Unusual Regioselectivity in the Di-π-methane Rearrangement. Inhibition and Control by Electron-Donating Substituents. Mechanistic and Exploratory Photochemistry[1,2]

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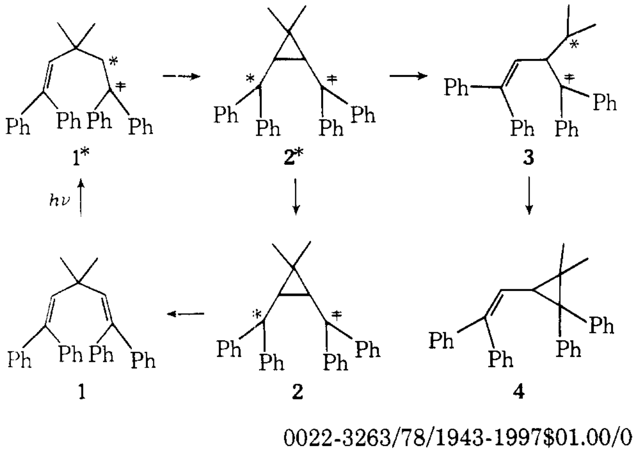
1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene were synthesized and their photochemistry was studied. The excited singlets underwent the di-π-methane rearrangement, while the triplets proved unreactive. In the case of the dianisyl diene unusual regioselectivity was observed in which 2,2-dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane predominated 3.3:1 over 1,1-bis(*p*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. This suggests that ionic factors may dominate over odd-electron stabilization in control of regioselectivity in the di-π-methane rearrangement. The reaction quantum yield was determined to be $\phi = 0.097$ for the dianisyl diene and $\phi = 0.044$ for the tetraanisyl diene. The rates of excited singlet rearrangement and decay to ground state were determined. Markedly lower rates of rearrangement were encountered for the anisyl systems compared with the parent 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. Additionally, the photochemistry of 1,1-bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene was explored. Here the vinylcyclopropane with the vinyl group bearing the dimethylaminophenyl groups proved to be the exclusive product, again suggesting ionic control of the reaction regioselectivity.

Eleven years ago we reported the occurrence of a general photochemical rearrangement of systems in which an sp^3-hybridized carbon bears two π moieties; we termed this the di-π-methane rearrangement. We proposed the general mechanistic sequence depicted in Scheme I.[3,4] In the intervening years, our investigations of the reaction mechanism have included stereochemistry,[5,6] multiplicity,[5a,6,8] excited-state reaction-rate measurement[6,9] and reaction regioselectivity.[6,9a,10] Our efforts and those of the literature[6] have been pleasingly consonant with the mechanism proposed.

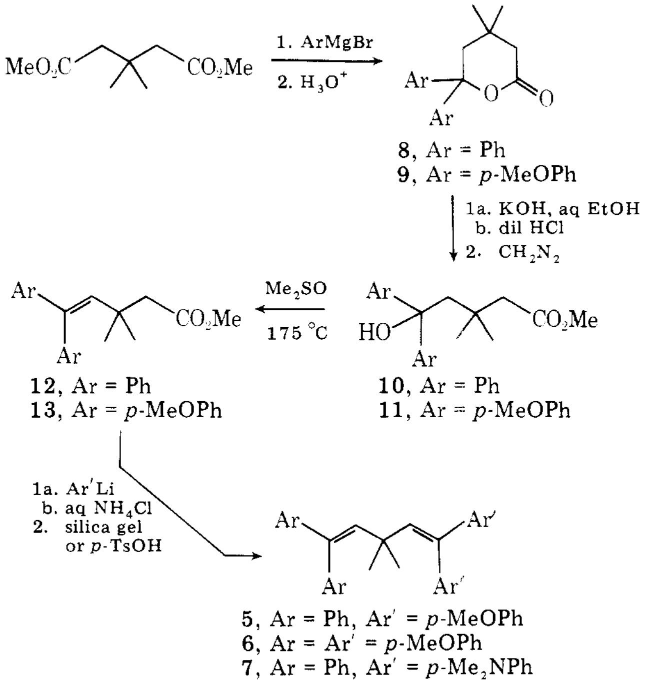
In this mechanism, the asterisk and double dagger of Scheme I have been depicted as odd electrons and the diradical character of the reacting species was emphasized. Nevertheless, despite the success of this picture, it was deemed of interest to determine if there was appreciable ionic character observable in the reaction. Thus, the photochemistry of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**5**), 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4 pentadiene (**6**), and 1,1-bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**7**) was examined.

Synthesis of Photochemical Reactants. The syntheses of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**5**), 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene (**6**), and 1,1-bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**7**) were carried out as delineated in Scheme II and described in the Experimental Section. Treatment of methyl and ethyl 3,3-dimethylglutarate with aryllithium and Grignard reagents did not lead to 1,5-diol precursors of the dienes of interest; rather, the diaryl δ-lactones **8** and **9** resulted. Thus, the sequence utilizing the Me_2SO elimination[11] of the δ-hydroxy esters **10** and **11** proved both convenient and necessary.

Scheme I. Resonance Version of the Di-π-methane Rearrangement



Scheme II. Syntheses of *p*-Methoxy and *p*-*N*,*N*-Dimethylamino Substituted Dienes



Results

Exploratory Photolyses. The exploratory runs were made both in benzene and *tert*-butyl alcohol solvent using a 450-W medium-pressure lamp, immersion well, and Pyrex filter. Each of the three dienes—the dianisyl diene **5**, the tetraanisyl diene **6**, and the bis(dimethylaminophenyl) diene **7**—led nicely to photochemical products with irradiations up to ~40% conversion. Beyond this, secondary photochemistry was encountered.

From the tetraanisyl diene **6**, a single photoproduct resulted. Typically, irradiation of 265 mg of tetraanisyl diene

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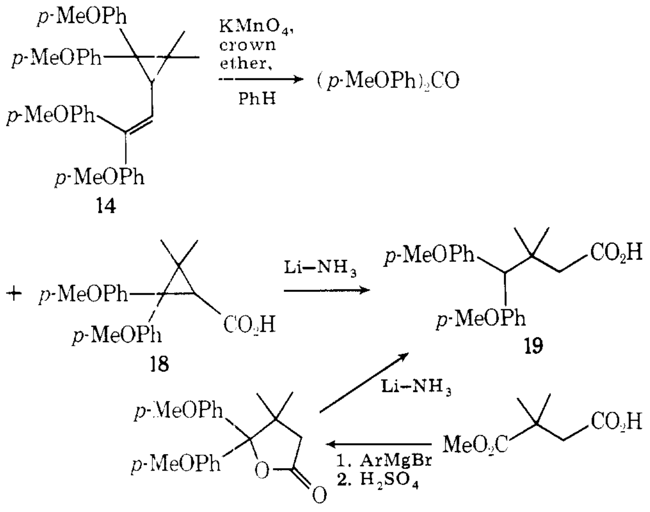
Scheme III. Structure Elucidation of Tetraanisyl Photoproduct 14



6 afforded 81 mg of photoproduct **14**, mp 149–150 °C, along with 125 mg of recovered diene reactant.

In the case of dianisyl diene **5** two photoproducts were isolated by column chromatography. In a typical run, irradiation of 780 mg of dianisyl diene **5** led to 257 mg of photoproduct **15** and 77 mg of photoproduct **16**, together with 297 mg of recovered reactant. The ratio of major to minor photoproduct thus proved to be 3.3:1, a value not far from that observed in quantum yield runs made to much lower conversion (vide infra).

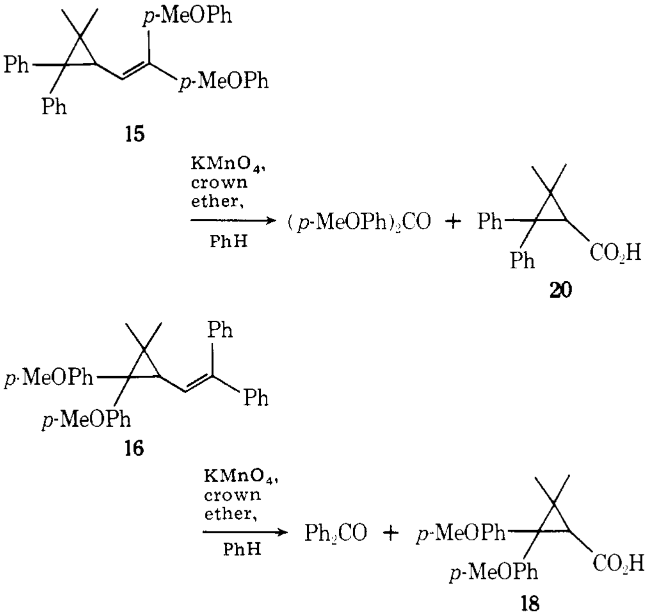
Finally, photolysis of 47 mg of bis(dimethylaminophenyl) diene **7** to complete conversion afforded 21 mg of a single photoproduct (**17**).

