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Effect of Triplet-State Sensitization on Inter- and Intramolecular 2+2 Photocycloadditions of 2,5-Cyclohexadien-1-ones

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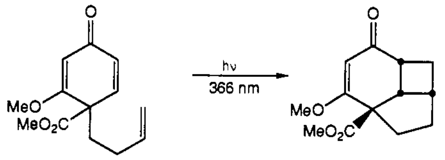
Abstract: The intramolecular 2+2 photocycloadditions of 4-carbomethoxy-4-(4′-phenyl-3′-butenyl)-2,5-cyclohexadien-1-ones **5a**, **5b**, and **12** give 6-phenyltricyclo[5.2.1.0^{5,10}]dec-2-en-4-ones **6** and **13** in excellent yields. In contrast to 4-(3′-butenyl)-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-one (**1**), both **5a** and **5b** undergo photocyclization via triplet-state sensitization by Michler's ketone (MK). The mechanism for the sensitized photocyclization must involve energy transfer from MK to the styrene chromophore in **5a** and **5b**. The sensitized intermolecular photoaddition of indene to 4-carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one (**14**) gives at least eight cycloadducts. Two major cycloadducts (~60%) are trans-fused **16** and cis-fused **17**. It is suggested that the formation of trans-fused **16** is the result of conformational energetics of an intermediate 1,4-biradical.

Direct irradiation of 4-(3′-butenyl)-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-one (**1**) at 366 nm gives the intramolecular 2+2 cycloadduct **2**[1] rather than type A photoproducts.[2]



1 2

A related photocycloaddition has been shown to occur by triplet-state sensitization with benzophenone or xanthone.[1] The sensitized process (and presumably the direct irradiation) must occur from the triplet state of the 2,5-cyclohexadienone; it has been suggested that an intermediate 1,4-biradical precedes cyclobutane formation. In this paper, we show that it is possible to obtain 2+2 cycloadducts via the triplet excited state of a suitably substituted 4-(3′-butenyl) substituent. This modification has important mechanistic consequences and should prove to be synthetically useful, especially with 2,5-cyclohexadienones that are prone to undergo type A photorearrangements rather than 2+2 photocycloaddition. A triplet-state-sensitized intermolecular 2+2 cycloaddition of indene to a 2,5-cyclohexadien-1-one also is described.

Results and Discussion

Styrene has an excited-triplet-state energy (E_T) of 61.7 kcal/mol.[3] The 4-(4′-phenyl-3′-butenyl) substituent in 2,5-cyclohexadienones **5a** and **5b** should have a similar E_T, substantially below the E_T of the 2,5-cyclohexadienone chromophore.[4] It was expected that a sensitizer of $E_T \approx 62$ kcal/mol would be capable of sensitizing the styrene chromophore in **5a** and **5b** but not the 2,5-cyclohexadienone unit. As a control, it was shown that Michler's ketone ($E_T \approx 62$ kcal/mol)[3] does not sensitize the conversion of **1** to **2**[5] (see Experimental Section).

Scheme I

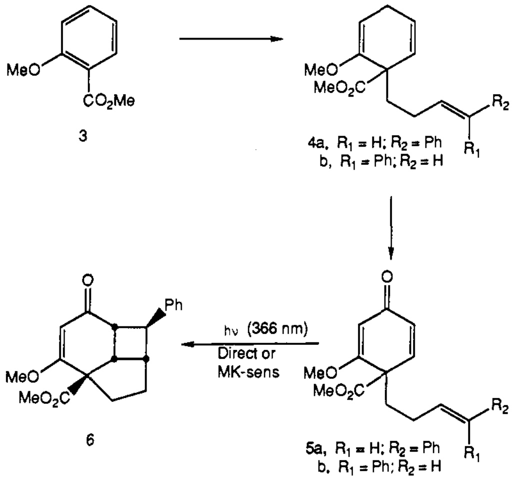


Table I. Product Distribution after 366-nm Irradiation of **5a** or **5b** (25 °C)

starting material[a]	conditions	transmission at 366 nm[b] (%)	composition[c] (%) **5b**	composition[c] (%) **5a**	composition[c] (%) **6**
5a	direct	31		82 (82)	18 (18)
5a	MK-sens			36 (33)	64 (67)
5b	direct	44	57 (55)[d]	19 (21)	24 (24)
5b	MK-sens		47 (47)	7 (5)	46 (48)

[a] Initial concentration of 3.36 × 10^{-2} M. [b] Calculated from initial absorbance of photoreaction mixture. [c] Measured by HPLC. [d] Yields in parentheses measured by ^{1}H NMR integration.

The syntheses of **5a** and **5b** are outlined in Scheme I. Preparative irradiation of **5a** or **5b** in benzene solution at 366 nm gave 1-carbomethoxy-2-methoxy-6-phenyltricyclo[5.2.1.0^{5,10}]dec-2-en-4-one (**6**) in quantitative yield. None of the stereoisomeric tricyclodecenone with inverted configuration at C(6) was observed in these experiments. Furthermore, it was noted that photo-

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(1) (a) Schultz, A. G.; Plummer, M.; Taveras, A. G.; Kullnig, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 5547. (b) For an excellent review of the applications of intramolecular 2+2 photocycloadditions in organic synthesis, see: Becker, D.; Haddad, N. *Org. Photochem.* **1989**, *10*, 1.

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

(3) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(4) The triplet-state energies of 2,5-cyclohexadienones, without substituents at C(3), have been reported to be 67–71 kcal/mol; see: (a) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1964**, *86*, 1436. (b) Zimmerman, H. E.; Binkley, R. W.; McCullough, J. J.; Zimmerman, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 6589.

