mL of benzene was added 0.40 mL of a 0.1 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was stirred for 5 min at room temperature, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 26 mg of a yellow solid. The material was subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[44] Elution with 35% ether in hexane at a flow rate of 4.8 mL/min gave two bands: band 1, retention time 11 min, 13 mg (48%) of 4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one as faint yellow microcrystals, mp 178–179 °C; band 2, retention time 15 min, 11 mg (45%) of starting monobromo ketone. No 1-cyano-4-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (retention time 21 min) was observed.

Control Experiment. Treatment of 1-Cyano-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Potassium *tert*-Butoxide. To a solution of 18 mg (0.066 mmol) of the 3-oxobicyclic compound in 4 mL of *tert*-butyl alcohol and 1 mL of benzene was added 0.66 mL of a 0.1 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was stirred for 5 min at room temperature, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 18 mg of a colorless oil. NMR analysis indicated pure starting ketone.

Control Experiment. Treatment of 5-Cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one with Potassium *tert*-Butoxide. To a solution of 27 mg (0.1 mmol) of the 5-cyano enone in 4.0 mL of *tert*-butyl alcohol and 1.0 mL of benzene was added 1.0 mL of a 0.1 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was stirred for 5 min at room temperature, diluted with ether, washed with saturated aqueous ammonium chloride, water, and brine, dried, and concentrated in vacuo to give 27 mg of a white solid. NMR analysis indicated pure starting enone.

Emission Measurements. Phosphorescence measurements were made on an Aminco-Kiers spectrophosphorimeter equipped with a Hanovia 901C-1, 150-W, xenon arc lamp and modified with internal baffles to eliminate scatter. The spectra were obtained at 77 K in ethanol–ether (2:1) with the samples being thoroughly degassed immediately before measurements were made. The emission spectra were calibrated by use of a low-pressure mercury lamp in each run.

Acknowledgment. Support of this research by National Institutes of Health Grant GM07487, the National Science Foundation, and the U.S. Army Research Office is gratefully acknowledged. Also we acknowledge the technical assistance of Mr. Bruce Berris, an undergraduate research student, in synthetic efforts.

Registry No. **12**, 75010-94-5; **14**, 22612-62-0; **15**, 75011-32-4; **16**, 75011-33-5; **17**, 75011-34-6; **18**, 75011-35-7; **19**, 75011-36-8; **20**, 75011-37-9; **21**, 53102-14-0; **22**, 75011-38-0; **23**, 34250-16-3; **24**, 75011-39-1; **25**, 930-60-9; **26**, 75011-40-4; **27**, 75011-41-5; **28a**, 75011-42-6; **28b**, 75045-13-5; *endo,endo*-**29**, 75011-43-7; *endo,exo*-**29**, 75011-44-8; *endo,endo*-**30**, 75011-45-9; *endo,exo*-**30**, 75011-46-0; **31**, 75011-47-1; **32**, 75011-48-2; **33**, 75011-49-3; **34**, 75011-50-6; **35**, 75011-51-7; **36**, 75011-52-8; **37**, 75011-53-9; **39**, 75011-54-0; **40**, 75011-55-1; trimethylsilyl cyanide, 7677-24-9; diphenyldiazomethane, 833-40-9; *exo*-3-(phenylseleno)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexan-2-one, 75011-56-2; *exo*-2-chloro-*exo*-3-(phenylsulfenyl)-5-cyano-6,6-diphenylbicyclo[3.1.0]hexane, 75011-57-3; isopropenyl acetate, 108-22-5; *N*-bromosuccinimide, 128-08-5.

Type A Zwitterions and Cyclohexadienone Photochemical Rearrangements. Mechanistic and Exploratory Organic Photochemistry[1,2]

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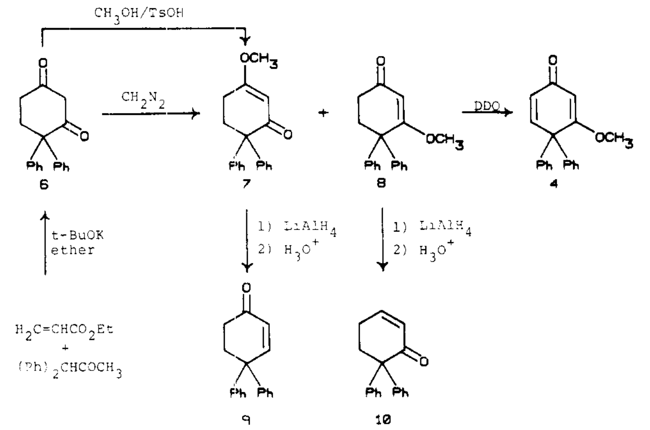
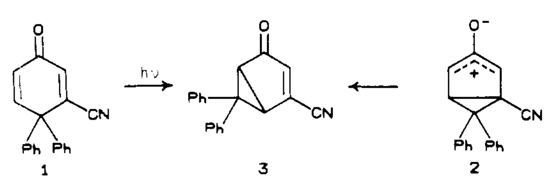
The photochemistry of 3-methoxy-4,4-diphenyl-2,5-cyclohexadienone was studied. The type A rearrangement proved to be regioselective with a preference for formation of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one relative to 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (1.4:1 in benzene). An unexpected product was 3-methoxy-4,5-diphenylphenol, a product deriving from phenyl migration; normally phenyl migration in dienones is considerably slower than the type A rearrangement. The quantum yields in benzene were $\phi = 0.27$ for the 4-methoxy bicyclic enone, $\phi = 0.19$ for the 5-methoxy bicyclic enone, and $\phi = 0.12$ for the methoxyphenol formation. Acetophenone sensitization gave the same product distribution with the same quantum efficiencies. Interestingly, in methanol the type A efficiencies increased without appreciable change in the regioselectivity, and the phenyl migration efficiency decreased. In this solvent the quantum yields were $\phi = 0.49$, $\phi = 0.30$, and $\phi = 0.069$, respectively. Rearrangement rates for the triplet excited state were obtained by a Stern–Volmer treatment using cyclohexadiene quenching. The rate for the methoxy dienone triplet undergoing the type A rearrangement was comparable to that of the parent diphenylcyclohexadienone but faster than the 3-cyano-4,4-diphenylcyclohexadienone triplet. SCF–CI calculations were performed with a truncated basis orbital set consisting of the n orbital and the π system AO's. The calculations were carried out on the parent dienone, the presently studied methoxy dienone, and the corresponding 3-cyano dienone. Triplet and singlet energies for the lowest $n-\pi^*$ and $\pi-\pi^*$ states were derived as well as the corresponding wave functions, bond orders, and electron densities. As in previous studies of the triplets, only the $n-\pi^*$ state is β,β bonding while the $\pi-\pi^*$ state tends to be β,β antibonding. For comparison purposes the type A zwitterion was generated from a series of α-bromo-, α-chloro-, and α,α'-dibromo-1-methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-ones. 4-Methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was formed completely regioselectively, thus defining the behavior of the zwitterion. The difference between the zwitterion behavior and the photochemical regioselectivity is construed to mean that part of the β,β-bridged $n-\pi^*$ excited state undergoes bicycling to a product geometry concomitant with radiationless decay without formation of a zwitterion.

Previously we have studied the regioselectivity of both the type A cyclohexadienone photochemistry and the dark type A zwitterion rearrangement. In these studies[1,2] we investigated the photochemistry of 3-cyano-4,4-di-

Scheme I. Synthesis of 3-Methoxy-4,4-diphenylcyclohexadienone



phenylcyclohexadienone (1) and the related zwitterion 2 (eq 1). Both the photochemistry and the zwitterion behavior were totally regioselective with 4-cyano-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (3) being the only observed product. This provided necessary but not mandatory evidence that the zwitterion is a reaction intermediate in the type A dienone rearrangement.[3]



(1)

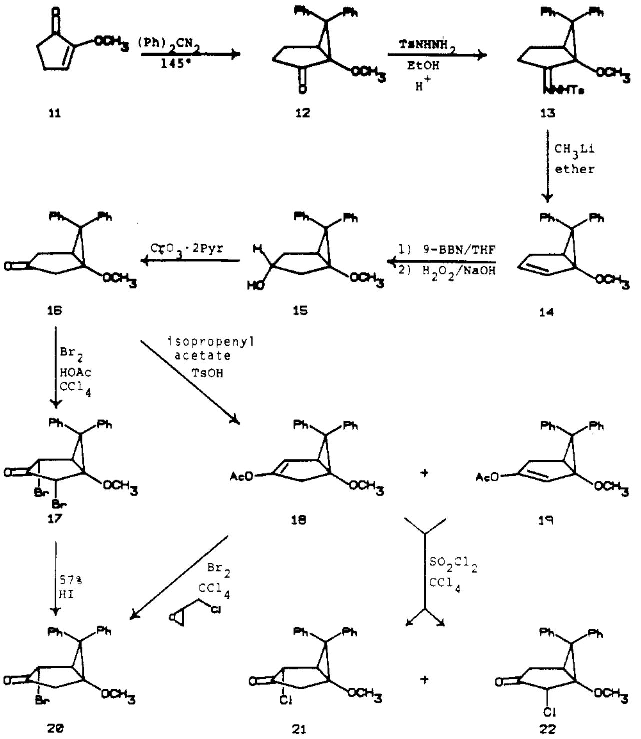
It was of considerable interest to investigate an example with an electron-donating substituent in place of the cyano moiety. The aim was twofold: namely, to determine the effect on the direction of the regioselectivity and to search for an example where the regioselectivity was less than complete. The latter promised to allow a more definitive comparison of the type A photochemistry and the behavior of the type A zwitterion. Thus, a study of the photochemistry of 3-methoxy-4,4-diphenylcyclohexadienone (4) and the reactivity of the derived zwitterion 5 became the goal of the present study.

Results

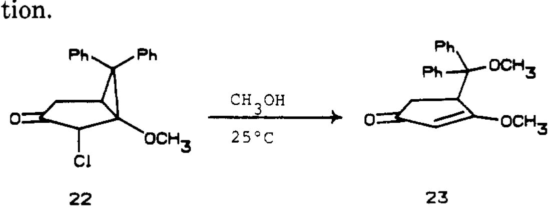
Synthesis of the Methoxy Dienone Reactant and Precursors to the Type A Zwitterion. The synthesis of methoxy dienone 4 is outlined in Scheme I. While enol ether formation from β-diketone 6 with p-toluenesulfonic acid and methanol gave only one enol ether (i.e., 7), diazomethane led to both possible regioisomers 7 and 8. The spectral characteristics of the two isomers were rather similar, and structural assignments proved most easily determined by conversion to the corresponding enones 9 and 10 as shown in Scheme I. This showed enol ether 8 to be the desired 3-methoxy-4,4-diphenylcyclohexenone (8), which was then converted with DDQ to the desired methoxy dienone 4. Details of these conversions are given in the Experimental Section.

Scheme II describes the approach to the desired zwitterion precursors. A key intermediate was the 3-oxobicyclohexane 16. Functionalization of C-3 in the synthesis of this compound was sufficiently selective when 9-borabicyclononane[4] was employed with bicyclohexene 14; in contrast, the borane–THF complex led to a mixture of regioisomers.

Scheme II. Synthesis of Zwitterion Precursors



While synthesis of the 4-bromo bicyclic ketone 20 was readily accomplished and while the 2,4-dibromo ketone 17 was also accessible, all attempts at the synthesis of the corresponding 1-methoxy-2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one were fruitless. The synthesis of the corresponding α-chloro ketones 21 and 22 proved less difficult. A clue to the instability of the 2-bromo bicyclic ketone came from the solvolysis of the corresponding 2-chloro bicyclic ketone 22 which afforded 3-methoxy-4-(methoxydiphenylmethyl)cyclopentenone (23; note eq 2). Details of these syntheses are given in the Experimental Section.



(2)

Exploratory Photolysis of 3-Methoxy-4,4-diphenylcyclohexadienone. It was found that irradiation of 3-methoxy-4,4-diphenylcyclohexadienone (4) in methanol led to formation of three photoproducts. The major photoproduct proved to be the known[2] 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (24). Two more minor products were isolated. The first appeared from spectral data (note Experimental Section) to be an isomeric enone (25). The second was a phenol (26). The product ratio in methanol was 4:2.6:1.

The enone 25 was found by elemental analysis and high-resolution mass spectral analysis to be isomeric with

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(1) This is paper 123 of our photochemical series.

(2) For paper 122, see: Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.*, previous paper in this issue.

(3) (a) Zimmerman, H. E. 17th National Organic Symposium of the American Chemical Society, June 1961; American Chemical Society: Washington, DC; Abstracts, p 31. (b) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486–4487. (c) Zimmerman, H. E.; Schuster, D. I. *Ibid.* **1962**, *84*, 4527–4540.

(4) (a) Scouten, C. G.; Brown, H. C. *J. Org. Chem.* **1973**, *38*, 4092–4094. (b) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5280–5281. (c) *Ibid.* **1968**, *90*, 5281–5283.

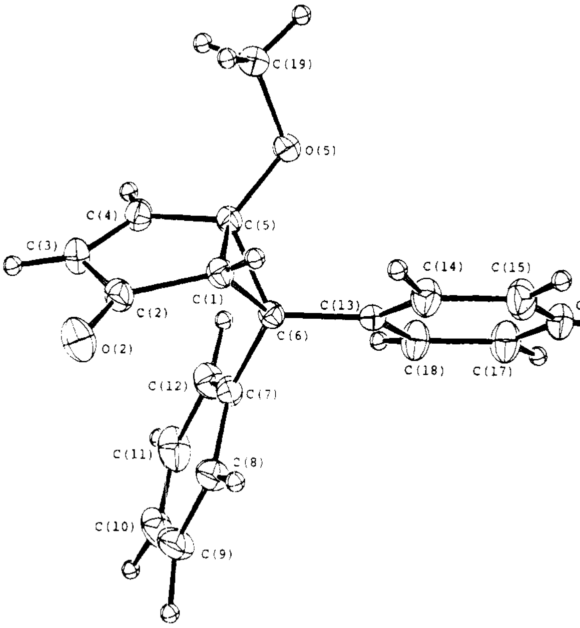


Figure 1. ORTEP II drawing of photoenone **25**.

the major photoproduct (i.e., methoxy enone **24**). However, the NMR spectrum showed a methoxyl methyl peak at δ 3.40, indicating that this was substituted on an sp^3-hybridized carbon. Also a vinyl doublet at δ 5.54 and an unsplit methine at δ 3.08 were observed in addition to absorption deriving from two phenyl groups and a hidden CH under this peak. Two structures were considered: 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**25**) and 6-methoxy-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**27**). Formation of the latter (i.e., **27**) would have involved a phenyl migration to a methoxyl-bearing carbon in the dienone photochemistry. The former (i.e., **25**) would arise from a type A rearrangement.