Elucidation of Photoproduct Structures. In the case of photoproduct **14**, derived from tetraanisyl diene **6**, a vinylcyclopropane structure (note **14** in Scheme III) was strongly suggested by the NMR spectrum. Thus an AB quartet, corresponding to the τ 4.57 vinyl and the τ 7.99 cyclopropyl methine, was observed. This is closely analogous to the NMR situation observed for similar vinylcyclopropanes.[8a,10b] Also, there were observed two three-hydrogen singlets ascribed to nonequivalent methyl groups, two three-hydrogen singlets and one six-hydrogen singlet corresponding to the four methoxy groups, and also aromatic absorption. These NMR features supported the structural assignment, but unambiguous proof was desired. This was obtained by Sam–Simmons[12] "purple benzene" oxidation of photoproduct **14** (note Scheme III) to give 4,4′-dimethoxybenzophenone and 2,2-bis(*p*-methoxyphenyl)-3,3-dimethylcyclopropanecarboxylic acid (**18**), whose structure was suggested by its NMR spectrum and confirmed by lithium–ammonia degradation to 4,4-bis(*p*-methoxyphenyl)-3,3-dimethylbutanoic acid (**19**) as depicted in Scheme III. The structure of the latter compound was established by independent synthesis (note Scheme III again).

Turning now to the photoproducts obtained from dianisyl diene **5**, we again noted the characteristic AB quartet, two nonequivalent methyls, two nonequivalent methoxy groups, and aromatic hydrogens for each photoproduct. The major photoproduct exhibited its vinyl hydrogen absorption at τ 4.52, which was remarkably close to the τ 4.57 shift for the tetraanisylvinylcyclopropane **14**. In the case of the minor photoproduct, the vinyl absorption at τ 4.30 was strongly reminiscent of the τ 4.25 vinyl peak in the NMR spectrum of the known 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**4**).[8a]

The upfield shift expected for a vinyl hydrogen β to an electron donor suggested that the major photoproduct contained a dianisylvinyl moiety, while the minor photoproduct had a diphenylvinyl group. The degradative scheme using "purple benzene"[12] oxidation was again employed in each case. The major photoproduct **15** afforded 4,4′-dimethoxybenzophenone and 3,3-dimethyl-2,2-diphenylcyclopropanecarboxylic acid (**20**)[8a] as shown in Scheme IV. The minor photoproduct **16** led to benzophenone and 2,2-bis(*p*-methoxyphenyl)-3,3-dimethylcyclopropanecarboxylic acid (**18**). This, too, is shown in Scheme IV.

Scheme IV. Degradation of Dianisyl Diene Photoproducts



Finally, the single photoproduct **17** derived from irradiation of the bis(dimethylaminophenyl) diene **7** revealed an NMR spectrum showing the typical AB quartet, the nonequivalent pair of methyl groups, and aromatic absorption. Also, there were observed two six-hydrogen singlets ascribed to the four *N*-methyl groups. Additionally, the vinyl portion of the AB quartet was centered at τ 4.73, still further upfield from that observed in the anisyl-substituted vinyl groups, indicating the presence of the electron-donating dimethylaminophenyl groups on the double bond. These data lead us then to 2,2-dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-*N*,*N*-dimethylaminophenyl)vinyl]cyclopropane (**17**).

Quantum Yield Determinations. These determinations were made both on the black box apparatus and the semimicrooptical bench described by us earlier.[13,14] In using the former, filter solutions were employed giving 272- and 310-nm light with band widths of 50 nm baseline to baseline; ferrioxalate actinometer was employed.[15] Details are given in the Experimental Section. The usual precautions were taken as previously described[16] for quantum yield determinations. Assay of product was by isolation with gravimetric determination or by high-speed liquid chromatography. The results of direct irradiations are summarized in Table I.

Sensitized runs were made with acetophenone and with benzophenone. In the benzophenone runs benzhydrol was also added, since to the extent that energy transfer was occurring, benzopinacol formation would be inhibited relative to runs omitting the di-π-methane reactant. In these runs, quenching of the benzophenone–benzhydrol reaction was observed and yet no reaction of the diene occurred. It can thus be concluded that despite energy transfer to the di-π-methane dienes, no rearrangement of triplet occurs. These runs are also included in Table I.

Emission Measurements and Single Photon Counting Determination of Excited-State Rate Constants. With the quantum yields in hand, we turned our attention toward a

Table I

Reactants (M)	λ_{irrad}, nm	Φ_r	% conversion
5 (0.000 25)	285	0.085,[a] 0.025[b]	5.6
5 (0.000 87)	272	0.070,[a] 0.023[b]	8.8
5 (0.001 49)	310	0.071,[a] 0.017[b]	6.0
5 (0.000 813), $PhCOCH_3$ (0.309)	331	<0.004[c]	0
6 (0.001 23)	272	0.040[d]	3.3
6 (0.001 53)	310	0.042[d]	6.7
6 (0.001 80)	310	0.051[d]	3.4
6 (0.000 705), Ph_2CO (0.0449)	345	0.002[c]	0
7 (0.000 92)	310	<0.0054[c]	0
7 (0.000 493)	310	0.0027[e]	9.2
Ph_2CO (0.0110), Ph_2CHOH (0.005 45)	345	0.123[f]	24.0
Ph_2CO (0.0110), Ph_2CHOH (0.005 45), **5** (0.000 545)	345	0.031[f]	8.0
Ph_2CO (0.0110), Ph_2CHOH (0.005 45), **6** (0.000 400)	345	0.039[f]	18.0

[a] Formation of dianisylvinyl product **15**. [b] Formation of diphenylvinyl product **16**. [c] Limit of detection. [d] Formation of tetraanisyl product **14**. [e] Formation of bis(dimethylaminophenylvinyl) product **17**. [f] Formation of benzopinacol.

Table II. Results of Emission and Single-Photon Counting Studies

Compd	λ_{em},[a] nm	M	$k_{dt}{}^{77}$, s^{-1}	τ^{77}, ns	$k_{dt}{}^{RT}$, s^{-1}	τ^{RT}, ps	$k_r{}^{RT}$, s^{-1}
Dianisyl diene **5**	330	95	3.7×10^8	2.7	3.5×10^{10}	28	3.4×10^9
Tetraanisyl diene **6**	335	75	5.2×10^8	1.9	3.9×10^{10}	25	1.7×10^9
Dimethylaminophenyl diene **7**	360	70	2.9×10^8	3.5	2.0×10^{10}	50	5.4×10^7
1,1-Dianisylethylene **21**	325	77	2.26×10^8	4.4	1.7×10^{10}	57	
1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene **26**[b]	310	225	8.1×10^9	0.12	1.8×10^{12}	0.55	1.4×10^{11}

[a] λ_{em} refers to wavelength of maximum emission in nanometers. [b] Reference 9b.

more meaningful measure of molecular reactivity, namely the rates with which the excited states rearrange.

It was first necessary to inspect the fluorescence behavior of the di-π-methane diene reactants. 1,1-Dianisylethylene (**21**) was included for comparison. The compounds under study showed similar absorption and emission spectra. The emission was typically diarylvinyl-like with little difference between the dienes and the monoethylenic models. Note Table II. The small shift in wavelength between absorption and emission curves, along with the overlap of these showing a common 0–0 energy difference, indicated emission from S_1 and absence of emission from exciplexed species of either the inter- or intramolecular varieties.

It was important to ascertain that no self-quenching of excited singlets was occurring under experimental conditions. The case of the bis(dimethylaminophenyl) diene **7** was most critical, since its photochemical reactivity was lowest (vide supra). At very low concentration, fluorescence intensity is linear with concentration and deviations due to self-quenching are readily detected. However, in the medium concentration range, we have noted[16,17] that fluorescence emitted mid-cell at 90° increases with concentration until a maximum intensity is obtained at a 0.87 absorbance, whereupon the intensity diminishes. A complex function of concentration is obtained[16] as given in the equation

$$I_f = KI_0\phi_f A \times 10^{-(A/2)} \tag{1a}$$

where A is the absorbance, I_f is the fluorescence intensity at 90° through a slit placed midway along the cell depth, ϕ_f is the fluorescence efficiency, I_0 is the light intensity, and K is an instrumental constant. While our previous study[16] utilized a complete plot of this function to test lack of self-quenching, a convenient two-point test is provided by the equation

$$A_1 10^{-A_1/2} = A_2 10^{-A_2/2} \tag{1b}$$

Here we select as A_1 the optical density used for the single-photon counting studies. One then solves eq 1b for A_2 and determines if a solution of this absorbance really does emit with the same intensity as that with absorbance A_1. This test applied to the diene of present interest showed absence of self-quenching.

With static emission information in hand, we were able to turn our attention to single-photon counting measurements. The primary data derivable are the rate of excited singlet decay (i.e., k_{dt}) and the corresponding excited singlet lifetimes (i.e., $\tau = 1/k_{dt}$). The method used has been described by us previously[9b] and is detailed as necessary in the Experimental Section.

As has been observed in a number of instances in the past, the room-temperature decay rates proved too rapid, especially in the case of the methoxy dienes, to measure directly at room temperature. As before[9b] it was observed that the decay rates decreased dramatically with decrease in temperature and were quite measureable at 77 K. These rates are summarized in Table II.