(5) For an example of quenching of a long-lived triplet state of $\pi \rightarrow \pi^*$ character by high concentrations of Michler's ketone (exciplex quenching), see: (a) Schultz, A. G.; DeBoer, C. D.; Herkstroeter, W. G.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6086. (b) DeBoer, C. D.; Herkstroeter, W. G.; Marchetti, A. P.; Schultz, A. G.; Schlessinger, R. H. *Ibid.* **1973**, *95*, 3963. Exciplex quenching appears unlikely in the case of **1** because of the relatively low concentration of Michler's ketone (3.5 × 10^{-3} M) utilized and the relatively inefficient quenching of **1** with triplet-state quenchers such as piperylene.[1]

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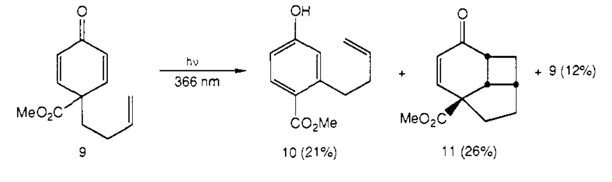
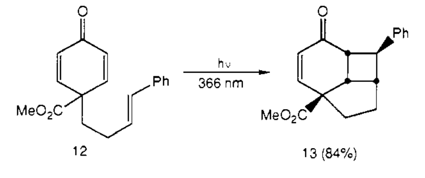
isomerization to **5a** occurred during photolysis of **5b**, but detectable quantities (≥2%) of **5b** were not observed during irradiation of **5a**.

In contrast to the photochemistry of **1**, both **5a** and **5b** underwent photocyclization to **6** in the presence of Michler's ketone (MK) at concentrations such that >99% of the incident light at 366 nm was absorbed by MK. Irradiations of **5a** and **5b** were carried to partial completion so that isomerization of the 4'-phenyl-3'-butenyl group could be examined (Table I). It is noteworthy that proportionally more **5a** is present in the direct irradiation of **5b** than in the sensitized irradiation. A tentative explanation for this difference in product distribution is based on the observation that direct irradiation of **5a** appears to give **6** with poorer quantum efficiency than that of **5b**. On the other hand, MK-sensitized irradiation of **5a** gives **6** with higher efficiency than that of **5b**. These apparent differences in quantum efficiencies would result in a relatively greater accumulation of **5a** on direct compared to sensitized irradiation of **5b**; however, we reserve further comment on this point until accurate quantum yield determinations and kinetic studies have been made.

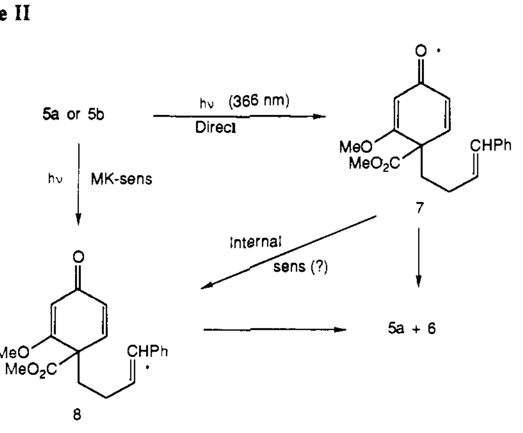
Selected mechanistic aspects of the photochemistry of **5a** and **5b** are illustrated in Scheme II. MK-sensitized irradiation of **5a** or **5b** must produce **8** with triplet-state energy localized in the styrene chromophore. This supposition is based on control experiments with **1** (vide supra). Direct irradiation would necessarily produce **7** with excitation energy localized in the 2,5-cyclohexadiene portion of the molecule. Excited-state **7** could give tricyclodecenones **6** and **5a** (via a 1,4-biradical intermediate),[6] but competitive internal energy transfer in **7** would give **5a** and **6** via excited-state **8**. There is no definitive evidence at present to support the notion of internal energy transfer as shown in Scheme II; however, experiments with 2,5-cyclohexadien-1-ones **9** and **12** (vide infra) suggest that the process **7** → **8** is worthy of further consideration.[7-9]

The presence of the 3-methoxy substituent in **1** is crucial for the complete diversion of photoreactivity from the type A rearrangement to intramolecular 2+2 cycloaddition. Irradiation of **9** in benzene solution at 25 °C has been reported to give phenol **10**, a product of type A photoreactivity, along with the intramolecular 2+2 cycloadduct **11**.[10] In a subsequent study, it was found that enhanced yields of 2+2 cycloadducts could be obtained from 2,5-cyclohexadien-1-ones lacking the 3-methoxy substituent by performing the photoreaction in pentane at −78 °C.[11]





Scheme II



Scheme III

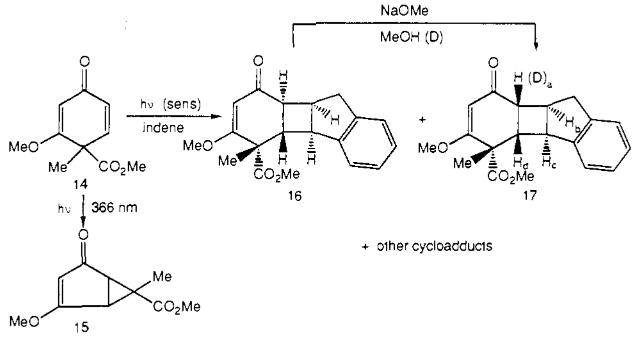


Table II. Cycloadduct Distribution after 366-nm Irradiation of 0.05 M **14** and 0.10 M Indene (25 °C)

	composition of **14**–indene cycloadducts[a,b] (%)							
conditions	A	B	C	D	**16**	E	**17**	F
direct[c]	0.39	0.96	0.68	2.37	37.8		24.3	25.1
MK-sens	0.10	0.10	0.16	3.25	20.4	3.27	40.4	32.3
thioxanthone-sens	0.39	0.45	0.46	2.17	23.3	0.35	40.1	32.7

