Singlet Photochemistry of Vinylcyclopropenes. Regioselectivity and Mechanism: Mechanistic and Exploratory Organic Photochemistry[1]

Howard E. Zimmerman* and David W. Wilson

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

Received September 12, 1994[⊗]

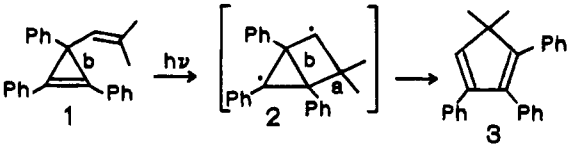
A study of the direct photochemistry of 1-anisyl-2-phenyl-3-methyl-3-isobutenylcyclopropene (**5**) was pursued with the objective of elucidating the reaction regioselectivity and casting light on alternative reaction mechanisms for this reaction known to afford cyclopentadienes. Two mechanisms had previously been advanced—one proceeding by an initial three-ring bond fission to afford an intermediate vinyl carbene and the other by vinyl–vinyl bonding to afford a housane diradical intermediate. The two reaction mechanisms predict different reaction regiochemistry. The experimental observation in the case of vinylcyclopropene **5** was a preference for formation of that product in which the C1–C3 three-ring single bond is severed to give an anisyl-substituted carbene. Then bonding occurs between the isobutenyl moiety and the carbene center. CASSCF computations were run on S_1 of the reactant cyclopropene as well as S_0 and S_1 of the two regioisomeric carbenes. The preferred carbene, both in the ground state and the first excited singlet, was that having the anisyl group on the carbene center. The S_1 carbenes were linear at the carbene center while the S_0 carbenes were bent. The aryl group at the carbene center of S_1 preferred to overlap with a pentadienyl π-system. The lower energy of the excited singlet carbenes with anisyl at the carbene center accounts for the regioselectivity of opening with internal conversion occurring during or subsequent to bond stretching.

Introduction

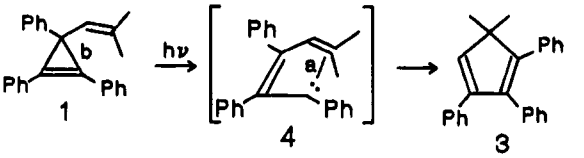
Previously, our group[2] and that of Padwa[3] have uncovered a singlet photochemical rearrangement of vinylcyclopropenes leading to cyclopentadienes. Both groups have considered two alternative reaction mechanisms as outlined in Scheme 1. Mechanism A involves an initial vinyl–vinyl bridging to afford a housane diradical (i.e. **2**) which then undergoes a 1,4-(2,3)-fragmentation. Thus, this mechanism proceeds by (i) formation of bond a followed by fission of bond b. Mechanism B proceeds with initial carbene **4** formation, followed by electrocyclic closure to afford cyclopentadiene product **3**. Interestingly, this mechanism, in proceeding by (i) scission of bond b followed by (ii) formation of bond a, differs from mechanism A only in reversal of the order of bond formation and bond breaking. In view of the subtle difference of the two mechanisms,[4] differentiation proved difficult.

Scheme 1. Two Alternative Mechanisms for the Singlet Vinylcyclopropene Rearrangement

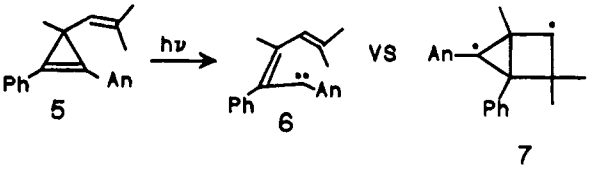
Mech A:



Mech B:



Scheme 2. Carbene vs Housane Diradical Intermediates in the Phenyl Anisyl Case



Results

Our approach to the problem involved a study of 1-anisyl-2-phenyl-3-methyl-3-isobutenylcyclopropene (**5**) and its regioselectivity. Each mechanism promised to afford a different major cyclopentadiene isomer as discussed below.

Synthesis of the Reactant Vinylcyclopropene 5. The required photochemical reactant was prepared using

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1995.

(1) (a) This is part 173 of our photochemical series and 236 of our general sequence. (b) For Part 235 see: Zimmerman, H. E. *The Spectrum*; Center for Photochemical Sciences; Bowling Green, OH, 1994; Vol. 7(3). (c) Part 234: In *Photochemical Key Steps in Organic Synthesis*; Zimmerman, H. E., Mattay, J., Griesbeck, A. G., Eds.; Verlag Chemie: Weinheim, 1994. (d) Part 233: Zimmerman, H. E.; Kutateladze, A. G.; Maekawa, Y.; Mangette, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 9795–9796. (e) Zimmerman, H. E.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 1579–1580.

(2) (a) Zimmerman, H. E.; Aasen, S. *J. Am. Chem. Soc.* **1977**, *99*, 2342–2344. (b) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506. (c) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345. (d) Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *37*, 2060–2075. (e) See also ref 4 for related cyclopropene photochemistry.

(3) Padwa, A.; Blacklock, T.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1978**, *99*, 2344–2345.

(4) (a) For triplets an entirely different mechanism ("mechanism C") has been established[4b]. (b) Zimmerman, H. E.; Fleming, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 622–624.