The structural assignment of this photoproduct derived from X-ray crystal structure determination which led to structure **25** (note Figure 1).[5]

We now consider the second minor photoproduct (i.e., phenol **26**), where high-resolution mass spectral and elemental analysis again showed this compound to be isomeric with the photochemical reactant and other photoproducts. A low-field (δ 3.73) methyl seemed attributable to an aryl or vinyl methoxyl group. A two-proton singlet at δ 6.50, just upfield from a ten-hydrogen aromatic multiplet, seemed ascribable to two aryl hydrogens ortho or para to methoxyl and/or hydroxyl moieties. A broad singlet at δ 5.2 corresponded to a phenolic hydroxyl group. With this information and with possible reaction mechanisms in mind, both 3-methoxy-4,5-diphenylphenol (**26**) and 3-methoxy-5,6-diphenylphenol (**28**) were synthesized (note Scheme III). The second minor photoproduct proved identical with the 3-methoxy-4,5-diphenylphenol (**26**).

Scheme III. Synthesis of Photophenol 26

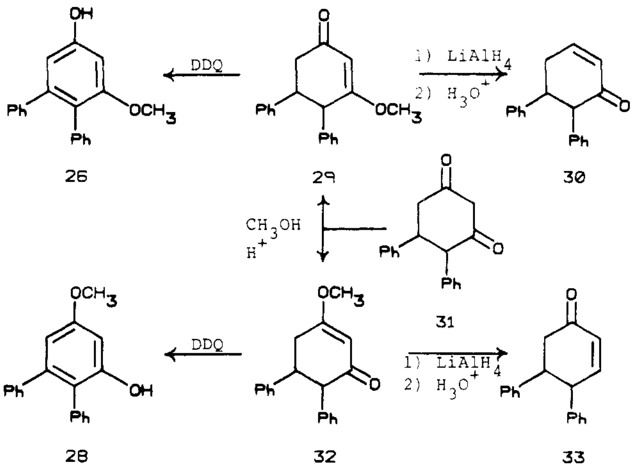
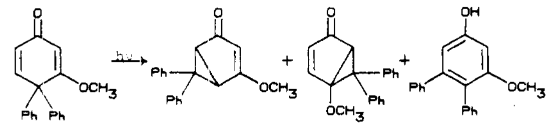


Table I. Summary of Quantum Yield Data[a]

		quantum yield[b]		
solvent	additive	24	25	26
methanol	none	0.49	0.30	0.069
benzene	none	0.27	0.19	0.12
benzene	acetophenone	0.26	0.19	0.11

[a] For details of individual runs see the Experimental Section. [b] Extrapolated to 0% conversion.

Thus we can depict the photochemistry of 3-methoxy dienone **4** as in eq 3. As long as the conversion was under 30%, secondary photochemistry[3c,6] deriving from further reaction of the bicyclic enones was minimal. Thus, direct irradiation proved of preparative value in contrast to the parent 4,4-diphenylcyclohexadienone (**34**) system where sensitization was really necessary[3c,6] for appreciable buildup of the bicyclic ketone primary product. Of the two bicyclic enones presently obtained, the β-methoxy bicyclic enone (i.e., the major photoproduct **24**) was relatively unreactive. Sensitization of the dienone in either benzene or methanol provided the same products preparatively and in slightly improved yields due to lowered competition by secondary photochemistry.



(3)

4 24 25 26

Quantum Yield Determinations. Quantum yields were determined on the semimicrobench described earlier[7] along with the electronic actinometer[8] used in much of our photochemistry. Each run was calibrated with ferrioxalate actinometry.[9] Interestingly, for any given wavelength, the calibration factors (i.e., millieinsteins/count of the actinometer[8]) showed an average deviation of only 0.25% when used with a seasoned HBO 200-W lamp. Products were assayed by use of high-pressure LC with internal standards. Individual runs are tabulated in the Experimental Section. Zero-time quantum yields were obtained by extrapolation to zero conversion; this obviated problems due to product light absorption. The lowest conversions were 2.8%. The extrapolated quantum yields are summarized in Table I.

Direct irradiations in both benzene and in methanol were carried out. Also, sensitized quantum yields were obtained in benzene. Interestingly, the sensitized runs gave the same product distribution and the same quantum yields as the corresponding direct irradiations. This indicated that a triplet is the reactive species even in the

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[5] (a) We thank Dr. Lawrence G. Hoard for collaboration in this structure determination. (b) Hoard, L. G.; Pasteris, R. J., to be submitted for publication. (c) Pasteris, R. J., Ph.D. Thesis, University of Wisconsin, 1980.

[6] Zimmerman, H. E.; Keese, R.; Nasielski, J.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895–4904.

[7] Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.

[8] Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weigt, T. J. *Mol. Photochem.* **1977**, *8*, 379–385.

[9] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

Table II. Triplet Rate Data for 3-Methoxy-4,4-diphenylcyclohexadienone[a,b]

photoproduct	$k_q\tau$, M	τ, s	$k_{d(tot)}$, s^{-1}	k_r, s^{-1} [c]	k_d, s^{-1} [d]
4-methoxy enone **24**	1.02	1.0×10^{-10}	9.8×10^{9}	2.9×10^{9}	
5-methoxy enone **25**	0.96	9.6×10^{-11}	1.0×10^{10}	2.0×10^{9}	4.8×10^{9}
photophenol **26**	0.84	8.4×10^{-11}	1.2×10^{10}	1.3×10^{9}	
average value	0.94	9.4×10^{-11}	1.1×10^{10}		

[a] Obtained from Stern–Volmer analysis of cyclohexadiene quenching data in benzene at 22 °C. [b] k_{diff} taken to be (note ref 11) 1.0×10^{10} M^{-1} s^{-1} and to be equal to k_q. [c] k_r calculated by using the average value of $k_{d(tot)}$. [d] $k_d = k_{d(tot)}$ minus the sum of all k_r's.

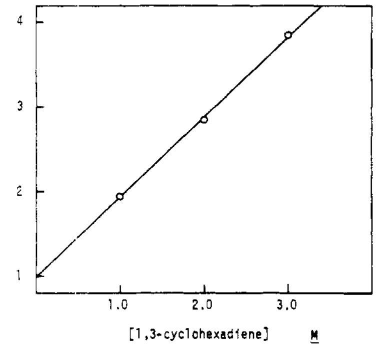


Figure 2. Stern–Volmer plot of quenching data for methoxy dienone 4. Product distribution constant is within experimental errors.

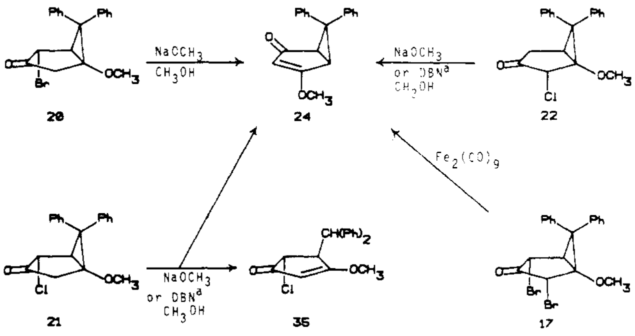
direct irradiations. The reasoning here is based on the "fingerprint comparison"[10] wherein the distribution of products derived from the direct run is the same as that characteristic of the independently generated triplet.

The change from benzene to methanol produced a dramatic alteration in quantum yields and product distributions. Thus the type A product quantum yields increased markedly (note Table I) while the phenyl migration product quantum yield decreased dramatically. However, the regioselectivity of the type A rearrangement (i.e., the ratio of **24** to **25**) was not appreciably changed.

Triplet Rate Determinations. Quenching Studies. Stern–Volmer quenching studies were carried out by using cyclohexadiene (53 kcal/mol) as a quencher in benzene as solvent. The slope (note Figure 2) obtained is $k_q\tau$. Interestingly, within experimental error the same excited-state lifetime, τ, was derived for quenching of the three different photoproducts: **24**, **25**, and **26**. Also, from $k_{d(tot)}$, the total rate of decay of the reacting triplet, which is just the inverse of the lifetime τ, it was possible to obtain the rate of triplet reaction, k_r, and the rate of triplet decay, k_d, by other processes such as radiationless decay. Thus $k_r = \phi k_{d(tot)} = \phi/\tau$ allows one to solve for k_r, since both quantum yields and lifetime (or total rate of triplet decay) are known. Also, $k_d = k_{d(tot)} - k_r$ allows one to obtain k_d. These rate constants are given in Table II.

Phosphorescence Measurements. The phosphorescence spectrum of 3-methoxy-4,4-diphenylcyclohexadienone (**4**) was determined at 77 K in 2:1 ethanol-ether. In contrast to the spectra of the parent 4,4-diphenylcyclohexadienone,[12] 4,4-dimethylcyclohexadienone,[12] 4-methyl-4-(dichloromethyl)cyclohexadienone,[12] 4-methyl-4-(trichloromethyl)cyclohexadienone,[12] and 3-cyano-4,4-diphenylcyclohexadienone,[2] the emission spectrum of the 3-methoxy dienone **4** was broad and was without the vibrational structure characteristic of n–π^* emission. The energy was estimated as 70.5 kcal/mol; here the 0–0 band was estimated as halfway between the onset of the emission and the maximum. The emission was exceptionally weak, and part of the structureless nature of the spectrum derives from the wide monochromator slits required.

Scheme IV. Zwitterion Generation



[a] Diazabicyclononene.

Zwitterion Generation. The desired zwitterion was generated (note Scheme IV) from the monobromo bicyclic ketone **20**, from the monochloro bicyclic ketones **21** and **22**, and from the dibromo bicyclic ketone **17** by using the approach we described in our earlier zwitterion studies.[2,13-15] The monohalo ketones were treated with sodium methoxide in methanol. Alternatively, the two monochloro ketones **21** and **22** were treated with diazabicyclononene in methanol. The dibromo ketone was treated with diiron nonacarbonyl in benzene by using the method of Noyori.[16] In all cases the only bicyclic enone detectable was 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**24**). In the case of the 4-chloro bicyclic ketone **21**, a byproduct of 3-methoxy-4-benzhydryl-5-chlorocyclopentenone (**35**) was formed. The mass balances were excellent (>95%) in the monohalo ketone reactions with complete conversion to product. The dibromo ketone reaction proceeded in only 72% yield, but no regioisomeric methoxy bicyclic ketone (i.e., no **25**) was found.

The monochloro bicyclic ketone **22** was run to partial conversion in order to determine if it was equilibrating under the reaction conditions. Only the usual 4-methoxy bicyclic enone **24** was discernible, and the recovered reactant was the original regioisomer of the monochloro ketone (i.e., **22**). Significantly, the absence of ring-opened product **35** emphasized the lack of equilibration, since any

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[10] Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749–3760.

[11] (a) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 627. (b) A value of 5.0×10^9 M^{-1} s^{-1} for the rate of diffusion in benzene has also been measured, see: (c) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–4777; (d) Wagner, P. J.; Hammond, G. S. *Ibid.* **1966**, *88*, 1245–1251.

[12] Zimmerman, H. E.; Binkley, R. W.; McCullough, J. J.; Zimmerman, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 6589–6595.

[13] Zimmerman, H. E.; Döpp, D.; Huyffer, P. S. *J. Am. Chem. Soc.* **1966**, *88*, 5352–5353.

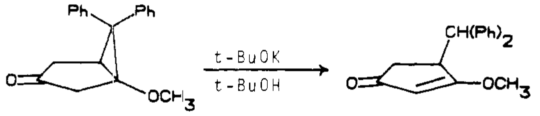
[14] Zimmerman, H. E.; Crumrine, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 5612–5614.

[15] Zimmerman, H. E.; Crumrine, D. S.; Döpp, D.; Huyffer, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 434–445.

[16] Noyori, R.; Hayakawa, Y.; Takaya, H.; Murai, S.; Kobayashi, R.; Sonoda, N. *J. Am. Chem. Soc.* **1979**, *100*, 1759–1765.

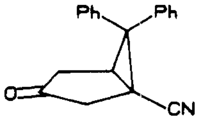
isomeric chloro ketone **21** would have led to such ring opening. Also, treatment of 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**25**) with sodium methoxide led to no reaction, showing the stability of this molecule to the reaction conditions and that it would have survived if formed in the zwitterion generation experiment. The results of zwitterion generation are outlined in Scheme IV.

In order to determine the behavior of this system in the absence of a departable anion, we ran one further experiment. This was the base treatment of 1-methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-one (**16**). Under the same conditions as those used for zwitterion generation, the nonhalogenated bicyclic ketone **16** underwent three-ring opening to afford 3-methoxy-4-benzhydrylcyclopentenone (**36**; see eq 4). This contrasts with the behavior of 1-cyano-6,6-diphenylbicyclo[3.1.0]hexan-3-one (**37**)[2] and the parent 6,6-diphenylbicyclo[3.1.0]hexan-3-one (**38**),[15] both of which are stable to base under the conditions which form zwitterions from the corresponding monohalo bicyclic ketones.



(4)

16 36



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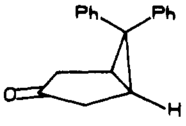
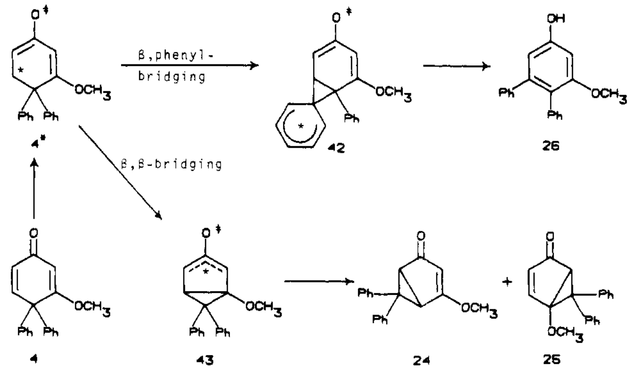


38

Discussion

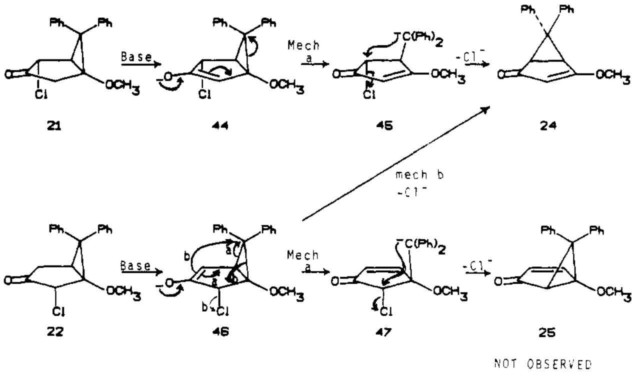
Gross Details of the Rearrangement Mechanisms. The rearrangement products derived from the photochemistry of 3-methoxy-4,4-diphenylcyclohexadienone (**4**) are of two varieties. Thus, both 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**24**) and 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**25**) are typical type A rearrangement[3] products, differing from one another only in the regioselectivity of the mechanism giving rise to them. In contrast, the third photoproduct, 3-methoxy-4,5-diphenylphenol (**26**), arises from a phenyl migration from carbon 4 of the dienone reactant to carbon 5. This striking result is without precedent. Thus, while migration of an aryl group from C-4 to the β carbon of an enone triplet is a known photochemical rearrangement,[10,17-24] normally the type A rearrangement is much more facile both in terms of quantum yields and rates.[10]

Scheme V. Mechanistic Pathways Available to 3-Methoxy Dienone[a]

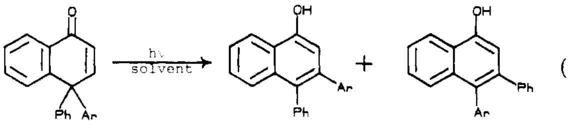


[a] The asterisk and double dagger denote free valencies.