[a] Arranged in order of elution from GC column (A elutes first): 6 ft × 1/8 in. stainless steel column filled with 3% OV-17 on Chromosorb WHP-80/100 mesh size; 170 °C for 2 min and then 4 °C/min to 300 °C. [b] Preparative chromatography fractions (silica gel) of the photoreaction mixture gave CIMS m/z (relative intensity) 313 ($M^+ + 1$, 100.0) with no higher molecular ions. These fractions were judged to contain only dimers of **14** + indene by analysis of ^{1}H NMR spectra and retention times on the GC column. [c] Under these conditions, the product ratio of bicyclohexenone **15** and cycloadducts A–F is 5.5:1.

The 4-(4'-phenyl-3'-butenyl) analogue **12** provided an opportunity to examine the effect of a tethered styrene chromophore on the type A photoreactivity of an unsubstituted 2,5-cyclohexadienone. Direct irradiation of **12** gave 1-carbomethoxy-6-phenyltricyclo[5.2.1.0^{5,10}]dec-2-en-4-one (**13**) in 84% isolated yield. The absence of significant quantities of type A photoproducts from **12** is compatible with a mechanism involving efficient quenching of the photoexcited 2,5-cyclohexadienone by the styrene chromophore. However, an alternative explanation involving faster rates of cyclization of the excited 2,5-cyclohexadienone to the 4'-phenyl-3'-butenyl group compared to that of the simple 3'-butenyl substituent also must be considered.[12]

Intermolecular 2+2 photocycloadditions of 4-carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one (**14**) to cyclopentene

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(6) See ref 1b (p 19) for a discussion of the first successful interception of a 1,4-biradical intermediate generated from an intramolecular enone–olefin cycloaddition.

(7) Pirrung and co-workers have shown that 3-(3'-butenyloxy)-2-cyclo-octen-1-ones undergo intramolecular 2+2 photocycloaddition when the olefin is substituted with a vinyl or phenyl group. However, it was concluded that intramolecular triplet-state energy transfer from the enone to the diene or styrene chromophore is insignificant; see Pirrung, M. C.; Webster, N. J. G. *J. Org. Chem.* **1987**, *52*, 3603.

(8) For examples of intramolecular energy transfer in 4,4-diaryl-2-cyclohexenones, see: Zimmerman, H. E.; Jian-hua, X.; King, R. K.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724.

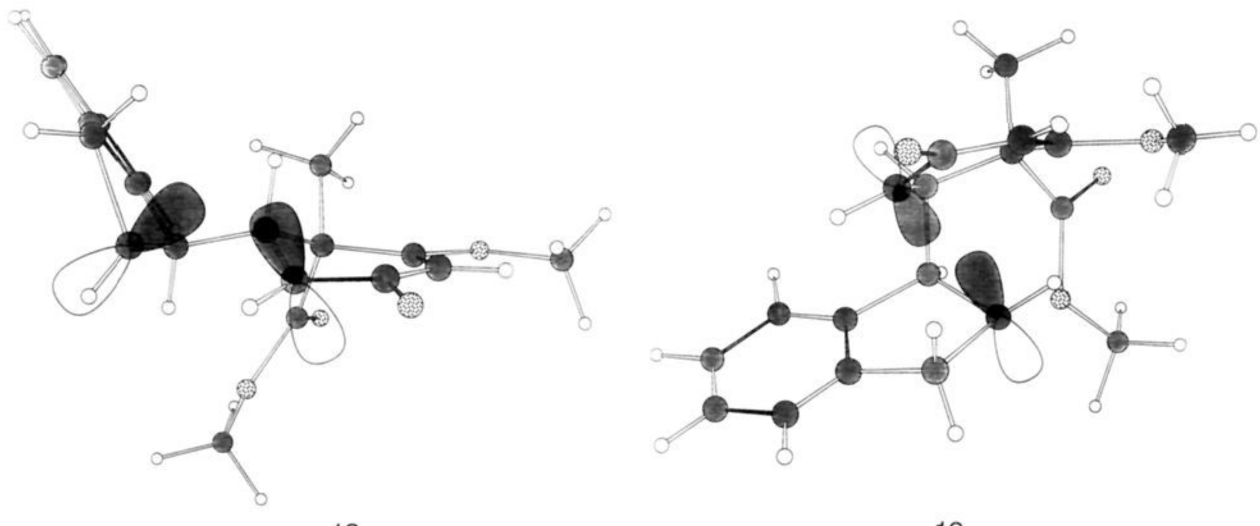
(9) For a strong dependence of internal quenching on chain length and double bond substitution in the photochemistry of alkenyl-substituted aryl ketones, see: Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4404.

(10) Plummer, M. S. Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY, 1986.

(11) Schultz, A. G.; Geiss, W.; Kullnig, R. K. *J. Org. Chem.* **1989**, *54*, 3158.

(12) An estimate of relative rates of photocyclization of **9** and **12** is not available from literature data. See ref 7 for a discussion of this point from the basis of quenching and sensitization studies. For a discussion of rates of intermolecular enone–olefin cycloadditions, see: de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41.

Chart I



18

19

have been reported, but high concentrations of cyclopentene are required to minimize competing type A photoreactivity.[13] One of the **14**–cyclopentene adducts (formed in at least 25% yield) has trans substitution at the cyclohexenone ring fusion. It is probable that the $\pi \rightarrow \pi^*$ triplet state of **14** is responsible for cycloadditions to cyclopentene.[14]

Photocycloaddition of **14** to aryl-substituted olefins was expected to be complicated by intermolecular energy transfer to the aryl olefin.[15] Indene was initially selected for study because its well-characterized triplet-state photodimerization[16] provides a convenient monitor of energy transfer (Scheme III). As expected, irradiation of **14** in high concentrations of indene (4.3 M) resulted in indene dimerization along with **14**–indene cycloaddition and type A photorearrangements.