Previously we have noted that the ratio of fluorescence intensities at two temperatures gives the inverse of the ratio of the two rates of decay; note the equation

$$k_{dt}{}^{RT}/k_{dt}{}^{77} = I_f{}^{77}/I_f{}^{RT} = M \tag{2}$$

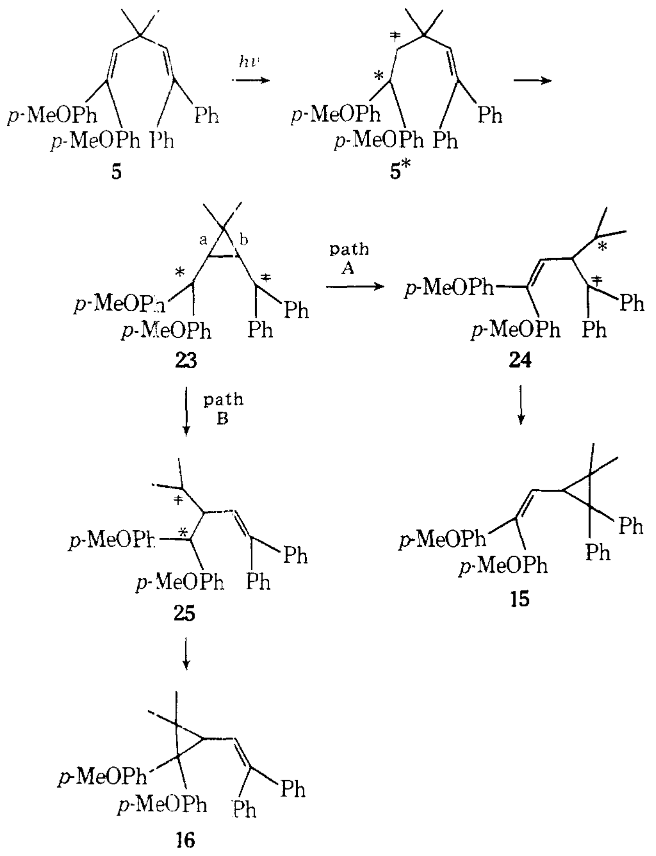
We should note that eq 2 is derived[9b] with the assumption that the rate of fluorescence k_f is temperature independent. While this cannot be taken to be invariably the case, it has proven[9b,17] valid for systems of the type presently under study. The ratio in eq 2, termed[9b] the magic multiplier M, is obtained experimentally from the ratio of fluorescence intensities at the two temperatures.

With M available and with the low-temperature decay rates measureable, one can thus calculate the very rapid room-temperature rates of decay (i.e., the $k_{dt}{}^{RT}$'s). Both the M's and the $k_{dt}{}^{RT}$'s are included in Table II.

Interpretative Discussion

The first observation to be made is that the di-π-methane rearrangement proceeds to afford the usual vinylcyclopropane

Scheme V. Mechanism of the Reaction



type product and does this via the singlet excited state as expected[8] for acyclic systems.

Unexpected and striking is the regioselectivity encountered. With the usual formulation, where the free valences in the cyclopropyldicarbinyl species 2 (note Scheme I) are represented as odd-electron centers, one would have anticipated a preference for path B in Scheme V rather than the observed path A, since *p*-methoxyphenyl is known[18,19] to stabilize odd-electron centers in excited states better than phenyl and *p*-*N*,*N*-dimethylaminophenyl would be expected to behave similarly. We have noted,[8c,9b] however, that the S_1 excited state consists heavily of ionic terms of the type $\chi_1^{\alpha}(i)\chi_1^{\beta}(j)$, where the χ's refer to atomic orbitals of the system, i and j are two electrons, and α and β refer to the electron spin.[20-22] Thus S_1 states are likely to be quite polarizable; and the dot-dot representation of the excited states, while convenient, should not be construed to exclude polarization.

Also, we need to recognize that the qualitative resonance picture (e.g., note Scheme V) used conveniently is not inconsistent with the Möbius cyclic orbital array 22 (Figure 1), which we have used previously[8a] to rationalize the reaction stereochemistry and photochemical allowedness. Thus, the resonance picture in Scheme V merely dissects the two main mechanistic processes of the rearrangement, namely vinyl–vinyl bridging and accompanying three-ring reopening, for convenience in presentation and to allow consideration in traditional organic terms.

At this point there are two experimental observations which are particularly striking and deserve discussion. One is the rate inhibition by anisyl and dimethylaminophenyl substitution (note Table II) and the other is the regioselectivity encountered wherein electron-donating aryl groups preferentially appear on the double bond of the photoproduct.

In our previous studies[9b,10b] we have suggested that π–π bridging is rate limiting. We have also suggested that one significant mode of S_1 decay derives from such bridging, followed by internal conversion of the cyclopropyldicarbinyl diradical (here 2*) to its ground-state counterpart (i.e., 2), which then reverts to diene reactant 1 by Grob fragmentation. Inspection of Table II reveals that for the presently studied molecules k_{dt}, the total rate of singlet decay, is not appreciably more rapid than that of an isolated dianisylethylene excited singlet. This contrasts with such systems as 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (26),[8a,9b] where an ultrarapid decay is encountered with a lifetime of 0.55 ps. Thus in the present anisyl and dimethylaminophenyl systems a slow rate of bridging seems the likely source of a low S_1 reaction rate rather than any exceptional amount of return of bridged diradical to reactant. Hence the effect of these electron-donating groups must be in the bridging process.

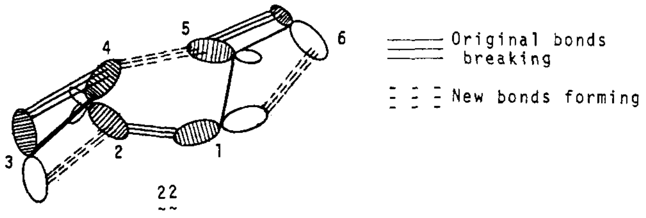


Figure 1. Möbius orbital array in the di-π-methane rearrangement.

SCF–CI calculations[1b,23] reveal that the dramatic rate inhibition derives from excessive stabilization of the vertical excited states for these molecules with considerably less stabilization of the cyclopropyldicarbinyl diradical by these electron-donating aryl groups.

The regioselectivity provides evidence that in the three-ring opening of the cyclopropyldicarbinyl diradical the carbinyl carbon destined to become the final vinyl group becomes much less electron rich. This leads to stabilization by anisyl and other donating groups. Conversely, the carbon destined to become a three-ring atom becomes more electron rich with consequent stabilization by electron-withdrawing groups. SCF–CI calculations[1] show the cyclopropyldicarbinyl diradical to be electron rich at the carbinyl carbons before opening; however, one might expect such a diradical to be quite polarizable.[23]

In this discussion we recognize that the excited state has all gradations of charge separation possible, and that the less than complete regioselectivity for anisyl suggests that we are not dealing with a heavily polar species.

Thus, we can formulate the reaction mechanism as in Scheme V, where the free valences are represented by an asterisk and a double dagger. The significance of these two symbols is not constant along the reaction coordinate, and one might equally validly use the dot–dot formulation presented by us in earlier publications.

Conclusion

In conclusion, we comment that again our mechanistic reasoning in photochemistry has involved the implicit concept that excited-state transformations are controlled by the demand of these species for minimum energy pathways along the excited-state hypersurface.[24] While consideration of ways in which these excited states can convert themselves into ground-state counterparts is of interest, this seems to be related to the photochemical course of a reaction only in a secondary fashion.[25]

Experimental Section[30]

3,3-Dimethyl-5,5-diphenyl-5-hydroxypentanoic Acid Lactone. Phenylmagnesium bromide prepared from 42 mL (0.40 mol) of bromobenzene in 200 mL of anhydrous ether and 9.52 g (0.39 mol) of magnesium turnings was transferred under nitrogen to a constant-pressure addition funnel and added over 2.0 h to a solution of 34.3 g (0.18 mol) of dimethyl 3,3-dimethylglutarate in 400 mL of anhydrous ether. The reaction was stirred for 1.0 h, quenched with cold 10% sulfuric acid, ether extracted, washed with 5% aqueous sodium bicarbonate solution and with saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under vacuum to a yellow oil. Crystallization from hexane gave 10.0 g of 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoic acid lactone. A second crop of lactone was obtained after removal of anisole and unreacted dimethyl 3,3-dimethylglutarate by vacuum distillation. The product was recrystallized from hexane to mp 90.5–91.5 °C (lit.[31] mp 90.0–91.0 °C), giving a total of 20.0 g (80% based on unrecovered starting material).

The spectral data were: IR ($CHCl_3$) 3.32, 3.36, 3.47, 5.77, 6.26, 6.69, 6.90, 7.27, 7.41, 7.58, 7.61, 7.9, 8.0–8.3, 8.73, 9.15, 9.45, 10.00, 10.92, 14.43, 15.25 μm; NMR ($CDCl_3$) τ 8.97 (s, 6 H, $C(CH_3)_2$), 7.85 (s, 2 H, CH_2), 7.43 (s, 2 H, CH_2), 2.73 (s, 10 H, arom).

Methyl 3,3-Dimethyl-5,5-diphenyl-5-hydroxypentanoate. A solution of 4.98 g (0.0178 mol) of 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoic acid lactone, 2.35 g of potassium hydroxide, and 300 mL of 95% ethanol was refluxed for 2.5 h, concentrated under vacuum, taken up in ether and water, and acidified to a methyl orange end point with 10% hydrochloric acid. The ether layer was dried over magnesium sulfate and concentrated under vacuum to 4.84 g (91%) of white crystalline 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoic acid, mp 114–117 °C, which was used without further purification.

The spectral data were: IR ($CHCl_3$) 2.71, 2.76–4.0, 5.92, 6.26, 6.71, 6.91, 7.15, 7.29, 7.70, 8.0–8.3, 8.55, 8.98, 9.42, 9.73, 9.97, 10.24, 14.43, 15.43 μm; NMR ($CDCl_3$) τ 9.22 (s, 6 H, $C(CH_3)_2$), 7.52 (s, 2 H, CH_2), 7.47 (s, 2 H, CH_2), 3.93 (br s, 2 H, $CO_2\mathbf{H}$ and $CPh_2O\mathbf{H}$), 2.97–2.45 (m, 10 H, arom).