Scheme VI. Push-Pull Mechanistic Alternative for Dark Rearrangement



The case of 4-(p-cyanophenyl)-4-phenyl-1(4H)-naphthalenone (**39**; cf. eq 5), which is formally a benzo dienone, is interesting since aryl migration occurs in preference to the type A rearrangement.[23] This case, however, is not inconsistent with the generalization that dienones prefer the type A reaction since in this naphthalenone case β,β bonding, needed for the type A reaction, introduces a new requirement of disruption of aromaticity.



(5)

39 40 41

Scheme V outlines the gross reaction mechanisms leading to the three photoproducts.

Significance of the Zwitterion Reactivity. Two aspects of the zwitterion chemistry need consideration. One is the regioselectivity shown by the zwitterion in which there was a preference for rearrangement to give the bicyclic enone with the methoxy substituent on the bicyclic enone double bond. The other is the relevance of the zwitterion results to the dienone photochemistry.

In order to discuss the regioselectivity encountered in the dark generation and the reaction of the bicyclic zwitterion, we need to convince ourselves that an alternative "push-pull" mechanism is not operating. Looking at Scheme VI, we see that this mechanism (mechanism a) involves enolate formation and benzhydryl carbanion formation from three-ring opening, followed by intramolecular S_N2 displacement of halide. Such a mechanism might be stepwise or concerted. However, the consequence of such a mechanism is that each regioisomer of the

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(17) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036-4042.

(18) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033-2047.

(19) Zimmerman, H. E.; Lewin, N. *J. Am. Chem. Soc.* **1969**, *91*, 879-886.

(20) Zimmerman, H. E.; Elser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 887-896.

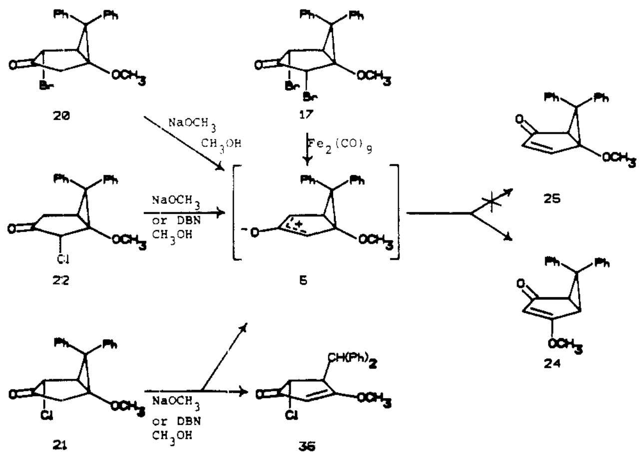
(21) Zimmerman, H. E.; Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954-966.

(22) Zimmerman, H. E.; Sam, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 4905-4914.

(23) Zimmerman, H. E.; Hahn, R. C.; Morrison, H.; Wani, N. C. *J. Am. Chem. Soc.* **1965**, *87*, 1138-1140.

(24) (a) Zimmerman, H. E.; Little, R. D. *J. Chem. Soc., Chem. Commun.* **1972**, 698-700. (b) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623-4630. (c) Agosta, W. C.; Wolff, S. *J. Chem. Soc., Chem. Commun.* **1972**, 226-227.

Scheme VII. Mechanism for Rearrangement of the Type A Zwitterion



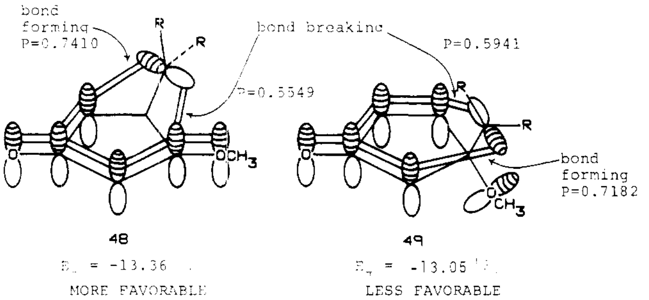


Figure 3. Two alternative transition states controlling regioselectivity in the zwitterion rearrangement.

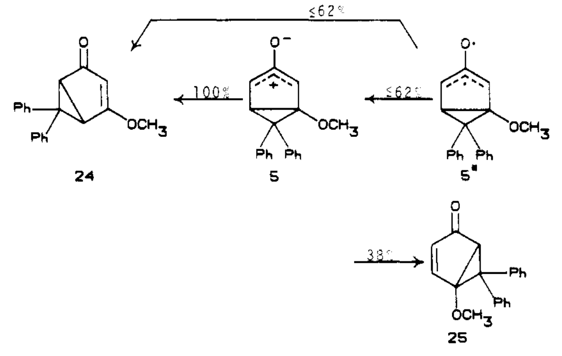
reactant α-halo ketone would lead to one regioisomer of the methoxy bicyclic enone (i.e., to **24** or **25**).[25] Such a reaction would be regiospecific.[26] However, such regiospecificity was not observed, with both α- and α′-halo ketones giving the same 4-methoxy bicyclic enone product, **24**. The formation of the same regioisomer, independent of reactant regiochemistry, suggests a common intermediate. This intermediate is the zwitterion **5**.

The zwitterionic mechanism is outlined in Scheme VII. It is seen that there is a preferred regioselectivity[26] in which the bicycling of the benzhydryl group is counterclockwise (away from the methoxy group), thus giving rise to the bicyclic enone with the methoxy moiety on the product double bond.

The regioselectivity, interestingly, is the same as that observed in our previous studies on the corresponding cyano zwitterion **2**. Since simple one-electron calculations were useful in understanding the regioselectivity of the cyano system, these were employed presently. The calculated π energies for the two alternative transition states derived from the zwitterion **5** were found to favor a rearrangement leaving the methoxy group on the product double bond (i.e., **48** vs. **49**; note Figure 3). Also, in comparing the two transition states, one observes that the bond being broken has a lower bond order in the preferred transition state, and the bond being formed has a higher bond order for this preferred transition state. In addition, at half-reaction for both transition states the bond order of the bond breaking is weaker than that for the bond forming.

We turn now to the relevance of the zwitterion regioselectivity to the understanding of the dienone photochemistry. We see that the photochemistry led to both regioisomers of the bicyclic enone (i.e., to **24** and **25**) while the zwitterion formed independently led only to the product with the methoxy on the double bond (i.e., to **24**). This result means that the zwitterion cannot be the sole species responsible for the photochemistry. At most the zwitterion could account for $1.6/(1.6 + 1) \times 100 = 62\%$ of the photochemistry. This obtains only if all of the 4-methoxy bicyclic enone **24** arises from zwitterion and all of the 5-methoxybicyclic enone **25** arises from some other mechanism. Formation of the 4-methoxy bicyclic enone **24** as the major product in both the zwitterion and photochemical reactions could be fortuitous.

The alternative mechanism leading to 5-methoxy bicyclic enone **25** in the photochemistry of 3-methoxy dienone **4** is then the rearrangement of an electronically excited (triplet) bridged species, **5***, concomitant with conversion to the singlet ground state of the bicyclic enone product. This is shown in eq 6.



(6)

There is a large body of literature (vide infra) providing strong support for the presence of zwitterions in dienone type A rearrangements. Thus, the present findings either bear on only a portion of the mechanism (here, e.g., 62%), indicate that the methoxy dienone **4** is unique in rearranging without prior decay to zwitterion, or indicate operation of some further factor.

SCF–CI Calculations. In order to understand the nature of the electronic excited states of the dienones studied, we carried out SCF–CI calculations (note Calculations in the Experimental Section). These calculations were of the type described earlier[28] and used a truncated set of basis orbitals of the π system and the oxygen p_y orbital. The derived SCF MO's were subjected to con-

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(25) One alternative is that bromo ketone **21** follows mechanism a in Scheme VI while bromo ketone **22** uses mechanism b. This leads to the same methoxy enone **24** from **21** and **22**. While possible, the use of two different mechanisms is less likely.

(26) It is convenient to define *regiospecificity* and *regioselectivity* in parallel to our definition[27] of *stereospecificity* and *stereoselectivity*. Thus, a regiospecific reaction is one where each of two regioisomeric reactants gives predominantly (or totally) different regioisomers of product. Where instead the two regioisomeric reactants give the same product distribution but where there is a preference for formation of one regioisomeric product, the reaction is termed *regioselective*. To the extent that the specificity or selectivity is partial, one can indicate this with the appropriate adjective. If only one regioisomeric reactant is possible and shows selectivity, the definition still holds. The advantage of this definition is that specificity does not mean formation of only one product, an experimental observation which is a function of the mode of analysis, the skill of the experimentalist, and other related factors. This definition is a modification of the original one of Hassner.[27c]

(27) (a) Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1959**, *81*, 108–116, footnote 16. (b) Eliel, E. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 436. (c) Hassner, A. *J. Org. Chem.* **1968**, *33*, 2684–2691.

(28) (a) Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131–4145. (b) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *Ibid.* **1978**, *100*, 4146–4162.

(29) Brand, J. C. D. *J. Chem. Soc.* **1956**, 858–872.

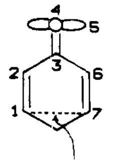
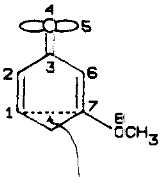
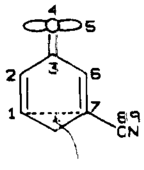
(30) (a) Zimmerman, H. E.; Gruenbaum, W. T.; Klun, R. T.; Steinmetz, M. G.; Welter, T. R. *J. Chem. Soc., Chem. Commun.* **1978**, 228–230. (b) Zimmerman, H. E.; Steinmetz, M. G. *Ibid.* **1978**, 230–232.

Table III. Calculated and Experimental Singlet and Triplet Energies[a]

molecule	singlets			triplets		
	calcd	obsd	config	calcd	obsd	config
4,4-diphenylcyclohexadienone (**34**)	3.28	3.25[b]	n–π*	2.99	2.98[b,e]	n–π*
	5.67	5.50[b]	π–π*	3.10	*f*	π–π*
3-cyano-4,4-diphenylcyclohexadienone (**1**)	2.92	2.99[c]	n–π*	2.88	2.82[c,e]	n–π*
	5.13	4.96[c]	π–π*	2.87	*f*	π–π*
3-methoxy-4,4-diphenylcyclohexadienone (**4**)	3.30	3.35[c]	n–π*	3.20	3.06[c,g]	n–π*
	4.79	4.80[c]	π–π*	2.58	*f*	π–π*
4,4-diphenylcyclohexenone	3.33	3.32[b]	n–π*	3.14	3.09[b]	n–π*
	6.28	5.61[b]	π–π*	3.36	*f*	π–π*
formaldehyde	3.31	3.50[d]	n–π*	3.24	3.12[d]	n–π*
	8.02	8.05[d]	π–π*	4.86	*f*	π–π*

[a] Energies in eV. [b] Reference 12. [c] This study. [d] Reference 29. [e] Strong, highly structured emission. [f] Unknown. [g] Weak, broad, featureless emission; configuration assumed.

Table IV. Electron Densities and β,β-Bond Orders for Substituted Cyclohexadienones

molecule	orbital	ground state	singlets		triplets	
			n–π*	π–π*	n–π*	π–π*
	1	0.9624	1.1634	0.9290	1.1526	0.9904
	2	0.9877	1.0789	0.8305	1.0841	0.9376
	3	0.6870	0.9275	0.9113	0.9346	0.8478
	4	1.4128	1.5880	1.5696	1.5919	1.2962
	5	2.0000	1.0000	2.0000	1.0000	2.0000
	6	0.9877	1.0789	0.8305	1.0841	0.9376
	7	0.9624	1.1634	0.9290	1.1526	0.9904
β,β-bond order	($P_{1,7}$)	−0.0676	+0.1315	+0.3859	+0.1204	−0.0371
	1	1.0169	1.2474	1.2260	1.2287	1.2282
	2	0.9673	1.1019	1.0629	1.1000	1.1143
	3	0.6874	0.9132	0.8882	0.9272	0.8149
	4	1.4517	1.5997	1.4337	1.6057	1.3874
	5	2.0000	1.0000	2.0000	1.0000	2.0000
	6	1.1853	1.2395	0.8078	1.2549	0.8484
	7	0.9403	1.0994	0.9774	1.0833	0.9997
	8	1.7511	1.7990	1.6071	1.8003	1.6071
β,β-bond order	($P_{1,7}$)	−0.0589	+0.1281	+0.1538	+0.1168	+0.0044
	1	0.9583	1.0799	0.8235	1.0767	1.0239
	2	0.9901	1.0449	0.7952	1.0528	0.9882
	3	0.6871	0.8526	0.8404	0.8549	0.8181
	4	1.4128	1.5451	1.4330	1.5442	1.3476
	5	2.0000	1.0000	2.0000	1.0000	2.0000
	6	0.9550	1.1147	0.9821	1.1128	0.8826
	7	0.9828	1.1812	1.0793	1.1735	0.9619
β,β-bond order	8	0.8333	0.9020	0.8602	0.9062	0.8528
	9	1.1805	1.2797	1.1863	1.2788	1.1250
	($P_{1,7}$)	−0.0626	+0.0619	+0.1400	+0.0506	−0.0079

figurational interaction with both singly and doubly excited configurations. The present calculations are similar in philosophy to those we carried out much earlier[12] except for the inclusion of doubly excited configurations. Additionally, somewhat different parameters were used.

The excited-state energies derived from these calculations on the three cyclohexadienones of interest, as well as on formaldehyde and cyclohexenone for comparison purposes, are given in Table III. Also included in Table III are the experimental singlet and triplet energies where available. Table IV summarizes some selected bond orders and electron densities for the states of interest.

It is seen that the calculated energies are in good agreement with observation. Interestingly, the methoxy substitution raised both the singlet and triplet n–π* energies, as might be expected from selective ground-state stabilization, while lowering the corresponding π–π* energies. Cyano substitution lowered the energy of all excited states.

The most striking effect noted was the β,β-bond orders of the n–π* and π–π* triplets of the three dienones **1**, **4**, and **34**. These bond orders are positive and strongly bonding for the n–π* states but negative or near zero and thus antibonding for the π–π* excited states (note Table IV).