Irradiation of a 0.05 M solution of **14** in benzene in the presence of only 0.10 M indene produced a mixture of two diastereoisomeric bicyclohexenones **15**[17] together with several **14**–indene cycloadducts in a product ratio of 5.5 to 1 (Table II). Bicyclohexenone formation was eliminated by performing the photolysis in the presence of MK[18] or, more effectively, thioxanthone (E_T = 65 kcal/mol).[3] Under these conditions, the photocycloaddition could be driven to 80–84% completion to give at least eight 2+2 cycloadducts.

The structures of two of the major cycloadducts have been determined, e.g., **16** with a *trans*-bicyclooctene ring fusion and the cis-fused **17**. Cycloadduct **17** (mp 154 °C) was isolated and completely characterized (X-ray determined molecular structure shown in Figure 1), but it proved impossible to obtain each of the other cycloadducts in pure form. It was easily shown that **16** and **17** were related by base-catalyzed epimerization and that the proton adjacent to the carbonyl group in **16** could be completely substituted with deuterium during epimerization to **17** in MeOD.[19]

Table III. Product Distribution after 366-nm Irradiation of **14** (25 °C)

conditions	transmission at 366 nm[b] (%)	composition[a] (%)	
		14	**15**
direct	15	90	10
benzophenone-sens		88	12
MK-sens		100	<0.01[c]
direct[d]	38	83	17

[a] ^{1}H NMR analysis. [b] Calculated from initial absorbance of photoreaction mixture. [c] ^{1}H NMR and GC analysis. [d] [**14**] = 3.6 × 10^{-2} M; [styrene] = 0.10 M; no **14**–styrene cycloadducts were observed.

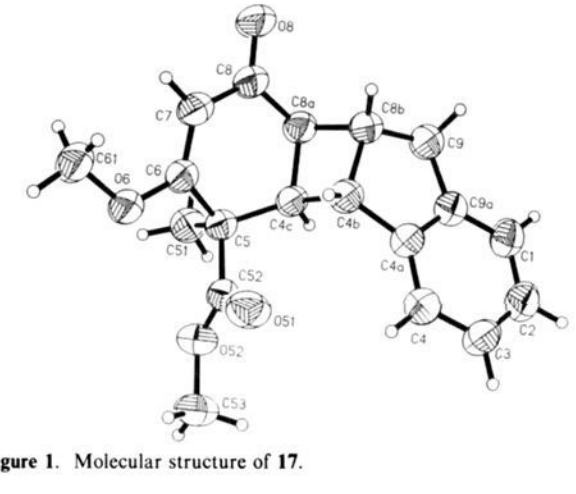


Figure 1. Molecular structure of **17**.

It was of interest to demonstrate that, as with **1**, MK was incapable of transferring triplet-state energy to **14** (Table III).

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[13] Schultz, A. G.; Taveras, A. G. *Tetrahedron Lett.* **1988**, *29*, 6881.

[14] The $n \rightarrow \pi^*$ triplet state of 4-methyl-4-(trichloromethyl)-2,5-cyclohexadien-1-one undergoes photocycloaddition to olefins to give oxetanes rather than cyclobutanes; see: Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 5145.

[15] (a) Irradiation of 2-cyclohexenone and butadiene in benzene solution through Pyrex glassware gives five isomeric 2+2 cycloadducts along with dimers of butadiene. Butadiene dimers were suggested to be formed by triplet-state energy transfer from the enone to butadiene; see: Cantrell, T. S. *J. Org. Chem.* **1974**, *39*, 3063. (b) For a related report, see: Chapman, O. L.; Lenz, G. *Org. Photochem.* **1967**, *1*, 297. (c) The 2+2 photoaddition of 4,4-dimethyl-2-cyclohexenone to 1,1-diphenylethylene occurs on direct irradiation of the enone at >300 nm. Since the photocycloaddition is not sensitized by benzophenone nor quenched by triplet-state quenchers, it was suggested that a singlet state of the enone adds to the 1,1-diphenylethylene; see: Rettig, T. A. Ph.D. Thesis, Iowa State University, Ames, IA, 1965; see also ref 15b (p 304). However, for the triplet-state addition of this same enone to other olefins, see: Chapman, O. L.; Koch, T. H.; Klein, F.; Nelson, P. J.; Brown, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 1657.

[16] (a) Schenck, G. O.; Hartman, W.; Mannsfield, S.-P.; Metzner, W.; Krauch, C. H. *Chem. Ber.* **1962**, *95*, 1642. (b) Bowyer, J.; Porter, Q. N. *Aust. J. Chem.* **1965**, *19*, 1455. (c) DeBoer, C. *J. Am. Chem. Soc.* **1969**, *91*, 1855.

[17] Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991.

[18] It has been shown that Michler's ketone is an effective sensitizer of indene dimerization; see ref 16c.

[19] (a) Cycloadduct F is recovered unchanged from reaction conditions that resulted in complete epimerization of **16** to **17**. This result is consistent with cis substitution at the cyclohexenone ring fusion, but we cannot rule out trans substitution at the other cyclobutane ring fusion; for a relevant example, see: Tobe, Y.; Doi, A.; Kunai, A.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1977**, *42*, 2523. (b) It is noteworthy that **16** and **17** were formed with the same regioselectivity as the cycloadduct reported to be formed from indene and coumarin; see ref 16b.