A solution of 9.20 g (0.031 mol) of 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoic acid in 100 mL of ether was added over 15 min to an ether solution of diazomethane generated from 16.8 g of DuPont EXR-101 (*N,N′*-dinitroso-*N,N′*-dimethylterephthalimide with 30% inert filler) as described by Moore and Reed.[32] After 7 h of stirring, excess diazomethane was removed with a stream of nitrogen. The white solid residue was dissolved in ether, filtered, and concentrated to a colorless oil. Recrystallization from hexane gave 8.52 g (89%) of methyl 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoate, mp 70–70.5 °C.

The spectral data were: IR ($CHCl_3$) 2.91, 3.21, 3.25, 3.31, 3.37, 3.48, 5.86, 6.25, 6.71, 6.91, 7.18, 7.30, 7.41, 7.50, 7.72, 8.28, 8.69, 8.83, 9.40, 9.63, 9.72, 9.97, 10.22, 10.82, 11.29, 11.71, 14.34, 15.39 μm; NMR ($CDCl_3$) τ 9.22 (s, 6 H, $C(CH_3)_2$), 7.48 (s, 4 H, two CH_2), 6.42 (s, 3 H, CO_2CH_3), 5.97 (s, 1 H, OH), 2.93–2.42 (m, 10 H, arom).

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.90; H, 7.74. Found: C, 77.06; H, 7.82.

Methyl 3,3-Dimethyl-5,5-diphenyl-4-pentenoate. Following the general method of Traynelis,[11] a solution of 0.642 g (2.05 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoate and 2.8 mL of dimethyl sulfoxide was heated at 175 °C for 2 h, diluted with water, ether extracted, dried over magnesium sulfate, and concentrated to an oil residue which was immediately chromatographed on a 2.5 × 40 cm silica gel[33] column. Elution with 2 L of 5% ether gave: fraction 1, 300 mL, nil; fraction 2, 1000 mL, 0.550 g (91%) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate, a colorless oil; fraction 3, 700 mL, nil.

The spectral data were: IR ($CHCl_3$) 3.35, 5.78, 6.26, 6.71, 6.82, 6.93, 7.31, 7.42, 7.60, 7.72, 8.0–8.4, 8.62, 9.02, 9.48, 9.8, 10.02, 14.43 μm; NMR (CCl_4) τ 8.97 (s, 6 H, $C(CH_3)_2$), 7.78 (s, 2 H, CH_2), 6.42 (s, 3 H, CO_2CH_3), 3.90 (s. 1 H, vinyl), 2.90–2.68 (m, 10 H, arom).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.49; H, 7.40.

1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 0.500 g (1.70 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate in 75 mL of anhydrous ether was added over 10 min to a solution of *p*-methoxyphenyllithium prepared from 2.5 mL (19.8 mmol) of *p*-bromoanisole in 60 mL of ether and 16.8 mmol of *n*-butyllithium in 8.4 mL of hexane. The reaction was stirred for 4 h, quenched with cold saturated ammonium chloride solution, ether extracted, dried over magnesium sulfate, and concentrated to a yellow oil. The crude oils from two similar runs (total mass of starting ester used was 1.00 g (3.40 mmol)) were combined and chromatographed on a 2.5 × 85 cm silica gel column.[33] Elution proceeded as follows: fraction 1, 800 mL, hexane, nil; fraction 2, 2000 mL, hexane, 2.63 g of anisole; fraction 3, 1000 mL, 0.5% ether in hexane, nil; fraction 4, 1000 mL, 0.5% ether, 0.072 g of bianisole; fraction 5, 500 mL, 0.5% ether, nil; fraction 6, 4700 mL, 0.5–2.0% ether, 1.42 g (91%) of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene as a colorless glass.

The spectral data were: IR ($CHCl_3$) 3.32, 3.36, 3.38, 3.47, 3.50, 6.23, 6.36, 6.63, 6.83, 6.94, 7.07, 7.28, 7.77, 8.04, 8.24, 8.51, 8.69, 9.02, 9.34, 9.69, 11.4, 12.05, 14.4 μm; NMR (CCl_4) τ 8.98 (s, 6 H, $C(CH_3)_2$), 6.34, (s, 3 H, OCH_3), 6.30 (s, 3 H, OCH_3), 4.21 (s, 1 H, $-C\mathbf{H}{=}CAr_2$), 4.10 (s, 1 H, $-C\mathbf{H}{=}CPh_2$), 3.44–2.84 (m, 18 H, arom); UV (95% EtOH) 245 nm (ϵ 30 600).

Anal. Calcd for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00. Found: C, 85.98; H, 7.11.

5,5-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic Acid Lactone. *p*-Methoxyphenylmagnesium bromide prepared from 16.0 mL (0.125 mol) of *p*-bromoanisole in 100 mL of anhydrous tetrahydrofuran and 2.91 g (0.120 mol) of magnesium turnings was added over 45 min to a solution of 9.47 g (0.050 mol) of dimethyl 3,3-dimethylglutarate in 120 mL of anhydrous tetrahydrofuran. The reaction was stirred for 5 h, quenched with cold 3% sulfuric acid, ether extracted, washed with saturated sodium chloride solution and with water, dried over magnesium sulfate, and concentrated under vacuum to 19.9 g of yellow oil. Removal of additional volatile material by vacuum distillation left 16.2 g of yellow oil which was chromatographed on a 4 × 78 cm column of silica gel.[33] Elution with 4 L of hexane, 2 L of 2.5%, 2 L of 5%, 3 L of 10%, 2 L of 12.5%, 4 L of 15%, 1 L of 17.5%, and 1 L of 20% ether in hexane, and 1 L of 5% chloroform, 25% ether, and 70% hexane gave in 1000-mL fractions: fractions 1–4, 1.38 g of a mixture of anisole and bianisole; fractions 5–10, 3.13 g of a mixture containing unreacted dimethyl 3,3-dimethylglutarate and bianisole; fraction 11, 0.172 g of material containing ~0.08 g of 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid lactone; fractions 12–14, 7.31 g of 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid lactone; fractions 15–16, 2.57 g of a mixture of 1.99 g of lactone and 0.58 g of 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-pentenoic acid; fractions 17–18, 0.419 g of the pentenoic acid. Crystallization of fractions 11–14 from hexane gave 9.35 g (55%) 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid lactone as a white crystalline solid, mp 88.5–89.5 °C.

The spectral data were: IR ($CHCl_3$) 3.31, 3.36, 3.51, 5.79, 6.21, 6.63, 6.84, 6.95, 7.30, 7.42, 7.7, 7.85, 8.05, 8.25, 8.49, 9.36, 9.70, 10.07 μm; NMR ($CDCl_3$) τ 8.95 (s, 6 H, $C(CH_3)_2$), 7.83 (s, 2 H, CH_2), 7.48 (s, 2 H, CH_2), 6.25 (s, 6 H, OCH_3), 3.21–2.64 (q, 8 H. arom).

Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.36; H, 7.18.

The structure of 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-pentenoic acid was assigned on the basis of the spectral data: IR ($CHCl_3$) 2.8–3.9, 3.32, 3.36, 3.51, 5.88, 6.22, 6.35, 6.72, 6.83, 7.06, 7.27, 7.31, 7.77, 8.05, 8.25, 8.53, 9.04, 9.67, 12.05 μm; NMR (CCl_4) τ 8.92 (s, 6 H, $C(CH_3)_2$), 7.72 (s, 2 H, CH_2), 6.31 (s, 3 H, OCH_3), 6.24 (s, 3 H, OCH_3), 4.02 (s, 1 H, vinyl), 3.40–2.80 (m, 8 H, arom).

Methyl 5,5-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoate. An ether solution of 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid was prepared by refluxing a mixture of 14.6 g (0.043 mol) of 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoic acid lactone, 15.0 g of potassium hydroxide, 15 mL of water, and 500 mL of 95% ethanol for 2.0 h, concentrating to near dryness under vacuum, dissolving the residue in water, acidifying to the methyl orange end point with 10% hydrochloric acid, and extracting with ether. The resulting solution was added over 90 min to an ether solution of diazomethane generated from 23.7 g of DuPont EXR-101 (*N,N′*-dinitroso-*N,N′*-dimethylterephthalimide with 30% inert filler) as described by Moore and Reed.[32] After 4 h of stirring, excess diazomethane was removed with a stream of nitrogen. The residue was dissolved in ether, filtered, and concentrated under vacuum to 16.0 g (99%) of methyl 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoate, pure by NMR, which was used without further purification.

The spectral data were: IR ($CHCl_3$) 2.95, 3.34, 3.39, 3.41, 3.44, 3.53, 5.80, 6.25, 6.38, 6.65, 6.85, 6.95, 7.09, 7.21, 7.33, 7.45, 7.59, 7.79, 8.05, 8.20, 8.49, 8.54, 8.93, 9.70, 12.02 μm; NMR (CCl_4) 9.24 (s, 6 H, $C(CH_3)_2$), 7.58 (s, 2 H, CH_2), 7.54 (s, 2 H, CH_2), 6.40 (s, 3 H, CO_2CH_3), 6.28 (s, 6 H, $C_6H_4OC\mathbf{H}_3$), 3.35–2.65 (q, 8 H, arom).