Hence the n–π* excited triplet is an especially suited species for β,β bridging and formation of the necessary bridged species, independent of whether or not decay to zwitterion occurs, and the π–π* triplet is a uniquely ill-suited excited state for type A reactivity. This point has been made earlier.[12]

Another observation in the β,β-bond orders calculated (note Table IV) is that the highest β,β-bond order is for the parent dienone n–π* triplet (i.e., +0.120 (**34***)) which is the fastest reacting triplet (2.5×10^{10} s^{-1}).[31] A somewhat lower (but still high) β,β-bond order was obtained for the 3-methoxy dienone **4** (note Table IV), and the observed triplet rate of type A rearrangement was somewhat lower (4.6×10^9 s^{-1}, as the sum of type A processes). The β,β-bond order for the cyano dienone **1** was still lower (Table IV), and the type A rate was considerably slower than for either of the two other dienones (i.e., here $k_r = 1.3 \times 10^8$ s^{-1}).[2] Thus there seems to be a correlation between the

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[31] Schuster, D. I.; Lau, N. K. *Mol. Photochem.* **1969**, *1*, 415–432.

Table V. Calculated Triplet $\Delta P_{r,t}$ Values for Substituted Cyclohexadienones

bond or orbital[a]	$\Delta P_{r,t}$					
	34		4		1	
r,t	n–π*	π–π*	n–π*	π–π*	n–π*	π–π*
1,1	0.1925	0.0302	0.2234	0.2229	0.1202	0.0674
2,2	0.0935	−0.0530	0.1401	0.1543	0.0602	−0.0044
3,3	0.2615	0.1747	0.2508	0.1386	0.1769	0.1400
4,4	0.1666	−0.1291	0.1462	−0.0721	0.1275	−0.0691
5,5	−1.0000	0.0000	−1.0000	0.0000	−1.0000	0.0000
6,6	0.0935	−0.0530	0.0493	−0.3571	0.1547	−0.0755
7,7	0.1925	0.0302	0.1512	0.0676	0.1909	−0.0208
8,8			0.0391	−0.1541	0.0747	0.0214
9,9					0.0948	−0.0591
1,2	−0.1251	−0.3204	−0.1698	−0.2056	−0.0763	−0.1529
2,3	0.0608	0.1239	0.0787	0.0895	0.0257	0.0688
3,4	−0.2033	−0.2379	−0.1859	−0.1320	−0.1457	−0.1823
3,6	0.0608	0.1239	−0.0038	0.0441	0.0879	0.1465
6,7	−0.1251	−0.3204	−0.0676	−0.3723	−0.1673	−0.3962
7,8			−0.0767	0.0664	0.0560	0.1498
8,9					−0.0798	−0.1526
1,7	0.1925	0.0350	0.1824	0.0700	0.1185	0.0600

[a] Refer to structures in Table IV for orbital numbering sequences.

Table VI. Photolysis of 3-Methoxy-4,4-diphenylcyclohexadienone

run	cond[a]	additive, M	mmol of rctnt (×10^2)	mmol of prdt (×10^4)	mEinsteins absd (×10^3)	% conv	Φ(24)[e]	Φ(25)[f]	Φ(26)[g]
1	A	*b*	16.6	39.1	84.0	27.7	0.305	0.197	0.0466
2	A	*b*	15.9	15.5	28.0	13.1	0.421	0.265	0.0554
3	A	*b*	17.2	8.10	12.9	6.05	0.460	0.282	0.0628
4	A	*b*	18.6	4.30	6.55	3.05	0.505	0.295	0.0656
5	B	*b*	33.2	60.8	78.5	8.03	0.157	0.106	0.0775
6	B	*b*	32.5	47.2	48.9	6.02	0.173	0.131	0.0965
7	B	*b*	34.0	30.2	29.0	3.98	0.217	0.143	0.108
8	B	*b*	32.8	22.7	19.1	2.90	0.228	0.161	0.105
9	C	0.06[c]	7.38	11.7	10.8	7.30	0.215	0.177	0.109
10	C	0.06[c]	7.31	8.62	7.24	5.10	0.225	0.181	0.110
11	C	0.06[c]	6.95	4.07	3.62	2.80	0.241	0.187	0.112
12	D	*b*	11.5	19.4	22.0	6.50	0.132	0.120	0.0880
13	D	1.00[d]	11.5	10.7	22.0	3.36	0.0705	0.0564	0.0486
14	D	2.00[d]	11.5	7.61	22.0	2.29	0.0425	0.0425	0.0346
15	D	3.00[d]	11.5	5.47	22.0	1.69	0.0330	0.0302	0.0249

[a] A, 40 mL of methanol, 313 nm; B, 40 mL of benzene, 313 nm; C, 40 mL of benzene, 334 nm; D, 40 mL of benzene, 366 nm, no nitrogen purge. [b] None. [c] Acetophenone. [d] 1,3-Cyclohexadiene. [e] Φ for 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. [f] Φ for 5-methoxy isomer. [g] Φ for 3-methoxy-4,5-diphenylphenol.

n–π* triplet β,β-bond order and the experimental rate of type A rearrangement. This is satisfying theoretically and also provides support for the assumption that β,β bridging in the n–π* triplet is an important component of the rate-limiting stage of the rearrangement.

The above discussion is predicated on the methoxy dienone 4 photochemistry deriving from the 70-kcal/mol n/π* triplet rather than from the low-energy (60 kcal/mol) π–π* triplet. Further, supporting this idea (vide supra), triplet sensitizers of 61–65 kcal/mol were ineffectual. It appears that the observed methoxy dienone rearrangements are more rapid than decay from T_2 to T_1.

Additionally, ΔP calculations[28,30] were carried out by using the wave functions generated from SCF–CI. Each ΔP is the change in bond order, or electron density in the case of the $P_{r,r}$'s, resulting from excitation of the molecule from S_0 to the given electronically excited state. Table V lists those ΔP values of special interest.

Of further interest, we note in Tables IV and V the flow of electron density from the p_y, or n orbital (orbital 5), to the π system on n–π* excitation. Another item of interest is the finding that in the π–π* singlets and triplets it is the α-carbons which are most electron deficient, with the β-carbons coming next. This has been found in our earlier work[12] and is ubiquitous enough that it must play a role in π–π* photochemistry. Finally, the ΔP values in Table V tell us which bonds stretch and which compress on excitation. Bonds with negative ΔP values stretch while those with positive ΔP's compress.[28,30]

The most striking result seen in Table V derives from the ΔP_{17} values (i.e., β,β bonding; note final entry in table). Thus, for all three dienones (**1**, **4**, and **34**) the ΔP values observed for n–π* excitation are large and positive while the ΔP values for π–π* excitation are much smaller. Of course these are just the changes in bonding tendency on excitation; and we note (see Table VI) that the β,β-bond orders in the ground-state dienones are all negative or very near zero and antibonding. The small ΔP values for the π–π* excited state are scarcely enough to offset this antibonding tendency.

One other consequence of the ΔP treatment is seen in the methoxy dienone n–π* triplet where the ΔP values for the enone system not bearing the substituent are much larger than those for the moiety bearing the substituent. Thus the preferential migration of phenyl to the unsubstituted β-carbon is reasonable since the more perturbed portion of the dienone triplet proves more reactive.

Additionally, this unusual phenyl migration to methoxy dienone **4** does not derive from an inhibited type A process, since the β,β-bond order is not the lowest, nor is the triplet type A rate the slowest as we compare the parent dienone **34**, the methoxy dienone **4**, and the cyano dienone **1**. The cyano dienone **1** has the lowest β,β-bond order and the slowest type A triplet rate, yet it exhibits no competing phenyl migration. Thus the phenyl migration must be inherently more rapid and therefore competitive for the methoxy dienone.

Similar SCF–CI calculations were carried out on the bridged dienone. However, here the σ framework is no longer orthogonal to the π system, and the three-ring Walsh orbitals were included as well as the five-ring σ orbitals.

The species does have an S_0 ground state which corresponds to the type A zwitterion discussed so often in connection with dienone photochemistry. The next highest state is T_1.

A correlation diagram can be drawn for the β,β bridging of dienone MO's. The SCF–MO's are qualitatively the same for the parent dienone **34** as those derived by us earlier using Hückel calculations.[32] However, the HOMO–LUMO crossing characteristic of this correlation is permitted only because of the different symmetries of these MO's. In the methoxy dienone this symmetry is broken, and a HOMO–LUMO crossing is avoided. This seems to be the source of the excited state of the bridged species rearranging rather than decaying first to the ground-state zwitterion (note Figure 4).

There is an interesting point which can be seen in the correlation diagram (Figure 4). This is that adiabatic conversion of the dienone triplet to the bridged species converts an n–π^* triplet to a triplet which is best designated π–π^*. Thus the LUMO(dienone) of the dienone reactant becomes the LUMO(zwitterion) of bridged product species when there is an avoided crossing due to substitution of methoxy on the β-carbon. The species obtained in this adiabatic fashion is hardly termed an n–π^* state but rather seems better pictured as a π–π^* species, since promotion is to the LUMO(zwitterion) from the HOMO(zwitterion), and the latter has no p_y (i.e., n) orbital weighting. Even without the β-substituent perturbation, an adiabatic conversion to an excited (triplet) bridged species affords a configuration hardly termed n–π^* since, again, the bonding MO with one electron has no p_y character.

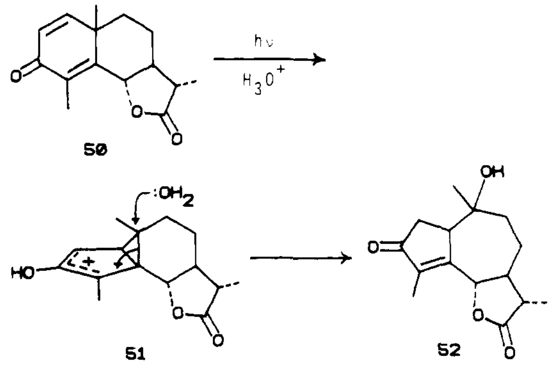
Thus, as carbon 4 moves out-of-plane with incipient β,β bridging (either vibrationally or in reaction), the n–π^* excited state begins to mix with the π–π^* excited triplet, and one is really dealing with a mixed state. This mixing results from the out-of-plane Walsh orbitals overlapping with both the π system and the in-plane p_y orbital and σ system. Hence, much of the controversy[33-35] about the nature of the reacting dienone triplet is not meaningful until one defines the geometry of the reacting dienone excited state.

Paraphrased in terms of states, the introduction of a β substituent tends to destroy the bifunnel leading to the ground-state product. It is interesting to speculate whether this not only assists formation of a bridged triplet but also leads to the structureless phosphorescence emission observed in so many β-alkyl and (here) methoxy dienones and, perhaps, to an extended triplet lifetime.

Role of Zwitterions in Dienone Photochemistry. In the preceding sections we have provided evidence that at least a portion of the 3-methoxy dienone photochemistry derives from rearrangement of the bridged triplet dienone without prior radiationless decay to the type A zwitterion. However, in our earlier work we provided evidence in favor of intervention of type A zwitterions in the photochemistry of 2,5-cyclohexadienones. Because of these differing conclusions, it is worthwhile to summarize the reasons for believing that type A zwitterions are involved in much of dienone photochemistry.

The initial postulate suggesting zwitterion involvement derived[3] from the nature of the type A rearrangement both in the case of 4,4-diphenylcyclohexadienone[3] and in santonin (**49**) photochemistry. Thus, we noted that the rearrangements were typically cationic, of the cyclopropylcarbinyl variety, despite the n–π^* triplet being a diradical-like species. The zwitterion postulate[3] resolved the dilemma of this ambivalency.

We also noted[3] that the behavior of santonin in acidic solvents,[37] leading to products such as isophotosantonic lactone (**52**), was best understood on the basis of a protonated zwitterion (**51**) followed by three-ring opening by nucleophile (note eq 7).



50 **51** **52**

(7)

Since that time further support has been found in many additional examples of diversion of the zwitterion by the medium acidity. In one interesting set of examples Kropp[38] and Jeger[39] found not only the isophotosantonic lactone type opening of eq 7 but also opening of the alternate bond C(1)–C(10) on substitution of a methyl group at C-2 rather than C-4.

Beyond this, in a large number of examples we were able to generate type A zwitterions independently, without the use of light, and found that in each case the photochemical product was generated.[2,13-15]

Perhaps the most convincing evidence derives from the very elegant work of Samuel[40] in which an adduct of the type A zwitterion, derived from irradiation of 4-(trichloromethyl)-4-methylcyclohexadienone, and cyclo-

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[32] (a) Zimmerman, H. E.; Binkley, B. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (b) Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551.

[33] Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 906–912.

[34] Fisch, M. H.; Richards, J. H. *J. Am. Chem. Soc.* **1963**, *85*, 3029–3030.

[35] (a) Marsh, G.; Kearns, D. R.; Fisch, M. *J. Am. Chem. Soc.* **1970**, *92*, 2252–2257. (b) Fisch, M.; Nonnenmacker, R. "Abstracts of Papers", 157th National Meeting of the American Chemical Society, Apr 1969, American Chemical Society: Washington, DC, 1969; Abstracts, ORGN 88. (c) Note: Swenton, J. S.; Saurborn, E.; Srinivasan, R.; Sonntag, F. I. *J. Am. Chem. Soc.* **1968**, *90*, 2990–2991. These authors note evidence for a nonionic pathway in the gas phase.

[36] (a) Schuster, D. I.; Prabhu, K. V. *J. Am. Chem. Soc.* **1974**, *96*, 3511–3523. (b) Schuster, D. I.; Barile, G. C.; Liu, K. C. *Ibid.* **1975**, *97*, 4441–4443.

[37] (a) Barton, D. H. R.; De Mayo, P.; Shafig, M. *J. Chem. Soc.* **1958**, 140–145. (b) Barton, D. H. R.; De Mayo, P.; Shafig, M. *Proc. Chem. Soc., London* **1957**, 205. (c) Barton, D. H. R.; De Mayo, P.; Shafig, M. *J. Chem. Soc.* **1958**, 3314–3319.

[38] Kropp, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 4053–4061.

[39] Ganter, C.; Utzinger, E. C.; Schaffner, K.; Arigoni, D.; Jeger, O. *Helv. Chim. Acta* **1962**, *45*, 2403–2419.

[40] Samuel, C. J. *J. Chem. Soc., Chem. Commun.* **1979**, 275–276.

pentadiene was isolated and characterized. The relatively slow rearrangement of the type A zwitterion in this system permitted its trapping.

Thus it may be concluded that the photochemistry of 2,5-cyclohexadienone derives for the most part from the type A zwitterions postulated almost 20 years ago.[3] Where special substitution exists, it seems from the present study that some chemistry of the excited bridged species, namely, the excited state of the type A zwitterion, does occur.

Overview of n-π* vs. π-π* Reactivity in Dienone Photochemistry. Over the years there have been several viewpoints expressed regarding the nature of the excited state responsible for the type A dienone rearrangement.