As a control, benzophenone (E_T = 69 kcal/mol)[3] was found to efficiently sensitize the type A photorearrangement to bicyclohexenones **15**. However, irradiation of **14** in the presence of MK (>99% light at 366 nm absorbed by MK) resulted in no detectable photoisomerization to **15**; it was estimated that at least 0.01% of **15** could have been detected by the gas chromatographic analysis of the photoreaction mixture. Thus, it is clear that formation of cycloadducts A–F by MK or thioxanthone sensitization occurs by triplet-state energy transfer from sensitizer to indene and that the excited state of indene adds to ground-state **14**.

It is remarkable that trans-fused **16** is obtained from sensitized (and direct) irradiations of **14** and indene. The formation of trans-fused cyclobutanes from photocycloadditions of 2-cyclohexenones[20] to olefins has been suggested to involve intermediate ground-state *trans*-cyclohexenones[21a] and highly twisted triplet excited states.[21b] Ground-state *trans*-cyclohexenes have been detected with use of flash techniques.[22] On the other hand, Bauslaugh has proposed that conformational energetics of the intermediate 1,4-biradical determine the distribution of trans and cis adducts.[23]

The existence of a *trans*-2,5-cyclohexadienone, such as **14**, with three additional trigonal centers in the six-membered ring is difficult to imagine. Consequently, we did not discuss the issue of stereocontrol in our earlier report of the 2+2 cycloaddition of photoexcited **14** to cyclopentene.[13] The formation of trans-fused **16** (and **17**) from 2+2 cycloaddition of excited indene to **14** demonstrates that stereoselectivity in this case depends on the reactivity of an intermediate 1,4-biradical rather than the conformation of the reacting enone.

Lewis has pointed out that the carbon skeleton of a substituted 1,4-biradical probably is nonplanar so as to minimize 1,2-eclipsing interactions.[24] Two conformations for a 1,4-biradical resulting from addition of indene to C(5) of **14** are shown qualitatively as **18** and **19** (Chart I). The biradical C(2) and C(3) hydrogen atoms are antiperiplanar in **18**, and the indenyl residue is pseudoequatorial with respect to the cyclohexenone ring. This conformation accommodates overlap of the p orbitals on the radical centers in the transition state leading to formation of *trans*-**16**. The conformer **19** leading to *cis*-**17** has the hydrogen atoms at C(2) and C(3) in a gauche relationship. Evidently there is little difference in stabilities of **18** and **19** (cf. distribution of **16** and **17**, Table II). Similar observations could be made regarding the biradical produced by initial bonding of indene to C(6) of the 2,5-cyclohexadienone ring.[25]

At least two questions emerge from consideration of the rather significant differences in distributions of cycloadducts **16**, **17**, and F resulting from direct vs sensitized irradiation (Table II): (1) On direct irradiation, how much of each product is formed by the addition of **14*** to indene and how much by the addition of indene* to **14**? (2) If the excited state of **14** is directly involved, are the structures and reactivities of biradicals resulting from **14*** and indene* the same? While of great mechanistic interest, these questions are beyond the scope of this report.

Direct irradiation of **14** in the presence of styrene by utilizing concentrations that gave not only **15** but also substantial quantities of **14**–indene cycloadducts resulted only in type A photorearrangements of **14**. The absence of **14**–styrene cycloadducts is consistent with the relatively inefficient reactivity of the styrene triplet state in photocycloaddition reactions.[26] This photochemical behavior once again underscores the importance of entropic factors in the intramolecular process (e.g., **5** → **6** and **12** → **13**).[27]

Experimental Section

General Procedures. Solvent purification and analytical and photochemical reaction procedures have been described previously.[17]

Direct and Sensitized Irradiation of 4-(3′-Butenyl)-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-one (1). Test tubes A containing **1** (21.1 mg, 8.93 × 10^{-2} mmol; ϵ_{366} = 12.5) in benzene (2.0 mL) and B containing **1** (21.1 mg) and Michler's ketone (1.9 mg, 7.1 × 10^{-3} mmol; ϵ_{366} = 28 100; MK absorbs >99% of the incident light at 366 nm) in benzene (2.0 mL) were degassed, sealed, and irradiated with the 366-nm light source[17] for 30 min. ^{1}H NMR (integration of vinyl and methyl ester resonances) and gas chromatographic analysis (Table II) indicated the following compositions: tube A, ratio of **1** to **2** was 6.1:1 (NMR) and 5.8:1 (GC); tube B, no detectable **2** by ^{1}H NMR analysis, ratio of **1** to **2** was 270:1 by GC analysis.

3-Carbomethoxy-2-methoxy-3-[(*E*)-4′-phenyl-3′-butenyl]-1,4-cyclohexadiene (4a). Methyl 2-methoxybenzoate (978 mg, 5.88 mmol) and *tert*-butyl alcohol (0.55 mL, 5.9 mmol) were placed into an oven-dried three-neck flask along with 25 mL of THF. Ammonia was condensed into the flask at −78 °C, and lithium metal was added until the blue coloration persisted for 0.5 h. Anhydrous piperylene was added to the reaction mixture until the blue coloration was dissipated. The reaction mixture was allowed to warm to room temperature while a slow stream of nitrogen was passed through the flask to facilitate removal of ammonia. After the solution was recooled to −78 °C, (*E*)-4-bromo-1-phenylbut-1-ene[28] (1.61 g, 7.63 mmol) in 10 mL of THF (−78 °C) was added. The reaction mixture was allowed to warm to room temperature over 1 h and after 19 h was quenched with ammonium chloride. Water was added, and extraction with ethyl acetate followed by chromatography on silica gel (1:2 ethyl acetate–hexane) provided **4a** (1.27 g, 72%) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 5 H), 6.36 (d, 1 H, *J* = 15.9 Hz), 6.20 (dt, 1 H, *J* = 15.9, 6.0 Hz), 5.93 (ddt, 1 H, *J* = 1.0, 9.8, 3.4 Hz), 5.43 (dt, 1 H, *J* = 9.8, 2.0 Hz), 4.87 (t, 1 H, *J* = 3.2 Hz), 3.67 (s, 3 H), 3.53 (s, 3 H), 2.85 (m, 2 H), 2.34–1.73 (m, 4 H); IR (film) 3080, 3060, 3020, 3000, 2950, 2830, 1725, 1685, 1650, 1430, 1160, 965, 750, 695 cm^{-1}; chemical ionization mass spectrometry (CIMS) *m*/*z* (relative intensity) 299 (M^+ + 1, 4.7), 267 (18.2), 168 (42.0), 121 (100.0). A combustion analysis was obtained for derivative **5a**.