0022-3263/95/1960-0692$09.00/0

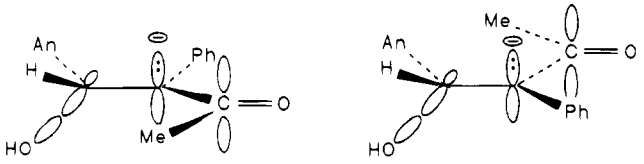
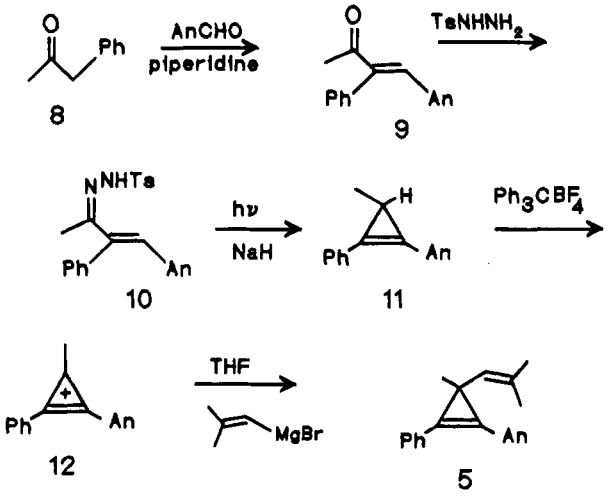
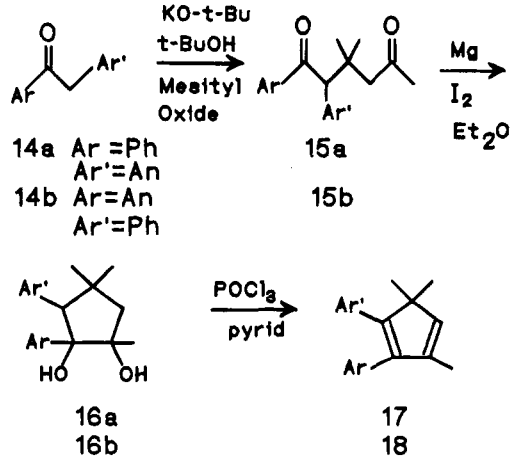


Figure 1. Overlap control leading to more hindered product.

Scheme 3. Synthesis of the Reactant Vinylcyclopropene



Scheme 4. Synthesis of the Potential Photoproducts



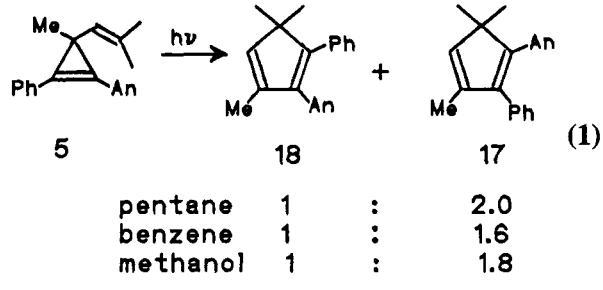
the approach[5] outlined in Scheme 3. One particularly interesting facet was encountered in the aldolization of anisaldehyde with phenylacetone which led regioselectively to the thermodynamically less stable geometric isomer, (*E*)-4-anisyl-3-phenyl-buten-2-one (**9**), with the large aryl groups cis. This is understood on the basis of the very general concept of "overlap control" which we described four decades earlier.[6] Thus, there are many reactions in which the kinetic product is the less stable one with two large groups cis due to a requirement that a small delocalizing group remain trans and unhindered in order to maximally delocalize a negative charge. In the present case of aldolization, the preferred enolate intermediate is **13c** rather than **13t** (Figure 1).

One other intriguing finding was that, in the synthesis of vinylcyclopropene **5**, unless the reaction mixture was quickly quenched at −75 °C, an unusual rearrangement to two cyclopentadienes, **17** and **18**, took place.

Synthesis of Potential Photoproducts. The general synthetic method, outlined in Scheme 4, was a modification of a sequence utilized by Wislicenus.[7] Interestingly, the reaction of **14a** was more facile than that of **14b**; this can be ascribed to the enhanced enolate stabilization by the α-phenyl relative to α-anisyl and hence a less reactive nucleophile derived from **14b**. Also, the conversion in the case of **14b** had to be limited to a greater extent due to secondary conversion of **15b** by intramolecular aldolization to the corresponding cyclohexenone.

One interesting aspect is the pattern of NMR shifts of cyclopentadienyl vinyl hydrogens. From this study and previous efforts[2,4] cyclopentadienes with a vinyl hydrogen vicinal to an aryl group appear consistently at δ 6.28 ± 0.02 while vinyl hydrogens vicinal to alkyl or hydrogen absorb at δ 6.01 ± 0.01.

Photochemistry of Vinylcyclopropene 5. The direct irradiation of vinylcyclopropene **5** was carried out in benzene, pentane, and in methanol. In each case, at various conversions, the NMR spectrum showed the presence of reactant and the two cyclopentadienes. Independent synthesis of the two 1,2-diarylcyclopentadienes **17** and **18** is described above. The photolysis led to these photoproducts without any further discernable NMR peaks. The ratio of the two cyclopentadiene photoproducts (**18**:**17**) was determined as 1.6:1 in benzene irradiations and 2:1 in pentane. In methanol a 1.8:1 ratio was observed. Runs with various conversions ranging from 10−70% showed no variation in these ratios. Product ratios were determined by NMR analysis and products were identified by HPLC isolation. The reaction course is shown in eq 1.



Interpretative Discussion

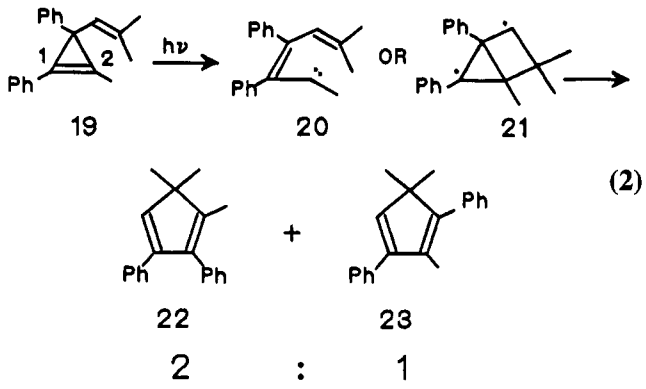
In the previous studies[2,3] the reaction regiochemistry of 1-phenyl-2-alkyl-substituted cyclopropenes led preferentially to 3-phenyl-1-alkyl cyclopentadienes. For example, note eq 2. We note that the regioselectivity can be understood on either of two bases. One might decide that mechanism A (vide supra) involving housane diradical **21** in this case would account for the observed regioselectivity as a consequence of the extra benzylic delocalization resulting from isobutenyl to C-2 bridging rather than the alternative isobutenyl to C-1 bridging.