Arguing in favor of an n-π* excited triplet as the reacting species are several pieces of evidence. The first is that SCF-CI calculations, almost independent of choice of parameterization,[12] lead to the prediction of a very high β,β-bond order for the n-π* triplet but an antibonding tendency for the corresponding π-π* triplet. This effect is seen even in simple Hückel calculations.[33] Thus, the n-π* triplet reactivity parallels that expected of its high β,β bonding tendency while the π-π* triplet would have to form a bond between two centers which are antibonding.

A second piece of evidence suggesting the n-π* excited state as the reacting species is the Zimmerman and Keck[41] generation of this state specifically from a dioxetane under conditions where evidence argued against n-π* and π-π* triplet equilibration prior to bridging and subsequent rearrangement.[42]

A third source of evidence arises from the present inability to effect the type A rearrangement of the 3-methoxy dienone 4 with sensitizers of energy below that of the n-π* state despite prediction of a low-energy π-π* triplet. Coupled with this evidence is the identification of the n-π* triplet as the only strongly emitting species in a number of dienone systems which rearrange efficiently.[3,12] As the n-π* energy is lowered, rearrangement rates tend to diminish as would be expected by selectively lowering the starting-state energy in a reaction.

The main evidence in favor of a π-π* configuration in the type A rearrangement is the observation of lower energy emitting species than the n-π* triplet and the assumption that it will be the low-energy triplet which rearranges. Another source of support for the π-π* configuration was differential quenching in a Stern-Volmer treatment with expulsion of a trichloromethyl radical following one slope and the type A rearrangement following another;[36a] however, the different slopes were found[36b] to be an artifact deriving from a chain process in trichloromethyl expulsion.

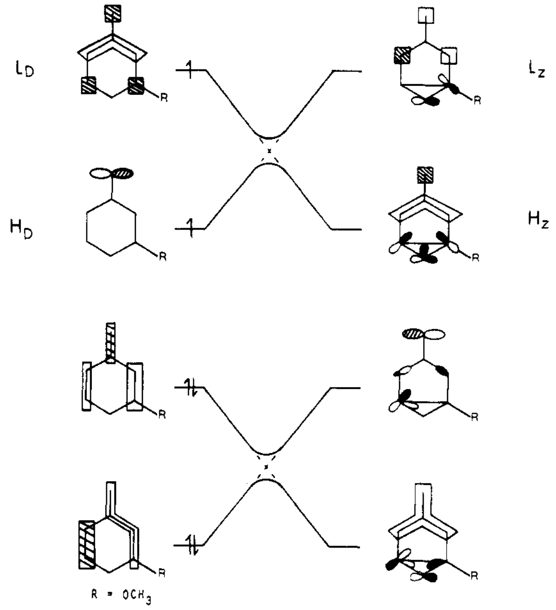

Figure 4. MO correlation diagram for closure of dienone to 3,5-bridged species: wave function positive, shaded lobes; wave function negative, unshaded lobes. H_D refers to the HOMO of the dienone, H_Z to the HOMO of the zwitterion, L_D to the LUMO of the dienone, and L_Z to the LUMO of the zwitterion. The magnitude of the shadings qualitatively gives weightings.

Conclusion

While after bridging designation of an n-π* triplet configuration is ambiguous due to admixture with π-π*-type contributions, this is a semantic problem of minor consequence. Otherwise, the evidence favors an n-π* triplet as the bridging and reacting species in the type A dienone rearrangement. Further, it is seen that in selected cases not all of the mechanism proceeds via the type A zwitterion.

Experimental Section[43]

4,4-Diphenylcyclohexane-1,3-dione. To a suspension of 5.61 g (50 mmol) of alcohol-free potassium *tert*-butoxide in 150 mL of anhydrous ether was added 10.5 g (50 mmol) of 1,1-diphenylacetone in 50 mL of anhydrous ether followed by 5.40 mL (50 mmol) of ethyl acrylate in 50 mL of anhydrous ether. The solution was stirred at room temperature for 18 h during which time a precipitate formed. The hygroscopic solid was filtered under nitrogen, washed thoroughly with anhydrous ether, dissolved in water, acidified with dilute hydrochloric acid, and

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[41] (a) Zimmerman, H. E.; Keck, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 3527-3528. (b) Zimmerman, H. E.; Keck, G. E.; Pflederer, J. L. *Ibid.* **1976**, *98*, 5574-5581.

[42] (a) Our dioxetane work[41] has been discussed by Schuster,[42b] who has, however, misquoted our conclusions and then criticized these. Thus, this work did not conclude that the dioxetane study proved that the n-π* configuration of 4,4-diphenylcyclohexadienone was its lowest energy triplet state (although other evidence indicates this). Rather, the dioxetane study reveals that there is lack of equilibration of the cyclohexadienone n-π* triplet initially formed with a low-energy β-acetonaphthone molecule generated in the same solvent cage and that the rate of dienone rearrangement is found to be faster. Furthermore, the formation of the 68.9-kcal/mol dienone triplet in preference to the β-acetonaphthone 59-kcal/mol π-π* triplet would be unreasonable if the 68.9-kcal/mol dienone triplet has the same configuration as the 59-kcal/mol β-acetonaphthone triplet. Subsequent work by Richardson[42c] has shown that in absence of rearrangements the lower energy of two possible triplets is formed from dioxetanes. However, the unusual energy partition is understood on the basis of a kinetic preference for n-π* triplets in thermal dioxetane cleavages. The virtually constant partition of triplet energy in our series of dioxetanes, independent of the higher or lower triplet energy of the second ketone being generated, would otherwise be difficult to understand unless the low-energy β-acetonaphthone π-π* state were unavailable. Then the ketone byproduct excited states potentially available are *all* of higher energy than the dienone. (b) Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65-73. (c) Richardson, W. H.; Lovett, M. B.; Price, M. E.; Anderegg, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4683-4687. (d) Despite this criticism, Schuster does conclude[42b] that no experimental evidence exists which is "inconsistent" with the n-π* excited state being the reactive species in cyclohexadienone photochemistry.

[43] All melting points were determined by using a calibrated hot-stage apparatus. Mass spectra were obtained by using an AEI MS-902 mass spectrometer at 70 eV. Proton nuclear magnetic resonance spectra were obtained by using a JEOL MH-100 or Bruker WH-270 spectrometer. Carbon nuclear magnetic resonance spectra were obtained by using a JEOL FX-60 spectrometer. All reactions were run under an atmosphere of dry nitrogen, with magnesium sulfate being used as the drying agent. High-pressure liquid chromatography was performed on a Waters Model ALC-100 liquid chromatograph employing an LDC 254-nm UV detector which was calibrated for the relative responses of detected compounds and standards. Column chromatography was performed on silica gel (Matheson Coleman and Bell, grade 62, 60-200 mesh) packing mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored by a hand-held UV lamp.

chloroform extracted. The extract was washed with water and brine, dried, and concentrated in vacuo to give 12.3 g of the dione as a white solid. Recrystallization from dioxane afforded 12.1 g (92%) of colorless needles: mp 196–198 °C (lit.[44] mp 197–198 °C); 100-MHz NMR (acetone-d_6) δ 10.2–9.1 (br, 1 H, OH), 7.5–7.0 (m, 10 H, arom), 5.52 (s, 1 H, vinyl), 2.77 (t, 2 H, J = 7 Hz, CH_2), 2.35 (t, 2 H, J = 7 Hz, CH_2); IR (KBr) 3400–3110, 1615 cm^{-1}; high-resolution mass spectrum calcd for $C_{18}H_{16}O_2$ *m/e* 264.1150, found *m/e* 264.1150.

3-Methoxy-6,6-diphenylcyclohex-2-en-1-one. A solution of 132 mg (0.50 mmol) of 4,4-diphenylcyclohexane-1,3-dione in 25 mL of benzene containing 3.0 mL of methanol and 5 mg of *p*-toluenesulfonic acid was refluxed for 0.5 h, cooled, diluted with ether, washed with saturated aqueous sodium bicarbonate solution, dried, and concentrated in vacuo to yield 145 mg of a slightly yellow solid. Recrystallization from cyclohexane afforded 112 mg (0.402 mmol, 80%) of the 3-methoxy enone as colorless crystals: mp 143–144 °C; 100-MHz (CDCl$_3$) δ 7.4–7.0 (m, 10 h, arom), 5.52 (s, 1 H, vinyl), 3.60 (s, 3 H, OCH_3), 2.68 (t, 2 H, J = 6 Hz, CH_2), 2.31 (t, 2 H, J = 6 Hz, CH_2); IR (KBr) 2850, 1655, 1607, 1190 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{18}O_2$ *m/e* 278.1307, found *m/e* 278.1307.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.51. Found: C, 82.06; H, 6.41.

Structure Proof of 3-Methoxy-6,6-diphenylcyclohex-2-en-1-one. To a suspension of 35 mg (0.9 mmol) of lithium aluminum hydride in 1.0 mL of anhydrous ether was slowly added 200 mg (0.72 mmol) of the methoxy enone in 1.0 mL of dry tetrahydrofuran. The solution was refluxed for 0.5 h and cooled, and excess lithium aluminum hydride was destroyed by the careful addition of 1 mL of water. The solution was diluted with ether and washed with 10% sulfuric acid, water, and brine, dried, and concentrated in vacuo to give 181 mg (100%) of a colorless oil. The oil was recrystallized from 95% ethanol to give 110 mg (61%) of colorless prisms (mp 88–90 °C) identified as 4,4-diphenylcyclohexenone by comparison of physical and spectral data with those of authentic material.[3c]

3-Methoxy-4,4-diphenylcyclohex-2-en-1-one. Into an ice-cooled solution of 7.93 g (30.0 mmol) of 4,4-diphenylcyclohexane-1,3-dione in 200 mL of tetrahydrofuran was distilled 40.0 mmol of diazomethane prepared by mixing 7.5 g of EXR-101 (70% *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide in mineral oil), 270 mL of ether, 27 mL of 2-(2-ethoxyethoxy)ethanol and 13.2 g of potassium hydroxide in 40 mL of water at 0 °C. The mixture was stirred at room temperature for 18 h, purged with a stream of nitrogen to remove excess diazomethane, and concentrated in vacuo to give 8.52 g of a yellow oil. Chromatography on a 2.5 cm × 90 cm silica gel column slurry packed in 15% ether in hexane with collection of 1-L fractions and elution with 15% ether in hexane gave the following fractions: 1–5, nil; 6–9, 2.69 g (32%) of the previously obtained 3-methoxy-6,6-diphenylcyclohex-2-en-1-one, pure by NMR; 10–14, 3.83 g (46%) of the desired 3-methoxy-4,4-diphenylcyclohex-2-en-1-one. Recrystallization of this methoxy enone from cyclohexane gave 3.42 g (41%) colorless prisms: mp 132–133 °C; 100-MHz NMR (CDCl$_3$) δ 7.4–7.0 (m, 10 H, arom), 5.60 (s, 1 H, vinyl), 3.68 (s, 3 H, OCH_3), 2.68 (t, 2 H, J = 6 Hz, CH_2), 2.22 (t, 2 H, J = 6 Hz, CH_2); IR (KBr) 2840, 1645, 1590, 1220 cm^{-1}; UV (EtOH) λ_{max} 249 nm (ϵ 19 500); high-resolution mass spectrum calcd for $C_{19}H_{18}O_2$ *m/e* 278.1307, found *m/e* 278.1306.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.51. Found: C, 81.99; H, 6.63.

Structure Proof of 3-Methoxy-4,4-diphenylcyclohex-2-en-1-one. To a suspension of 35 mg (0.9 mmol) of lithium aluminum hydride in 1.0 mL of anhydrous ether was slowly added 200 mg (0.72 mmol) of the methoxy enone in 1 mL of tetrahydrofuran. The solution was refluxed for 0.5 h and cooled, and excess lithium aluminum hydride was destroyed by the careful addition of 1 mL of water. The solution was diluted with ether and washed with 10% sulfuric acid, water, and brine, dried, and concentrated in vacuo to give 185 mg (101%) of a colorless oil. The oil was recrystallized from 95% ethanol to give 100 mg (56%) of colorless prisms of 6,6-diphenylcyclohex-2-en-1-one: mp 94–95 °C (lit.[45] 94.5–96 °C); 100-MHz NMR (CDCl$_3$) δ 7.4–7.0 (m, 10 H, arom), 6.76 (dt, 1 H, J = 3.5, 10 Hz, vinyl), 6.16 (dt, 1 H, J = 1.5, 10 Hz, vinyl), 2.72 (t, 2 H, J = 5.5 Hz, CH_2), 2.28 (m, 2 H, CH_2); IR (KBr) 1675 cm^{-1}; high-resolution mass spectrum calcd for $C_{18}H_{16}O$ *m/e* 248.1201, found *m/e* 248.1201.

3-Methoxy-4,4-diphenylcyclohexadienone. A solution of 1.39 g (5.0 mmol) of 3-methoxy-4,4-diphenylcyclohex-2-en-1-one and 1.50 g (6.0 mmol) of dichlorodicyanobenzoquinone in 30 mL of dioxane was refluxed for 30 h, cooled, filtered, and concentrated in vacuo to yield a dark oil. The oil was dissolved in ether, washed with 10% sodium hydroxide, dried, and concentrated to give 1.32 g of a brown solid which was chromatographed on a 2.5 cm × 80 cm silica gel column slurry packed and eluted with 15% ether in hexane to give 1.28 g (92%) of the dienone, pure by NMR. Recrystallization from ethanol gave 0.89 g (64%) of colorless prisms: mp 160–161 °C; 100-MHz NMR (CDCl$_3$) δ 7.4–7.0 (m, 10 H, arom), 6.85 (d, 1 H, J = 9 Hz, vinyl), 6.20 (dd, 1 H, J = 1, 9 Hz, vinyl), 5.73 (d, 1 H, J = 1 Hz, vinyl), 3.70 (s, 3 H, OCH_3); IR (KBr) 2840, 1655, 1620, 1590, 1225 cm^{-1}; UV (EtOH) λ_{max} 242 nm (ϵ 10 600), λ_{sh} 275 (6200); high-resolution mass spectrum calcd for $C_{19}H_{16}O_2$ *m/e* 276.1150, found *m/e* 276.1146.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.35; H, 5.85.

Exploratory Sensitized Photolysis of 3-Methoxy-4,4-diphenylcyclohexadienone in Methanol. A solution of 1.00 g (3.62 mmol) of 3-methoxy-4,4-diphenylcyclohexadienone and 100 g (833 mmol) of acetophenone in 650 mL of methanol was purged with purified nitrogen for 1 h prior to and during photolysis. The photolysis was performed on the "Wisconsin Black Box"[7] apparatus utilizing the following filter combination: cell 1, 0.55 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 0.8 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 0.075 M stannous chloride dihydrate in 10% hydrochloric acid. The transmission was 0% below 305 nm, 35% at 330 nm, and 0% above 365 nm. Light output was measured by a digital electronic actinometer[8] calibrated by ferrioxalate actinometry[9] and indicated that the sample absorbed 7.40 mEinsteins of light.