4-Carbomethoxy-3-methoxy-4-[(*E*)-4′-phenyl-3′-butenyl)]-2,5-cyclohexadien-1-one (5a). A solution of **4a** (398 mg, 1.3 mmol) and pyridinium dichromate (PDC; 1.50 g, 3.99 mmol) in 75 mL of chloroform was refluxed for 20 h. The reaction mixture was filtered through Florisil (ethyl acetate); chromatography on silica gel (2:1 ethyl acetate–hexane) provided **5a** (140 mg, 34%) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 5 H), 6.52 (d, 1 H, *J* = 9.9 Hz), 6.35 (dd, 1 H, *J* = 1.3, 9.9 Hz), 6.33 (d, 1 H, *J* = 15.8 Hz), 6.10 (dt, 1 H, *J* = 15.8, 6.5 Hz), 5.72 (d, 1 H, *J* = 1.3 Hz), 3.73 (s, 3 H), 3.70 (s, 3 H), 2.44 (m, 1 H), 2.18 (m, 1 H), 1.97 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 186.97, 172.27, 169.23, 142.37, 137.04, 130.47, 130.14, 128.52, 128.17, 126.76, 125.62, 104.29, 55.64, 54.82, 52.81, 33.51, 26.75; IR (film) 3020, 2940, 2840, 1730, 1655, 1595, 1430, 1365, 1220, 1170, 860 cm^{-1}; CIMS *m*/*z* (relative intensity) 313 (M^+ + 1, 38.3), 281 (4.6), 195 (8.3), 182 (10.4), 131 (100.0). Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.17; H, 6.40.

(1*R,5*R**,6*S**,7*S**,10*S**)-1-Carbomethoxy-2-methoxy-6-phenyltricyclo[5.2.1.$0^{5,10}$]dec-2-en-4-one (6).** Irradiation of **5a** (51.4 mg, 0.16 mmol) at 366 nm in benzene (5 mL) for 1.5 h and solvent evaporation gave **6** in quantitative yield: mp 103–104 °C; ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 4 H), 7.24 (m, 1 H), 5.50 (s, 1 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 3.31–2.99 (m, 5 H), 2.13–1.84 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.52, 178.09, 173.70, 143.26, 128.47, 126.40, 126.35, 101.06, 56.31, 55.69, 52.74, 47.19, 46.12, 43.60, 43.11, 38.33, 30.58; IR (KBr) 3060, 3025, 2955, 2855, 1730, 1645, 1605, 1435, 1350, 1215, 1065, 840, 700 cm^{-1}; CIMS *m*/*z* (relative intensity) 313 (M^+ + 1, 70.0), 281 (4.6), 253 (2.4), 131 (100.0). Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.99; H, 6.35.

3-Carbomethoxy-2-methoxy-3-[(*Z*)-4′-phenyl-3′-butenyl]-1,4-cyclohexadiene (4b). The procedure described for preparation of **4a**, except that (*Z*)-4-iodo-1-phenylbut-1-ene[29] was utilized, provided **4b** (1.10 g, 61%) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.34–7.15 (m, 5 H), 6.38 (d, 1 H, *J* = 11.7 Hz), 5.89 (dt, 1 H, *J* = 9.8, 3.4 Hz), 5.66 (dt, 1 H, *J* = 11.6,

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7.4 Hz), 5.41 (dt, 1 H, *J* = 9.8, 2.0 Hz), 4.82 (t, 1 H, *J* = 3.5 Hz), 3.69 (s, 3 H), 3.52 (s, 3 H), 2.84–2.65 (m, 2 H), 2.15 (m, 3 H), 1.82 (m, 1 H); IR (film) 3080, 3060, 3030, 3010, 2955, 2835, 1730, 1690, 1445, 1435, 1230, 1210, 1165, 1070, 1030, 950, 920, 790, 770, 705 cm^{-1}; CIMS *m/z* (relative intensity) 299 (M$^+$ + 1, 2.4), 267 (20.0), 168 (9.4), 121 (100.0). A combustion analysis was obtained for derivative **5b**.