Superficially, "mechanism B" appears inconsistent with the observed regioselectivity, since the methyl-stabilized

(5) Zimmerman, H. E.; Bunce, R. A. *J. Org. Chem.* **1982**, *47*, 3377–3396.

(6) (a) Zimmerman, H. E.; Ahramjian, L. *J. Am. Chem. Soc.* **1959**, *81*, 2086–2091. (b) Zimmerman, H. E.; Ahramjian, L. *J. Am. Chem. Soc.* **1960**, *82*, 5459–5466. (c) Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1959**, *81*, 108–116.

(7) Wislicenus, J.; Carpenter, H. *Justus Liebigs Ann. Chem.* **1898**, *302*, 223.



carbene **20** needs to be invoked rather than the alternative benzylic carbene resulting from C_1-C_3 fission. However, as Padwa has noted, in the excited state the phenyl group in cyclopropene **19** will be coplanar with the three-membered ring and thus not in a conformation to overlap with the breaking σ bond. In this conformation, the phenyl group was noted to lead to inductive destabilization of the carbene center. Additionally, Padwa[8] has noted that the excited state might tend to preferentially decay to the less stable of the two alternative carbenes as a consequence of a smaller energy gap. This point involves the tendency of conical intersections to be utilized in excited state to ground state decay (i.e. Michl "funnel" and Zimmerman "bifunnel" effects).[9,10] In previous publications both mechanisms, "A" and "B", have been considered reasonable by the Padwa and Zimmerman groups.

As noted earlier, the study of anisyl phenyl cyclopropene **5** promised to avoid the inductive destabilization effect, since both aryl groups should be coplanar with the original three-ring double bond in the excited singlet. However, odd-electron stabilization by anisyl in the housane diradical would favor housane diradical **24** and cyclopentadiene photoproduct **18** while carbene stabilization by anisyl in the carbene mechanism would favor cyclopentadiene **17** (Scheme 5). The experimental observation of preferential formation of isomer **17** suggests operation of mechanism B.

Theoretical Aspects. Computations were run on five species: the S_1 excited state of anisylphenylcyclopropene **5**, the S_0 singlets of the two alternative vinyl carbenes, **25** and **26**, and the corresponding S_1 singlets of the two carbenes. Approximate geometries were obtained with AM1[11a] and final geometry and energy optimization was with GAUSSIAN92[11b] using CASSCF with an active space of 6 and STO-3G. The optimized geometries are drawn in Figure 2 with C-1, C-2, C-3 in the paper plane and hydrogens not shown. For computational simplicity the *gem*-dimethyls were not included. Interestingly, in

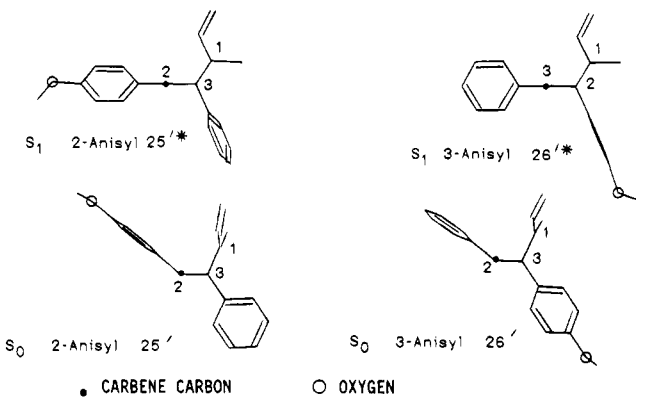


Figure 2. Four carbenes of interest.

Scheme 5. Role of Anisyl in Stabilizing the Two Alternative Intermediates

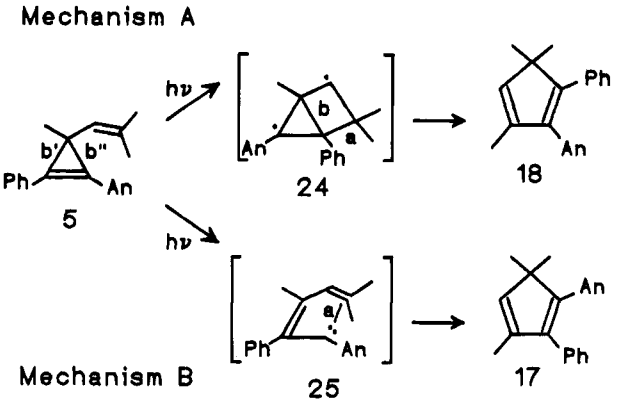


Table 1. CASSCF Energies

species	energy[a]	species	energy[a]
cyclopropene **5'***	−794.755		
2-anisylcarbene S_0 **25'**	−794.906	2-anisylcarbene S_1 **25'***	−794.837
3-anisylcarbene S_0 **26'**	−794.901	3-anisylcarbene S_1 **26'***	−794.807

[a] The energies are in Hartrees (627.5 kcal/Hartree). In **5'***, **25'**, **26'**, **26'***, and **26'*** the primes refer to omission of the *gem*-dimethyl groups and the energies are thus for the bis-nor compounds.

the S_1 carbenes the aryl group substituted at the carbene center, C-2, and the original vinyl appear coplanar with a pentadienyl system comprised of the vinyl group and the π system at C1−C3−C2 while in S_0 the conformation is twisted and more suitable for three- or five-ring closure. As shown in Table 1, the energy of the cyclopropene excited singlet is above either of the opened carbenes of either S_0 or S_1 configurations. The lower energy excited singlet carbene was **25** in which the anisyl group is substituted on the carbene center. The ground state (i.e. S_0) carbenes differ less in energy but still favor **25**. Thus, it may be concluded that ring opening occurs with its regioselectivity controlled by anisyl stabilization on the excited singlet hypersurface. Internal conversion of the S_1 carbenes seems likely to occur either during or after ring-opening has reached irreversibility. The bifunnel rationale, arising from a less stable ground state carbene being formed, cannot be correct.