The photolysate was concentrated in vacuo, the acetophenone removed via bulb-to-bulb distillation at 35 °C (0.005 mmHg), and the residue taken up in ether to slowly give 352 mg (35%) of starting methoxy dienone as colorless crystals, pure by NMR. The mother liquor was concentrated in vacuo and chromatographed on a 2.5 cm × 180 cm silica gel column slurry packed in 10% ether in hexane. Elution with 10% ether in hexane with collection of 40-mL fractions gave the following fractions: 1–30, nil; 31–50, 75 mg of acetophenone; 51–77, 15 mg of unidentified oil; 78–86, 12 mg of unidentified oil; 87–120, 80 mg (8%) of 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, by NMR; 121–190, nil; 191–280, 65 mg (0.23 mmol, 6.5%) of 3-methoxy-4,5-diphenylphenol, by NMR; 281–380, nil; 381–510, 230 mg (0.83 mmol, 23%) of starting methoxy dienone, by NMR; 511–680, 229 mg (0.83 mmol, 23%) of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, by NMR.

Fractions 87–120 were recrystallized from ether–pentane to give 42 mg of the 5-methoxy bicyclic enone as colorless prisms, mp 130–132 °C with darkening. The material was identified by X-ray crystallography (vide infra) and displayed the following spectral data: 100-MHz NMR (CDCl$_3$) δ 7.52 (d, 1 H, J = 5.5 Hz, vinyl), 7.4–7.0 (m, 10 H, arom), 5.54 (d, 1 H, J = 5.5 Hz, vinyl), 3.40 (s, 3 H, OCH_3), 3.08 (s, 1 H, bridgehead); IR (KBr) 1700, 1500, 1450, 1355, 1240, 1155 cm^{-1}; UV (cyclohexane) λ_{max} 270 nm (ϵ 1400), λ_{max} 357 (127); high-resolution mass spectrum calcd for $C_{19}H_{16}O_2$ *m/e* 276.1150, found *m/e* 276.1153.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.57; H, 6.03.

Fractions 191–280 were recrystallized from benzene–hexane to give 54 mg of the phenol as colorless needles (mp 160–161 °C) whose spectral properties were identical with those of independently prepared material (vide infra).

Fractions 511–680 were recrystallized from methanol to give 171 mg of the 4-methoxy bicyclic enone as colorless prisms (mp 125.5–126.5 °C) whose spectral properties were identical with those

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(44) A melting point but no details of the occurrence of this as a byproduct was reported by: Walker, G. N.; Alkalay, D. *J. Org. Chem.* **1967**, *32*, 2213–2225.

(45) Burger, A.; Bennet, W. B. *J. Am. Chem. Soc.* **1950**, *72*, 5414–5415.

of independently prepared material (vide infra).

Exploratory Sensitized Photolysis of 3-Methoxy-4,4-diphenylcyclohexadienone in Benzene. A solution of 500 mg (1.81 mmol) of 3-methoxy-4,4-diphenylcyclohexadienone and 35.0 g (292 mmol) of acetophenone in 700 mL of 3% methanol in photolysis grade benzene[47] was purged with purified nitrogen[46] for 1 h prior to and during photolysis. The photolysis was performed on the "Wisconsin Black Box"[7] apparatus utilizing the following filter combination: cell 1, 1.0 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 1.0 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 0.05 M stannous chloride dihydrate in 10% hydrochloric acid. The transmission was 0% below 315 nm, 16% at 335 nm, and 0% above 365 nm.

The light output was measured as described above and indicated the sample absorbed 9.20 mEinsteins of light.

The photolysate was concentrated in vacuo, and the acetophenone was removed via bulb-to-bulb distillation at 35 °C (0.005 mmHg) and chromatographed on a 2.5 cm × 180 cm silica gel column slurry packed in 5% ether in hexane. Elution with 5% ether in hexane with collection of 40-mL fractions gave the following fractions: 1–165, 14 mg of unidentified oils; 166–220, 30 mg (6%) of 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, pure by NMR (mp 130–132 °C after recrystallization from ether–hexane); 221–280, nil; 281–330, 62 mg (12%) of 3-methoxy-4,5-diphenylphenol, pure by NMR (mp 160–161 °C after recrystallization from benzene–hexane); 431–600, 253 mg (51%) of starting methoxy dienone, pure by NMR (mp 160–161 °C after recrystallization from ether–hexane); 601–845, 112 mg (22%) of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, pure by NMR (mp 125–126.5 °C after recrystallization from ether–hexane).

Exploratory Direct Photolysis of 3-Methoxy-4,4-diphenylcyclohexadienone. A solution of 300 mg (1.09 mmol) of 3-methoxy-4,4-diphenylcyclohexadienone in 250 mL of methanol was purged with purified nitrogen[46] for 30 min prior to and during photolysis. The photolysis was performed on the "Wisconsin Black Box"[7] apparatus utilizing the following filter combination: cell 1, 0.2 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 1.0 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 0.05 M stannous chloride dihydrate in 10% hydrochloric acid. The transmission was 0% below 305 nm, 17% at 335 nm, and 0% above 375 nm.

The light output was measured as described above and indicated the sample absorbed 2.50 mEinsteins of light.

The photolysate was concentrated in vacuo, dissolved in ether, and stored at −20 °C for 12 h to give 119 mg (39%) of starting methoxy dienone as colorless crystals which were pure by NMR. The mother liquor was concentrated in vacuo and subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with ether at a flow rate of 4.8 mL/min gave two bands: band 1, 86 mg (0.31 mmol, 29%) of a complex mixture; band 2, 95 mg (0.34 mmol, 32%) of a 6:10 mixture of starting methoxy dienone and 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (by NMR analysis).

Band 1 from above was subjected to preparative high-pressure LC on the same column with elution with 25% ether in hexane to give three bands: band 1, 21 mg (7%) of a complex mixture; band 2, 16 mg (5%) of 3-methoxy-4,5-diphenylphenol, pure by NMR (mp 160–161 °C after recrystallization from ether–hexane); band 3, 38 mg (13%) of 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, pure by NMR (mp 130–131.5 °C after recrystallization from ether–hexane).

Summary of Quantum Yield Results for 3-Methoxy-4,4-diphenylcyclohexadienone. All direct, sensitized, and quenched quantum yield determinations were performed by using a microoptical bench[7] employing a Bausch and Lomb Model 33-86-79 monochromator having a 5.4-mm entrance slit and a 3.0-mm exit slit (22-nm half-width theoretical band-pass) and an Osram HBO 200-W high-pressure mercury lamp. Light output was monitored by a digital electronic actinometer[8] calibrated with ferrioxalate actinometry.[9]

Analysis was by high-pressure liquid chromatography using a 25 cm × 0.4 cm column packed with 5–10-μm porous silica beads[48] with elution with 2.5% ether in dichloromethane at a flow rate of 1.1 mL/min. The internal standard used was 4-(diphenylmethoxy)-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.[2]

All direct and sensitized runs were purged with purified nitrogen[46] for 1 h prior to and during each run. All runs are summarized in Table VI.

Single-Crystal X-ray Structure of 5-Methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The crystal chosen for the X-ray study had dimensions 0.60 × 0.45 × 0.40 mm and was sealed in a glass capillary which was placed on a Syntex P$\bar{1}$ four-circle autodiffractometer (θ–2θ scans) equipped with a graphite-monochromated Mo K_α (0.7107 Å) source. Lattice parameters were obtained from 15 diffraction maxima well distributed in 2θ, χ, and ω. The compound is monoclinic with $a = 10.947$ (2) Å, $b = 10.924$ (2) Å, $c = 12.344$ (3) Å, $\beta = 96.003$ (12)°, and $V = 1468.1$ Å^3. Systematic absences [(0k0) with $k = 2M + 1$ and (h0l) with $h = 2M + 1$] indicated the space groups $P2_1/a$ (equivalent positions: $\pm[x, y, z; {}^1/_2 - x, {}^1/_2 + y, -z]$). For $z = 4$, the calculated density is 1.25 g/mL.

Intensity data were collected in the range $3° \leq 2\theta \leq 60°$ by using a variable scan speed mode of 4–24°/min. The intensities of three standard reflections were monitored every 97 reflections and indicated no significant decay in intensity throughout the data collection.

Data reduction[49] yielded 4530 unique reflections of which 2513 were considered observed ($I > 2\sigma(I)$).

The solution of the structure was accomplished by direct methods[50] and was refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogens were included in the structure factor calculations, but their parameters were not refined. The final anisotropic temperature factors resulted in $R_1 = 0.0630$ and $R_2 = 0.0677$. A final difference map resulted in no peak greater than 0.25 e, and the final "goodness of fit" value was 0.6002.

3-Methoxy-4,5-diphenylcyclohex-2-en-1-one and 3-Methoxy-5,6-diphenylcyclohex-2-en-1-one. A solution of 7.93 g (30 mmol) of 4,5-diphenylcyclohexane-1,3-dione[51] and 25 mL of methanol in 150 mL of benzene containing 0.10 mL of concentrated sulfuric acid was refluxed for 3 h, cooled, and concentrated in vacuo to give a yellow oil. The oil was chromatographed on a 5 cm × 60 cm silica gel column slurry packed in 20% ether in hexane. Elution with 20% ether in hexane with collection of 1000-mL fractions gave the following: fractions 1–4, nil; 5–8, 3.20 g (11.5 mmol, 38.3%) of 3-methoxy-4,5-diphenylcyclohex-2-en-1-one, by NMR; 9–14, 3.80 g (46%) of 3-methoxy-5,6-diphenylcyclohex-2-en-1-one, by NMR.

The 4,5-diphenyl enone was recrystallized from chloroform–hexane to give 2.50 g (30%) of colorless prisms: mp 128.5–129.5 °C; 100-MHz NMR ($CDCl_3$) δ 7.3–6.9 (m, 10 H, arom), 5.62 (s, 1 H, vinyl), 3.90 (d, 1 H, $J = 7$ Hz, CH), 3.60 (s, 3 H, OCH_3), 3.40 (m, 1 H, CH), 2.70 (d, 2 H, $J = 7$ Hz, CH_2); IR (KBr) 1635, 1580, 1480, 1355, 1215 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{18}O_2$ m/e 278.1307, found m/e 278.1307.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.51. Found: C, 81.70; H, 6.62.

The 5,6-diphenyl enone was recrystallized from chloroform–hexane to give 3.0 g (36%) of colorless prisms: mp 143.5–145 °C; 100-MHz NMR ($CDCl_3$) δ 7.3–6.9 (m, 10 H, arom), 5.58 (s, 1 H, vinyl), 3.64 (s, 3 H, OCH_3), 3.99–3.35 (m, 2 H, methines), 2.90–2.64 (m, 2 H, CH_2); IR (KBr) 1630, 1600, 1480, 1370, 1205 cm^{-1};

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(46) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

(47) Benzene for photolysis was purified by repeated washing with acidic, saturated potassium permanganate solution followed by repeated washing with concentrated sulfuric acid, water, and brine, drying over magnesium sulfate, and distillation through a 30-cm column of metal helices from CaH.

(48) Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D., unpublished results.

(49) Whitesides, T. H.; Slaven, R. V.; Calabrese, J. *Inorg. Chem.* **1974**, *13*, 1895–1899.

(50) Programs used in the structure determination: MULTAN (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B.* **1974**, *B26*, 274); data reduction and merging, Fourier calculations, and least squares by J. Calabrese; ORTEP II (Johnson, C. K. *USAEC.* **1970**, *ORNL-3794*, 1).

(51) Borsche, W. *Chem. Ber.* **1909**, *42*, 4496–4499.

high-resolution mass spectrum calcd for $C_{19}H_{18}O_2$ *m/e* 278.1307, found *m/e* 278.1309.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.51. Found: C, 81.82; H, 6.51.

Structure Proof of 3-Methoxy-4,5-diphenylcyclohex-2-en-1-one. To a suspension of 35 mg (0.92 mmol) of lithium aluminum hydride in 2.0 mL of dry tetrahydrofuran was added a solution of 200 mg (0.72 mmol) of the methoxy enol ether in 2 mL of anhydrous tetrahydrofuran. The mixture was stirred at reflux for 30 min, cooled, cautiously quenched with 10% sulfuric acid, and ether extracted. The extract was washed with water and brine, dried, and concentrated in vacuo to give 185 mg (103%) of a colorless oil. The oil was taken up in hot hexane and allowed to cool. Recrystallization of the crystalline product gave 156 mg (87%) of 5,6-diphenylcyclohex-2-en-1-one as colorless prisms, mp 92.5–93.5 °C (lit.[3c] mp 93–94 °C). A mixture melting point with authentic enone was undepressed. Spectral data proved to be identical.

Structure Proof of 3-Methoxy-5,6-diphenylcyclohex-2-en-1-one. The above procedure was used; thus 200 mg (0.72 mmol) of methoxy enol ether yielded 180 mg (0.72 mmol, 100%) of a colorless oil which was recrystallized from hexane to give 120 mg of 4,5-diphenylcyclohex-2-en-1-one as colorless prisms, mp 96.5–97.5 °C (lit.[22] mp 97–98 °C). A mixture melting point with authentic material was undepressed. Spectral data proved to be identical.

3-Methoxy-4,5-diphenylphenol. A solution of 640 mg (2.3 mmol) of 3-methoxy-4,5-diphenylcyclohex-2-en-1-one and 700 mg (3.1 mmol) of dicyanodichlorobenzoquinone in 20 mL of dry dioxane was refluxed for 36 h, cooled, filtered, and concentrated in vacuo to give a dark oil which was chromatographed on a 2.5 cm × 90 cm silica gel column slurry packed in 10% ether in hexane. Elution with 6 L of 10% ether in hexane gave 240 mg (38%) of a white solid, pure by NMR. Recrystallization from benzene–cyclohexane gave pure phenol: mp 160–161 °C; 100-MHz NMR ($CDCl_3$) δ 7.4–6.9 (m, 10 H, arom), 6.50 (s, 2 H, arom), 5.20 (br s, 1 H, OH), 3.73 (s, 3 H, OCH_3); IR (KBr) 3600–3100, 1612, 1583, 1565, 1462, 1440, 1300, 1180, 1132 cm^{-1}; UV (EtOH) λ_{max} 294 nm (ϵ 3900), λ_{sh} 240 (20 000), λ_{sh} 226 (26 000); high-resolution mass spectrum calcd for $C_{19}H_{16}O_2$ *m/e* 276.1150, found *m/e* 276.1151.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.38; H, 5.79.