Methyl 5,5-Bis(*p*-methoxyphenyl)-3,3-dimethyl-4-pentenoate. A mixture of 15.7 g (0.042 mol) of methyl 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-5-hydroxypentanoate and 60 mL of dimethyl sulfoxide[11] was heated at 176 °C for 2.5 h, cooled, and partitioned between water and ether. The ether phase was washed with saturated sodium chloride solution, dried over sodium sulfate, and concentrated to a yellow oil which was immediately chromatographed on a 2.5 × 45 cm silica gel column.[33] Elution with 2.0 L of 1% ether in hexane gave 13.4 g (90%) of methyl 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-pentenoate as a colorless oil.

The spectral data were: IR ($CHCl_3$) 3.36, 3.50, 5.75, 6.22, 6.35, 6.63, 6.84, 6.93, 7.76, 8.00, 8.5, 8.9, 9.65, 12.05 μm; NMR (CCl_4) 8.98 (s, 6 H,

$C(CH_3)_2$), 7.80 (s, 2 H, CH_2), 6.42 (s, 3 H, CO_2CH_3), 6.29 (s, 3 H, $C_6H_4OCH_3$), 6.21 (s, 3 H, $C_6H_4OCH_3$), 4.07 (s, 1 H, vinyl), 3.42–2.95 (m, 8 H, arom).

Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.55; H, 7.33.

3,3-Dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene. A solution of 4.27 g (12.0 mmol) of methyl 5,5-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-pentenoate in 75 mL of anhydrous ether was added over 30 min to a solution of *p*-methoxyphenyllithium prepared from 5.0 mL (38.9 mmol) of *p*-bromoanisole in 45 mL of ether and 39 mmol of *n*-butyllithium in 27 mL of hexane. The reaction was stirred for 2.5 h, quenched with cold saturated ammonium chloride solution, ether extracted, dried over magnesium sulfate, and concentrated under vacuum to 8.98 g of yellow oil which was chromatographed on a 4 × 80 cm silica gel column.[33] Elution with 4 L of hexane, 1 L of 0.5%, 2 L of 1.0%, 1 L of 1.5%, 8 L of 2.5%, 4 L of 10%, 1 L of 12%, 1 L of 15%, and 1 L of 20% ether in hexane proceeded as follows (1000-mL fractions): fraction 1 (4000 mL), 1.23 g of anisole; fractions 2–3, nil; fractions 4–5, 0.196 g of bianisole; fractions 6–8, nil; fractions 9–12, 0.686 g of 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene; fractions 13–14, 0.091 g of overlap; fractions 15–19, 5.42 g of 3,3-dimethyl-1,1-5,5-tetrakis(*p*-methoxyphenyl)pent-4-en-1-ol; fraction 20, nil. The combined yield of pentadiene and pentenol was 95%. The pentenol was dehydrated (vide infra) without further purification. Crystallization from ether–hexane gave white crystals, mp 183–186 °C.

The spectral data were: IR ($CHCl_3$) 2.86, 3.34, 3.39, 3.41, 3.45, 3.53, 6.25, 6.38, 6.65, 6.77, 6.85, 6.96, 7.19, 7.30, 7.81, 8.06, 8.23, 8.50, 8.55, 8.96, 9.22, 9.73, 11.49, 12.03, 12.44 µm; NMR ($CDCl_3$) τ 9.20 (s, 6 H, $C(CH_3)_2$), 7.42 (s, 2 H, CH_2), 6.51 (s, 6 H, OCH_3), 6.22 (s, 3 H, OCH_3), 6.16 (s, 3 H, OCH_3), 5.29 (s, 1 H, OH), 4.12 (s, 1 H, vinyl), 3.48–2.19 (m, 16 H, arom).

A solution of 1.54 g (3.50 mmol) of 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)pent-4-en-1-ol in 10 mL of chloroform was added to a solution of 0.073 g of *p*-toluenesulfonic acid in 100 mL of chloroform, stirred at room temperature for 1.0 h, and poured into aqueous sodium bicarbonate solution. The organic layer was dried over sodium sulfate and concentrated to 1.67 g of material containing no trace of starting alcohol (NMR analysis). Chromatography of the crude product on a 2.5 × 80 cm silica gel[33] column eluting with 2 L of hexane, and 4 L of 1.5% and 4 L of 2.5% ether proceeded as follows: fraction 1, 6000 mL, nil; fraction 2, 3000 mL, 1.42 g (96%) of 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene, a colorless glass; fraction 3, 1000 mL, nil.

The spectral data were: IR ($CHCl_3$) 3.32, 3.37, 3.51, 6.23, 6.37, 6.64, 6.83, 6.94, 7.07, 7.28, 7.77, 8.0–8.3, 8.52, 8.68, 9.04, 9.68 µm; NMR (CCl_4) τ 9.00 (s, 6 H, $C(CH_3)_2$), 6.33 (s, 6 H, OCH_3), 6.31 (s, 6 H, OCH_3), 4.29 (s, 2 H, vinyl), 3.49–3.00 (m, 16 H, arom); UV (95% EtOH) 244 (ϵ 31 600), 264 nm (ϵ 27 800).

Anal. Calcd for $C_{35}H_{36}O_4$: C, 80.74; H, 6.97. Found: C, 80.93; H, 7.09.

1,1-Bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 0.831 g (2.83 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate in 25 mL of anhydrous ether was added over 10 min to a solution of *p*-*N*,*N*-dimethylaminophenyllithium prepared from 1.58 g (7.9 mmol) of *p*-bromo-*N*,*N*-dimethylaniline in 25 mL of anhydrous ether and 7.5 mmol of *n*-butyllithium in 5.2 mL of hexane. The reaction was stirred for 90 min, quenched with cold saturated aqueous ammonium chloride solution, ether extracted, dried over magnesium sulfate, and concentrated under vacuum to 1.96 g of material which was chromatographed on a 2.5 × 45 cm silica gel column.[33] Elution with 1 L of hexane and 0.5 L of 1%, 1 L of 3%, and 1 L of 6% ether in hexane proceeded as follows: fraction 1, 1000 mL, nil; fraction 2, 800 mL, 0.384 g of aryl coupling products; fraction 3, 1500 mL, 1.23 g (89%) of the dehydrated product, 1,1-bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, a clear, viscous oil.

The spectral data were: IR ($CHCl_3$) 3.38, 3.50, 3.57, 6.21, 6.43, 6.58, 6.68, 6.85, 6.92, 7.38, 8.59, 8.87, 10.00, 10.24, 10.56, 11.23, 11.59 µm; NMR (CCl_4) τ 8.97 (s, 6 H, $C(CH_3)_2$), 7.17 (s, 6 H, two of the N-CH_3 groups), 7.15 (s, 6 H, two N-CH_3 groups), 4.27 (s, 1 H, $-CH{=}CAr_2$), 4.08 (s, 1 H, $-CH{=}CPh_2$), 2.8–3.6 (m, 18 H, arom); UV (95% EtOH) 262 nm (ϵ 26 400).

Anal. Calcd for $C_{35}H_{38}N_2$: C, 86.37; H, 7.87. Found: C, 86.08; H, 7.61.

Exploratory Photolysis of 1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 0.510 g (1.11 mmol) of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 1.0 L of *tert*-butyl alcohol was purged with purified nitrogen[34] for 1 h before and during photolysis. The diene solution was irradiated for 0.5 h with a 450-W medium-pressure mercury lamp through a Pyrex filter. Removal of solvent under vacuum left a yellow oil which was chromatographed on a 2.5 × 125 cm silicic acid[35] column. Elution proceeded as follows: fraction 1, 5000 mL, 0–1% ether in hexane, nil; fraction 2, 1300 mL, 1%, 0.432 g of the starting diene; fraction 3, 550 mL, 1%, 0.005 g of starting diene and 0.029 g of 2,2-dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane; fraction 4, 900 mL, 1%, 0.028 g of 2,2-dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane; fraction 5, 1300 mL, 1%, 0.015 g of 1,1-bis(*p*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. Yield of major product is 11% and yield of minor product is 3%.

The spectral data for 2,2-dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane were: IR ($CHCl_3$) 3.28, 3.34, 3.40, 3.41, 3.53, 6.25, 6.35, 6.64, 6.70, 6.85, 6.94, 7.12, 7.28, 7.78, 8.05, 8.26, 8.50, 8.53, 9.01, 9.26, 9.70, 12.12, 14.35 µm; NMR (CCl_4) τ 9.01 (s, 3 H, CH_3), 8.71 (s, 3 H, CH_3), 7.86 (d, J = 10 Hz, 1 H, cyclopropyl methine), 6.28 (s, 3 H, OCH_3), 6.16 (s, 3 H, OCH_3), 4.52 (d, J = 10 Hz, 1 H, vinyl), 3.36–2.48 (m, 18 H, arom).

Anal. Calcd for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00. Found: C, 85.94; H, 7.02.

The spectral data for 1,1-bis(*p*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane were: IR ($CHCl_3$) 3.28, 3.34, 3.39, 3.41, 3.53, 6.25, 6.64, 6.71, 6.85, 6.95, 7.14, 7.28, 7.78, 8.05, 8.25, 8.53, 9.00, 9.70, 12.00 µm; NMR (CCl_4) τ 9.04 (s, 3 H, CH_3), 8.72 (s, 3 H, CH_3), 7.98 (d, J = 10 Hz, 1 H, cyclopropyl methine), 6.37 (s, 3 H, OCH_3), 6.28 (s, 3 H, OCH_3), 4.30 (d, J = 10 Hz, vinyl), 3.52–2.60 (m, 18 H, arom).