Conclusion. As pointed out in the introduction, the two alternative mechanisms differ mainly in the chronology of fission of bond b and formation of bond a. A complete spectrum of mechanisms spanning these extremes is conceptually possible. Thus we can conclude that bond b scission operates to a greater extent in the

(8) See Padwa, A. *Org. Photochem.* **1977**, *4*, 261−326 for a review and general references.

(9) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1566−1567. (b) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538−3548. (c) *Topics in Photochemistry*. Zimmerman, H. E. *Topics Curr. Chem.* **1982**, *100*, 45−73 (Springer-Verlag, Heidelberg-New York). (d) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272−280. (e) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393−401.

(10) Michl, J. *J. Mol. Photochem.* **1972**, *4*, 243.

(11) (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909 (MOPAC Vers 6.0). (b) Gaussian 92, Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1992.

reaction mechanism than formation of bond a. Yet both processes may overlap in timing.

Experimental Section

General Procedures. Melting points were determined on a mel-Temp heating block and are reported uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville TN 37950-1610. All reactions were run under an atmosphere of calcium sulfate-dried nitrogen with magnetic stirring. All the column chromatography was performed on silica gel (J. T. Baker Inc., 60–200 mesh) mixed with Sylvania 2282 green phosphor and hexane slurry packed into quartz columns, which permitted monitoring by hand-held UV lamps. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing a Milton Roy LDC 6000-psi minipump with a LDC 254-nm detector. Tetrahydrofuran (THF) was purified by successive distillation, under a nitrogen atmosphere, from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Hexane used for HPLC was washed with 1:1 nitric acid and sulfuric acid, water, saturated sodium bicarbonate, and saturated sodium chloride before being dried with calcium chloride, passed through alumina, and distilled over calcium hydride. Spectral grade and HPLC benzene was prepared with successive washes of saturated potassium permanganate in 10% sulfuric acid, water, concentrated sulfuric acid until colorless, saturated sodium bicarbonate, and saturated sodium chloride before distillation from calcium hydride. For the photolysis experiments all apparatus was stored at 50 °C and all solutions were purged with deoxygenated and dried nitrogen[12] for 30 min before turning on the lamp. Exploratory irradiations were carried out using a Hanovia 450-W medium-pressure mercury vapor lamp equipped with a 2 mm Pyrex filter ($\lambda > 280$ nm). Quantum yield determinations were carried out with a 200-W (HBO-200) high-pressure xenon/mercury lamp using a Bausch & Lomb monochromator grating (1200 Grooves/mm).

(*E*)-4-(*p*-Methoxyphenyl)-3-phenylbuten-2-one. Following the general procedure for synthesis of 3,4-diarylbutenones,[2] a mixture of 134 g (1.00 mol) of phenylacetone,[13] 122 mL (1.00 mol) of *p*-anisaldehyde, and 10 mL (0.10 mol) piperidene in 1.0 L of benzene was refluxed until no more water was collected. Then the cooled solution was extracted with 500 mL of 1% aqueous hydrochloric acid and the benzene layer was concentrated. Filtration of the butenone and recrystallization from 95% ethanol afforded 151 g (59.7%) of clear needles, mp 59.5–61.0 °C.

The spectral data were the following: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.62 (s, 1H, =C*H*), 7.45–7.38 (m, 3H, arom), 7.20–7.17 (m, 2H, arom), 6.99–6.96 (m, 2H, arom), 6.70–6.67 (m, 2H, arom), 3.75 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3(CO)); MS *m/e* 252.1149 (calcd for $C_{17}H_{16}O_2$ 252.1151). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.86; H, 6.32.

(*E*)-4-(*p*-Methoxyphenyl)-3-phenylbuten-2-one Tosylhydrazone. Following the general procedure of Closs[14a] modified by Dürr,[14b] a methanol solution of 15.1 g (59.9 mmol) of 4-(*p*-methoxyphenyl)-3-phenylbuten-2-one and 11.2 g (59.9 mmol) of tosylhydrazine[15] was brought to a light reflux before the addition of 0.50 mL of concd hydrochloric acid. Heating an additional five min, followed by cooling to 0 °C, filtering, and recrystallization from 95% ethanol, afforded 17.0 g (67.5%) of a white powder, mp 142.5–143.5 °C.

The spectral data follow: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.53–7.51 (m, 2H, arom), 7.41–7.36 (m, 4H, arom and NN*H*Tos), 7.18–7.16 (m, 2H, arom), 7.07–7.04 (m, 2H, arom), 6.88 (s, 1H, =C*H*), 6.85–6.82 (m, 2H, arom), 6.65–6.62 (m, 2H, arom), 3.73 (s, 3H, OCH_3), 2.41 (s, 3H, ArCH_3), 1.96 (s, 3H, CH_3(CNNH)); MS *m/e* 420.1526 (calcd for $C_{24}H_{24}N_2O_3S$, 420.1509). Anal. Calcd for $C_{24}H_{24}N_2O_3S$: C, 68.55; H, 5.75. Found: C, 68.56; H, 5.75.

1-(*p*-Methoxyphenyl)-3-methyl-2-phenylcyclopropene. A modification of the combined procedures by Dürr[14b] and Breslow[16] for cyclopropene and cyclopropenium tetrafluoroborate synthesis was found to give an enhanced overall yield. In a Hanovia photolysis flask 0.52 g (13 mmol) of 60% sodium hydride dispersion was rinsed with pentane. With vigorous stirring, 450 mL of spectral grade tetrahydrofuran and 4.20 g (9.98 mmol) 4-(*p*-methoxyphenyl)-3-phenylbuten-2-one tosylhydrazone were then added. After 60 min, the Hanovia cell was wrapped with aluminum foil and irradiated for 90 min, with agitation of the reaction mixture to break up the white flocculent precipitate after 30 and 60 min. This resulted in a cloudy solution containing a fine white powder. The tetrahydrofuran was removed *in vacuo* and the 1-(*p*-methoxyphenyl)-2-phenyl-3-methylcyclopropene was taken up in anhydrous acetonitrile and transferred to an addition funnel.