3-Methoxy-5,6-diphenylphenol. A solution of 1.40 g (5.0 mmol) of 3-methoxy-5,6-diphenylcyclohex-2-en-1-one and 1.50 g (6.0 mmol) of dicyanodichlorobenzoquinone in 30 mL of dry dioxane was refluxed for 24 h, cooled, filtered, and concentrated in vacuo to give a dark oil. The oil was chromatographed on a 2.5 cm × 90 cm silica gel column slurry packed in 10% ether in hexane. Elution with 5 L of 10% ether in hexane gave 400 mg (1.45 mmol, 29%) of the methoxy phenol as a white solid, pure by NMR. Recrystallization from ether–hexane gave colorless crystals: mp 115.5–117 °C; 100-MHz NMR ($CDCl_3$) δ 7.4–6.9 (m, 10 H, arom), 6.61 (s, 2 H, arom), 5.14 (s, 1 H, hydroxyl), 3.84 (s, 3 H, methoxyl); IR (KBr) 3500–3150, 1607, 1590, 1570, 1480, 1462, 1450, 1422, 1345, 1223, 1160, 1122, 1058 cm^{-1}; UV (EtOH) λ_{max} 296 nm (ϵ 4200), λ_{sh} 232 (24 000); high-resolution mass spectrum calcd for $C_{19}H_{16}O_2$ *m/e* 276.1150, found *m/e* 276.1149.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.34; H, 5.91.

1-Methoxy-6,6-diphenylbicyclo[3.1.0]hexan-2-one. To 20.0 g (180 mmol) of 2-methoxycyclopent-2-en-1-one[52] heated at 145 °C was added 10.0 g (50 mmol) of neat liquid (mp 32 °C) diphenyldiazomethane at such a rate that only a faint red color was present in solution (~1 drop/30 s). The mixture was cooled, the excess enone removed by vacuum distillation, and the residue chromatographed on a 2.5 cm × 90 cm silica gel column slurry packed in 5% ether in hexane. Elution with 5% ether in hexane with collection of 1-L fractions gave, in fractions 3–6, 4.5 g (32%) of a slightly yellow solid. Recrystallization from methanol gave 3.82 g (27%) of the bicyclo ketone as colorless prisms: mp 115–116 °C; 100-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 3.28 (s, 3 H, OCH_3), 2.95 (d, 1 H, *J* = 6 Hz, bridgehead), 2.4–1.6 (m, 3 H, aliph), 1.1–0.6 (m, 1 H, HCH); IR (KBr) 1720, 1450, 1170, 1080, 1000 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{18}O_2$ *m/e* 278.1307, found *m/e* 278.1312.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.51. Found: C, 82.16; H, 6.52.

1-Methoxy-6,6-diphenylbicyclo[3.1.0]hexan-2-one Tosylhydrazone. A solution of 4.30 g (15.5 mmol) of the bicyclic ketone and 5.80 g (31.0 mmol) of tosylhydrazine in 60 mL of absolute ethanol containing 0.02 mL of concentrated hydrochloric acid was refluxed for 5 h, cooled in ice, and filtered to yield 6.83 g (15.3 mmol, 98%) of the tosylhydrazone as colorless crystals, mp 220–22 °C dec (pure by NMR). An analytical sample was prepared by recrystallization from ethyl acetate: mp 240–242 °C dec; 270-MHz NMR ($CDCl_3$) δ 7.93 (d, 2 H, *J* = 8.6 Hz, arom), 7.39 (d, 2 H, *J* = 8.6 Hz, arom), 7.3–7.0 (m, 10 H, arom), 3.28 (s, 3 H, OCH_3), 2.71 (d, 1 H, *J* = 6.3 Hz, bridgehead), 2.49 (s, 1 H, NH), 2.4–2.2 (m, 1 H, HCH), 2.2–2.0 (m, 1 H, HCH), 1.9–1.7 (m, 1 H, HCH), 1.57 (s, 3 H, CH_3), 0.6–0.4 (m, 1 H, HCH); IR (KBr) 3300–3120, 1400, 1340, 1170 cm^{-1}; high-resolution mass spectrum calcd for $C_{26}H_{26}N_2O_3S$ *m/e* 446.1664, found *m/e* 446.1668.

Anal. Calcd for $C_{26}H_{26}N_2O_3S$: C, 69.93; H, 5.87. Found: C, 69.74; H, 5.85.

1-Methoxy-6,6-diphenylbicyclo[3.1.0]hex-2-ene. To an ice-cooled suspension of 6.70 g (15.0 mmol) of 1-methoxy-6,6-diphenylbicyclo[3.1.0]hexan-2-one tosylhydrazone in 75 mL of anhydrous ether were added 41 mL (37.5 mmol) of a 0.90 M methyllithium in ether solution. The ice bath was removed, the mixture stirred at room temperature for 12 h and recooled in ice, and the excess methyllithium carefully destroyed by addition of water. The solution was partitioned between hexane and water, and the organic layer was washed with water and brine, dried, and concentrated in vacuo to give a yellow solid which was chromatographed on a 2.5 cm × 50 cm silica gel column slurry packed in hexane. Elution with 4 L of 1% ether in hexane with collection of 1-L fractions gave the following: fractions 1 and 2, nil; 3 and 4, 3.47 g (88%) of the olefin as a fluffy white solid, mp 83–85 °C. An analytical sample was prepared by recrystallization from hexane: mp 88–90 °C; 270-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 6.02 (ddt, 1 H, *J* = 5.5, 2.1, 0.6 Hz, vinyl), 5.23 (dt, 1 H, *J* = 5.5, 2.1 Hz, vinyl), 3.28 (s, 3 H, OCH_3), 2.79 (ddt, 1 H, *J* = 18.6, 6.8, 2.1 Hz, HCH), 2.55 (br d, 1 H, *J* = 6.8 Hz, bridgehead), 2.01 (ddt, 1 H, *J* = 18.6, 2.1, 0.7 Hz, HCH); IR (KBr) 1495, 1450, 1370, 1330, 1060 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{18}O$ *m/e* 262.1358, found *m/e* 262.1354.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.91. Found: C, 87.20; H, 7.12.

***exo*-1-Methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-ol.** The general method of Brown et al.[4] was used. To a refluxing solution of 38.5 mmol of 9-borabicyclononane, prepared by adding 4.16 g (38.5 mmol) of 1,5-cyclooctadiene to an ice-cooled solution of 0.94 M borane–tetrahydrofuran complex in tetrahydrofuran followed by refluxing for 1 h, was added a solution of 9.18 g (35 mmol) of 1-methoxy-6,6-diphenylbicyclo[3.1.0]hex-2-ene in 20 mL of tetrahydrofuran. The mixture was refluxed for 12 h and cooled in ice, and 20 mL of absolute ethanol was added followed by 10 mL (50 mmol) of 5.0 N sodium hydroxide and 15 mL (50 mmol) of 30% hydrogen peroxide. The mixture was refluxed for 1.5 h, cooled, poured into 100 mL of brine and ether extracted. The extract was washed with brine, dried, and concentrated in vacuo to give 17 g of a waxy solid which was heated with vigorous shaking in 400 mL of water and filtered hot to give 11 g of a white powder. The powder was dissolved in chloroform, dried, concentrated in vacuo, and recrystallized from benzene–hexane to give 8.39 g (86%) of the desired exo alcohol as colorless needles: mp 138–139 °C; 270-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 3.22 (s, 3 H, OCH_3), 2.75 (dd, 1 H, *J* = 14.7, 7.4 Hz, HCH), 2.58 (dd, 1 H, *J* = 13.2, 7.4 Hz, H cH), 2.43 (d, 1 H, *J* = 5.5 Hz, bridgehead), 2.3–1.9 (m, 3 H, 2 HCH and HOCH), 1.56 (br s, 1 H, OH); IR (KBr) 3600–3000, 1495, 1450, 1080, 1060, 1045, 1030 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{20}O_2$ *m/e* 280.1463, found *m/e* 280.1457.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.18; H, 7.24.

1-Methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-one. To a solution of 135 mmol of chromium trioxide–pyridine complex,[53]

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[52] Ackeson, R. M. *J. Chem. Soc.* **1956**, 4232–4237.

prepared by the addition of 13.5 g of anhydrous chromium trioxide to 21.5 g of pyridine in 400 mL of dichloromethane, was added in one portion 6.31 g (22.5 mmol) of *exo*-1-methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-ol in 20 mL of dichloromethane. The mixture was stirred at room temperature for 30 min and decanted, the solids were washed with anhydrous ether, and the combined dichloromethane and ether solution was washed with saturated sodium bicarbonate, 10% hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and concentrated in vacuo to give 5.90 g of a yellow oil. Recrystallization from methanol gave 5.02 g (80%) of the 1-methoxy bicyclic ketone as colorless prisms: mp 120–122 °C; 270-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 3.25 (s, 3 H, OCH_3), 2.95 (dt, 1 H, $J = 18.7, 1.3$ Hz, HCH), 2.86 (br dd, 1 H, $J = 18.9, 6.6$ Hz, HCH), 2.84 (dd, 1 H, $J = 18.7, 0.9$ Hz, HCH), 2.74 (d, 1 H, $J = 6.6$ Hz, HCH); IR (KBr) 1755, 1495, 1450, 1200 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{18}O_2$ *m/e* 278.1307, found *m/e* 278.1302.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.51. Found: C, 81.83; H, 6.69.

1-Methoxy-3-acetoxy-6,6-diphenylbicyclo[3.1.0]hex-2-ene and 1-Methoxy-3-acetoxy-6,6-diphenylbicyclo[3.1.0]hex-3-ene. A mixture of 1.39 g (5.0 mmol) of 1-methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-one, 50 mg of *p*-toluenesulfonic acid, and 25 mL of isopropenyl acetate was refluxed for 24 h, the bulk of the isopropenyl acetate removed by distillation, and the residue chromatographed on a 2.5 cm × 50 cm silica gel column slurry packed in 10% ether in hexane. Elution with 2 L of 10% ether in hexane gave 1.49 g of a cream-colored solid. Recrystallization from ether–hexane gave colorless crystals (mp 150–152 °C) which were shown by NMR analysis to be a 1:1 mixture of the two isomeric enol acetates: 100-MHz NMR ($CDCl_3$) δ 7.5–7.0 (m, 20 H, arom), 5.95 (m, 1 H, vinyl), 5.60 (m, 1 H, vinyl), 3.28 (s, 3 H, OCH_3), 3.24 (s, 3 H, OCH_3), 3.1–2.0 (m, 6 H, 2 CH_2 and bridgeheads), 1.90 (s, 6 H, acetyl); IR (KBr) 2840, 1765, 1755, 1650, 1220 cm^{-1}; high-resolution mass spectrum calcd for $C_{21}H_{20}O_3$ *m/e* 320.1412, found *m/e* 320.1410.

Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29. Found: C, 78.76; H, 6.37.

1-Methoxy-4-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one. To an ice-cooled solution of 132 mg (0.41 mmol) of the enol acetate mixture in 4.0 mL of carbon tetrachloride containing 0.065 mL (0.82 mmol) of epichlorohydrin was added 66 mg (0.41 mmol) of molecular bromine in 1 mL of carbon tetrachloride. The solution was stirred for 5 min at 0 °C, concentrated with a stream of dry nitrogen, and subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with 40% ether in hexane at a flow rate of 4.4 mL/min gave 67 mg (46%) of the monobromo ketone as a colorless oil, retention time 8 min. The bromo ketone was recrystallized from ether–hexane to give colorless prisms: mp 113–115 °C dec; 100-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 4.20 (s, 1 H, CH), 3.40 (d, 1 H, $J = 18$ Hz, HCH), 3.32 (s, 3 H, OCH_3), 2.96 (s, 1 H, bridgehead), 2.71 (d, 1 H, $J = 18$ Hz, HCH); IR (KBr) 1750, 1495, 1450 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{17}O_2Br$ *m/e* 356.0411, found *m/e* 356.0406.

Anal. Calcd for $C_{19}H_{17}O_2Br$: C, 63.87; H, 4.80. Found: C, 63.93; H, 4.76.

1-Methoxy-2-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one and 1-Methoxy-4-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one. A solution of 320 mg (1.0 mmol) of the enol acetate mixture and 0.09 mL (1.1 mmol) of sulfuryl chloride in 10 mL of carbon tetrachloride was stirred for 12 h at room temperature. The mixture was diluted with hexane, washed with saturated sodium bicarbonate, water, and brine, dried, and concentrated in vacuo to give 357 mg of a yellow oil. The oil was subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with 30% ether in hexane at a flow rate of 4.8 mL/min gave 200 mg (0.64 mmol, 64%) of the two isomeric monochloro ketones in a 1:1 ratio, retention time 12 min. The mixture was dissolved in ether and stored in a pentane-saturated atmosphere (i.e., Erlenmeyer flask in a desiccator with pentane at the bottom) to give 70 mg (22%) of 1-methoxy-4-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one as colorless prisms: mp 145–146 °C dec; 270-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 4.12 (s, 1 H, CH), 3.38 (d, 1 H, $J = 18.4$ Hz, HCH), 3.34 (s, 3 H, OCH_3), 2.87 (s, 1 H, bridgehead), 2.78 (d, 1 H, $J = 18.4$ Hz, HCH); IR (KBr) 1745, 1485, 1440, 1360 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{17}O_2Cl$ *m/e* 312.0917, found *m/e* 312.0916.

Anal. Calcd for $C_{19}H_{17}O_2Cl$: C, 72.95; H, 5.48. Found: C, 73.05; H, 5.68.

The mother liquor from above was concentrated in vacuo and subjected to preparative high-pressure LC using a 60 cm × 0.8 cm column packed with 15–25-μm porous Carbowax 400 coated silica beads.[48] Elution with 30% ether in hexane in the recycle mode gave 30 mg of the previously obtained 4-chloro ketone as the faster eluting component and 89 mg of 1-methoxy-2-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one as the slower eluting component. The 2-chloro ketone was recrystallized from ether–pentane to give 62 mg (20%) of colorless plates: mp 97–99 °C dec; 270-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 4.42 (d, 1 H, $J = 0.9$ Hz, CH), 3.22 (ddd, 1 H, $J = 18.4, 5.9, 0.9$ Hz, HCH), 3.22 (s, 3 H, OCH_3), 2.97 (d, 1 H, $J = 5.9$ Hz, bridgehead), 2.40 (d, 1 H, $J = 18.4$ Hz, HCH); IR (KBr) 1750, 1490, 1440 cm^{-1}; high-resolution mass spectrum, no parent ion was observable at low-electron-volt values.

Anal. Calcd for $C_{19}H_{17}O_2Cl$: C, 72.95; H, 5.48. Found: C, 73.05; H, 5.65.

1-Methoxy-2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one. To an ice-cooled solution of 278 mg (1.0 mmol) of 1-methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-one in 2.0 mL of carbon tetrachloride and 1 mL of glacial acetic acid was added 350 mg (2.2 mmol) of molecular bromine in 1 mL of carbon tetrachloride in one portion. The solution was stirred at 0 °C for 15 min, diluted with 1:1 ether–hexane, washed with ice-cold water and cold dilute sodium thiosulfate, dried, and concentrated in vacuo to give a yellow oil. The oil was subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with 30% ether in hexane at a flow rate of 4.8 mL/min gave 211 mg (48%) of the dibromo ketone as a slightly yellow solid (95% pure by NMR), retention time 10 min. Recrystallization from ether–pentane gave 160 mg (38%) of colorless prisms: mp 105–108 °C dec; 100-MHz NMR ($CDCl_3$) δ 7.5–7.0 (m, 10 H, arom), 4.64 (s, 1 H, CH), 4.24 (s, 1 H, CH), 3.30 (s, 1 H, bridgehead), 3.10 (s, 3 H, OCH_3); IR (KBr) 1750 cm^{-1}; high-resolution mass spectrum, no parent ion was observable at low-electron-volt values.