Anal. Calcd for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00. Found: C, 86.20; H, 7.08.

Exploratory Photolysis of 3,3-Dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene. A solution of 0.265 g (0.51 mmol) of the diene in 125 mL of benzene was purged with purified nitrogen[34] for 30 min before and during photolysis. The diene solution was irradiated for 30 min through a 1-mm Pyrex filter with a 450-W medium-pressure mercury lamp. Removal of solvent under vacuum left an orange oil which was chromatographed on a 2.5 × 45 cm silicic acid[35] column. Elution with 9 L of 0.0–2.5% ether in hexane gave nil; 2 L of 2.5% gave 0.125 g (47%) of the starting diene; 2 L of 2.5–5.0% gave 0.081 g (31%) of 1,1-bis(*p*-methoxyphenyl)-2,2-dimethyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane. Recrystallization from hexane gave the vinylcyclopropane as white needles, mp 149–150 °C.

The spectral data were: IR ($CHCl_3$) 3.34, 3.39, 3.41, 3.44, 3.53, 6.25, 6.64, 6.85, 6.95, 7.14, 7.27, 7.39, 7.78, 8.03, 8.53, 9.01, 9.68, 11.99 µm; NMR (CCl_4) τ 9.03 (s, 3 H, CH_3), 8.75 (s, 3 H, CH_3), 7.99 (d, J = 10 Hz, 1 H, cyclopropyl CH), 6.40 (s, 3 H, OCH_3), 6.30 (s, 6 H, two OCH_3), 6.21 (s, 3 H, OCH_3), 4.57 (d, J = 10 Hz, 1 H, $CH{=}CAr_2$), 2.72–3.71 (m, 16 H, arom).

Anal. Calcd for $C_{35}H_{36}O_4$: C, 80.74; H, 6.97. Found: C, 80.66; H, 6.91.

Exploratory Photolysis of 1,1-Bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 0.047 g (0.097 mmol) of 1,1-bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 125 mL of benzene was purged with purified nitrogen[31] for 1.0 h before and during photolysis. The solution was irradiated for 70 min through a Pyrex filter with a Hanovia 450-W medium-pressure lamp. Removal of solvent in vacuo and elution of the crude product through a 2 × 12 cm silicic acid column yielded 0.021 g (45%) of 2,2-dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-*N*,*N*-dimethylaminophenyl)vinyl]cyclopropane in 200 mL of 5% ether in hexane. No starting diene or isomeric vinylcyclopropane was detected.

Spectral data for the bis(dimethylaminophenyl)vinyl product are as follows: NMR (CCl_4) τ 9.01 (s, 3 H, CH_3), 8.74 (s, 3 H, CH_3), 7.81 (d, J = 10 Hz, 1 H, cyclopropyl methine), 7.20 (s, 6 H, NCH_3), 7.10 (s, 6 H, NCH_3), 4.73 (d, J = 10 Hz, 1 H, vinyl), 3.6–2.5 (m, 18 H, arom).

Anal. Calcd for $C_{35}H_{38}N_2$: exact mass, 486.30330. Found: exact mass, 486.30350.

4,4-Bis(*p*-methoxyphenyl)-3,3-dimethyl-4-hydroxybutanoic Acid Lactone. A solution of 4.49 g (0.026 mol) of 3-carbomethoxy-3-methylbutanoic acid[36] in 60 mL of anhydrous tetrahydrofuran was added over 100 min to a solution of *p*-methoxyphenylmagnesium bromide prepared from 11.6 mL (0.090 mol) of *p*-bromoanisole in 100 mL of anhydrous tetrahydrofuran and 2.19 g (0.090 mol) of magnesium turnings, stirred for 14 h, quenched with cold 7% sulfuric acid, partitioned between ether and saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under vacuum to 12.6 g of orange oil. Removal of anisole by vacuum distillation yielded 7.92

g of material which was chromatographed on a 4 × 73 cm silica gel column.[33] Elution with 3 L of hexane, 1 L of 2.5%, 1 L of 5%, 1 L of 7.5%, 2 L of 10%, 2 L of 12.5%, 3 L of 15%, and 1 L of 25% ether in hexane, and 1 L of 2% methanol, 38% ether, and 60% hexane proceeded as follows (500-mL fractions): fractions 1–5, 1.21 g of anisole; fractions 6–9, 0.140 g of bianisole; fractions 10–11, 0.082 g of overlap; fractions 12–13, 0.326 g of 4,4-bis(*p*-methoxyphenyl)-2,2-dimethyl-4-hydroxybutanoic acid lactone; fraction 14, 0.594 g of 2,2-dimethyllactone and 0.100 g of the expected 4,4-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-hydroxybutanoic acid lactone; fraction 15, 0.30 g of 2,2-dimethyllactone and 0.75 g of 3,3-dimethyllactone; fraction 16, 0.090 g of 2,2-dimethyllactone and 1.42 g of 3,3-dimethyllactone; fraction 17, 1.15 g of 3,3-dimethyllactone; fractions 19–26, 0.050 g, unidentified. The major product (3.42 g, 40%), 4,4-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-hydroxybutanoic acid lactone, was recrystallized from hexane to give white prisms, mp 114–115 °C.

The special data were: IR ($CHCl_3$) 3.32, 3.36, 3.39, 3.50, 5.66, 6.20, 6.32, 6.62, 6.82, 6.92, 7.04, 7.17, 7.26, 7.70, 8.0–8.3, 8.46, 8.94, 9.64, 9.75, 10.02, 10.19, 10.81, 10.96, 12.06 μm; NMR ($CDCl_3$) τ 8.78 (s, 6 H, $C(CH_3)_2$), 7.56 (s, 2 H, CH_2), 6.22 (s, 6 H, OCH_3), 3.15–2.49 (q, 8 H, arom).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.83; H, 6.71.

The minor product (1.31 g, 15%), 4,4-bis(*p*-methoxyphenyl)-2,2-dimethyl-4-hydroxybutanoic acid lactone, was recrystallized from hexane as white prisms, mp 129–130 °C.

The spectral data were: IR ($CHCl_3$) 3.38, 3.53, 5.70, 6.22, 6.33, 6.63, 6.83, 7.04, 7.19, 7.26, 7.72, 8.02, 8.13, 8.47, 8.95, 9.66, 10.03, 10.21, 10.82, 10.99, 12.11 μm; NMR ($CDCl_3$) τ 8.85 (s, 6 H, $C(CH_3)_2$), 7.12 (s, 2 H, CH_2), 6.24 (s, 6 H, OCH_3), 3.06–2.57 (q, 8 H, arom).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.55; H, 7.01.

4,4-Bis(*p*-methoxyphenyl)-3,3-dimethylbutanoic Acid. Lithium wire (0.014 g, 2.0 mmol) was added in four pieces to 0.280 g (0.86 mmol) of 4,4-bis(*p*-methoxyphenyl)-3,3-dimethylbutanoic acid lactone dissolved in a mixture of 10 mL of ether, 10 mL of tetrahydrofuran, and 60 mL of liquid ammonia. The intense blue color persisted after addition of the fourth piece of lithium. The reaction was stirred for an additional 20 min, then quenched with excess solid ammonium chloride. Evaporation of ammonia left a white solid which was taken up in ether and water. The water layer was extracted with more ether and the combined organic layer was dried over magnesium sulfate and concentrated to 0.28 g of colorless oil, pure by NMR. Recrystallization from hexane gave 4,4-bis(*p*-methoxyphenyl)-3,3-dimethylbutanoic acid as white needles, mp 74–74.5 °C.

The spectral data were: IR ($CHCl_3$) 2.8–4.0, 3.37, 3.51, 5.88, 6.21, 6.33, 6.64, 6.83, 6.94, 7.11, 7.29, 7.68, 7.9–8.3, 8.48, 8.97, 9.67 μm; NMR ($CDCl_3$) τ 8.84 (s, 6 H, $C(CH_3)_2$), 7.70 (s, 2 H, CH_2), 6.25 (s, 6 H, OCH_3), 6.04 (s, 1 H, (p-$CH_3OC_6H_4)_2C\mathbf{H}$), 3.24–2.60 (q, 8 H, arom), 0.3 (br s, 1 H, $COO\mathbf{H}$).

Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 73.33; H, 7.40.