Examination of representative crude photolysis product mixtures, by ^{1}H-NMR, show it to be consistently composed of 35% 1-(*p*-methoxyphenyl)-2-phenyl-3-methylcyclopropene and 65% 5-(*p*-methoxyphenyl)-3-methyl-4-phenylpyrazole. An alternative workup, consisting of adding an equivalent volume of wet diethyl ether followed by water extractions, caused the pyrazole to precipitate. The pyrazole could be filtered as a white solid with the cyclopropene resulting as a clear viscous oil from the concentration of the ether fraction. This compound proved unstable to chromatography and was thermally unstable. Thus it was carried on to the cyclopropenium salt immediatly.

The spectral data for 1-(*p*-methoxyphenyl)-3-methyl-2-phenylcyclopropene were as follows: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.48–7.43 (m, 2H, arom), 7.39–7.18 (m, 3H, arom), 7.07–7.03 (m, 2H, arom), 6.83–6.76 (m, 2H, arom), 3.76 (s, 3H, OCH_3), 2.82 (s, 1H, cyclopropyl-*H*), 2.32 (s, 3H, cyclopropyl-CH_3); MS *m/e* 236.1207 (calcd for $C_{17}H_{16}O$, 236.1202).

The spectral data for the 5-(*p*-methoxyphenyl)-3-methyl-4-phenylpyrazole fine white needles, mp 179.0–180.5 °C, were as follows: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 13.5 (bs, 1H, pyrazole-N*H*), 7.34–7.19 (m, 7H, arom), 6.80–6.77 (m, 2H, arom), 3.78 (s, 3H, OCH_3), 2.26 (s, 3H, ArCH_3). Anal. Calcd for $C_{17}H_{16}N_{20}$: C, 77.25; H, 6.10. Found: C, 77.26; H, 6.25.

1-(*p*-Methoxyphenyl)-3-methyl-2-phenylcyclopropenium Tetrafluoroborate. The cyclopropene extract, from above, was then added dropwise to a solution of fresh trityl tetrafluoroborate that had been prepared from 5.2 mL (40 mmol) of 48% aqueous tetrafluoroboric acid slowly added to 5.2 g (20 mmol) of triphenylmethanol dissolved in 50 mL of acetic anhydride at 0 °C, followed by precipitation with 100 mL of anhydrous ether, decanting, rinsing with additional anhydrous ether, and dissolving in 50 mL of anhydrous acetonitrile. The yellow solution was poured into 200 mL of diethyl ether, resulting in the formation of a tan precipitate. Cooling to 0 °C, filtering, and rinsing with ether afforded 1.11 g (34.5%) of tan solid. The 1-(*p*-methoxyphenyl)-3-methyl-2-phenylcyclopropenium tetrafluoroborate was recrystallized twice by dissolution in a minimum amount of acetonitrile followed by precipitation with double the volume of ether to give 0.997 g (31.0%) of white powder, mp 219.0–221.0 °C with decomposition.

The spectral data for 1-(*p*-methoxyphenyl)-3-methyl-2-phenylcyclopropenium tetrafluoroborate was as follows: ^{1}H-NMR (CD_3CN, 200 MHz) δ 8.41–8.34 (m, 4H, arom), 7.97 (m, 1H, arom), 7.82 (m, 2H, arom), 7.32 (m, 2H, arom), 4.01 (s, 3H, OCH_3), 3.15 (s, 3H, cyclopropenium-CH_3). Anal. Calcd for $C_{17}H_{15}OBF_4$: C, 63.39; H, 4.69. Found: C, 63.57; H, 4.76.

3-Isobutenyl-1-(*p*-methoxyphenyl)-3-methyl-2-phenylcyclopropene. On the basis of the work of Breslow[16] and previous workers,[2] in a flame dried system 0.700 g (2.17 mmol) of 1-(*p*-methoxyphenyl)-2-methyl-3-phenycyclopropenium tetrafluoroborate was partially dissolved in 30 mL of THF. The mixture was then cooled to −78 °C before the rapid dropwise

(12) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984.
(13) (a) Renfrow, W. B. *J. Am. Chem. Soc.* **1944**, *66*, 144. (b) Walker, H. G.; Hauser, H. G.; Hauser, C. R. *J. Am. Chem. Soc.* **1946**, *68*, 1386.
(14) (a) Closs, H. E.; Closs, L. E. *J. Am. Chem. Soc.* **1961**, *83*, 2015. (b) Dürr, H. *Angew. Chem.* **1967**, *79*, 1104.
(15) Friedman, L.; Litle, R. L.; Reichle, W. R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 1055.
(16) (a) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168. (b) Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729.

addition of an isobutenylmagnesium bromide solution (which was prepared from 0.851 g (6.30 mmol) of isobutenyl bromide, 0.238 g (9.81 mmol) of dry magnesium turnings, 0.50 mL of ethylene dibromide, and 30 mL of anhydrous THF). The bright yellow solution was quenched after 10 min at −78 °C. In runs where the solution was allowed to warm to room temperature, the reaction mixture turned a dark orange color and there was complete conversion of the vinylcyclopropene to the two 1,2-diarylcyclopentadienes: 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene and 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene in a 1.0:1.2 ratio, respectively.

The yellow solution was quenched by quickly pouring it into 30 mL of ice−water. The organic phase was separated and concentrated to give 0.500 g of 3-isobutenyl-1-(*p*-methoxyphenyl)-3-methyl-2-phenylcyclopropene as a yellow oil. The crude product was chromatographed on a 50 cm × 2.5 cm silica column eluted with hexane giving: fraction 1, 150 mL, discarded. Fraction 2, 225 mL, 0.4389 g (69.6%) of a clear oil. This was recrystallized from methanol, resulting in formation of small white kernels, mp 68.0−69.0 °C.