Anal. Calcd for $C_{19}H_{16}O_2Br_2$: C, 52.32; H, 3.70. Found: C, 52.14; H, 3.73.

Reaction of 1-Methoxy-4-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Sodium Methoxide. To a solution of 36 mg (0.1 mmol) of the monobromo ketone in 2.0 mL of methanol was added 1.0 mL of 0.10 M sodium methoxide in methanol. The mixture was stirred for 5 min at room temperature, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 28 mg of a white solid. NMR analysis indicated that only the 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one isomer was formed. The material was subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with ether at a flow rate of 4.8 mL/min gave one band: retention time 15 min; 27 mg (98%) of the pure enone as colorless microcrystals; mp 125–126 °C, mixture melting point was undepressed at 125–127 °C. No 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (retention time 2.5 min) was observed by high-pressure LC.

The above reaction was also carried out at 0 °C for 2 min; workup gave 28 mg (100%) of the 4-methoxy enone as a white solid (mp 124–126 °C) which was pure by NMR analysis.

Reaction of 1-Methoxy-2-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Sodium Methoxide. To a solution of 62 mg (0.20 mmol) of the monochloro ketone in 4.0 mL of methanol was added 1.0 mL of 0.20 M sodium methoxide in methanol. The mixture was stirred for 5 min at room temperature, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 57 mg (100%) of a colorless oil. NMR analysis indicated that only the 4-methoxy-6,6-diphenylbicyclo[3.1.0]-

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hex-3-en-2-one isomer was formed. The material was subjected to preparative high-pressure LC on a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with ether at a flow rate of 4.8 mL/min gave one band: retention time 15 min; 53 mg (96%) of the pure 4-methoxy enone as colorless microcrystals; mp 125–126 °C. No 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (retention time 2.5 min) was observed by high-pressure LC.

Reaction of 1-Methoxy-2-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one with DBN. To a solution of 62 mg (0.20 mmol) of the monochloro ketone in 4.0 mL of methanol was added 0.05 mL (0.40 mmol) of 1,5-diazabicyclo[3.4.0]non-5-ene (DBN). The mixture was stirred for 2 min at room temperature, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated to give 57 mg of a white solid. NMR analysis indicated that only the 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one isomer was formed. The material was subjected to preparative high-performance LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with ether at a flow rate of 4.8 mL/min gave one band: retention time 15 min; 54 mg (98%) of the pure enone as colorless microcrystals; mp 125–127 °C. No 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (retention time 2.5 min) was observed by high-pressure LC.

Reaction of 1-Methoxy-4-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Sodium Methoxide. To a solution of 62 mg (0.20 mmol) of the monochloro ketone in 4 mL of methanol was added 1.0 mL of 0.20 M sodium methoxide in methanol. The mixture was stirred for 10 min, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated to give 50 mg of a slightly yellow oil. NMR analysis indicated approximately 70% conversion to 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one along with several other compounds; however, no 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was discernible.

The above reaction was repeated with stirring for only 1 min, and workup gave 58 mg of a slightly yellow oil whose NMR was identical with that obtained above.

The two reaction products were combined and subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with ether at a flow rate of 4.8 mL/min gave three bands: band 1, retention time 5 min, 10 mg (8%) of an unidentified yellow oil; band 2, retention time 9 min, 23 mg (19%) of a colorless oil identified as 3-methoxy-4-(diphenylmethyl)-5-chlorocyclopent-2-ene-1-one (vide infra); band 3, retention time 15 min, 78 mg (71%) of the 4-methoxy enone as colorless microcrystals, mp 124–126 °C.

Band 2 was recrystallized from hexane to give 20 mg (16%) of the cyclopentenone as colorless needles: mp 88–89 °C; 100-MHz NMR ($CDCl_3$) δ 7.6–7.0 (m, 10 H, arom), 5.30 (d, 1 H, J = 0.5 Hz, vinyl), 4.56 (d, 1 H, J = 7 Hz, $(Ph)_2CH$), 4.12 (d, 1 H, J = 2 Hz, ClCH), 3.8 (m, 1 H, CH), 3.76 (s, 3 H, OCH_3); IR (KBr) 1680, 1585, 1250 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{17}O_2Cl$ *m/e* 312.0917, found *m/e* 312.0915.

Anal. Calcd for $C_{19}H_{17}O_2Cl$: C, 72.95; H, 5.48. Found: C, 73.17; H, 5.63.

Reaction of 1-Methoxy-4-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one with DBN. To a solution of 31 mg (0.10 mmol) of the monochloro ketone in 4.0 mL of methanol was added 0.025 mL of 1,5-diazabicyclo[3.4.0]non-5-ene (DBN). The mixture was stirred for 2 min at room temperature, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 30 mg of a slightly yellow oil. The material was subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with ether at a flow rate of 4.8 mL/min gave two bands: band 1, retention time 9 min, 8 mg (26%) of 3-methoxy-4-(diphenylmethyl)-5-chlorocyclopent-2-en-1-one, by NMR; band 2, retention time 15 min, 20 mg (72%) of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, mp 124–126 °C.

No 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (retention time 2.5 min) was observed by high-pressure LC.

Reaction of 1-Methoxy-2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Diiron Nonacarbonyl. A solution of 110 mg (0.25 mmol) of the dibromo ketone and 110 mg (0.30 mmol) of diiron nonacarbonyl[16] in 4.0 mL of benzene was stirred for 3.5 h at room temperature. The mixture was diluted with ether, washed with saturated sodium bicarbonate, water, and brine, dried, and concentrated in vacuo to give 150 mg of a yellow solid. NMR analysis indicated that only the 4-methoxy isomer and no 5-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one isomer was formed. The material was dissolved in ether, filtered through a short plug of silica gel, and concentrated in vacuo to give 50 mg (72%) of the enone as a white solid. Recrystallization from cyclohexane gave 34 mg of the 4-methoxy enone as colorless prisms, mp 125–126 °C.

Reaction of 1-Methoxy-2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Hydriodic Acid. To an ice-cooled solution of 44 mg (0.1 mmol) of the dibromo ketone in 2.0 mL of acetone was added 0.027 mL (0.2 mmol) of 57% hydriodic acid. The solution was stirred for 1 min, 1 mL of dilute sodium thiosulfate was added, and the mixture was diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 38 mg of a clear oil. The material was subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with 30% ether in hexane at a flow rate of 4.8 mL/min gave two bands: band 1, retention time 10 min, 9 mg (21%) of unreacted dibromo ketone, by NMR; band 2, retention time 14 min, 26 mg (73%) of 1-methoxy-4-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one.

No 1-methoxy-2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one was observed.

Control Experiment. Reaction of 1-Methoxy-2-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one with a Deficiency of Sodium Methoxide. To a solution of 62 mg (0.20 mmol) of the monochloro ketone in 4.0 mL of methanol was added 0.5 mL (0.10 mmol) of 0.2 M sodium methoxide in methanol. The solution was stirred for 5 min at room temperature, quenched with 1 mL of ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 58 mg of a colorless oil. NMR analysis indicated a 1:1 ratio of the starting monochloro ketone and 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The material was subjected to preparative high-pressure LC using a 50 cm × 0.8 cm column packed with 10–20-μm porous silica beads.[48] Elution with ether at a flow rate of 4.8 mL/min gave two bands: band 1, retention time 4 min, 28 mg (45%) of unreacted monochloro ketone, pure by NMR; band 2, retention time 15 min, 29 mg (52%) of the 4-methoxy enone as colorless microcrystals, mp 124–126 °C.

No 1-methoxy-4-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one was observed.

Control Experiment. Treatment of 5-Methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one with Sodium Methoxide. To a solution of 10 mg (0.036 mmol) of the 5-methoxy enone in 2.0 mL of methanol was added 0.18 mL (0.036 mmol) of 0.2 M sodium methoxide in methanol. The mixture was stirred for 5 min at room temperature, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 10 mg (100%) of recovered enone, pure by NMR analysis.

Control Experiment. Treatment of 1-Methoxy-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Potassium *tert*-Butoxide. To a solution of 28 mg (0.10 mmol) of the ketone in 4.0 mL of *tert*-butyl alcohol and 1.0 mL of benzene was added 1.0 mL (0.10 mmol) of 0.10 M potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was stirred for 5 min at room temperature, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 28 mg of a colorless oil. Recrystallization from hexane gave 22 mg (79%) of colorless needles, mp 95–97 °C. The compound was identified as 3-methoxy-4-(diphenylmethyl)-cyclopent-2-en-1-one on the basis of the following spectral data: 270-MHz NMR ($CDCl_3$) δ 7.3–7.0 (m, 10 H, arom), 5.21 (d, 1 H, J = 0.9 Hz, vinyl), 4.55 (d, 1 H, J = 5.3 Hz, $(Ph)_2CH$), 3.76 (s, 3 H, OCH_3), 3.72 (m, 1 H, CH), 2.67 (dd, 1 H, J = 18.0, 7.2 Hz, HCH), 2.39 (dd, 1 H, J = 18.0, 2.6 Hz, HCH); IR (KBr) 1680, 1580, 1345, 1250, 1200 cm^{-1}; high-resolution mass spectrum calcd for $C_{19}H_{18}O_2$ *m/e* 278.1307, found *m/e* 278.1305.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.51. Found: C, 82.02; H, 6.59.

Control Experiment. Treatment of 6,6-Diphenylbicyclo[3.1.0]hexan-3-one with Potassium *tert*-Butoxide. To a solution of 25 g (0.10 mmol) of 6,6-diphenylbicyclo[3.1.0]hexan-3-one[15] in 4.0 mL of *tert*-butyl alcohol and 1 mL of benzene was added 1.0 mL of 0.10 M potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was stirred for 5 min at room temperature, quenched with 1 mL of saturated ammonium chloride, diluted with ether, washed with water and brine, dried, and concentrated in vacuo to give 25 mg (100%) of unreacted enone as a colorless oil, pure by NMR analysis.

Reaction of 1-Methoxy-2-chloro-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Methanol. A solution of 31 mg (0.1 mmol) of the monochloro ketone in 5.0 mL of methanol was stirred for 5 h at room temperature. Concentration in vacuo gave 31 mg of a slightly yellow solid which was recrystallized from ether to give 25 mg (0.081 mmol, 81%) of prisms, mp 183–185 °C.

The material was identified as 3-methoxy-4-(methoxydiphenylmethyl)cyclopent-2-en-1-one on the basis of the following spectral data: 100-MHz NMR ($CDCl_3$) δ 7.4–7.0 (m, 10 H, arom), 5.02 (s, 1 H, vinyl), 4.26 (br t, 1 H, J = 5 Hz, CH), 3.68 (s, 3 H, OCH_3), 2.98 (s, 3 H, OCH_3), 2.61 (br d, 2 H, J = 5 Hz, CH_2); IR (KBr) 1685, 1600, 1350, 1257 cm^{-1}; high-resolution mass spectrum calcd for $C_{20}H_{20}O_3$ m/e 308.1412, found m/e 308.1416.

Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.79; H, 6.67.

Emission Measurements. Phosphorescence measurements were made on an Aminco-Kiers spectrophosphorimeter equipped with a Hanovia 901C-1, 150-W, xenon arc lamp and modified with internal baffles to eliminate scatter. The spectra were obtained at 77 K in ethanol–ether (2:1) with the samples being thoroughly degassed immediately before measurements were made. The emission spectra were calibrated by use of a low-pressure mercury lamp in each run.

Calculations. The Pople semiempirical SCF method[54,55] (complete neglect of differential overlap) was used for closed-shell, SCF, ground-state calculations. Excited-state energies and wave functions were obtained by a configuration-interaction treatment applied to SCF molecular orbitals, including single- and double-excitation calculations. Important configurations were selected from this set, as determined by the extent of the perturbations on the first two excited states by a representative set of dominant singly excited configurations and then checking to see which doubly excited configurations interacted with this group of singly excited configurations.

Configurations were represented as a linear combination of Slater determinants such that each configuration was an eigenfunction of the spin operator S^2 as described by Murrell and McEwen.[56] Matrix elements between configurations were calculated from general formulas obtained by the standard methods for reduction of many electron integrals.[57]

Valence-state ionization potentials were obtained from Hinze and Jaffe,[58] except for nitrogen, where values compiled by Nishimoto[59] were used. Two-electron-repulsion integrals were calculated by the Pariser–Parr method. Resonance integrals were calculated by the following expression:[60b]

$$\beta_{ij} = (S_{ij}/1 + S_{ij})(I_i + I_j)K$$

where S_{ij} is the overlap integral,[60a] and I_i and I_j are the valence-state ionization potentials for orbitals i and j, respectively. Nearest-neighbor and selected 1,3-resonance integrals were used. The constant K was obtained by fitting β to the spectral transition of ethylene by using a configuration-interaction calculation that included single and double excitations. The resonance integral for the carbon–nitrogen triple bond was obtained empirically by spectral fitting to benzonitrile.[57d]

Standard geometries for the 2,5-cyclohexadienones and the bicyclo[3.1.0]hexenyl systems were assumed, on the basis of reported model compounds.[61]

Calculations were performed with Fortran IV programs on a PDP-11/T55 computer having 32K words of memory. Direct access to and from two disks of 1.2 × 10^6 words/disk allowed storage and use of the large matrices encountered in configuration-interaction calculations.[57d]

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Registry No. **1**, 75010-94-5; **4**, 75010-95-6; **6**, 13128-74-0; **7**, 75010-96-7; **8**, 75010-97-8; **9**, 4528-64-7; **10**, 73982-28-2; **11**, 22323-97-3; **12**, 75024-09-8; **13**, 75010-98-9; **14**, 75010-99-0; **15**, 75011-00-6; **16**, 75011-01-7; **17**, 75011-02-8; **18**, 75011-03-9; **19**, 75011-04-0; **20**, 75011-05-1; **21**, 75024-10-1; **22**, 75011-06-2; **23**, 75011-07-3; **24**, 75011-41-5; **25**, 75011-08-4; **26**, 75011-09-5; **28**, 75011-10-8; **29**, 75011-11-9; **30**, 75011-12-0; **31**, 75011-13-1; **32**, 75011-14-2; **33**, 13304-13-7; **34**, 13304-12-6; **35**, 75011-15-3; **36**, 75011-16-4; **38**, 22524-15-8; 1,1-diphenylacetone, 781-35-1; ethyl acrylate, 140-88-5; diphenyldiazomethane, 883-40-9.

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