Characterization of 2,2-Dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane. A solution of 0.090 g (0.195 mmol) of 2,2-dimethyl-1,1-diphenyl-3-[2,2-bis(*p*-methoxyphenyl)-vinyl]cyclopropane in 15 mL of benzene was added to a solution of 0.427 g of dicyclohexyl-18-crown-6 and 0.172 g of potassium permanganate in 40 mL of benzene (the Sam–Simmons reagent[12]), stirred at room temperature for 37 h, poured into 100 mL of 0.5% hydrochloric acid, ether extracted, washed with water, dried over magnesium sulfate, and concentrated to 0.559 g of yellow oil which was partitioned between ether and 5% aqueous sodium hydroxide solution. The organic phase was washed again with sodium hydroxide solution, dried, and concentrated to an oily residue. Crystallization of the oil from ether–hexane gave 0.020 g (44%) of 4,4′-dimethoxybenzophenone as white needles, the melting point and spectral data of which were identical with that of commercially available 4,4′-dimethoxybenzophenone. The alkaline phase was neutralized to the methyl orange end point with 10% hydrochloric acid, ether extracted, dried, and concentrated to a white solid which gave 0.021 g (40%) of 3,3-dimethyl-2,2-diphenylcyclopropanecarboxylic acid after crystallization from ether–hexane. The melting point and spectral data were identical with the values reported previously.[8a]

Characterization of 1,1-Bis(*p*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. A solution of 0.048 g (0.10 mmol) of 1,1-bis(*p*-methoxyphenyl)-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane in 10 mL of benzene was added to the Sam–Simmons reagent[12] prepared from 0.153 g of dicyclohexyl-18-crown-6 and 0.064 g of potassium permanganate in 15 mL of benzene, stirred for 22 h, poured into 1% hydrochloric acid, ether extracted, dried over magnesium sulfate, and concentrated to 0.193 g of colorless oil which was chromatographed on a 2.5 × 88 cm column of silicic acid.[35] Elution proceeded as follows: fraction 1, 4500 mL, 0–1% ether in hexane, nil; fraction 2, 1800 mL, 1–2%, 0.011 g (60%) of benzophenone; fraction 3, 5100 mL, 2–40%, 0.045 g of material including some unreacted vinylcyclopropane; fraction 4, 1700 mL, 40–60%, 0.022 g (67%) of 2,2-bis(*p*-methoxyphenyl)-3,3-dimethylcyclopropanecarboxylic acid; fraction 5, 1600 mL, 60–100%, 0.015 g of crown ether. Crystallization from hexane gave 2,2-bis(*p*-methoxyphenyl)-3,3-dimethylcyclopropanecarboxylic acid as white prisms, mp 182–183 °C.

The spectral data were: IR ($CHCl_3$) 2.9–3.6, 3.21, 3.31, 3.36, 3.41, 3.52, 5.87, 6.22, 6.32, 6.61, 6.83, 6.94, 7.27, 7.78, 8.00, 8.13, 8.51, 8.99, 9.64, 10.81 μm; NMR ($CDCl_3$) τ 8.92 (s, 3 H, CH_3), 8.54 (s, 3 H, CH_3), 7.76 (s, 1 H, CH), 6.26 (s, 6 H, OCH_3), 3.28–2.68 (m, 8 H, arom), 2.5–0.5 (1 H, CO_2H, detectable only with integrator).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.42; H, 6.76.

Characterization of 1,1-Bis(*p*-methoxyphenyl)-2,2-dimethyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane. A solution of 0.135 g (0.26 mmol) of 1,1-bis(*p*-methoxyphenyl)-2,2-dimethyl-3-[2,2-bis(*p*-methoxyphenyl)vinyl]cyclopropane in 10 ml of benzene was added to the Sam-Simmons reagent[12] prepared from 0.436 g of dicyclohexyl-18-crown-6 and 0.118 g of potassium permanganate in 40 ml of benzene, stirred for 40 h, poured into 2% hydrochloric acid, ether extracted, dried over sodium sulfate, and concentrated under vacuum to 0.544 g of clear, viscous oil which was partitioned between ether and 5% aqueous sodium hydroxide solution. The ether layer was dried over sodium sulfate and concentrated under vacuum to 0.471 g of material from which 0.057 g (95%) of 4,4′-dimethoxybenzophenone was obtained by crystallization from hexane. The aqueous layer was acidified to the methyl orange end point with 10% hydrochloric acid, ether extracted, dried over sodium sulfate, concentrated under vacuum, and crystallized from ether–hexane to give 34 mg (40%) of 2,2-bis(*p*-methoxyphenyl)-3,3-dimethylcyclopropanecarboxylic acid.

Characterization of 2,2-Bis(*p*-methoxyphenyl)-3,3-dimethylcyclopropanecarboxylic Acid. Lithium wire (0.007 g, 1.0 mmol) was added to a solution of 0.023 g (0.07 mmol) of 2,2-bis(*p*-methoxyphenyl)-3,3-dimethylcyclopropanecarboxylic acid in 4 mL of anhydrous ether, 4 mL of tetrahydrofuran, and 20 mL of liquid ammonia. The reaction was stirred for 40 min, then quenched with excess solid ammonium chloride. Evaporation of the ammonia left a white slurry which was dissolved in ether and water. The aqueous layer was saturated with sodium chloride and extracted with ether. The combined ether layers were dried over magnesium sulfate, filtered, and concentrated to 0.021 g of clear, colorless oil. Crystallization from hexane gave 5 mg of the starting cyclopropanecarboxylic acid. The mother liquors were crystallized from hexane to give 15 mg (65%) of 4,4-bis(*p*-methoxyphenyl)-3,3-dimethylbutanoic acid identical in all respects with independently synthesized material (vide supra).

Photolysis Equipment for Quantum Yield Determinations. Quantum yield irradiations were performed on the "black box" apparatus or on the microoptical bench.[13] Light output was measured by ferrioxalate actinometry.[15] The light absorbed in the reaction cell was determined by the splitting ratio technique.[13]

For direct "black box" photolyses, the solution filters used were the following. Filter A: (a) 1.74 M nickel sulfate hexahydrate in 5% sulfuric acid; (b) 1.0 M cobalt sulfate heptahydrate in 5% sulfuric acid; (c) 0.0013 M stannous chloride dihydrate in 15% hydrochloric acid; this combination gave a transmission maximum at 310 nm (40% transmission) and was opaque above 345 nm and below 275 nm. Filter B: (a) 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid; (b) 0.8 M cobalt sulfate heptahydrate in 5% sulfuric acid; (c) 0.0002 M bismuth trichloride in 10% hydrochloric acid; this combination gave a transmission maximum at 272 nm (40% transmission) and was opaque above 305 nm and below 245 nm. For the microbench runs, the monochromator inlet slit was set at 5.4 mm and the exit slit at 2.9 mm, giving a band pass of 22 nm at half-peak height.

For sensitized "black box" runs, the solution filters used were as follows. Filter C:(a) 1.0 M nickel sulfate hexahydrate in 10% sulfuric acid; (b) 1.0 M cobalt sulfate heptahydrate in 10% sulfuric acid; (c) 0.047 M stannous chloride dihydrate in 15% hydrochloride acid; this combination gave a transmission maximum at 331 nm (17% transmission) and was opaque above 365 nm and below 312 nm. Filter D:(a) 0.1 M nickel sulfate hexahydrate in 10% sulfuric acid; (b) 0.4 M cobalt sulfate heptahydrate in 10% sulfuric acid; (c) 0.1 M stannous chloride dihydrate in 15% hydrochloride acid; this combination gave a transmission maximum at 345 nm (40% transmission) and was opaque above 380 nm and below 320 nm.

Direct Quantum Yields. 1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. Run 1 was performed on the microoptical bench, runs 2 and 3, on the black box apparatus.[13] All employed dry *tert*-butyl alcohol as solvent. Each solution was purged with purified nitrogen[34] for 1.0 h before and during irradiation. Runs 1 and 2 were analyzed with high-pressure liquid chromatography using a 2 ft × 1/8 in. column packed with a silicic acid like material developed in these laboratories[37] and eluting with 1.4% ether in hexane. 4-Bromobenzophenone was used as an internal standard. In run 3, the photoproducts were isolated by chromatography on a 2.5 × 45 cm silicic acid[35] column, eluting with 1% ether in hexane. The composition of the fraction containing the photoproducts was determined by manual integration of the vinyl hydrogen peaks in the expanded (108-Hz sweep width) τ 5.0–6.1 region of the 100-MHz NMR spectrum. Data for the individual quantum yields are as follows.

Run 1: monochromator set at 285 nm; starting diene used, 1.0×10^{-2} mmol in 40 mL; 5.1×10^{-2} mEinsteins absorbed; dianisylvinylcyclopropane formed, 4.3×10^{-3} mmol, $\Phi = 0.085$; diphenylvinylcyclopropane formed, 1.3×10^{-3} mmol, $\Phi = 0.025$; 5.6% conversion.

Run 2: filter B; starting diene, 6.45×10^{-1} mmol in 750 mL; 6.1×10^{-1} mEinsteins; dianisylvinylcyclopropane, 4.2×10^{-2} mmol, $\Phi = 0.070$; diphenylvinylcyclopropane, 1.4×10^{-2} mmol, $\Phi = 0.023$; 8.8% conversion.

Run 3: filter A; starting diene, 1.12 mmol in 750 mL; 7.7×10^{-1} mEinsteins; dianisylvinylcyclopropane, 5.7×10^{-2} mmol, $\Phi = 0.071$; diphenylvinylcyclopropane, 1.3×10^{-2} mmol, $\Phi = 0.017$; 6.0% conversion.

Sensitized Quantum Yield. 1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. A solution of 0.280 g (0.61 mmol) of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, 30.0 mL of acetophenone, and 720 mL of *tert*-butyl alcohol was purged with purified nitrogen[34] for 1.0 h before and during photolysis. The solution was irradiated in the "black box" apparatus[13] through filter combination C with 1.60 mEinsteins of light. Removal of solvent and acetophenone in vacuo left 0.286 g of material. Analysis by NMR spectroscopy showed only starting diene and a trace of acetophenone. No vinylcyclopropanes were detected, and assuming that 3.0 mg could be detected, $\Phi_{sens} < 4 \times 10^{-3}$.

Direct Quantum Yields. 3,3-Dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene. All three runs were performed on the "black box" apparatus.[13] Each 750-mL *tert*-butyl alcohol solution was purged with purified nitrogen[30] for 1.0 h before and during irradiation. Run 1 was analyzed using high-pressure liquid chromatography (vide supra), eluting with 10% ether in hexane. 4-Methoxybenzophenone was used as an internal standard. Runs 2 and 3 were analyzed by the silicic acid chromatography–NMR integration technique described above. Data for the individual quantum yields are as follows.