The spectral data follow: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.65−7.56 (m, 4H, arom), 7.46−7.39 (m, 2H, arom), 7.32−7.26 (m, 1H, arom), 7.00−6.96 (m, 2H, arom), 5.51−5.49 (bs, 1H, =C*H*), 3.86 (s, 3H, OCH_3), 2.17 (s, 3H, cyclopropyl-CH_3), 1.66 (s, 3H, =CCH_3), 1.57 (s, 3H, =CCH_3); UV (C_6H_6) λ_{max} 220 nm (ϵ 2580), 234 (2770), 242 (4430), 254 (5390), 274 (9760), 330 (26 900), 346 (22 200); MS *m/e* 290.1670 (calcd for $C_{21}H_{22}O$, 290.1672). Anal. Calcd for $C_{21}H_{22}O$: C, 86.86; H, 7.64. Found: C, 86.71; H, 7.70.

3,3-Dimethyl-1-(*p*-methoxyphenyl)-2-phenyl-1,5-hexanedione. Using a modification of Zimmerman and coworkers addition of 1,2-diarylethanones[2] to mesityl oxide, a vigorously stirred yellow slurry of 5.60 g (24.75 mmol) of 1-(*p*-methoxyphenyl)-2-phenylethanone,[17] 1.60 g (16 mmol) of potassium *tert*-butoxide in 5 mL of freshly distilled *tert*-butyl alcohol were combined with gentle warming before the addition of 3.5 mL (41 mmol) of mesityl oxide. After 20 min, the reaction was quenched with hydrochloric acid and ether extracted. Allowing the reaction to continue for longer periods of time increased the extent of conversion but the 1,5-hexanedione cyclization product, 5,5-dimethyl-3-methoxyphenyl-4-phenylcyclohexenone, rapidly became the major product. The concentrated organics were chromatographed on a 2.5 cm × 100 cm column resulting in: fraction 1, 2.4 L of 5% ether in hexane, discarded; fraction 2, 2 L of 5% ether in hexane, 2.10 g (9.29 mmol) of 1-(*p*-methoxyphenyl)-2-phenylethanone; fraction 3, 500 mL of 10% ether in hexane, discarded; fraction 4, 2.8 L of 20% ether in hexane, 3.68 g (11.3 mmol, 73.3% yield based upon unrecovered starting material) of 3,3-dimethyl-1-(*p*-methoxyphenyl)-2-phenyl-1,5-hexanedione as a tan solid; and fraction 5, 1.8 L of 20% ether in hexane, 1.27 g (4.16 mmol) of 5,5-dimethyl-3-(*p*-methoxyphenyl)-4-phenylcyclohexenone. The diketone from fraction 4 was recrystallized from 95% ethanol giving fine microcrystals, mp 95.0−96.0 °C. The cyclohexenone from the last fraction was recrystallized to give clear plates, mp 102.0−103.5 °C.

The spectral data for the diketone follow: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.96−7.91 (m, 2H, arom), 7.39−7.20 (m, 5H, arom), 6.86−6.81 (m, 2H, arom), 5.19 (s, 1H, ArC*H*(CO)), 3.80 (s, 3H, OCH_3), 2.83 (d, 1H, J = 17.5 Hz, CH_2(CO)), 2.37 (d, 1H, J = 17.5 Hz, CH_2(CO)), 2.07 (s, 3H, CH_3(CO)), 1.17 (s, 3H, RCH_3), 1.15 (s, 3H, RCH_3); MS *m/e* 324.1725 (calcd for $C_{21}H_{24}O_3$, 324.1726). Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.77; H, 7.67.

The spectral data for the cyclohexenone follow: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.46−7.40 (m, 2H, arom); 7.33−7.22 (m, 5H, arom), 6.84−6.78 (m, 2H, arom), 6.64 (s, 1H, =C*H*(CO)), 3.82 (s, 1H, ArC*H*C=), 3.76 (s, 3H, OCH_3), 2.47 (d, 1H, J = 16.8 Hz, CH_2(CO)), 2.09 (d, 1H, J = 16.8 Hz, CH_2(CO)), 1.26 (s, 3H, RCH_3), 0.83 (s, 3H, RCH_3). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 81.93; H, 7.37.

(17) The 1,2-diarylethanones were synthesized following the literature procedure: (a) Vanino, T. *Ber.* **1896**, *29*, 1727. (b) Buck, J. S.; Ide, W. S. *J. Am. Chem. Soc.* **1932**, *54*, 3012.

1-(*p*-Methoxyphenyl)-5-phenyl-2,4,4-trimethyl-1,2-cyclopentanediol. Magnesium subiodide,[18] prepared from 0.242 g (10.0 mmol) of magnesium powder and 1.30 g (5.14 mmol) of iodine in dry diethyl ether, heated until all the iodine had reacted, was added to 0.594 g (1.83 mmol) of 3,3-dimethyl-1-(*p*-methoxyphenyl)-2-phenyl-1,5-hexanedione dissolved in dry diethyl ether. The reaction mixture was refluxed for 20 h, cooled to 0 °C, and quenched with saturated aqueous ammonium chloride. The organic layer was separated and concentrated and the mixture was chromatographed on a 2.5 cm × 50 cm quartz column eluted with 20% diethyl ether in hexane. The first 700 mL were discarded and the next 500 mL collected was concentrated to afford 0.571 g (1.75 mmol, 95.1% yield) of diol diastereomers as a light yellow solid, mp 53−60 °C. This was suitable for the following dehydration step or it could be recrystallized to give clear crystals of a single diastereomer, mp 145.5−147.0 °C.

The spectral data for the isolated diol follow: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.46−7.38 (m, 4H, arom), 7.26−7.14 (m, 3H, arom), 6.83−6.78 (m, 2H, arom), 4.05 (bs, 1H, RO*H*), 3.74 (s, 3H, OCH_3), 2.13−1.95 (m, 3H, CH_2 and RO*H*), 1.25 (s, 3H, RCH_3), 1.20 (s, 3H, RCH_3), 1.04 (s, 3H, RCH_3), 1.03 (s, 1H, ArC*H*); MS *m/e* 326.1872 (calcd for $C_{21}H_{26}O_3$, 326.1883). Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.30; H, 8.08.