Preparation of 4-Carbomethoxy-3-methoxy-4-[(*Z*)-4′-phenyl-3′-butenyl]-2,5-cyclohexadienone (5b). A solution of **5** (126 mg, 0.42 mmol) and PDC (476 mg, 1.26 mmol) was refluxed in 20 mL of chloroform for 44 h. The reaction mixture was filtered through Florosil (ethyl acetate); chromatography on silica gel (1:1 ethyl acetate–hexane) provided **5b** (73.1 mg, 55%) as a colorless solid: mp 70 °C; ^{1}H NMR (CDCl$_3$) δ 7.24 (m, 5 H), 6.46 (d, 1 H, *J* = 9.8 Hz), 6.42 (d, 1 H, *J* = 9.5 Hz), 6.28 (dd, 1 H, *J* = 9.8, 1.4 Hz), 5.66 (d, 1 H, *J* = 1.3 Hz), 5.57 (dt, 1 H, *J* = 11.6, 7.3 Hz), 3.69 (s, 6 H), 2.40 (m, 1 H), 2.10 (m, 3 H); ^{13}C NMR (CDCl) δ 187.18, 172.35, 169,49, 142.38, 137.04, 130.40, 130.11, 128.40, 128.04, 126.63, 104.51, 55.77, 55.07, 53.05, 34.24, 22.68; IR (KBr) 3080, 3060, 3020, 2950, 2850, 1735, 1655, 1595, 1435, 1365, 920, 860, 770, 605 cm^{-1}; CIMS *m/z* (relative intensity) 313 (M$^+$ + 1, 100.0), 281 (1.4), 255 (5.8), 183 (12.2), 131 (13.0). Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.10; H, 6.36.

Direct and Sensitized Irradiation of 5a and 5b (Table I). Samples of **5a** and **5b** were prepared and irradiated as described for **1**. The HPLC analysis utilized a Partisil 5 column (ethyl acetate–hexane (1:3)).

3-Carbomethoxy-3-[(*E*)-4′-phenyl-3′-butenyl]-1,4-cyclohexadiene. The procedure described for preparation of **4a**, except that methyl benzoate and (*E*)-4-iodo-1-phenylbut-1-ene were utilized, provided 863 mg (58%) of the title compound as an oil: ^{1}H NMR (CDCl$_3$) δ 7.33–7.14 (m, 5 H), 6.37 (d, 1 H, *J* = 15.8 Hz), 6.17 (dt, 1 H, *J* = 15.8, 6.4 Hz), 5.93 (m, 2 H), 5.77 (dt, 2 H, *J* = 10.5, 1.9 Hz), 3.69 (s, 3 H), 2.66 (m, 2 H), 2.13 (m, 2 H), 1.84 (m, 2 H); IR (film) 3080, 3055, 3025, 2995, 2950, 2920, 2865, 2820, 1720, 1430, 1220, 1200, 1070, 965, 800, 745, 695 cm^{-1}; CIMS *m/z* (relative intensity) 269 (M$^+$ + 1, 100.0), 209 (12.4), 191 (1.0). A combustion analysis was obtained for derivative **12**.

Preparation of 4-Carbomethoxy-4-[(*E*)-4′-phenyl-3′-butenyl]-2,5-cyclohexadien-1-one (12). A solution of the diene (568 mg, 2.11 mmol) from the previous reaction together with Celite (3.18 g) in 40 mL of benzene was cooled to 10 °C. PDC (3.18 g, 8.45 mmol) and then 90% *tert*-butylhydroperoxide (0.94 mL, 8.4 mmol) were added, and the reaction was allowed to warm to room temperature. After 10 h, the reaction mixture was filtered through Celite and subsequent chromatography (1:1 ethyl acetate–hexane) provided **12** (336 mg, 56%) as an oil: ^{1}H NMR (CDCl$_3$) δ 7.30–7.16 (m, 5 H), 7.08 (m, 2 H), 6.39 (m, 2 H), 6.37 (d, 1 H, *J* = 15.7 Hz), 6.11 (dm, 1 H, *J* = 15.7 Hz), 3.74 (s, 3 H), 2.15 (d, 4 H, *J* = 2.8 Hz); IR (film) 3080, 3055, 3025, 2995, 2950, 1730, 1665, 1625, 1430, 1400, 1230, 1175, 860, 695 cm^{-1}; CIMS *m/z* (relative intensity) 283 (M$^+$ + 1, 58.9), 267 (1.0), 223 (1.1), 131 (100.0). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.42. Found: C, 76.45; H, 6.58.

Preparation of (1*R,5*R**,6*S**,7*S**,10*S**)-1-Carbomethoxy-6-phenyltricyclo[5.2.1.0^{5,10}]dec-2-en-4-one (13).** Irradiation of **12** (58.9 mg, 0.20 mmol) at 366 nm in pentane for 2.5 h and chromatography on silica gel gave **13** (49.5 mg, 84%): mp 80–82 °C; ^{1}H NMR (CDCl$_3$) δ 7.34 (d, 1 H, *J* = 10.5 Hz), 7.34 (m, 4 H), 7.25 (m, 1 H), 6.11 (d, 1 H, *J* = 10.5 Hz), 3.76 (s, 3 H), 3.44–3.19 (m, 4 H), 2.64 (m, 1 H), 2.09 (m, 2 H), 1.86 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 196.95, 175.08, 151.00, 143.24, 128.46, 127.61, 126.41, 126.30, 52.56, 51.59, 47.32, 46.79, 43.76, 42.44, 42.01, 30.41; IR (KBr) 3080, 3055, 3025, 2950, 1725, 1675, 1605, 1430, 1240, 1200, 1140, 815, 780, 750, 700 cm^{-1}; CIMS *m/z* (relative intensity) 283 (M$^+$ + 1, 100.0), 251 (5.3), 153 (6.7), 131 (45.8). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.44; H, 6.35.

Irradiation of 4-Carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one (14) and Indene. Irradiation of a solution of **14** (25.4 mg, 0.12 mmol) and indene (29.8 mg, 0.25 mmol) in 25 mL of benzene at 366 nm for 18 h gave bicyclohexenone **15** and seven cycloadducts in a ratio of 5.5 to 1 by ^{1}H NMR integration of the vinyl region and GC analysis (Table II).

