12. Found: C, 63.48; H, 8.02. To a solution of the *tert*-butyldimethylsilyl ether (99 mg, 0.3 mmol) in THF (4 mL) was added lithium aluminum hydride (24 mg, 0.5 mmol). The mixture was stirred overnight at room temperature, quenched with a saturated solution of sodium bicarbonate, extracted with ethyl acetate, and washed with brine. After the solution was dried over magnesium sulfate, the solvents were evaporated under reduced pressure to afford a clear, colorless oil (40 mg, 41%): ^{1}H NMR (CDCl$_3$) δ 7.02 (dd, 1 H, J = 17.5 Hz, J = 10.3 Hz), 6.59 (d, 1 H, J = 2.2 Hz), 6.35 (d, 1 H, J = 2.2 Hz), 5.62 (dd, 1 H, J = 17.5 Hz, J = 1.3 Hz), 5.36 (dd, 1 H, J = 10.3 Hz, J = 1.3 Hz), 4.72 (s, 2 H), 3.81 (s, 3 H), 2.65 (br s, 1 H), 1.1 (s, 9 H), 0.02 (s, 6 H); IR (film) 3360 (OH), 1600 (C=C) cm^{-1}. The alcohol (30 mg, 0.1 mmol) was dissolved in pyridine (1 mL) with a few crystals of 4-(*N*,*N*-dimethylamino)pyridine. Acetic anhydride (53 mL, 0.2 mmol) was added, and the reaction was stirred overnight at room temperature. Water (5 mL) was added, and after 10 min, the mixture was extracted with chloroform (3 × 10 mL). The combined extracts were washed with a 10% solution of aqueous hydrochloric acid (3 × 5 mL), a saturated solution of sodium bicarbonate, and then brine. After the solution was dried over magnesium sulfate, the solvent was removed under reduced pressure to afford a clear, colorless oil, whose spectral properties were identical to the *tert*-butyldimethylsilyl ether derivative prepared from **34**.

Acknowledgment. This work was supported by the National Institute of General Medical Science (Grant GM 33061).

Registry No. 4a, 138408-58-9; **4b**, 138408-55-6; **5a**, 138432-67-4; **5b**, 138408-56-7; **6a**, 138408-59-0; **6b**, 138408-57-8; **7**, 138408-60-3; **8**, 138408-61-4; **9**, 138408-62-5; **10**, 138408-63-6; **11**, 138408-64-7; **12a**, 138408-65-8; **17**, 138432-68-5; **18**, 138408-67-0; **19**, 138408-68-1; **20**, 138408-69-2; **21**, 138408-70-5; **22**, 138408-71-6; **23**, 138408-72-7; **24**, 138432-69-6; **25**, 138408-73-8; **26**, 85518-40-7; **34**, 138408-66-9; **35a**, 138408-74-9; **35b**, 138408-75-0; methyl 2-methoxybenzoate, 606-45-1; methyl benzoate, 93-58-3; 1,2-dibromoethane, 106-93-4.