2-(*p*-Methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene. Following the phosphoryl chloride pyridine-assisted dehydration procedure of Sauers,[19] a pyridine solution of 0.763 g (2.63 mmol) of 1-(*p*-methoxyphenyl)-5-phenyl-2,4,4-trimethyl-1,2-cyclopentanediol diastereomers and 1.0 mL (10.8 mmol) of phosphorus oxychloride was heated to reflux for 2 h. After cooling, the solution was poured onto ice in pentane and separated and the aqueous portion extracted with pentane. The combined organic layers were washed with 3 N aqueous hydrochloric acid and water before drying, filtration, and concentration. Column chromatography on a 2 cm × 30 cm column gave: fraction 1, 300 mL of 2% ether in hexane, discarded, and fraction 2, 300 mL of 2% ether in hexane. Concentration of fraction 2 gave 0.488 g of a 4.8:1 mixture of 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene and 4,4-dimethyl-2-(*p*-methoxyphenyl)-1-methylene-3-phenylcyclopent-2-ene as a clear oil. Seed crystals of the cyclopentadiene were obtained by HPLC chromatography of 20 mg injections on the system described below using 0.5% ether in hexane and collection of the peak at 390 min. Recrystallization in 95% ethanol gave the desired product as 0.090 g (0.310 mmol) of clear needles, mp 59.0−60.0 °C.

The spectral data follow: ^{1}H-NMR (C_6D_6, 300 MHz) δ 7.24−7.07 (m, 7H, arom), 6.65−6.62 (m, 2H, arom), 5.99 (q, 1H, J = 0.7 Hz, =C*H*), 3.18 (3H, s, OCH_3), 1.96 (3H, d, J = 0.7 Hz, =CCH_3), 1.29 (s, 6H, RCH_3); UV (C_6D_6) λ_{max} 220 nm (ϵ 1480), 236 (1910), 246 (2850), 254 (3660), 286 (8320); MS *m/e* 290.1667 (calcd for $C_{21}H_{22}O$, 290.1672). Anal. Calcd for $C_{21}H_{22}O$: C, 86.86; H, 7.64. Found: C, 86.50; H, 7.64.

3,3-Dimethyl-2-(*p*-methoxyphenyl)-1-phenyl-1,5-hexanedione. Following the previous example, 2.26 g (9.98 mmol) of 2-(*p*-methoxyphenyl)-1-phenylethanone[17] and 1.7 mL (20 mmol) of mesityl oxide were reacted using 0.406 g (4.05 mmol) of potassium *tert*-butoxide and 2 mL freshly distilled *tert*-butanol. Using the same workup and separation resulted in 1.48 g (4.55 mmol, 63.9% yield based upon unreacted starting material) of 3,3-dimethyl-2-(*p*-methoxyphenyl)-1-phenyl-1,5-hexanedione as a white powder, mp 88.0−89.5 °C, and 0.571 g (1.86 mmol) of 5,5-dimethyl-4-(*p*-methoxyphenyl)-3-phenylcyclohexenone, mp 109.0−110.0 °C.

The spectral data for the diketone follow: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.93−7.90 (m, 2H, arom), 7.43−7.24 (m, 5H, arom), 6.83−6.79 (m, 2H, arom), 5.18 (s, 1H, ArC*H*(CO)), 3.74 (s, 3H, OCH_3), 2.81 (d, 1H, J = 16.1 Hz, CH_2(CO)), 2.38 (d, 1H, J = 16.1 Hz, CH_2(CO)), 2.06 (s, 3H, CH_3(CO)), 1.17 (s, 3H, RCH_3), 1.14 (s, 3H, RCH_3); MS *m/e* 324.1728 (calcd for $C_{21}H_{24}O_3$, 324.1726). Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.71; H, 7.56.

(18) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1927**, *49*, 236.

The spectral data for the cyclohexenone follow: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.44–7.41 (m, 2H, arom), 7.30–7.26 (m, 3H, arom), 7.15–7.13 (m, 2H, arom), 6.84–6.81 (m, 2H, arom), 6.61 (s, 1H, =C*H*), 3.78 (s, 1H, ArC*H*C=); 3.76 (s, 3H, OCH_3), 2.48 (d, 1H, J = 11.1 Hz, CH_2(CO)), 2.10 (d, 1H, J = 11.1 Hz, CH_2(CO)), 1.25 (s, 3H, RCH_3), 0.83 (s, 3H, RCH_3).

5-(*p*-Methoxyphenyl)-1-phenyl-2,4,4-trimethyl-1,2-cyclopentanediol. Following the same coupling procedure for the cyclopentanediol regioisomer above with 0.365 g (15 mmol) of magnesium powder, 2.0 g (7.9 mmol) of iodine and 0.509 g (1.57 mmol) of 3,3-dimethyl-2-(*p*-methoxyphenyl)-1-phenyl-1,5-hexanedione gave 0.505 g (1.55 mmol, 98.7% yield) of a solid mixture of diastereomers, mp 59.0–64.0 °C, after column chromatography. Recrystallization in 95% ethanol gave clear prisms of a single diastereomer, mp 136.0–138.0 °C.

The spectral data follows: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.54–7.44 (m, 4H, arom), 7.41–7.13 (m, 3H, arom), 6.81–6.74 (m, 2H, arom), 4.04 (s, 1H, O*H*), 3.73 (s, 3H, OCH_3), 2.23–1.92 (m, 3H, CH_2RO*H*), 1.19 (s, 3H, RCH_3), 1.17 (s, 3H, RCH_3), 1.08 (s, 3H, RCH_3); and 1.01 (s, 1H, ArC*H*); MS *m/e* 326.1891 (calcd for $C_{21}H_{26}O_3$, 326.1883). Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.26; H, 8.32.

1-(*p*-Methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene. A solution of pyridine with 0.505 g (1.55 mmol) of 5-(*p*-methoxyphenyl)-1-phenyl-2,4,4-trimethyl-1,2-cyclopentanediol diastereomers and 0.50 mL (5.4 mmol) of phosphorus oxychloride was heated to reflux for 2 h. Workup as in the case above gave 0.388 g of a 6.4:1 mixture of 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene and 4,4-dimethyl-3-(*p*-methoxyphenyl)-1-methylene-2-phenylcyclopent-2-ene as a clear oil. Recrystallization in 95% ethanol gave 0.0734 g (0.253 mmol) of desired product as clear needles, mp 61.5–63.0 °C.