Michler's Ketone Sensitized Irradiation of 14 and Indene. Irradiation of a solution of **14** (23.0 mg, 0.11 mmol), Michler's ketone (2.5 mg, 9.3 × 10^{-3} mmol), and indene (26.8 mg, 0.23 mmol) in 2.3 mL of benzene at 366 nm for 3 h resulted in ~40% consumption of **14**. The cessation of reaction seemed to be caused by decomposition of Michler's ketone. Chromatography on silica gel (1:1 ethyl acetate–hexane) to remove decomposition products and reirradiation in 2.3 mL of benzene with additional Michler's ketone (1.5 mg, 5.6 × 10^{-3} mmol) and indene (15.9 mg, 5.9 × 10^{-2} mmol) for 2 h resulted in an 80% conversion to eight cycloadducts (^{1}H NMR and GC analysis; Table II).

Thioxanthone-Sensitized Irradiation of 14 and Indene. Irradiation of **14** (74.4 mg, 0.38 mmol), thioxanthen-9-one (24.8 mg, 0.11 mmol), and indene (87.6 mg, 0.75 mmol) in 7.5 mL of benzene at 366 nm for 22 h gave eight cycloadducts (Table II). GC analysis of the photolysis mixture showed the reaction had proceeded to 84% completion.

Cycloadducts 16 and 17. Irradiation of **14** (134 mg, 0.68 mmol), Michler's ketone (16.5 mg, 6.14 × 10^{-2} mmol), and indene (0.159 mg, 1.36 mmol) in 12 mL of benzene at 366 nm was carried out for 9 h. The reaction mixture was washed with 2 N HCl to remove the Michler's ketone and was irradiated through Pyrex glassware (>300 nm) to convert the remaining **14** to phenolic products.[17] Chromatography on silica gel (1:1 ethyl acetate–hexane) provided two fractions, each consisting of four cycloadducts. A: 16.0 mg contains 82% **16**; ^{1}H NMR (CDCl$_3$) δ 7.26–7.12 (m, 4 H), 5.17 (s, 1 H), 3.86 (s, 3 H), 3.76 (m, 1 H), 3.64 (s, 3 H), 3.26 (m, 2 H), 3.23–3.11 (m, 2 H), 2.53 (dd, 1 H, *J* = 8.2, 13.7 Hz), 1.35 (s, 3 H); IR (film) 3070, 3020, 2955, 2840, 1725, 1675, 1520, 1325, 1210, 1015, 985, 840, 760, 745 cm^{-1}. B: 69.9 mg. The less polar fraction A was treated with NaOH (8 mg, 0.2 mmol) in 1 mL of methanol and 0.5 mL of water for 1 h. Removal of solvents on a rotary evaporator was followed by addition of methylene chloride to the residue. The methylene chloride solution was washed with water; chromatography on silica gel (1:1 ethyl acetate–hexane) provided **17** (9.1 mg) as a colorless solid: mp 154 °C; ^{1}H NMR (CDCl$_3$) δ 7.26–6.96 (m, 4 H), 5.55 (s, 1 H), 4.11 (dd, 1 H, *J* = 7.2, 7.7 Hz), 3.84 (s, 3 H), 3.80 (s, 3 H), 3.49 (dd, 1 H, *J* = 17.4, 10.2 Hz), 3.19 (dd, 1 H, *J* = 17.4, 5.1 Hz), 2.93 (m, 1 H), 2.87 (m, 1 H), 2.71 (m, 1 H), 1.40 (s, 3 H); IR (film) 3075, 3020, 2995, 2955, 2850, 1730, 1645, 1605, 1460, 1345, 1225, 1110, 990, 765 cm^{-1}; CIMS *m/z* (relative intensity) 313 (M$^+$ + 1, 100.0), 197 (22.5), 116 (22.0). Crystals of **17** suitable for X-ray analysis were obtained from ethyl acetate–hexane solution by the isothermal distillation technique. Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.91; H, 6.28.

Determination of Structures of 16 and 17. The structure of **17** was initially determined by a combination of ^{1}H NMR and molecular modeling techniques. Decoupling studies with **17** enabled assignment of the resonances at δ 2.87 (H$_a$), 2.93 (H$_b$), 4.11 (H$_c$), and 2.71 (H$_d$). A two-dimensional NOESY experiment was performed on a sample of **17** in which H$_a$ was exchanged with deuterium. Positive NOEs involving the angular methyl group δ 1.40 and H$_d$ and also H$_b$ and H$_c$ were observed. Of the 16 possible diastereomers of **17**, only 4 were compatible with the NOE data. These four structures were minimized to a first-derivative root mean square (rms) of 0.01 kJ/A with use of the MM2 force field in Clark Still's MacroModel program to obtain representative conformations. A comparison of the actual coupling constants with those calculated for **17** with use of MacroModel follow: $J_{a,b}$ = 2.0 Hz (2.5 Hz calcd), $J_{b,c}$ = 7.8 Hz (9.7 Hz), $J_{c,d}$ = 6.9 Hz (9.7 Hz), and $J_{d,a}$ = 6.8 Hz (9.2 Hz). The validity of this analysis was confirmed by X-ray structure determination (Figure 1). Decoupling studies with **16** enabled assignment of the resonances at δ 3.23–3.11 (H$_a$, H$_b$), 3.76 (H$_c$), and 2.53 (H$_d$). A two-dimensional NOESY experiment was performed on **16**. Positive NOEs involving the angular methyl group δ 1.35 and H$_d$, H$_b$ and H$_c$, and also the benzylic methylene group δ 3.26 and H$_d$ were observed. A comparison of the actual coupling constants with those calculated for **16** with use of MacroModel follow: $J_{a,d}$ = 13.7 Hz (12.1 Hz calcd), $J_{d,c}$ = 8.2 Hz (11.0 Hz).

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Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates and figures of molecular models for **17** (8 pages). Ordering information is given on any current masthead page.