Run 1: filter B; starting diene used, 9.2×10^{-1} mmol; 7.6×10^{-1} mEinsteins absorbed; vinylcyclopropane formed, 3.0×10^{-2} mmol, $\Phi = 0.040$; 3.3% conversion.

Run 2: filter A; starting diene, 1.15 mmol; 1.87 mEinsteins; vinylcyclopropane, 7.9×10^{-2} mmol, $\Phi = 0.042$; 6.7% conversion.

Run 3: filter A; starting diene, 1.35 mmol; 9.1×10^{-1} mEinsteins; vinylcyclopropane, 4.6×10^{-2} mmol, $\Phi = 0.051$; 3.4% conversion.

Sensitized Quantum Yield. 3,3-Dimethyl-1,1,5,5-tetrakis-(*p*-methoxyphenyl)-1,4-pentadiene. A solution of 0.275 g (0.529 mmol) of 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene and 6.12 g of benzophenone in 750 mL of *tert*-butyl alcohol was purged with purified nitrogen[34] for 1.0 h before and during photolysis. The solution was irradiated in the "black box" apparatus[13] through filter D with 3.36 mEinsteins of light. Removal of solvent under vacuum left a colorless oil from which benzophenone crystallized. Chromatography on a 2.5 × 45 cm silicic acid[35] column eluting with 4.0 L of 0.5% ether in hexane removed benzophenone from the photolysate. Further elution with 1 L of 5% and 1 L of 10% ether in hexane gave 0.273 g of colorless oil. Analysis by NMR showed no evidence of vinylcyclopropane. Assuming that 3.0 mg could be detected, $\Phi_{sens} < 1.7 \times 10^{-3}$.

Direct Quantum Yields. 1,1-Bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene. Both runs utilized the "black box" apparatus[13] and filter combination A. Each 750-mL *tert*-butyl alcohol solution was purged with purified nitrogen[34] for 1.0 h before and during photolysis. Both runs were analyzed by the silicic acid[35] chromatography–NMR integration technique described above. Data for the individual quantum yields are as follows.

Run 1: starting diene used, 6.9×10^{-1} mmol; 1.14 mEinsteins absorbed; vinylcyclopropane formed, $<6.2 \times 10^{-3}$ mmol; $\Phi < 5.4 \times 10^{-3}$.

Run 2: starting diene, 3.7×10^{-1} mmol; 15.0 mEinsteins absorbed; vinylcyclopropane, 4.1×10^{-2} mmol; $\Phi = 2.7 \times 10^{-3}$.

Energy Transfer Tests. Quenching of Benzophenone Triplets by 1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and by 3,3-Dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene. The irradiations were carried out on the "black box" apparatus[13] using filter D. A solution of 0.500 g (2.74 mmol) of benzophenone and 0.250 g (1.36 mmol) of benzhydrol in 250 mL of *tert*-butyl alcohol was purged with purified nitrogen[34] for 1.0 h before and during the irradiation. Similarly, a solution of 0.500 g of benzophenone, 0.250 g of benzhydrol, and 0.063 g (0.136 mmol) of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene in 235 mL of *tert*-butyl alcohol and a solution of 0.500 g of benzophenone, 0.250 g of benzhydrol, and 0.052 g (0.100 mmol) of 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene in 235 mL of *tert*-butyl alcohol were purged and irradiated. Chromatography of each photomixture on a 2.5 × 45 cm silicic acid[35] column, eluting with 1% ether, completely separated benzopinacol from the other components.

Run 1: no quencher; 2.40 mEinsteins absorbed; benzophenone recovered, 0.380 g; benzpinacol, 0.108 g; $\Phi = 0.123$; 0% quenching.

Run 2: quencher, 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene; 2.41 mEinsteins; benzophenone, 0.460 g; benzpinacol, 0.027 g; $\Phi = 0.031$; 75% quenching.

Run 3: quencher, 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene; 2.41 mEinsteins; benzophenone, 0.410 g; benzpinacol, 0.034 g; $\Phi = 0.039$; 68% quenching.

Emission Studies. Purification of Solvent. Isopentane and methylcyclohexane were purified by repeated washings with 10% fuming sulfuric acid until the washings were colorless, washing with water, refluxing with 10% sulfuric acid saturated with potassium permanganate for 3–6 h, washing again with water, drying over phosphorus pentoxide, and passing through a 2.0 × 80 cm column of alumina containing 10% silver nitrate.[38] The early and late fractions were discarded. Solvents prepared in this manner were transparent in the ultraviolet and emission free.

Single-Photon Counting. The apparatus and procedure have been described in detail previously.[9b] The method uses a high-pressure (~80 psi) nitrogen flash lamp with a half-width of ~2 ns when run at 20–40 kHz, a 1P28 photomultiplier to trigger the start of a time-to-amplitude converter, monochromators before and after the sample, an RCA 8850 photomultiplier and Ortec model 463 constant fraction timing discriminator to signal emergence of a single photon, and a 12 bit Northern Scientific A/D converter interfaced with a PDP8/I-FPP12 minicomputer. The minicomputer was used as a 512-word multichannel analyzer and to do on-line deconvolution by reiterative convolution as previously described.[9b] Independent studies[39] establish a 16-ps error limit. Experiments were run for a time sufficient to collect a minimum of 2000 counts in the highest channel (about 300 000 counts in 512 channels), when collecting at 5% of the 22-kHz lamp frequency. The 5% factor assures that few double photons are collected. Excitation was generally at 280 nm. Optical densities were adjusted to 1.6–2.0 at the excitation wavelength. All runs were performed at 77 K in 4:1 methylcyclohexane–isopentane solvent. The data are reported as follows: compound, average lifetime, average rate of decay, number of runs, estimated error in rates.

1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene; 2.7 ns, $k_{dt}{}^{77} = 3.7 \times 10^8$ s^{-1}, five runs, 5%.

3,3-Dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene: 1.9 ns, $k_{dt}{}^{77} = 5.2 \times 10^8$ s^{-1}, 5 runs, 5%.

1,1-Bis(*p*-*N*,*N*-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene: 3.5 ns, $k_{dt}{}^{77} = 2.9 \times 10^8$ s^{-1}, 13 runs, 15%.

1,1-Bis(*p*-methoxyphenyl)ethylene: 4.4 ns, $k_{dt}{}^{77} = 2.3 \times 10^8$, one run.

Magic Multipliers. For each compound, the fluorescence spectrum was recorded in 4:1 methylcyclohexane–isopentane solution at 77 and 295 K under otherwise identical conditions using an Aminco–Kiers spectrofluorometer with a Hanovia 901C-1 150-W xenon lamp. Concentrations were adjusted to give an optical density in the range of 0.8–1.2, thus minimizing scatter. An excitation wavelength of 280 nm was used for each compound. The magic multipliers were obtained from a single sample by integrating the emission intensities obtained at the two temperatures. Values obtained were as follows: 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, $M = 95$ (2 runs); 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)-1,4-pentadiene, $M = 75$ (two runs); 1,1-bis(*p*-N,N-dimethylaminophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, $M = 70$ (two runs); 1,1-bis(*p*-methoxyphenyl)ethylene, $M = 77$ (two runs).

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Registry No.—**5**, 65366-58-7; **6**, 65366-59-8; **7**, 65366-60-1; **8**, 53392-28-2; **9**, 65366-61-2; **10**, 56405-96-0; **11**, 65392-12-3; **12**, 56405-97-1; **13**, 65366-62-3; **14**, 65366-63-4; **15**, 65366-64-5; **16**, 65366-65-6; **17**, 65366-66-7; **18**, 65366-67-8; **19**, 65366-68-9; **21**, 4356-69-8; dimethyl 3,3-dimethylglutarate, 19184-67-9; *p*-methoxyphenyllithium, 14774-77-7; *p*-methoxyphenyl bromide, 104-92-7; 3,3-dimethyl-1,1,5,5-tetrakis(*p*-methoxyphenyl)pent-4-en-1-ol, 65392-13-4; *p*-*N*,*N*-dimethylaminophenyllithium, 13190-50-6; 3-carbomethoxy-3-methylbutanoic acid, 32980-26-0; 4,4-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-hydroxybutanoic acid lactone, 65366-69-0; 4,4-bis(*p*-methoxyphenyl)-2,2-dimethyl-4-hydroxybutanoic acid lactone, 65366-70-3; Ph$_2$CO, 119-61-9; Ph$_2$CHOH, 91-01-0; 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoic acid, 65366-71-4; 5,5-bis(*p*-methoxyphenyl)-3-dimethyl-4-pentenoic acid, 65366-72-5.

References and Notes

(1) (a) This is paper 111 of the present series; (b) for a preliminary communication describing a part of these results, see H. E. Zimmerman, W. T. Gruenbaum, R. T. Klun, M. G. Steinmetz, and T. R. Welter, *J. Chem. Soc., Chem. Commun.*, 228 (1978).

(2) For the previous paper (110) on Mechanistic and Exploratory Organic Photochemistry, see H. E. Zimmerman and T. P. Cutler, *J. Chem. Soc., Chem. Commun.*, 232 (1978). In our previous papers we erroneously referred to this as a *J. Am. Chem. Soc.* publication forthcoming.

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