The spectral data follow: ^{1}H-NMR (C_6D_6, 300 MHz) δ 7.26–7.06 (m, 7H, arom), 6.68–6.64 (m, 2H, arom), 5.99 (q, 1H, J = 0.8 Hz, =C*H*), 3.21 (s, 3H, OCH_3), 1.93 (d, 3H, J = 0.8 Hz, =CCH_3), 1.30 (s, 6H, RCH_3); UV (C_6H_6) λ_{max} 224 nm (ϵ 1620), 246 (2850), 252 (4610), 290 (9500); MS *m/e* 290.1674 (calcd for $C_{21}H_{22}O$, 290.1672). Anal. Calcd for $C_{21}H_{22}O$: C, 86.86; H, 7.64. Found: C, 86.70; H, 7.84.

Exploratory Direct Photolysis of 3-Isobutenyl-1-(*p*-methoxyphenyl)-2-phenyl-3-methylcyclopropene. A solution of 0.125 g (0.430 mmol) of 3-isobutenyl-1-(*p*-methoxyphenyl)-2-phenyl-3-methylcyclopropene in 150 mL of photograde benzene was irradiated for 7 min with the 450 W medium pressure mercury vapor lamp through a Pyrex filter and then concentrated to 0.122 g of clear oil. A d_6-benzene ^{1}H-NMR determined that there was a 42% conversion of the isobutenylcyclopropene to 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene and 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene in a 1.6:1 ratio, respectively. The three compounds were distinguished by comparison of their *p*-methoxy peaks at 3.27, 3.21, and 3.18, respectively. The assignments were confirmed by addition of independently synthesized cyclopentadienes and by isolation of small quantities by HPLC separation (see below). All photolysis runs to conversions of 10–40% gave the same product ratios.

A similar irradiation in 150 mL of photograde pentane to 27.7% conversion gave a product ratio of 2.0:1 for 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene and 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene, respectively.

Photolysis in methanol solvent to 26.3% conversion gave a 1.8:1 product ratio for 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene and 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene, respectively.

HPLC Isolation of the Vinylcyclopropene and the Cyclopentadiene Photoproducts. The crude photolysate from the direct irradiations of the vinylcyclopropene was subjected to a HPLC system of two 50 cm and one 37.5 cm polished steel columns with a 0.72 cm i.d. These were packed with 3–5 μm porous silica beads in hexane using a Haskel high pressure packing pump.[20] The plate count was approximately 4000 measured against a standard of naphthalene/phenanthrene in hexane for each of the columns. The eluant used was 20% benzene in hexane for 10 mg injections of the concentrated photolysate. This obtained a clean separation of the vinylcyclopropene at a retention time of 790 min and overlapping peaks of the 1-(*o*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene and 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene at a retention time of 1190 min and 1260 min, respectively. The leading edge and tail of the peaks were collected to give pure cyclopentadienes that matched the physical data from the independently synthesized compounds.

Quantum Yield Determinations for the Cyclopentadiene Photoproducts. The quantum yields were run on the Zimmerman microbench at 325 nm in benzene using a digital actinometer calibrated by ferrioxalate actinometry to measure the light output.[21] The data are listed as follows: (1) mass (mmol) of 3-isobutenyl-1-(*p*-methoxyphenyl)-2-phenyl-3-methylcyclopropene; (2) mE light absorbed; (3) mmol of 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene, quantum yield; (4) mmol of 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene, quantum yield; (5) percent conversion. Analysis was by 300-MHz ^{1}H-NMR integration in d_6-benzene using the *p*-methoxy peaks listed above in the exploratory irradiation.

Run 1: (1) 25.2 mg (0.0868 mmol); (2) 0.114 mE; (3) 0.00500 mmol, ϕ = 0.0439; (4) 0.00313 mmol, ϕ = 0.0275; (5) 9.37%.

Run 2: (1) 22.3 mg (0.0768 mmol); (2) 0.0797 mE; (3) 0.00355 mmol, ϕ = 0.0445; (4) 0.00222 mmol, ϕ = 0.0279; (5) 7.52%.

Run 3: (1) 28.6 mg (0.0985 mmol); (2) 0.0679 mE; (3) 0.00305 mmol, ϕ = 0.0449; (4) 0.00191 mmol, ϕ = 0.0281; (5) 5.04%.

Run 4: (1) 24.5 mg (0.0844 mmol); (2) 0.0409 mE; (3) 0.00189 mmol, ϕ = 0.0462; (4) 0.00118 mmol, ϕ = 0.0289; (5) 3.64%.

The values for the quantum yield extrapolated to 0% conversion are ϕ = 0.048 for 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene and ϕ = 0.031 for 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene.

Control Direct Irradiation of the Cyclopentadienes. A test of the photostability of the cyclopentadiene products under the same conditions as the photolysis of the vinylcyclopropene above was carried out. Irradiations of a 52.0 mg (0.179 mmol) sample of 2-(*p*-methoxyphenyl)-1-phenyl-3,5,5-trimethylcyclopentadiene or 46.7 mg (0.161 mmol) of 1-(*p*-methoxyphenyl)-2-phenyl-3,5,5-trimethylcyclopentadiene for 10 min using the 450 W lamp with recovery of 55.1 and 43.2 mg, respectively, showed only a trace ($\leq$3%) of other compounds by 300 MHz ^{1}H-NMR analysis.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged. Additionally, thanks are due to Dr. Andrei G. Kutateladze for doing some of the computations.

JO9415667

(19) Sauers, R. R. *J. Am. Chem. Soc.* **1959**, *81*, 4873.

(20) Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D.; King, R. K.; St. Clair, J. D.; Baker, M. R.; Mangette, J. E.; Wilson, D. W. The University of Wisconsin, unpublished results.

(21) (a) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281. (b) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379. (c) Carrol, F. A.; Quina, F. H. *J. Am. Chem. Soc.* **1972**, *94*, 6246.